Name of faculty: Faculty of Environmental Science and Technology

Name of department: Department of Ecology and Natural Resource Management (INA)

Author: Søren Bang-Achton

Title: Impact of acetylation on the gluing properties of wood

Subtitle: Investigation on bonding of acetylated Radiata pine (*Pinus radiata* D. Don) with melamine-urea-formaldehyde adhesive (MUF).

Subject description: Investigation of factors affecting bonding properties of chemically modified Radiata pine with melamine-urea-formaldehyde adhesive (MUF) Prefere 4546/5022 produced by Dynea AS for load bearing constructions.

Academic advisor: Holger Militz, Norwegian University of Life Sciences (NMBU)

External advisors: Andreas Treu, Norwegian Institute of Bioeconomy Research (NIBIO)
                               Ronny Bredesen, Dynea AS

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ABSTRACT

Modified wood and the wood industry have a big potential in the future due to a growing global concern for non-environmental friendly chemicals and increasing focus on sustainability. The main purpose to modify wood is to increase the naturally durability of the wood and the ASE. One of the market's leading chemical wood modification methods is acetylation of wood. Acetylation of wood has showed to affect the bonding properties of several adhesives. Today there is no existing MUF adhesive system which can bond acetylated wood in service class 3. Development of a MUF adhesive system capable of bonding acetylated wood in services class 3 can have a positive impact throughout the value chain. The objective of this thesis was to increase the understanding of the interaction between MUF adhesive and acetylated wood. Rheology measurements of MUF adhesive directly on wood surfaces of acetylated and untreated wood have been made, as well as contact angle measurements, pH and buffer capacity determinations. Microscope analyses of the adhesive bond line and penetration in Radiata pine (*Pinus radiata* D. Don) have been made under fluorescence and normal light. Rheology analysis showed a lower increment in the complex viscosity for the tested MUF adhesive during the first three minutes on acetylated Radiata pine compared with untreated. No clear differences were seen in the microscope analyses except of a clear lack of adhesion between the cured MUF bulk adhesive and acetylated cell wall. As expected, a lower pH was found in acetylated wood; lowest in the core of the planks and higher in the outer part. Higher contact angle was found and thus poorer wetting properties of the acetylated wood in relation to the untreated wood. Furthermore, untreated wood did not show any alkaline buffer capacity in contrast to the acetylated wood.

Key words:

Chemical wood modification; acetylation; Melamine Urea Formaldehyde adhesive (MUF); gluing; rheology; rheometer; contact angle; pH; buffer capacity; microscopy analysis; adhesive penetration; *Pinus radiata* D. Don

RESUMÉ

Der ligger et stort potentiale i modificeret træ og træ industrien på grund af den globalt voksende bekymring for miljøskadelige stoffer og øget fokus på bæredygtighed. Hovedårsagen til at modificere træ er for at forbedre den naturlige holdbarhed og reducere dimensionsændringerne ved varierende fugtighed. Acetylering er blandt de markedsledende metoder til kemisk modificering af træ. Acetylering af træ har dog vist sig at påvirke limningsegenskaberne for flere typer lim. I dag findes der ikke nogle MUF lime, som kan binde acetyleret træ medhenblik på, at opfylde kravene for limtræ i service klasse 3. Udvikling af et MUF lim der kan binde acetyleret træ og er holdbar under service klasse 3, kan have en positiv virkning igennem hele værdikæden. Formålet med denne kandidatafhandling var, at øge forståelsen af samspillet mellem MUF lim og acetyleret træ. På acetyleret og ubehandlet radiata fyr (*Pinus radiata* D. Don) er der blevet udført reologi målinger af MUF lim direkte på træoverflader, kontaktvinkel målinger, pH og buffer kapacitets bestemmelser af træet, samt mikroskopi analyser af limfuger og indtrængning af lim i træet. Resultaterne viste en lavere hældningskvotient i øgningen af den komplekse viskositet af limen på acetyleret træ i de første 3 minutter efter påføring sammenlignet med ubehandlet træ. Ingen tydelig forskel blev fundet i forbindelse med mikroskopi analysen på nær manglende vedhæftning mellem lim massen (limfugen) og cellevæggen på det acetylerede træ. Som forventet blev der fundet en lavere pH og større kontaktvinkel, hvilket er et udtryk for dårligere befugtning af overfladen på det acetylerede træ sammenlignet med ubehandlet træ. I ubehandlet radiata fyr blev der ikke fundet nogen væsentlig buffer kapacitet i modsætning til acetyleret radiata fyr.

Nøgleord:

Kemisk modificeret træ; acetylering, Melamin Urea Formaldehyd lim (MUF); limning; reologi; reometer; kontaktvinkel; pH; buffer kapacitet; mikroskopianalyse; lim indtrængning; *Pinus radiata* D. Don

CONTENT

1. INTRODUCTION AND BACKGROUND

1.1. MOTIVATION

Adhesives are used in large amounts by the wood industry. In 1998 around 70 % by volume of all produced adhesive were for different wood applications (Pizzi 1998). Furthermore, in 1988 it was estimated that more than 70 % of all wood products were glued in one way or the other (Lambuth 1989). Today, wood together with paper, must still be considered the largest application purpose of adhesives (Frihart 2013).

The possibility of making structural wood composites has made wood a realistic alternative to other materials (Brandon et al. 2005; Shmulsky & Jones 2011). Wood can compete structurally, economically and on sustainability (Brandon et al. 2005; Shmulsky & Jones 2011). On the other hand, wood has some disadvantages such as dimensional changes with changing MC, and degradation in several ways – weather, fire, insects and fungal decay as the most common (Brandon et al. 2005; Shmulsky & Jones 2011). Wood modification can solve or reduce some of these disadvantages (Hill 2006). Within chemical modifications of wood, acetylation is the most research based (Frihart et al. 2004; Hill 2006), and probably the largest on the marked today (Hill 2011; Jensen 2015). A disadvantage with acetylated wood is the capability of being effectively bonded. Adhesives such as PRF and EPI can bond acetylated wood (Accoya® 2014; Ormstad 2007; Vick & Rowell 1990), but acid curing adhesives, such as MUF, do not perform well on acetylated wood (Ormstad 2007). Since MUF is one of the most widely used adhesives today in the European wood industry for loadbearing constructions (Bredesen 2015; Likozar et al. 2011; Schmidt et al. 2010), it is the aim to use MUF-based adhesive systems for acetylated wood as well.

Several experiments have shown the bonding problem of acetylated wood with MUF (Brandon et al. 2005; Ormstad 2007; Vick & Rowell 1990), some of them provide explanations and theories on what can be the cause. Ormstad (2007) has two theories i) the acetic acid in the acetylated wood makes the cold setting adhesive to a partly gelling in contact with the wood surface. ii) Due to the buffer capacity the adhesive will restrict the curing between the wood lamellas. Similar effects of chemical influence, probably from the acetic acid were observed by Vick and Rowell (1990). In addition there is no complete agreement about, the physical influence (penetration) on the curing (Kariz et al. 2013; Schmidt et al. 2010; Stoeckel et al. 2013).

A review of the literature did not reveal any studies that examined the specific reasons why MUF does not bond acetylated wood successfully. The most logical reason is mentioned among others by Brandon et al. (2005), the wood is more hydrophobic and the adhesive has reduced ability to form hydrogen-bonds with the wood due to the reduced amount of hydroxyl groups in acetylated wood. But this does not explain why PRF and EPI are working so much better, than MUF (Bredesen 2015; Chandler et al. 2005; Frihart et al. 2004).

1.2. ACETYLATION

Acetylation of wood is a chemically modification of the polymers in the cell wall. It occurs when the wood is impregnated with acetic anhydride. The acetic anhydride reacts and binds to the OH-groups on the polymers in the cell wall. In the reaction acetic acid is created as a by-product (see Figure 1) (Brandon et al. 2005; Hill 2006; Rowell 2005).
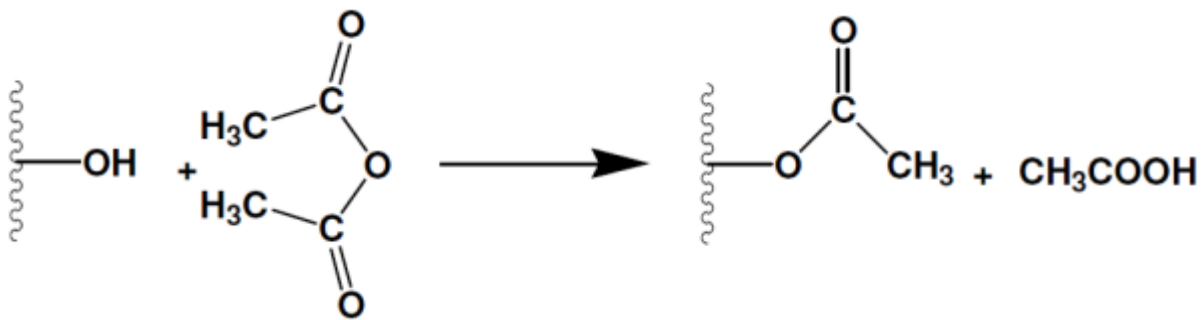
FIGURE 1: REACTION OF ACETIC ANHYDRIDE WITH AN OH-GROUP IN WOOD, FROM HILL (2006)

When the wood is acetylated the decay resistance is increased (Hill 2006), while the MOR (strength) is significant decreased, and MOE (stiffness) probably not decreased significantly (Jorissen et al. 2005). The average WPG of acetylated wood from Accsys Technologies is 20 % (Hill s.a.) which gives an ASE value of ca. 70 % (Hill & Jones 1996). Since WPG and ASE have a strong relationship, high WPG (%) results in low amount of swelling (Hill 2006). The relationship between ASE and WPG is due to bulking of the cell wall rather than the number of OH groups in the wood, which has been substituted (Hill 2006; Hill s.a.).

Acetylation of wood to prevent fungal decay and increase dimensional stability has been investigated since the late 1920's. In 1961 the first commercialization of acetylated wood was tried. Several other attempts have been made to commercialize the production of acetylated wood (Rowell, R. 2012). Previous trials probably failed mainly because of high competition from cheaper

and traditionally used salt impregnated products (mainly CCA). However the increasing environmental focus, especially in Europe has resulted in restrictions of the salt impregnated (CCA) products in many countries. Maybe because of this, the company Accsys Technologies seems to have succeeded in commercializing their acetylated wood under the product name Accoya® Wood. The company has currently such a high demand on their products that it surpasses their production (Jensen 2015). In response to this demand they are planning to open a new factory in Freiburg, Germany which can increase their production with 80.000 m^3 annually (Jensen 2015).

Accsys Technologies has several products on the market from MDF-boards over window frames to load bearing timber. Here, in this study, the use and focus have been on the load bearing construction timber. The main wood species for this use in the Accoya production is Radiata pine.

The very simplified explanation of the acetylation process described above and illustrated in Figure 1 is actual much more complex. The complexity is due to the variables before, during and after the impregnation and within the wood itself. Hill (2006) has a fine review of these variables and their influence.

1.3. RADIATA PINE

When wood is acetylated there will be only a minor colour change, compared with other wood treatments and modification methods e.g. CCA and furfuryl alcohol impregnation or heat treatment. With a minor colour changes after treatment, customers are not able to "see" the difference to untreated material. Introducing new tree species can therefore make sense; in the way that the customer can see that this is something different from the average wood on the marked. This gives Radiata pine an advantage, in the northern hemisphere, together with the optimal properties for acetylation (explained below) (Bongers 2015).

Radiata pine or Monterey Pine (*Pinus radiata* D. Don) is a well-known tree species for most foresters, especially for people who work with plantations in the southern hemisphere. Radiata pine is one of the world most planted species and it is originating from three small localities on the central-coast of California, North America (Berg 2012; Burns 1990).

In New Zealand, where plantations with Radiata pine is widespread, the mean annual growth is approximately 23 cubic meters per hectare and at sites with optimally conditions this increases to 30 m^3 with 28 year rotations (Berg 2012).

According to Ross (2010) Radiata pine will bond satisfactorily when high-quality adhesives are used and the conditions are controlled during the bonding. Radiata pine is generally described as a species which is easy to glue, paint, nail, treat with preservatives, finishes and easy to machine (Ross 2010). Ormstad (2007) did not report any problems in bonding untreated Radiata pine with MUF adhesive.

Accsys Technologies gets their timber from sustainable plantations in New Zealand, where wood for load bearing construction are specially sorted out. Accsys Technologies requires planks free of knots and only containing sapwood. The wood is picked out by local experts who have knowledge about where to find the right trees, and where the wood density is higher than average, which is also desirable (Bongers 2015). It is well known that the knot size and amount of knots, together with the density, affect the strength significantly (Shmulsky & Jones 2011). The reason Accsys Technologies requires pure sapwood is due to the uptake of acetic anhydride during impregnation and reaction within the wood. The sapwood cell wall swells up to a maximum when treated, while lower uptake in the heartwood only results in lower swelling. If heartwood is present together with sapwood in a treated plank, internal stress will occur due to the different swelling properties (Bongers 2015).

Although transportation costs are high, there are several reasons to explain the use of Radiata pine for acetylation. First, the fact that Radiata pine is very easy to impregnate and modify. Secondly it is not endangered. Thirdly, it can be produced under sustainable conditions with a high quality, short rotations, low cost and in amounts that follow the demands on the world marked, compared to several other tree species (Berg 2012; Bongers 2015; Burns 1990). Furthermore, Radiata pine has a large sapwood part, which is essential for modification purposes, when impregnation of the entire wood matrix is the aim. Other European wood species would fulfil the same requirements for being a potential wood species for acetylation. However, introducing a "new" non-European species might be able to compensate for the drawback of acetylated wood showing only light discoloration after treatment (Bongers 2015).

1.4. ADHESIVES AND ADHESION

MUF adhesives are characterised by having the advantages from the UF (Urea-Formaldehyde) adhesive, but contrary to a UF, it can be used in service class 3, due to the addition of melamine. UF adhesives have a high reactivity, are fast curing and cheaper, but the resistance to water are poor

and emissions of formaldehyde continues during its service life. MF adhesives have similar properties to MUF, but are more expensive due to higher melamine amount (Bredesen 2015; Frihart 2013; Likozar et al. 2011; Pizzi 1994; Zhang et al. 2013). MUF adhesives for load bearing constructions are usually two component system. The properties of the adhesive system is given by the ratio between melamine, urea and formaldehyde (Likozar et al. 2011; Pizzi 1994) as well as the hardener ratio and content (Bredesen 2015; Pizzi 1994; Viljugrein 2015).

Bonding wood with adhesives involves several factors and part of the central aspects are still not fully understood (Frihart 2013). The factors are difficult to separate because several of them are working together and are depending on each other (Frihart 2013; Nardin & Schultz 2003). The mechanical interlocking is often divided into a separate group, while the other functions come in a specific adhesion group (Nardin & Schultz 2003). The latter is often divided into secondary and primary bonds and occasionally donor-acceptor bonds after their typical bond energies (Frihart 2013; Nardin & Schultz 2003; Pizzi 1994). When discussing the different bond energies it is important to take the amount of bonds into account (Frihart 2013).

A complete understanding of bond strength, adhesion, performance and the forces around it will require a wide range of knowledge within mechanics, rheology, material science, organic chemistry and polymer science (Frihart 2013). A common way to differentiate between the working factors in adhesion with wood adhesive is as follows (Frihart 2013; Hass 2012; Nardin & Schultz 2003; Nussbaum 2001; Pizzi 1994):

- Mechanical interlock: Can be compared with "Velcro" or "hammer and nail", is the penetration of the adhesive into the porous wood surface. The "tentacles" from the glue line in the wood substrate contribute to the complete bond line strength. There seems to be a relationship between increasing roughness of the wood surface and the strength of the mechanical interlocking (Frihart et al. 2004; Frihart 2013; Nardin & Schultz 2003). The mechanical interlocking is generally more resistant to shear forces compared to normal forces (Frihart 2013). There is discussion about the importance of mechanical interlocking since perfectly smooth surfaces can be hold together with adhesives (Bredesen 2015; Hass 2012).
- Electronic attraction: Is a theory based on observations during failure processes, where a double electrical layer should exist. It has been concluded that the phenomenon is more

likely something which occurs as a consequence of debonding (Frihart 2013; Nardin & Schultz 2003).

- Boundary layers and interphases: This is a statistical based theory, where weak boundary layers are present in both the adhesive and wood substrate, and where interfaces of impurities or short polymer chains exist. The boundary layers have a thickness of molecular to microscopic (Nardin & Schultz 2003).

- Adsorption: Also known as the thermodynamic theory, is widely used and accepted in the adhesion science (Nardin & Schultz 2003). It can be explained as wetting parameters in a solid-liquid system consisting mainly of contact angle measurement, surface free energy and work of adhesion (Nardin & Schultz 2003; Nussbaum 2001). Not to confuse with absorption where a substance is taken up by a substrate.

- Diffusion theory: It can be described as mutual diffusion of polymers from both the wood and the adhesive, on a molecular level across the interface between the wood and the adhesive (Pizzi 1994).

- Chemical bonding: A term mainly used in wood adhesion, due to the fact that the wood substrate must be chemically reactive in combination with the adhesive system (Pizzi 1994). If this is not the case, the presence of coupling agents or promoter molecules increase the joint strength (Nardin & Schultz 2003). The coupling agents or promoter molecules react with the substrate and polymers in the adhesive to create chemical bridges at the interface (Nardin & Schultz 2003). Chemical bonding covers the primary bonds ionic, covalent and metallic coordination (the latter after e.g. an CCA impregnation) (Pizzi 1994).

Frihart (2013) divides the bonded assembly into three zones (see Figure 2): 1) The bulk wood, where the properties of the wood hasn't changed and no adhesive is present. 2) The interphase; the area where the properties differ from both the bulk wood and the bulk adhesive. 3) The bulk adhesive where the properties of the cured adhesive are unaffected of the other zones. Since the two bulk wood zones and interphase zones will be different, it may be preferable to look at the zones as five zones instead of three.
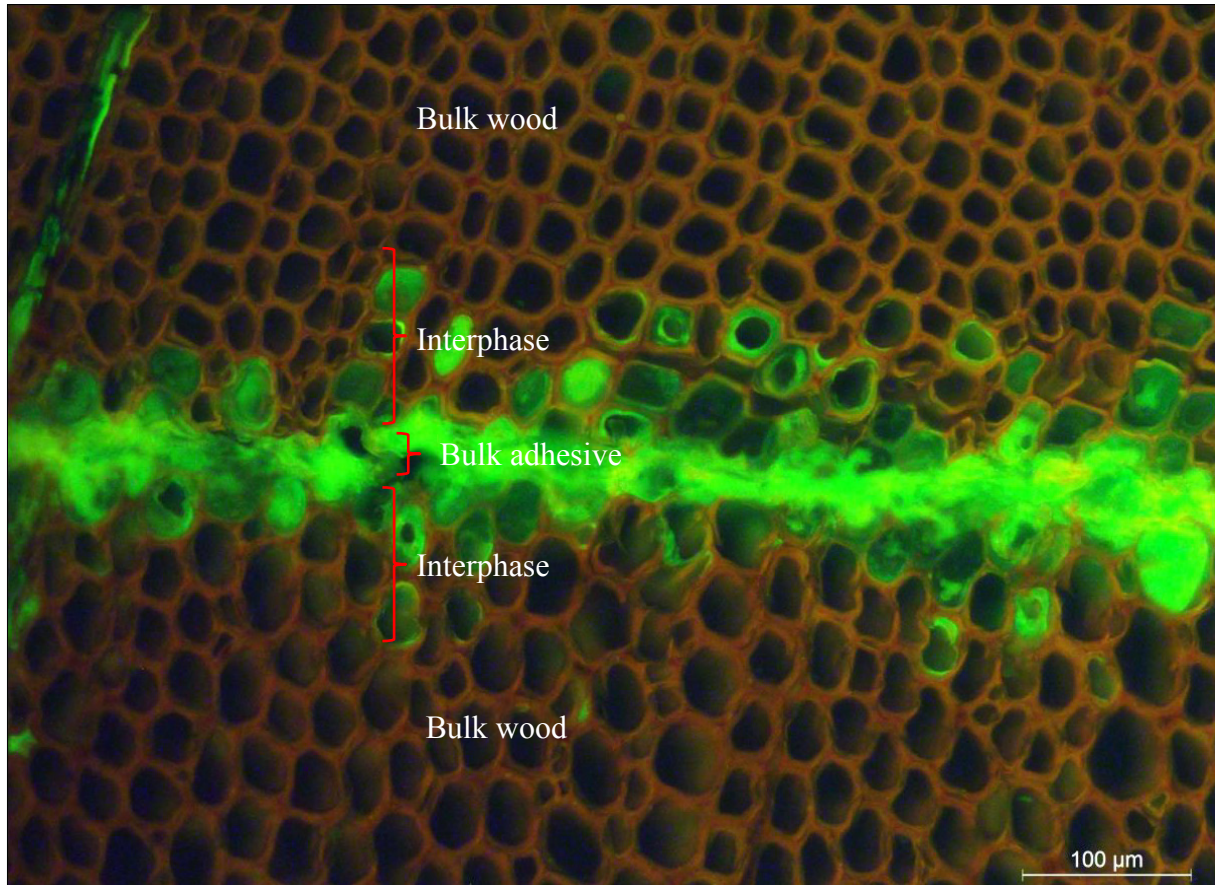
FIGURE 2: A GLUE LINE IN WOOD VIEWED FROM A CROSS SECTION, SHOWING THE BULK WOOD, INTERPHASE (ALSO REFERRED AS BOUNDARY LAYER SOME PLACES) AND BULK ADHESIVE.

1.4.1.   THE SELECTION OF MUF AS THE ADHESIVE SYSTEM

The choice of adhesive system from the product portfolio of MUF adhesives produced by Dynea AS was the glue Prefere 4546 together with the hardener Prefere 5022 (see Table 1). Prefere 4546/5022 is approved for gluing of wooden load bearing constructions in Europe and is very flexible. With Prefere 4546/5022 combination, cold-, hot- as well as radiofrequency curing will be possible and in a mixed application the hardener concentrations can be between 10-100 pbw (Bredesen 2015; Dynea 2014). The notification 100:20 Prefere 4546/5022 describes 20 pbw Prefere 5022 hardener, which correspond to 2 kg of hardener mixed together with 10 kg of glue, which gives 12 kg of "ready to apply" Prefere 4546/5022 adhesives.

TABLE 1: TECHNICAL DATA FOR MUF PREFERE 4546 AND HARDENER PREFERE 5022 FROM DYNEA (2014)

	Prefere 4546	Prefere 5022
	Liquid melamin urea adhesive	Liquid hardener
Appearance	Light grey/white viscous liquid	White viscous liquid
Solids content	63-64 %	-
Viscosity at 25 °C	3000-10000 mPa·s*	1800-2800 mPa·s*
pH at 25 °C	8.5-10.0	1.5-2.5
Density at 25 °C/4 °C	1.27±0.02 g/cm^3	1.08±0.02 g/cm^3

*The viscosity is measured by Brookfield, RVT, spindle 4 at 20 rpm

A large part of the global wood adhesives are MUF adhesives (see Figure 3) (Transparency Market Research 2014). MUF adhesives are similar to MF and UF adhesives and can be made with a mix of those, or by co-condensation. The variation is anyhow greater for MUF than for the MF and UF adhesives, since the ratio between melamine and urea can be varied together with temperature, pH, fillers and the way to cook the adhesive. The ratio between melamine and urea is important for obtaining the right combination between performance and costs (Frihart 2013; Zanetti & Pizzi 2003).
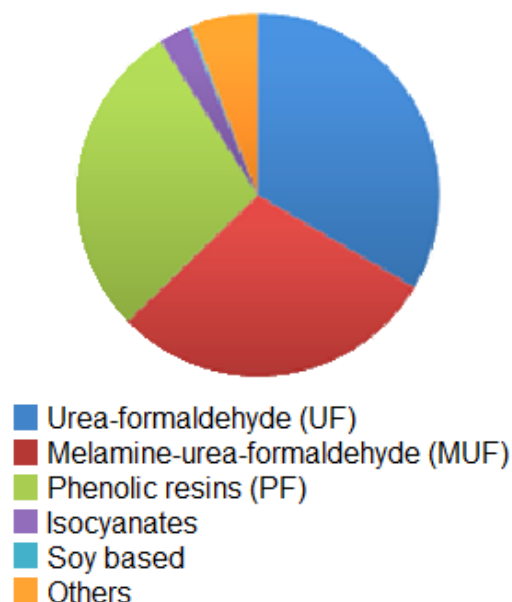

FIGURE 3: GLOBAL WOOD ADHESIVE AND BINDERS MARKET 2013 VOLUME SHARE, BY PRODUCT SEGMENT FROM TRANSPARENCY MARKET RESEARCH (2014) (SOURCE OMNEXUS4ADHESIVES, UNITED SOYBEAN BOARD, COMPANY PRESENTATIONS, PRIMARY INTERVIEWS, TRANSPARENCY MARKET RESEARCH).

1.5. GLUING OF ACETYLATED WOOD – HYPOTHESIS AND FACTORS

Accsys Technologies are continuously working on their process to optimize the acetylation, e.g. lowering the amount of free acetic acid (Bongers 2015). Most of the experiments with MUF on acetylated wood have been made before the last optimizations. The optimizations have not changed the bonding properties towards a better adhesion with MUF (Bredesen 2015). Several hypotheses can be put up why MUF doesn't work on acetylated wood: 1) The lower pH on the surface makes the curing too fast, so penetration into the wood does not occur. 2) A thin film of glue is cured in a very early stage when the adhesive system and the wood surface are in contact with each other. The partly pre-cured adhesive film hinders any surface penetration into the wood matrix. 3) The glue contains water molecules, which normally penetrates the wood and helps to dry out the glue line. Modified wood does not take up water in the same speed and through the same canals as unmodified wood. 4) Normally several phenomena work together in an adhesive to bond the elements. One or several of these functions can be put out or be radically decreased when trying to bond acetylated wood with adhesives developed for untreated wood. 5) The transport system of water in untreated wood is changed in acetylated wood. Capillary forces might be the first/main forces in the wetting of acetylated wood. Some of these hypotheses related to the changed properties are also mentioned in Accoya® (2014).

To locate the reason for the failing glue line and improve the adhesive to work optimally, one must have an overview of the possible reasons and factors that may cause the problem.

Several of the variables in Frihart's (2013) table of Wood Bonding Variables (see Table 2) are changed or affected when the wood is modified and the reason why the MUF adhesive fails must be found here. On the other hand there are also elements within acetylation which should work for a stronger glue line. These benefits are mainly the reduced swelling and shrinking, which reduces the stresses on the glue line. Another is the lower variation in moisture content, when the relative humidity of the surroundings is changing. This should make the environment in which the glue line needs to perform more stable and thereby reduce stress as well.

It has not been possible to study all variables and factors. The most obvious and important have therefore been selected and highlighted in Table 2 with bold text.

TABLE 2: WOOD BONDING VARIABLES AFTER FRIHART (2013), EXAMINATED VARIABLES ARE HIGHLIGHTED WITH BOLD TEXT.

Resin	Wood	Process	Service
Type	Species	Adhesive amount	Strength
Viscosity	Density	Adhesive distribution	Shear modulus
Molecular weight distribution	Moisture content	Relative humidity	Swell-shrink resistance
Mole ratio of reactants	Plane of cut: radial, tangential, transverse, mix	Temperature	Creepuf
Cure rate	Heartwood vs. sapwood	Open assembly time	Percentage of wood failure
Total solids	Juvenile vs. mature wood	Closed assembly time	**Failure type**
Catalyst	Earlywood vs. latewood	Pressure	Dry vs. wet
Mixing	Reaction wood	**Adhesive penetration**	Modulus of elasticity
Tack	Grain angle	Gas-through	Temperature
Filler	Porosity	Press time	Hydrolysis resistance
Solvent system	Surface roughness	Pre-treatments	Heat resistance
Age	Drying damage	Post-treatments	Biological resistance: fungi, bacteria, insects, marine organisms
pH	Machining damage	Adherend temperature	Finishing
Buffering	Dirt, contaminants		Ultraviolet resistance
	Extractives		
	pH		
	Buffer capacity		
	Chemical surface		
	Treatment (modification)		
	Distance from surface		

The same type of resin has been used in all the experiments and the variables within the MUF have been kept constant as far as possible. The viscosity of the mixed adhesive is depending on the glue-hardener ratio and time after mixing.

2. OBJECTIVE

2.1. MAIN PURPOSE

Increase the understanding of the interaction between MUF adhesive and acetylated wood. This understanding should be used to optimize the gluing of acetylated wood.

2.2. RESEARCH QUESTIONS

1. How does MUF perform on an acetylated wood surface during the curing process, compared to untreated wood?
2. How does MUF penetrate acetylated wood in comparison to untreated reference samples?
3. What influence can the wood pH and buffer capacity have on the hardening and polymerization processes of MUF properties afterwards?
4. How does the properties – here pH, buffer capacity and contact angle – of acetylated wood affect the bonding with MUF, in comparison with untreated wood.

2.3. APPROACH

An experimental approach has been used to obtain the objective and answer the research questions. Rheology measurements, microscopic analysis of penetration, contact angle measurement, determination of pH and buffer capacity of wood extractions have been used.

3. METHOD DEVELOPMENT

A great effort has been put into the development of reliable methods for some of the experiments. Method development was performed prior to the main part of the study and the final methods can be found in 4. Materials and methods. Only a few related studies were found. Experience gained from these studies was therefore used to select methods.

Rheology testing seemed to be an appropriate method, at least as a screening test. Microscopy should be able to help to analyse penetration of glue. pH and buffer capacity will influence curing and give important information on the further development of a new adhesive system.

When wood is acetylated, its properties will change (see 1.2. Acetylation). Planing to smooth surfaces of acetylated wood proved to be difficult compared to untreated surfaces. Problems arose similar to those which occur when the chip-angle is too big, the thickness of the chips is too big or if the wood is hard and brittle. Several things were tried out to overcome this problem including the use of new knives. The problem was reduced significantly when reducing maximum 0.5 mm in the plane every time and only 0.2 mm for the last five times before the final thickness.

3.1. RHEOLOGY PRE-TEST

"*Rheology is the science of deformation and flow of matter*" (Frihart 2013).

Rheology measurement of adhesives directly on wood surface with an oscillating plate is a relatively new method and not much experience exists in this field (Schmidt et al. 2010; Witt 2004).

The literature describes generally two ways to test the rheology of a curing adhesive on wood. One with the adhesive between two wooden surfaces where the upper part is oscillating (Schmidt et al. 2010). Another method is with the adhesive between a wooden surface and a metal surface (Kariz et al. 2013; Witt 2004). The most accurate way to measure the complex viscosity of the adhesive was found to be with metal-wood surface, because of the heterogeneous wood surface. It must be assumed that the surface variations will be bigger with a wood-wood surface compared to wood-metal surface. Furthermore, there already exist some experience in the metal-wood method and an almost complete developed method at Dynea AS, where the experiments of this study were carried out.

3.1.1.   SAMPLE PREPARATION FOR RHEOLOGY

50 cm from each of the ten selected planks (see 4.1. Material preparation and selection) were cut off and split tangentially in the longitudinal direction (see Figure 5). The bark side half was then planed from the pit side until a smooth surface was achieved. The test piece was then glued in the corners with EPI on top of a longer spruce plank, with the newly planed pit side facing the spruce. This made it possible to plane the plank down to the desired thickness from the bark side towards what was the core of the original plank. Still glued in the corners to the spruce board, a wood disc was cut out with a 60 mm (2-3/8") hole-saw (/core drill) from the "plank" (now veneer) (see Figure 4).
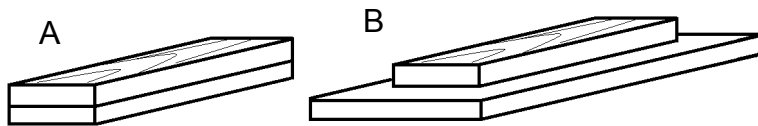

FIGURE 4: FRESHLY PLANED AND CUT ACETYLATED DISCS PREPARED FOR RHEOLOGY TESTING

FIGURE 5: A) SPLITTING OF THE 50 CM PLANK, B) GLUING THE HALF TOWARDS THE BARK FROM A WITH EPI ON A BIGGER SPRUCE PLANK.

The first samples in the pre-tests were stored in a climate room at 65 % RH and 20 °C for several weeks before testing. In the final method the tests were made on freshly planed discs (max 10h after planing).

To get the test samples to fit the Peltier Heated Basis Plate on the rheometer, a diameter as close as possible to 57 mm was necessary. For this purpose the special diameter in hole-saws 60 mm was ideal, because it makes wooden discs with a diameter of 56.8 mm. When cutting wooden discs with a hole-saw, one must remove the frayed edges afterwards with a knife.

3.1.2. EXPERIENCES FROM RHEOLOGY PRE-TESTS

The original metal holder to fixate the wooden discs to the rheometer, was found to have some weaknesses and was replaced by a modified holder printed in plastic on a 3D printer (see Figure 6). An advantage with the 3D-printed holder is also that it can fixate discs cut with a 57 mm hole-saw which is more common.

In the first tests with a glue/hardener concentration of 100:100 pbw huge differences between the samples from the same board were noted and reproducible results were difficult to achieve. It became clear that the time that the samples had been outside the climate room, prior to rheology measurements, accounted for a
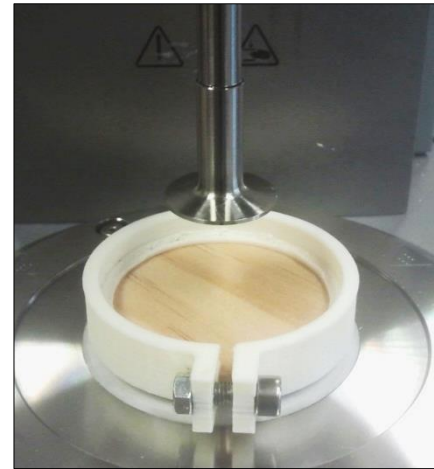
FIGURE 6: 3D PRINTED HOLDER TO FIXATE THE WOOD DISCS ON THE RHEOMETER

lot of the variation within the sample group. The procedure had been that a handful of discs were taken out of the climate room at the beginning of the day and used continuously over the next couples of hours. Therefore, the procedure was changed so the wooden discs would be outside the climate room for a maximum of 10 minutes before applying the adhesive and starting the measurement of the viscosity. To further reduce changing moisture content, the wood discs were carried in a sealed plastic bag from the climate room to the laboratory. The exposure to a different moisture-content was thus reduced to the time of fixing the plate in the rheometer and mixing the glue and hardener (maximum 10 min). To minimise the effect of the temperature difference between the laboratory and climate room (approx. 3-4 °C higher in the laboratory) the Peltier Temperature Device: Truly Peltier Heated Hood was applied on the rheometer. The first tests were only done with the Peltier Heated Basis Plate. The chosen temperature was 20 °C which corresponds to the temperature in the climate room (20 ± 2 °C / 65 ± 3 % RH) and a widely used temperature in test standards (Kucera 1992) and the minimum temperature recommended in practical application (Dynea 2014). After minimising some of the variables the results became more reproducible.

To further reduce variation within the viscosity measurement and make the tests more realistic in relation to the demands of a production line, the aging of the surface became the focus. Since the surfaces are changing with time after planing (Hass 2012; Nussbaum 2001), and adhesive application on newly planed surfaces are desired (Dynea 2014; Hass 2012; Ross 2010), the planing

procedure was changed. The test board was first planed down to 3 mm and test discs were cut out in one half of the 3 mm board. Later, the rest of the test board would be planed down to 1.5 mm and discs cut out from there. Using thinner discs would make it possible to make more tests from the same board with freshly planed surfaces. In this way all tests were able started within a maximum of 9 hours from planing.

The observations made in the method development and pre-test on contact angle measurement on acetylated wood led to a change of the disc thickness from a 1.5 mm to only using 3 mm thickness. The reason to this was the risk of water or adhesive penetrating through the disc (more about this in 3.2.1. Experiences from contact angle pre-tests).

The use of Ø25 mm spindler with a gap of 0.2 mm corresponds to an amount of 0.15 ml adhesive. If the applied amount of adhesive is too small, the area under the spindler will not be completely covered and unreliable results occur. Previous experiences made by Dynea AS showed no influence on results with a little extra adhesive (Viljugrein 2015). If using 0.15 ml adhesive under the spindler the placement must be very accurate in the middle of the wood disc (within 2-3 mm). Because of this, the amount of adhesive was increased to 0.2 ml.

The excess adhesive pressed out under the spindler will be in contact with the air. This can disturb the measurement since it creates a skin formation. To avoid this, oil was applied on the edge to the spindler and on top of the excess adhesive (see Figure 18 page 31). The pre-test showed that the viscosity of the oil was important. Two different oils were tried, one with a viscosity of approximately 100 mPa·s at 20 °C and another at approximately 1000 mPa·s at 20 °C. The viscosity of the first one seemed to be too low, since the measured viscosity of the adhesive would suddenly increase radically when using this oil (see Figure 7). This is probably because the oil runs off the adhesive and, as a result, creates the adhesive skin, which increases the resistance in the oscillation of the spindler. With the oil of an approximately viscosity of 1000 mPa·s at 20 °C, no suddenly increase in viscosity of adhesive was observed (see Figure 7).

Most of the pre-tests were run until the adhesive reached a viscosity of at least 10.000 mPa·s or 50 minutes, but about 10 minutes inexplicable variations started to occur, perhaps because of the reasons mentioned above. Depending on the amount of hardener, a viscosity of 10.000 mPa·s could take several hours to achieve. In the first 10 minutes a difference in the slope seemed to occur between the acetylated wood and the untreated wood. Based on this observation and the theory that

a reaction is created immediately when the adhesive is applied the test time was reduced to be between 7 and 10 minutes.
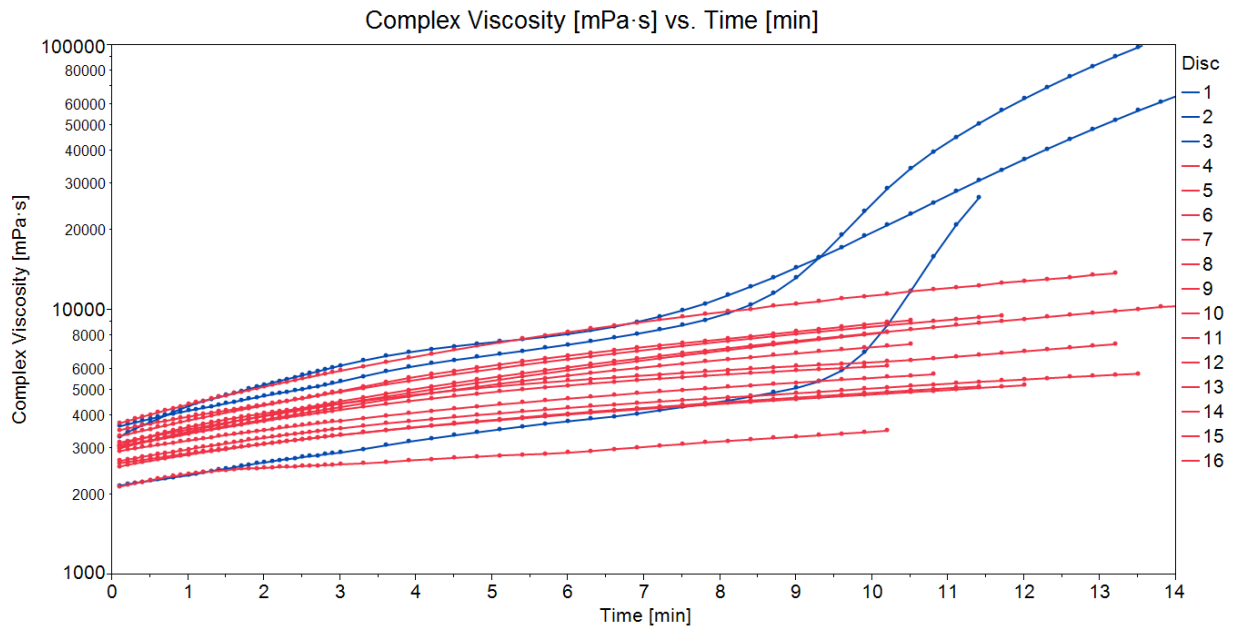
FIGURE 7: COMPLEX VISCOSITY DEVELOPMENT OVER TIME, EACH LINE REPRESENTING A DISC. BLUE LINES HAD THE EXCESS ADHESIVE COVERED WITH LOW VISCOSITY OIL AND RED LINES COVERED WITH HIGH VISCOSITY OIL, ALL DISCS ARE FROM SAME PLANK.

3.2. CONTACT ANGLE PRE-TEST

The reliability of contact angle measurements on wood is influenced by the great heterogeneity of the wood surface. Factors such as extractives, annual rings with changing density and swelling behaviour, roughness, time after planing and fibre direction can and will affect the measurement (Frihart 2013; Nussbaum 2001; Wålinder 2000). Wålinder (2000) gives more or less direct advice against the use of contact angle measurement with the droplet method on wood because of the high uncertainty, but this count especially when the aim is to find the surface energy. The aim here is to see if there exists a difference between acetylated and untreated wood and whether this might contribute to a better understanding of the problem. Due to this, and the lack of better equipment to measure contact angle on a wood surface, the droplet method was used.

A better method would be the Wilhelmy method where a wooden test piece is immersed vertically into a liquid (eg. Water) and the measured contact angle are influenced by several annual rings when withdrawn from the liquid. Several other methods for surface energy measurement exist as well (Wålinder 2000), but require other equipment.

3.2.1. EXPERIENCES FROM CONTACT ANGLE PRE-TESTS

The first pre-tests were made on 1.5 mm wooden discs identically to the first discs used in the rheometer pre-test. The result of this was a fast but continuous lowering of the (apparent[1]) contact angle on untreated wood. With the acetylated wood another phenomenon occurred, where the droplet was almost steady on the surface with only a slow lowering of the contact angle. Whether the lowering of the angle was due to evaporation, penetration or a combination is unknown. After around one minute or two on the acetylated surface the droplet just disappeared into the wood within a second. The 1.5 mm wood disc was placed on top of a stack of microscope glasses to get it at the right height. After the sudden disappearance of the droplet, it was observed that the water had penetrated all the way through the wooden disc and most of the water was located below the wooden disc on the glass. An explanation could be that the water had found e.g. a ray channel and capillary forces, maybe together with a small vacuum between the wood and glass, had sucked the water away from the wood's surface. This observation resulted in a change in the rheology method to thicker (3 mm) discs instead of 1.5 mm and to use 1-2 cm thick bars for the contact angle

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[1] See 4.3. Contact angle, for description of apparent contact angle vs. contact angle.

measurement instead. The bars were made from the full width of the plank and approximately 4 drops were placed for each 3 cm in width. The thought behind this was that with many droplets the frequency of droplets on early- and latewood would represent the area and distribution of early- and latewood. This applies as well to the direction of the annual rings. This way the full variation of a plank surface will be represented, which also corresponds to the surface on which the adhesive in the industry is applied.

Early and latewood can have an effect on the contact angle due the differences in the properties such as the density and swelling/shrinkage (Wålinder 2000).

Right after landing the droplets are very unstable and a lot of movement happens on the surface simultaneous with the natural spreading caused by gravity (see Figure 8 and Figure 9). This means that the first measurements are very unstable and not reliable. On untreated wood the penetration into the wood and spreading on the surface starts very quickly. A more or less stable period between measurement 7 (ca. 0.22 sec.) and measurement 15 (ca. 0.49 sec.) seems to exists (see the curly brackets in Figure 8 and Figure 9). The average contact angle in this interval was determined to represent the contact angle for the specific droplet. Another reason for this is that there, in this way, would come the same amount of measurements (9 units) for each droplet, since the start time for the first measurement is slightly different every time. The mean angle between the left and right sides of a droplet have been used since the information from contact angle hysteresis has been considered as less relevant in this case.
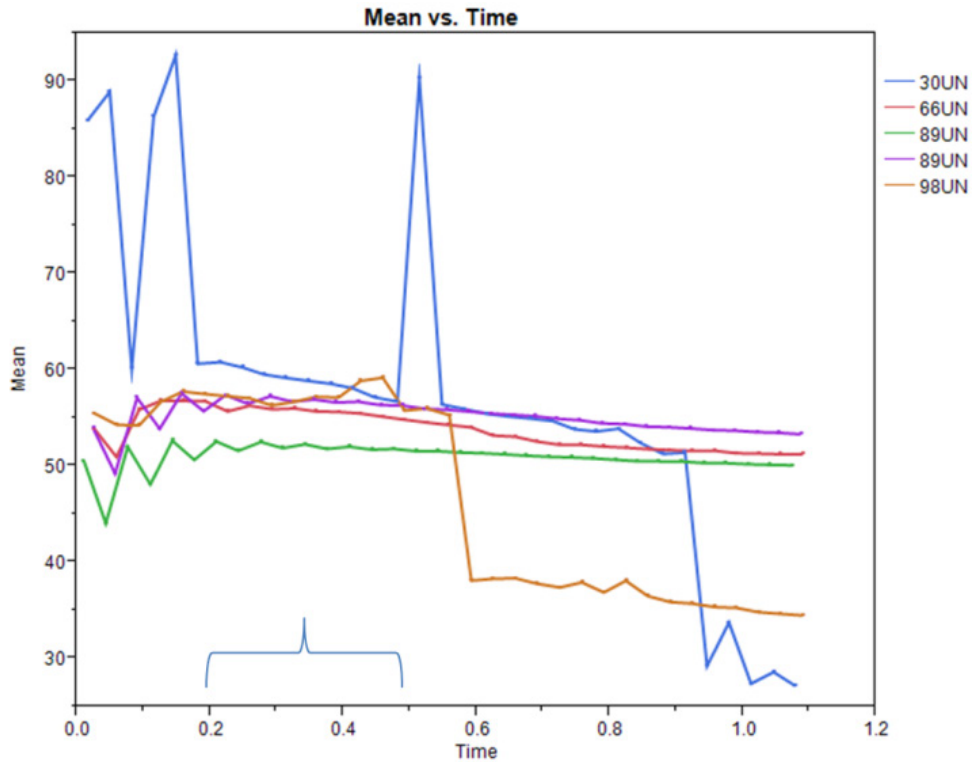
FIGURE 8: 5 RANDOM DROPS ON UNTREATED WOOD SHOWING THE MEAN APPARENT CONTACT ANGLE FROM THE LEFT AND RIGHT SIDE OF THE DROPLET AFTER LANDING ON THE WOOD SURFACE (TIME IN SEC.). "STABLE" PERIOD SHOWN WITH A CURLY BRACKET.
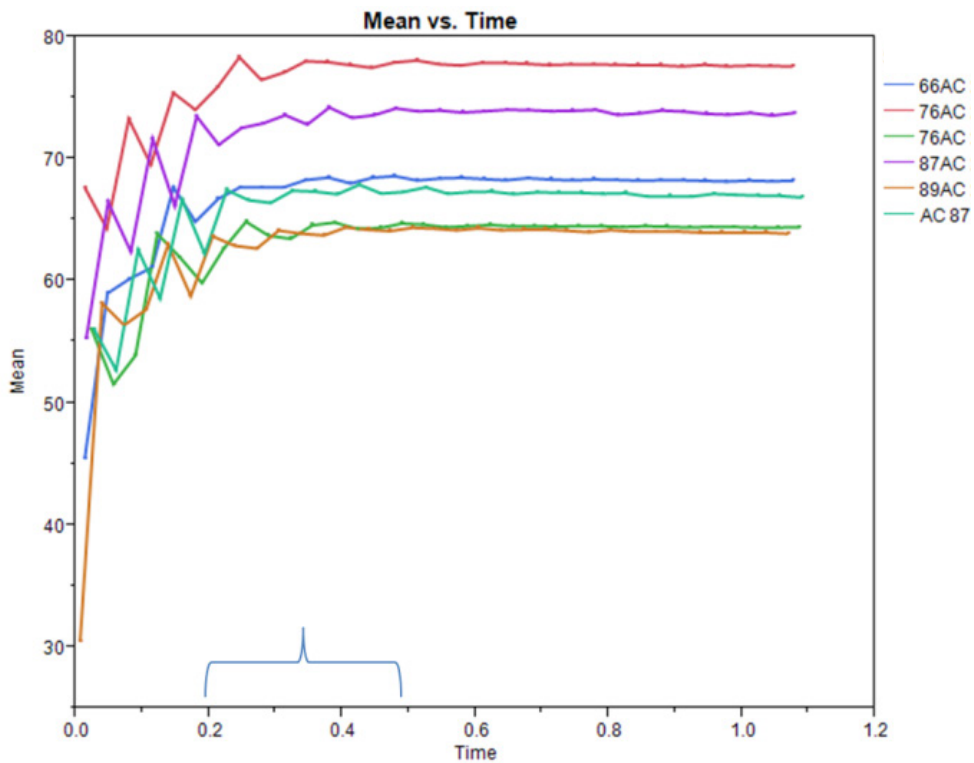

FIGURE 9: 6 RANDOM DROPS ON ACETYLATED WOOD SHOWING THE MEAN APPARENT CONTACT ANGLE FROM THE LEFT AND RIGHT SIDE OF THE DROPLET AFTER LANDING ON THE WOOD SURFACE (TIME IN SEC.). "STABLE" PERIOD SHOWN WITH A CURLY BRACKET.

4. MATERIALS AND METHODS

4.1. MATERIAL PREPARATION AND SELECTION

Wood is a heterogeneous material and natural variation within a wood trunk will occur (Hernandez 2013; Kollmann & Côté 1968). These variations will both be in the longitudinal and radial direction. The variations within a tree trunk will not only be due to the location in the trunk but also to the growth conditions (soil, altitude, temperature, light exposure, water, stress and completion, etc.) (Hernandez 2013; Høibø et al. 2013; Shmulsky & Jones 2011). The natural variations in the properties can affect the acetylation and bonding properties (Bongers 2015; Hass 2012).
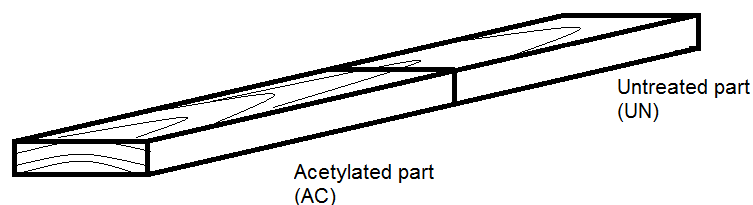

FIGURE 10: THE ORIGINAL UNTREATED (UN) PLANK BEFORE IT IS CUT IN HALF AND ONE HALF IS ACETYLATED (AC).

To minimise the variations within the groups of acetylated wood and the untreated reference wood, 4.2 meters pre-sorted planks in dimensions 38 x 200 mm were cut in half (lengthwise) and numbered (paired lengthwise) (see Figure 10). In total, 2 pallets with 80 lengthwise paired planks were delivered from Accsys Technologies in Arnhem, where one of the pallets was acetylated (batch 3298). The other pallet contained the untreated half of the original plank. From the untreated pallet 10 planks were chosen for the experiments, with different location in the pallet (see Figure 11, marked with green). From the pallet with the acetylated planks the corresponding other 10 half planks were chosen (same numbers).

30	29	28	27	26
35	34	33	32	31
40	39	38	37	36
45	44	43	42	41
50	49	48	47	46
55	54	53	52	51
60	59	58	57	56
65	64	63	62	61
70	69	68	67	66
75	74	73	72	71
80	79	78	77	76
85	84	83	82	81
90	89	88	87	86
95	94	93	92	91
100	99	98	97	96
105	104	103	102	101

FIGURE 11: LOCATION OF THE RECEIVED PLANKS AND THE 10 SELECTED PLANKS MARKED WITH GREEN.
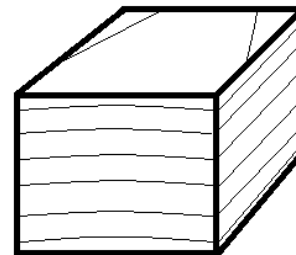

FIGURE 12: THE DIRECTION OF THE ANNUAL RINGS IN MANY TEST PIECES FOR STANDARD TESTS.

Straight-gained knotless wood can be viewed as an orthotropic material with three directions axial, radial and circumferential. In many standard tests, samples must be taken from the centre of a flat sawn plank with parallel annual rings (Kucera 1992). In small samples, the circumferential direction (annual ring) straightens and is then described as the tangential direction (see Figure 12).

It is not possible in an industrial and economic perspective to have the annual rings parallel and perpendicular to the cut surface. The angle between the annual rings and the sides of the plank will therefore differ. The wood used and received from Accsys Technologies is pure sapwood, knot free and contain planks cut tangentially to the core. An adhesive system must work regardless of the fibre and annual ring direction. Therefore, the annual ring and fibre direction in preparation of the test samples were not taken into account. Instead, it was attempted to reflect the natural variation of the surface on a flatsawn plank in the samples. This means that the tested surface area reflects the variation of the surface area where an adhesive in the industry would be applied.

Prefere 4546/5022 from Dynea AS explained in 1.4.1. The selection of MUF as the adhesive system was used in the ratio 100:20 pbw for all experiment if not anything else is mentioned.

4.2. DELAMINATION TEST

A single delamination test was carried out according to the standard EN 302-2:2013, mainly to verify the insufficient bonding of acetylated wood with MUF Prefere 4546/5022 100:20 pbw.

4.2.1. PURPOSE

The standard EN 302-2:2013 is a method for determining the resistance to delamination in the bond line for glued load-bearing timber structures. The principle is to stress test with water impregnation under high pressure and vacuum followed by fast drying in low humidity conditions. Similar stress tests exist in Japan (Japanese Agricultural Standard for Glued Laminated Timber) and American where ASTM D 2559 or ASTM International 2011b is applied. Conversely, what differentiates EN302-2 (2013) from other bond strength tests is that no external force is applied (Frihart 2013). The problems with applying external force in testing is pointed out by Steiger et al. (2010). Results from shear tests of bond lines in the control of glulam were influenced by the test equipment and the way the test specimen is supported (Steiger et al. 2010). When no external force is applied in testing and it's only swelling and shrinking which creates the internal stresses the issued pointed out by Steiger et al. (2010) is irrelevant.

4.2.2. METHOD

The resistance to delamination was performed according to the standard NS-EN 302-2:2013 Adhesives for load-bearing timber structures – Test methods – Part 2: Determination of resistance to delamination.

The planks number 39 and 89 were used in the test and laid up alternately with three lamellas from each and the annual rings in the same direction. This was done for both the acetylated and untreated part of the planks. The two laminated members (acetylated and untreated) were made under the same conditions, pressed at the same time in the same press, exposed to pressure in the same vessel at the same time as well dried in the same chamber and placed in a way that they wouldn't affect each other (across the air stream).

According to EN302-2 (2013) delamination should be expressed in percent rounded off to nearest 0.1% points and calculated for each test piece. The percentages are calculated with Equation 1.

EQUATION 1

$$D = \frac{l_1}{l_2} \cdot 100$$

D: Delamination in percent

l_1: The total delamination length on both end-grain surfaces in millimetres

l_2: The total nominal length of the glue lines on both end-grain surfaces after trimming, in millimetres.

4.3. CONTACT ANGLE

The properties of a wooden surface are highly important for the glueability. A surface can be described by several factors such as hardness, surface roughness, heterogeneity and apparent contact angle, among others (Wålinder 2000). The term "apparent contact angle" is used by Wålinder (2000) because the surface of wood is heterogeneous and never completely smooth, which is the criteria in the definition of "contact angle". Because only wood is used as surface in this case the term "contact angle" will be used, but it must be understood as the "apparent contact angle". The contact angle is the angle between the edge of a droplet on a surface and the surface itself, measured inside the liquid phase (see Figure 14) (Nussbaum 2001). The contact angle depends in this way both upon the surface and the polarity of the liquid (Wålinder 2000).

4.3.1. MATERIAL

The measurements are made on a ramé-hart Model 100-00-115, with a FOculus IEEE1394 Digital Camera and the program DROPimage Advanced Version 2.4.0. The droplets were generated with ramé-hart, inc. Auto Pipetting System (see Figure 13). A 15 µm hanging droplet of ion changed water was used in control and calibration of the surface tension together with a calibration sphere. The actual contact angle measurement was made with an 18 µL ion changed water droplet.

- Freshly planed wooden bars from the full width of a plank, 1-2 cm thick and approximately 1.5 cm width (in the longitudinal direction) (see E in Figure 13).
- Ramé-hart Goniometer and Tensiometer Model 100-00-115
- Ramé-hart Automated Dispensing System
- Digital camera – FOculus IEEE1394
- DROPimage Software
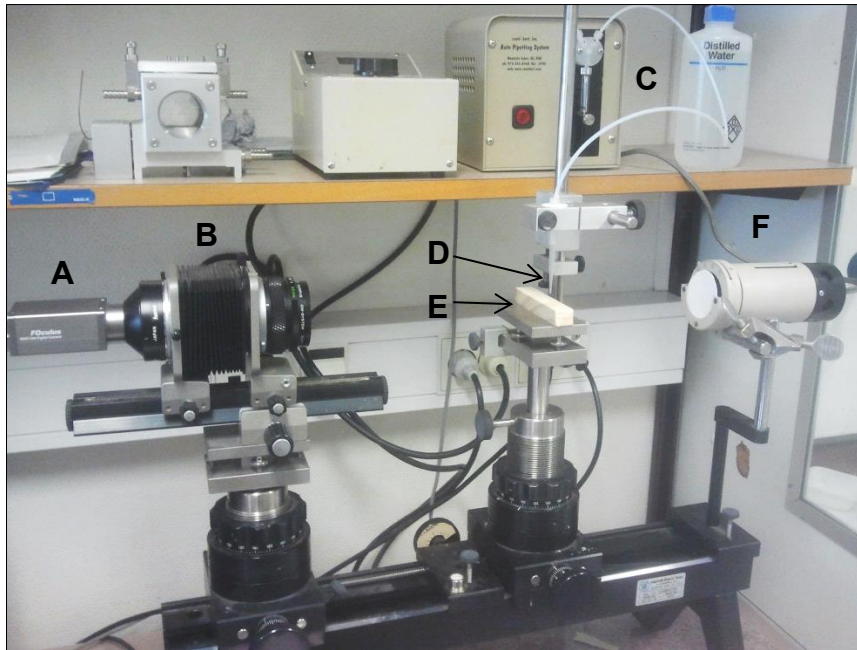
FIGURE 13: EXPERIMENT SETUP FOR CONTACT ANGLE MEASUREMENTS. BOX TO EXCLUDE DISRUPTIVE LIGHT MUST BE PUT OVER BEFORE MEASURING. A) DIGITAL CAMERA, B) CAMERA LENS, C) AUTOMATED DISPENSING SYSTEM WITH WATER, D) PIPETTE, E) PIECE OF WOODEN BAR, F) LIGHT SOURCE.

4.3.2.   METHOD

The software was programmed to measure an equidistant time making 33 measurements, with 0 sec. of delay and interval of 0.02 sec. These demands are too extreme for the set-up (camera, computer or software was to slow), but results in 33 measurements in just above one second and with a delay time of approximately 0.03 sec.

For more accurate measurements a trigger was used to start the measurements, its intensity was set to 100 and the offset to 20 (from the wooden surface).

In the Drop Volume Control the droplet was set to a Volume step on 18 µL and the full stroke time to 4.0 sec.

All the measurements were carried out on freshly planed surfaces (maximum 8 hours old) and on wood which had been stored for minimum two month in a climate room at 20 ± 2 °C and 65 ± 3 % RH. The temperature in the testing room was between 24 and 26 °C and the wood bars were stored in a plastic bag until start of the measurement. Time outside the climate room was reduced to a minimum to avoid unnecessary changes in temperature and MC.

The interpretation of the droplet was made along the grain, the profile of the interpreted picture was therefore taken from a cross sectional view of the underlying wood (see Figure 13 and Figure 14).

When the droplet hit the wood surface the measurements started. Directly after landing the droplet was very unstable. After around 0.2 seconds the drop stabilised and after 0.5 seconds a steady decrease in the contact angle was observed (see 3.2.1. Experiences from contact angle pre-tests, Figure 8 and Figure 9).

Besides the left and right angle of the droplet, the height, width, area and volume were measured/calculated, but only the mean angle between the left and right sides are used. If one or several measurements in the tests went wrong or if an angle has outliers above 90 degrees between 0.2 seconds and 0.5 seconds, the whole test was omitted. Tests mainly failed because the software DropImage was unable to make a correct interpretation of the picture.
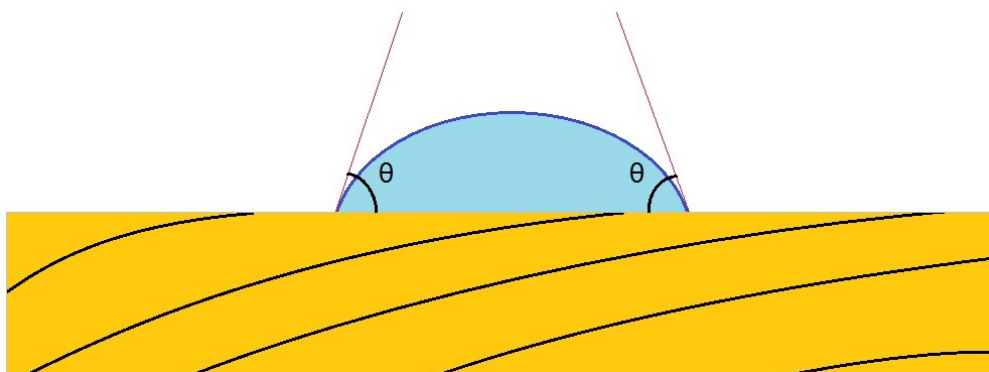
FIGURE 14: ILLUSTRATION OF A DROPLET'S CONTACT ANGLE (Θ) ON A WOODEN SURFACE

DropImage generates results for each measurement (droplet) in a LOG file with the time, contact angle, volume, etc. these results were imported and named to JMP with a script.

To get the same amount of readings from each drop the interval for the measurement point [7;15] was used instead of a time interval. This is due to a slight variation in start time for first reading which affected the following ones on the drop. In this way, an average of the mean contact angle for the left and right side were made for 9 readings (number 7, 8, 9, 10, 11, 12, 13, 14 and 15). Those 9 reading correspond very well to the time interval [0.2 ; 0.5] seconds.

On average, 4 drops were placed for each 3 cm across the width of a plank. The results are based on measurements of 731 droplets, if nothing else is mentioned. 513 of the droplets are on acetylated wood and 218 are on untreated wood.

4.4. pH AND BUFFER CAPACITY

Several studies have made buffer capacity and pH measurements on wood, but an official standard method was not found and there are only minor differences between many of the methods in the literature (Hernandez 2013; Ormstad 2007; Passialis et al. 2008; Schmidt et al. 2012; Sithole 2005; Xing et al. 2004). Based on the results from especially Sithole (2005) and Hernandez (2013) the following method was developed. The pH from a wood extraction is measured and the buffer capacity is identified by titration.

4.4.1. SAMPLE PREPARATION

3.5 cm long cross section slices were cut from 8 planks, which were stored for over a month at 20 ±2 °C and 65 ± 3 % RH. No surface preparation was done. The first 5-6 mm from the surface was cut off on all sides (except for the two cross section sides, which were freshly cut). In this way, four saw cuts of 3 mm were removed and not included in the test (see Figure 15). The separated outer part (O) and core (C) were then broken into small chips with a chisel.
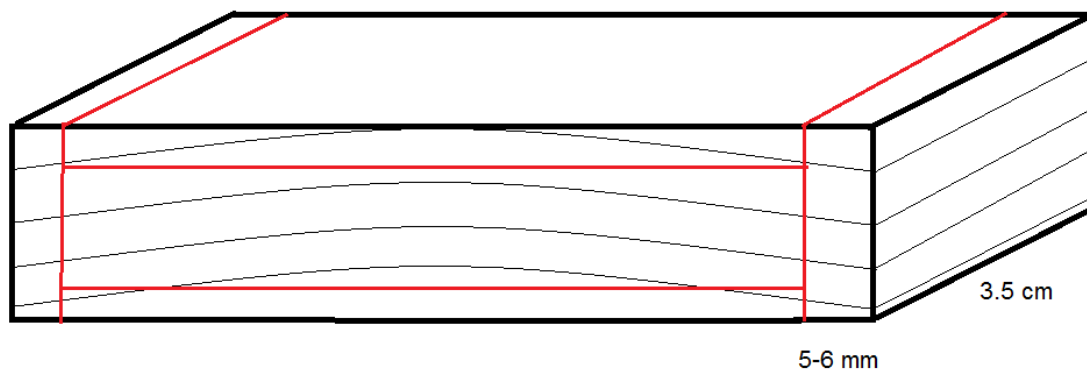

FIGURE 15: ILLUSTRATION OF A 3.5 CM PLANK PIECE, WITH RED LINES SHOWING CUTS FOR SEPARATING THE OUTER PART (5-6 MM) AND CORE OF THE PLANK, BEFORE PH AND BUFFER CAPACITY TEST.

Hence, 4 samples were taken for each plank. Two samples from the acetylated part and two from the untreated part, each part divided into a surface (O) sample and core (C) sample.

4.4.2. MATERIAL

- pH-meter: ORION model 420A
- Electrode: Thermo Scientific, Orion 8172BNWP, ROSS Sure-Flow Combination pH
- Ion changed water

- Hotplate

- Erlenmeyer flasks and beakers

- Magnetic stirrer

- Burette (10 mL)

- 0.025 M HCl and 0.025 M NaOH

- Wood chips from 8 planks (30, 76, 66, 57, 48, 98, 87, 80)

4.4.3.   METHOD

12.5 grams of chips boiled in an Erlenmeyer flask together with 250 mL of ion changed water (0.05 g wood / mL).

Samples from one plank (4 beakers), were boiled for 20 minutes.

Water incl. the wood was then stored for 24 hours before the wood was removed.

Titration was done manually with the same pH electrode for all measurements and calibrated with regular intervals.

60 mL of the water dissolved extractives from the wood (extractives from 3g wood per 60 mL solution) was used for each titration.

For the acid part 0.025 M HCl was used and for the alkaline part it was 0.025 M NaOH.

Before each titration the pH was measured, which means that each of the 32 solutions had their pH measured twice.
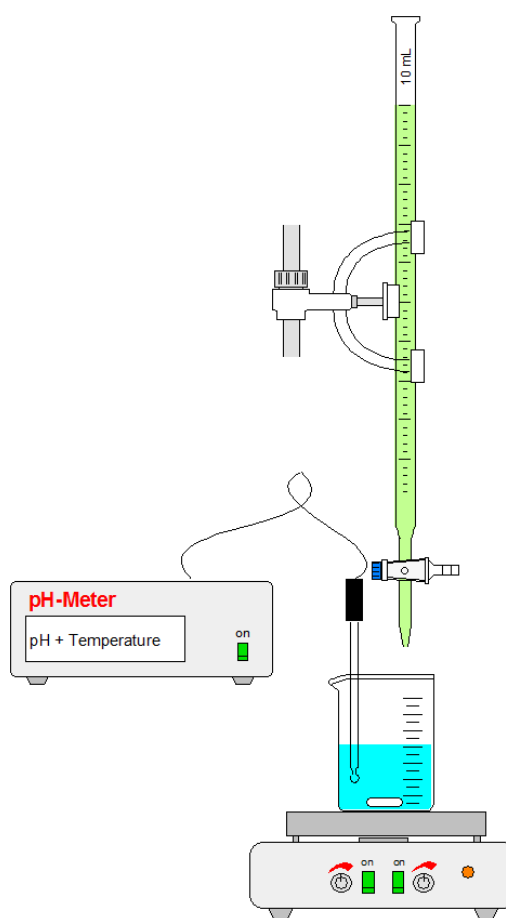
FIGURE 16: SETUP FOR TITRATION TO FIND BUFFER CAPACITY, CONSISTING OF BURETTE, MAGNETIC STIRRER, PH-METER AND BEAKER CONTAINING THE TEST SOLUTION.

4.5. RHEOLOGY

The purpose of using rheology measurements is to analyse how the complex viscosity changes after applying the adhesive (a mixture of the glue and hardener) on a wood surface. If free acid in the acetylated wood makes the curing faster, compared to the untreated wood, it will change the viscosity. It should in theory be possible to measure the difference with a small gap between the oscillating spindler and the wood surfaces.

4.5.1. MATERIAL

Measurements were made on the Anton Paar Rheometer MCR 302, using the software RHEOPLUS32 V6.22. The oscillating spindler was with a Ø25 mm plate and the same spindler was used on all the measurements (see Figure 17 and Figure 18).

- Wooden disc; 3 mm thick, with Ø 56.8 mm from the core of a plank, acclimatized and freshly planed (see 3.1.1. Sample preparation, for full description of the sample preparation)
- Holder for the wooden discs
- Glue and hardener: Prefere 4546/5022
- Weight within ±0.05 gram
- Mixer cup and stir bar
- Syringe 1.0 mL
- Rheometer: Anton Paar Rheometer MCR 302
- Software: RHEOPLUS32 V6.22
- Spindler: PP25 (diameter 25 mm)
- Anton Paar Truly Peltier Heated Hood device.
- Oil with an approximately viscosity of 1000 mPa·s at 20 °C

In the experiment focus was paid to the MUF Prefere 4546/5022 glue-hardener ratio 100:20, since this ratio is less reactive. The slower curing should make it easier to measure differences between acetylated and untreated wood.

4.5.2. METHOD

The steps in the method:

1. Preparation of the freshly planed wood discs (see 3.1.1. Sample preparation for rheology, for full description).

2. Placing and fixing the wooden discs in the rheometer (see Figure 17 and Figure 18).

3. Mixing the adhesive

4. Applying the 0.2 mL adhesive and oil to avoid skin

5. Start the measurement

     a. The measurement plant consisted of two intervals:

         i. Interval 1:

30 measurements, one every 0.1 minute, total duration 3 minutes

0.3 % oscillation (γ), 10 times every second (ω)

         ii. 100 measurements, one every 0.3 minute, total duration time 30 minutes

0.1 % oscillation (γ), 10 times every second (ω)

The last interval was stopped manually after 7-10 minutes.

6. Note the glue/hardener amount, the plank number, the treatment (AC or UN) and the disc/test number on the surface of the discs.

To make all the measurements as identical as possible, the following timeline in minutes was followed as closely as possible, when measuring the complex viscosity using the rheometer:

00:00   Transport of climatized sample to the measurement device (rheometer)

02:00   Disc-sample placed/fixed in rheometer and covered with the Truly Peltier Heated Hood at 20 °C

02:30   Zero-gap measurement between disc-sample and spindler

03:00   Weighing of the glue and hardener.

04:30   Stirring the adhesive for precisely one minute (timer on)

05:30   Using a 1 ml syringe to take out adhesive for precise application

06:00   Applying 0.2 ml adhesive in the centre of the wood disc directly under the spindler.

06:15   Lowering the spindler to the measurement position; 0.2 mm above the wood surface.

07:00   Adding oil on the glue edge and lowering the Truly Peltier Heated Hood

07:30   Write test name, number and starting measurement in RheoPlus software
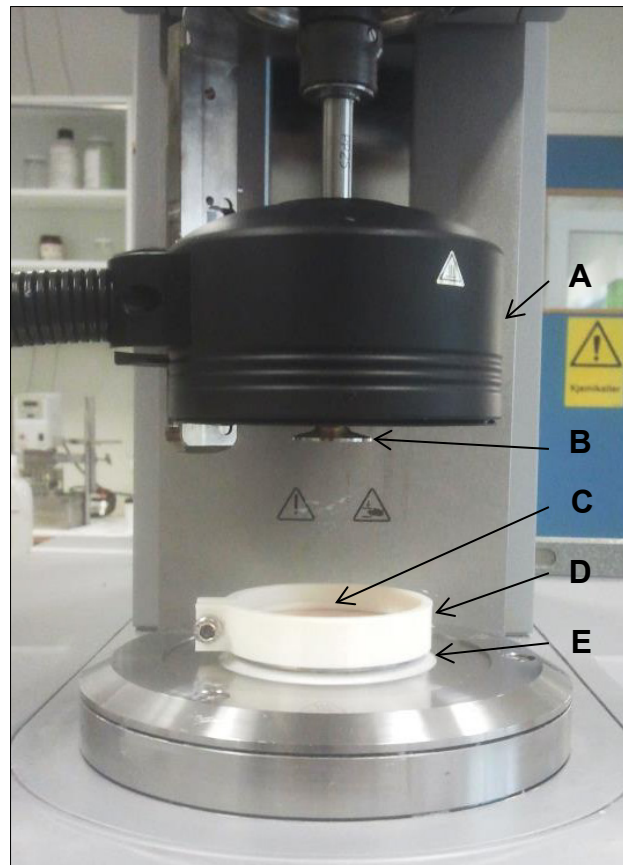
FIGURE 17: A) ANTON PAAR TRULY PELTIER HEATED HOOD DEVICE, B) SPINDLER 25 MM, C) FIXED WOOD DISC, D) HOLDER, E) TEMPERATURE PLATE.
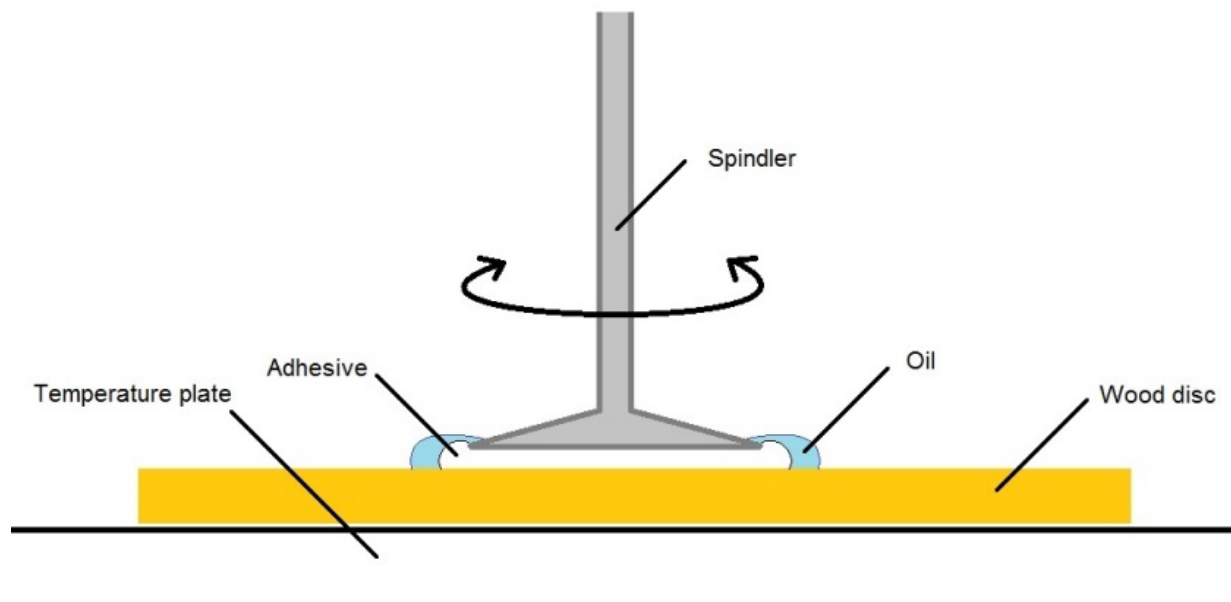

FIGURE 18: RHEOMETER MEASURING SETUP FOR MEASURING COMPLEX VISCOSITY ON A 3 MM THICK WOOD DISC. HEATED HOOD DEVICE AND HOLDER TO FIX THE WOOD DISCS ARE NOT SHOWN SEE FIGURE 18 A) & D)

The complex viscosity curves have been smoothed because the rheometer is very sensitive. A disturbance, for example, a small shock on the table or the instrument itself, will create an outlier from the curve, which can be minimised by smoothing.

Smoothing of the curves was performed with the analysis tool of the Rheoplus program. The following settings were used;

Method → Smoothing → Parameters:

- X-variable: Time
- Y-variables: Complex Viscosity
- Smoothing Type: Automatic smoothing
- Interpolation of X- and Y-Values: Use X-Values of Input Data, Y-Values are smoothened.

Input data: Complete Data Series

The data was after smoothing imported to excel, where each time measurement was named with help form a macro and then imported to JMP® Pro 10.0.0 for analysis.

The following formulation was used for the slope calculation:

EQUATION 2

$$slope = \frac{\log(y_2) - \log(y_1)}{x_2 - x_1}$$

Where y_2 is the complex viscosity after 3 minutes (= x_2) and y_1 is the complex viscosity at time 0.1 min (= x_1).

4.6. MICROSCOPY ANALYSIS

The glue lines were first investigated under a stereoscope without any good results in determining differences in penetration between the acetylated wood and the untreated. Better results were gained using a fluorescence microscope where the MUF adhesive lighted up.

4.6.1.   MATERIAL

- Sliding microtome
- Safranin
- Astra blue
- Pertex®, Histolab products AB
- Leica DMR fluorescence microscope with Leica DFC425 digital camera
- Zeiss SteREO Discovery. V20 with Zeiss PlanApo S 1.0x FWD 60mm lens and Zeiss AxioCam MRc5 digital camera.

4.6.2.   METHOD

The glue line and penetration were observed from the cross-section. Before cutting the thin sections the wood samples were boiled in water so they were fully soaked, in order to soften the samples and make it possible to make slides from the acetylated wood. Due to the acetylation it was not possible to cut the slices as thin as with untreated wood. The observed sections were cut with a thickness between 30-60 μm for the acetylated wood and 15-30 μm for the untreated wood. All the sections were stained with safranin and astra blue for getting a stronger contrast between the light glue line and wood. The acetylated wood had difficulty taking up colour, and was much less coloured than the untreated wood. The thin sections were glued on glass slides with Pertex from Histolab products AB.

The sections were studied under a Leica DMR fluorescence microscope with four different filters. The microscope was provided with a Leica DFC425 digital camera.

The samples were taken from the remainings of the laminated beam used for the delamination test, which means that the bond lines were made under very realistic circumstances and from the same wood and glue-mix as the delaminating test. It should be emphasized that the samples didn't undergo the stress test as the delamination blocks.

The thickness of the glue line was determined under a Zeiss SteREO Discovery V20 stereoscope without any colouring and from small blocks containing an intact glue line. The thickness was measured on six glue lines (three on from the acetylated delamination test and three from the untreated delamination test) and at three different places in each glue line. The thickness was measured from a cross section and on small blocks to maintain an undisturbed glue line.

4.7. STATISTICAL ANALYSIS

For the contact angle, pH and rheology analysis, Variance Component Model (or mixed model) was used. This model was used since it takes into consideration the possible variance between the planks as a random selection of a bigger population.

EQUATION 3

$$Y_{ij} = \mu + T_j + P_i + e_{ij}$$

Y_{ij} is the mean angle / pH / slope for a specific droplet j on a specific plank i.

μ is the intercept (a constant).

T_j is the treatment (fixed) effect.

P_i is the random plank effect. The deviations of the plank means from the overall mean, it is noted as a normally distributed random factor since the planks are random samples from a bigger population. $P_i \sim N(0, \sigma_P)$.

e_{ij} is the residuals (unexplained variance within the same plank).

To obtain the most correct analysis and results, only planks with results from the acetylated and untreated parts, were used.

All test were made with a 95 % significant level ($\alpha = 0.05$) and calculated using REML Variance Component Estimates in JMP® Pro, Version 10.0.0 (SAS Institute Inc., Cary, NC, 1989-2015).

5. RESULTS AND DISCUSSION

5.1. MATERIAL SELECTION

In the project's beginning, 10 random planks were selected (see 4.1. Material preparation and selection). The relationship between an acetylated plank and the corresponding untreated reference plank can be considered as good, since they originate from the same plank. However, it can be argued that a sample of 10 planks is too small to represent the total population. The spread can also be smaller when many tests have been made on only few of the 10 planks. The variation between the planks can result in a significant difference, even if this is small. Furthermore, none of the experiments contain all of the 10 planks. If one or two planks have characteristics which do not represent the general trend, they will substantially influence the results, compared to the more optimal situation with more planks and fewer tests on each plank. Some of the sub-experiments went wrong and led to an unequal amount of results between the acetylated and untreated part of a plank, as well as between the planks. This must be taken into consideration when reading the results.

5.2. DELAMINATION TEST – RESULTS AND DISCUSSION

The two acetylated members showed delamination of 88.2 % and 100 % respectively, while there was no delamination for the untreated members.

Glue lines were opened on both the acetylated members and untreated members. No wood failure occurred in the opening of the glue lines in the acetylated members. The only wood failure occurred in the opening of the untreated lamellas. This means that the glue lines in untreated wood are much stronger than those between the acetylated wood. This supports the previously observations within gluing of acetylated wood with MUF resins (Bredesen 2015; Ormstad 2007)

The result of high internal stresses within the untreated wood can visually be observed as cracks in the wood, compared to the acetylated wood with no cracks (see Figure 19). In the case of an adhesive which doesn't show any delamination with acetylated wood, the delamination test will not be valid or trustworthy, since these internal stresses are crucial for the test.

In this way it can be argued that the delamination test is not the right way of testing acetylated wood, due to the increases in ASE. A delamination test like EN 302-2:2013 or ASTM D 2559

works due to the wood's capability of having high swelling and shrinking at different moisture contents. For this reason is it also pointed out in the standard EN302-2 (2013) that this test is not suitable for modified and stabilised wood. However, as long as modified wood specimens does not pass the test, the limitations given by the standard can play a minor role; but this is far from the situation for all types of modification and adhesive combinations (Vick & Rowell 1990). Development of better methods which take the properties of modified wood into account must be done. The perfect alternative is not to use the shear tests as they are today, since it almost certainly will not lead to the same conclusion as a delamination test (Schmidt et al. 2009; Schmidt & Knorz 2010; Steiger et al. 2014). Shear tests can be an alternative for untreated wood, but only for service class 1 and 2 (Bredesen 2015).

FIGURE 19: DELAMINATION TEST WITH GLUE LINES OPENED ON TWO MEMBERS. AT LEFT UNTREATED AND AT RIGHT ACETYLATED.

The increased stability of acetylated wood should work for a stronger glue line, since the glue line will be exposed to less stress.

5.3. Contact Angle – Results and discussion

One has to distinguish between the capability of wetting a surface, flow on a surface and penetrating into the surface of the substrate (Frihart 2013). Wetting is determined by the contact angle of a droplet on the surface. Good wetting exists when the contact angle is low and bad wetting is when the contact angle is high (Frihart 2013). The great variation within wood can make this measurement difficult (Wålinder 2000). Wetting is highly correlated to the surface energy and contact angle measurement can be used to determine the surface energy. Flow, on the other hand, describes the properties of a liquid to spread on the surface. Here the viscosity will be of great importance in addition to the contact angle. Because the surface of wood is inhomogeneous, the physical appearances (pores and roughness) and penetration will also be major factors. Penetration is the movement of the liquid into the substrate and its pores. The porosity and size of the voids in the wood are important for the penetration. The surface of wood is normally quite polar but can vary a lot depending on the extractives (especially the oil and fats) or treatments (Frihart 2013).

The measurements were not performed at the exact same time. Reading number 7 had a mean time on 0.22 seconds after DropImage registered the droplet on the wood surface and a standard deviation on 0.0078. In the same way, measurement number 15 had a mean time on 0.49 seconds and a standard deviation on 0.0079.

The distributions of the mean contact angle between measurement points 7 and 15 are showed in Figure 20.

Contact angle in meas.No. [7;15] for acetylated wood		Contact angle in meas.No. [7;15] for untreated wood	
Mean μ	68.19	Mean μ	54.29
Std Dev σ	4.97	Std Dev σ	4.71
Std Err Mean	0.22	Std Err Mean	0.32
Upper 95% Mean	68.62	Upper 95% Mean	54.92
Lower 95% Mean	67.76	Lower 95% Mean	53.66
N	513	N	218
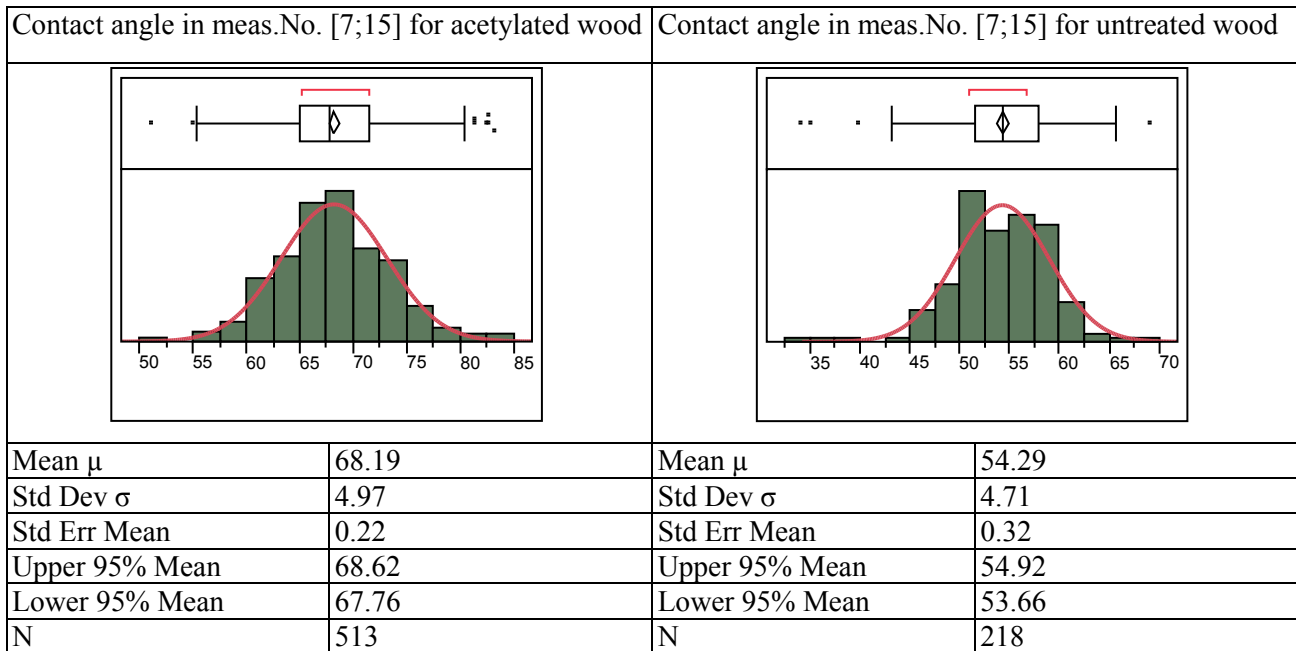
FIGURE 20: DISTRIBUTION OF THE MEAN CONTACT ANGLE FOR THE NINE MEASUREMENTS IN THE INTERVAL [7;15] OF EACH DROPLET.

The results in Figure 20 show a normal distribution of the measured angles for the acetylated wood, while the distribution for the untreated wood has a tail towards the lower angles. This can indicate two things. First that the droplets are more stable on the acetylated wood surface and the acetylated wood is more homogeneous. Secondly, the droplets on the untreated surface might flow out or penetrate into the wood in the interval from measurement No. 7 to 15 and thereby decrease the contact angle on the wood surface. With more measurements on untreated wood, the distribution would also become more normal, due to the central limit theorem.

If only measurement no. 7 is used, the distribution will look quite similar, but the normal distribution becomes a bit better for the untreated wood and the angle mean increases (see Figure 21). For the acetylated wood the mean is decreasing when only using measurement no. 7 compared to the interval [7;15] which can indicate that it's too early to have a stabilized drop. On the other hand, the increase for the untreated wood indicates that a penetration or flow is included in the [7;15] interval.

Contact angle at meas.No. 7 for acetylated wood		Contact angle at meas.No. 7 for untreated wood	
Mean	67.04	Mean	55.39
Std Dev	4.93	Std Dev	4.206
Std Err Mean	0.22	Std Err Mean	0.28
Upper 95% Mean	67.47	Upper 95% Mean	55.94
Lower 95% Mean	66.61	Lower 95% Mean	54.82
N	513	N	218
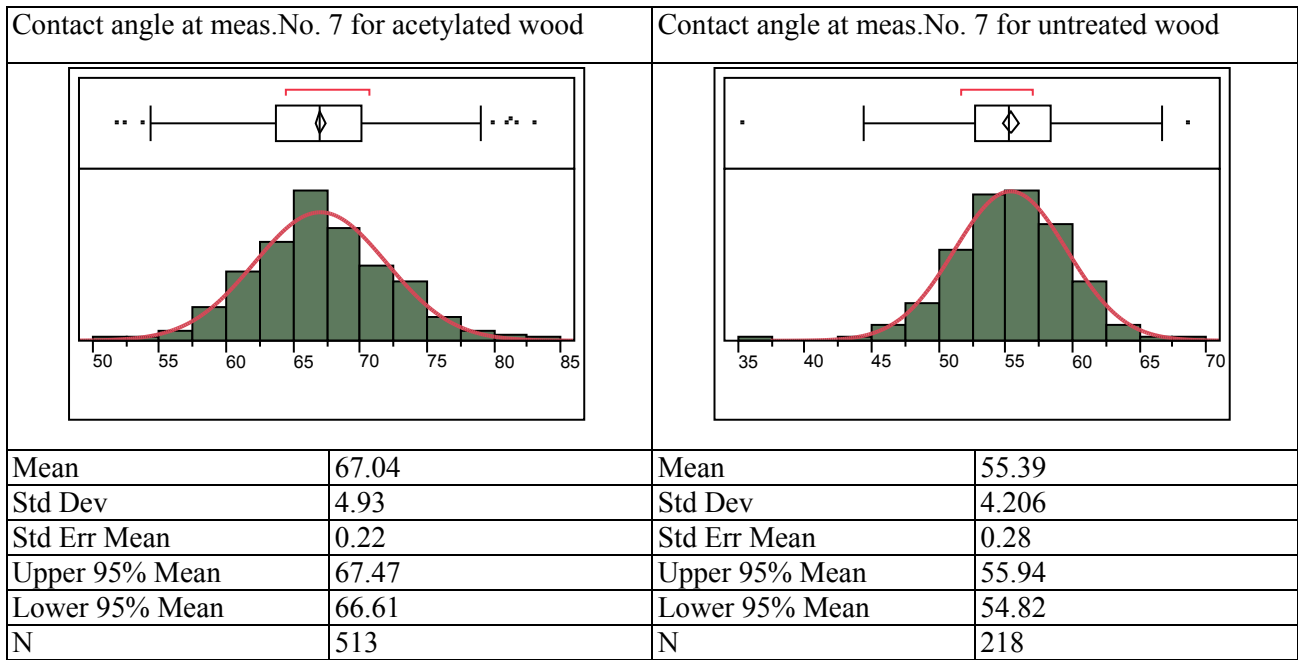
FIGURE 21: DISTRIBUTION OF THE MEAN CONTACT ANGLE FOR MEASUREMENT NUMBER 7 (APPROX. 0.22 SECOND AFTER LANDING) FOR ACETYLATED AND UNTREATED WOOD.

A clear difference seems to exist between the acetylated and untreated wood, but a great part of variation between the planks seems to exist as well (see Figure 22):
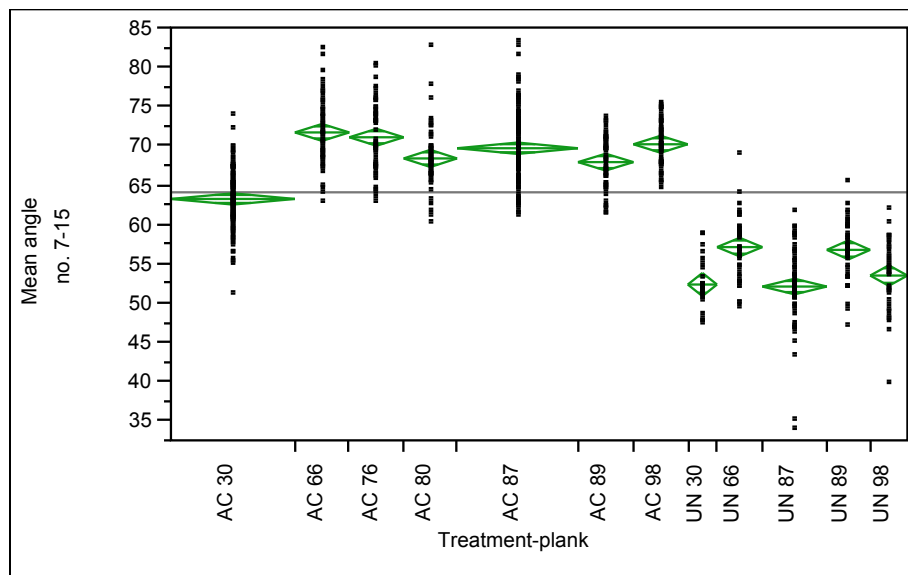
FIGURE 22: THE MEAN CONTACT ANGLE IN THE MEASUREMENT INTERVAL [7;15] FOR EACH DROPLET BY TREATMENT (AC = ACETYLATED AND UN = UNTREATED) AND PLANK

Not only the treatment can affect the droplet but several other factors such as amount of free acid, MC, density, extractives, early-latewood proportions, fibre direction, temperature, annual ring angle and pH can influence contact angle. These other variables should also be taken into consideration

when comparing the acetylated and untreated wood, since several of the factors are not measured. Not all of the factors are interesting in this case since the purpose was to get an average contact angle of each plank. A Variance component model (mixed model) with treatment as a fixed factor and plank as a random factor has been made.

Plank numbers 30, 66, 87, 89 and 98 have been used in the mixed model since contact angles have been measured on both the acetylated and untreated part on those planks (see Table 3).

TABLE 3: OVERVIEW OF PLANKS WHICH CONTACT ANGLE HAS BEEN TESTED ON

	Plank	30	66	87	89	98	76	80
UN	Drops	29	45	64	43	37		
	Mean angle	52.3	57.1	52.1	56.7	53.5		
AC	Drops	123	54	120	55	54	54	53
	Mean angle	63.2	71.7	69.7	67.9	70.2	71.0	68.4

The model showed a significant ($P < 0.0001$; $F = 1619.8$) effect on the mean angle for treatment.

The REML Variance Component Estimates calculates the variance not explained by the fixed factor treatment, which in total are 25.83. 31 % of the variance can be explained from variance between the planks and 69 % is due to variance within the same plank. A variance between the planks of 31 % seems to be high, but annual rings have not been taken into account when planing down the wood. The amount of latewood present can therefore differ substantially from plank to plank. The variance within the plank is probably caused by the properties of the annual rings, the annual ring degree and fibre direction. The amount of late- or earlywood could in principle be put in as a fixed factor in the model. But false annual rings can be common (Ross 2010) and a distinction between the early- and latewood can be challenging (Bamber & Burley 1983) especially when the discs only are 3 mm thick.

The model predicts a contact angle (least squares means) of 68.6 degrees for acetylated wood with a 95 % confidence interval from 65.0 degrees to 72.1 degrees. For the untreated wood the model predicts a contact angle of 54.0 degrees with a 95 % confidence interval from 50.5 degrees to 57.5 degrees.

As mentioned earlier, there are several factors which affect the contact angle and make the measurements inaccurate. Determination of the wetting properties with contact angle measurement

from water droplets is a method which must be used with caution. Gluing is often performed under high pressure and temperature and this can affect the wetting properties, even though the main part of most adhesives is water (Frihart 2013). But that untreated wood has better wetting than acetylated wood seems to be a fact, not only from these results (Hunt et al. 2007; Vick & Rowell 1990; Vick et al. 1993).

As mentioned in Experiences from contact angle pre-tests (3.2.1.) a sudden disappearing of the droplet was not unusual when testing on 1.5 mm thick acetylated wood. The best explanation of this phenomenon is that the water found its way through ray parenchyma cells or longitudinal tracheid with openings on both sides instead of entering the cell wall. With an average length of about 3.5 mm for longitudinal tracheids in Radiata pine (Bamber & Burley 1983) the fibre angle must be just around 25 degrees to be able to reach through a 1.5 mm thick disc. With such a high angle around half of the strength in untreated wood would be lost compared to a fibre direction parallel to the load (Kollmann & Côté 1968). Ray parenchyma is in this way the most logical way and reason for the phenomenon.

5.4. pH AND BUFFER CAPACITY – RESULTS AND DISCUSSION

The pH and the buffer capacity properties of wood are relevant, because they are parameters in the curing process of water based adhesives, in which polymerization is catalysed by acid, like MUF (Schmidt et al. 2012; Xing et al. 2004; Zanetti & Pizzi 2003).

The difference in pH between untreated and acetylated wood may be a part of the explanation for why MUF won't work on acetylated wood. The buffer capacity could also be helpful in developing new MUF adhesives, since the buffer capacity says something about the solution's (wood's) resistance to changes in pH (Schullery & Nord s.a.).

The definition of buffer capacity is not clearly defined. At least three ways to define buffer capacity exist: 1. "*The buffering capacity is defined as the quantity of mmol HCl required to reduce the starting pH of the extractive solution to a pH of 3, referenced to 100 g of dry net weight of wood flour."* (Schmidt et al. 2012). 2. The quantity (mL) of base required to raise the start pH of 1 mL extract to a pH 10 (or acid to lower it to a pH 3) (Passialis et al. 2008). 3. "*The buffering capacity of a solution refers to the amount of acid or base that can be added to the solution without going beyond the buffering range.*" And where "*The buffering range of a solution refers to the range of pH values where the solution acts as a buffer (resists changes in pH.)*" (Tavormina 2009). 4. *"...the moles of strong acid or base required to change the pH of 1 liter of the buffer by 1 pH unit (either higher or lower). It has units of moles/L"* (Schullery & Nord s.a.).

Under the boiling process it was noted that foam was created in the Erlenmeyer flask containing untreated samples, while only very small amount of foam was created in the flask containing acetylated samples (see Figure 23).
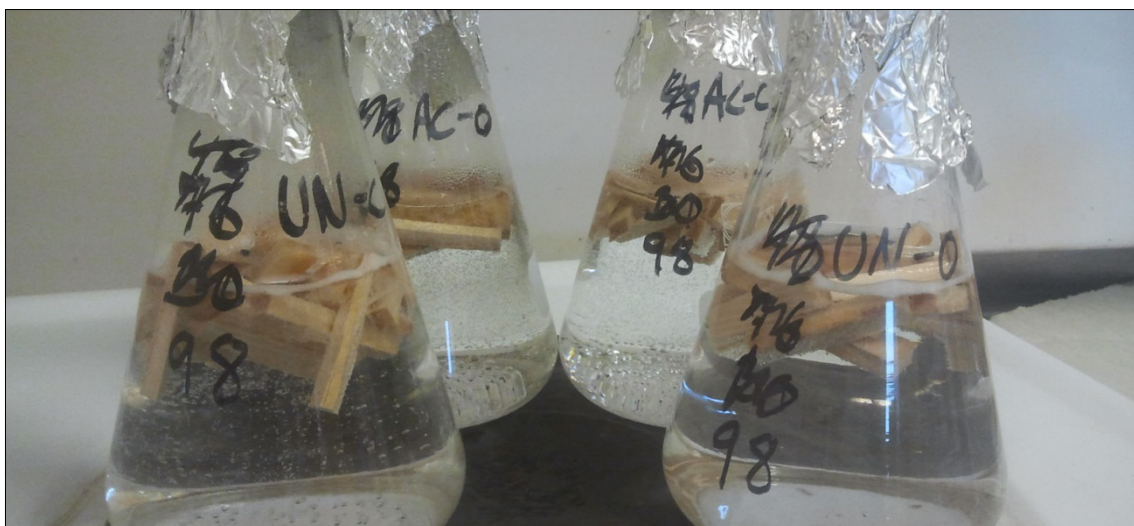
FIGURE 23: BOILING OF WOOD CHIPS FOR EXTRACTION OF EXTRACTIVES, UNTREATED IN FRONT AND ACETYLATED BACK. FOAM IS CREATED IN THE FLASKS WITH UNTREATED WOOD.

After cooling down and removing the wood from the water, a clear colour change of the water was observed. The colour change was strongest for the water which had contained the outer-part (-O) of the untreated wood (see Figure 24).
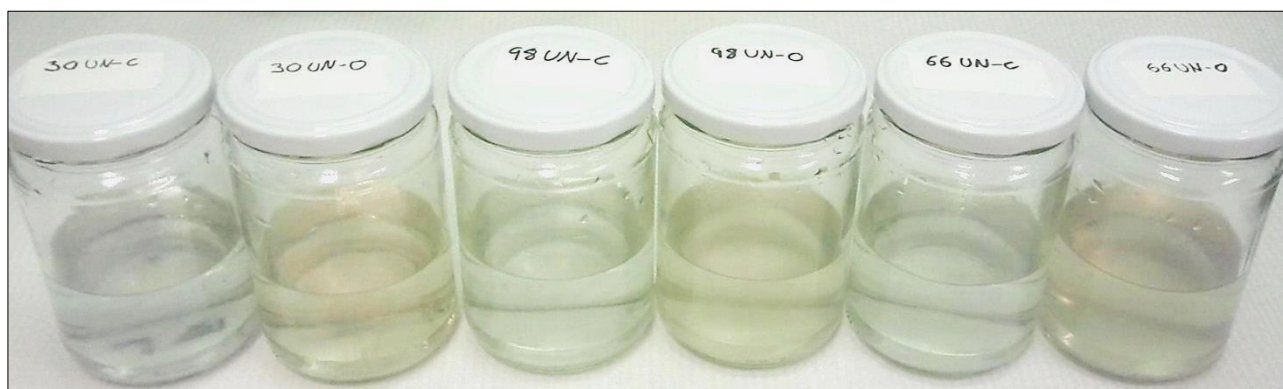
FIGURE 24: COLOUR OF WATER FROM THREE UNTREATED PLANKS AFTER EXTRACTION, UN = UNTREATED, C = CORE AND O = OUTER PART.

After titration with NaOH, the colour differences between water containing extractives from acetylated wood and untreated wood became more visible. There was barely any colour change in the water which had contained the acetylated wood (see Figure 25).
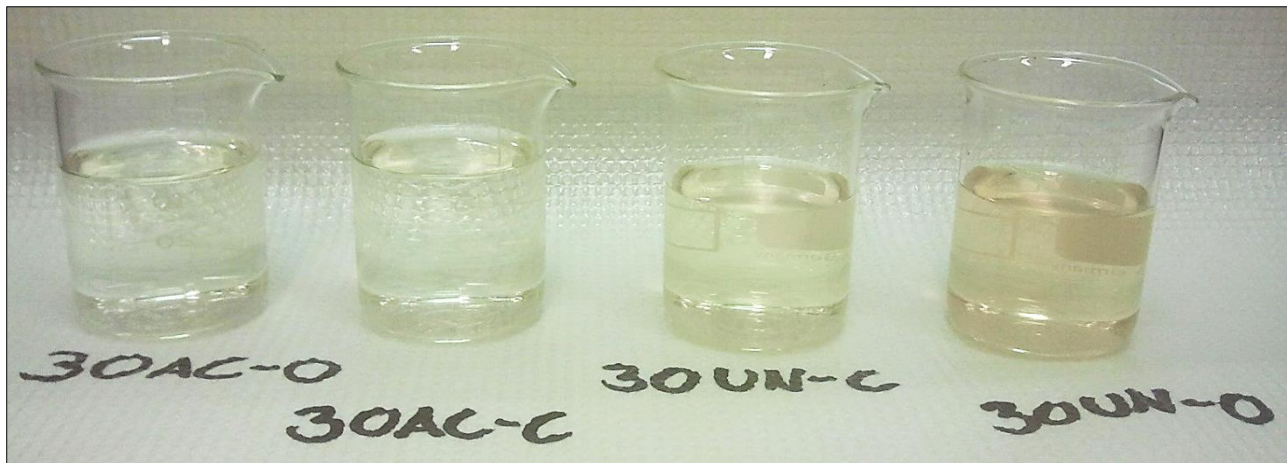
FIGURE 25: COLOUR OF WATER FROM PLANK 30 AFTER TITRATION WITH NAOH, FROM THE LEFT: ACETYLATED OUTER PART, ACETYLATED CORE, UNTREATED CORE AND UNTREATED OUTER PART.

B. Sithole (2005) has showed that the size of the wood chips doesn't influence the pH as well as the boiling time over 5 to 30 min. What can influence the pH is the moisture content of the wood since the amount of wood mass will be decreased with increasing moisture content. The wood used in this experiment was conditioned before use, and, due to the acetylation, the moisture content was much lower in the treated wood than in the untreated (see Table 7). Perhaps it would give a more accurate result if the wood was dried before the extraction, and the differences in moisture content thereby wouldn't influence the results. On the other hand, it can be argued that with conditioned wood one will get a more realistic result of the environment on the wood surface and within the wood. Drying can be looked upon as a relative increase in the concentration of the extractives, compared to using conditioned wood. When gluing wood for structural purposes it is not bone dry, and, therefore, experiments using conditioned wood will more accurately reflect the environment the wood offers the adhesive.

5.4.1.   BUFFER CAPACITY

When the amount (mL) of acid (HCl) and base (NaOH) are plotted on the x-axis, it is possible to see the titrations curves. Neither water containing extractives from the acetylated wood nor water with extractives from the untreated wood had any acid buffer capacity according to the titration curves (see left side, HCl in Figure 26). This might be the reason why PRF adhesive can bond acetylated wood satisfying (Accoya® 2014; Ormstad 2007; Vick & Rowell 1990) since PRF cures on the alkaline level of pH 7-10 (Ormstad 2007; Viljugrein 2015).

When looking on the alkaline side, we see that there are alkaline buffer capacities for the water containing the acetylated wood extractives. The alkaline buffer capacity is higher for the water

which contained wood from the core of the acetylated planks (AC-C) than for the water which contained acetylated wood from the outer-part of the plank (AC-O). For the water which contained the untreated wood, there is no alkaline buffer capacity.
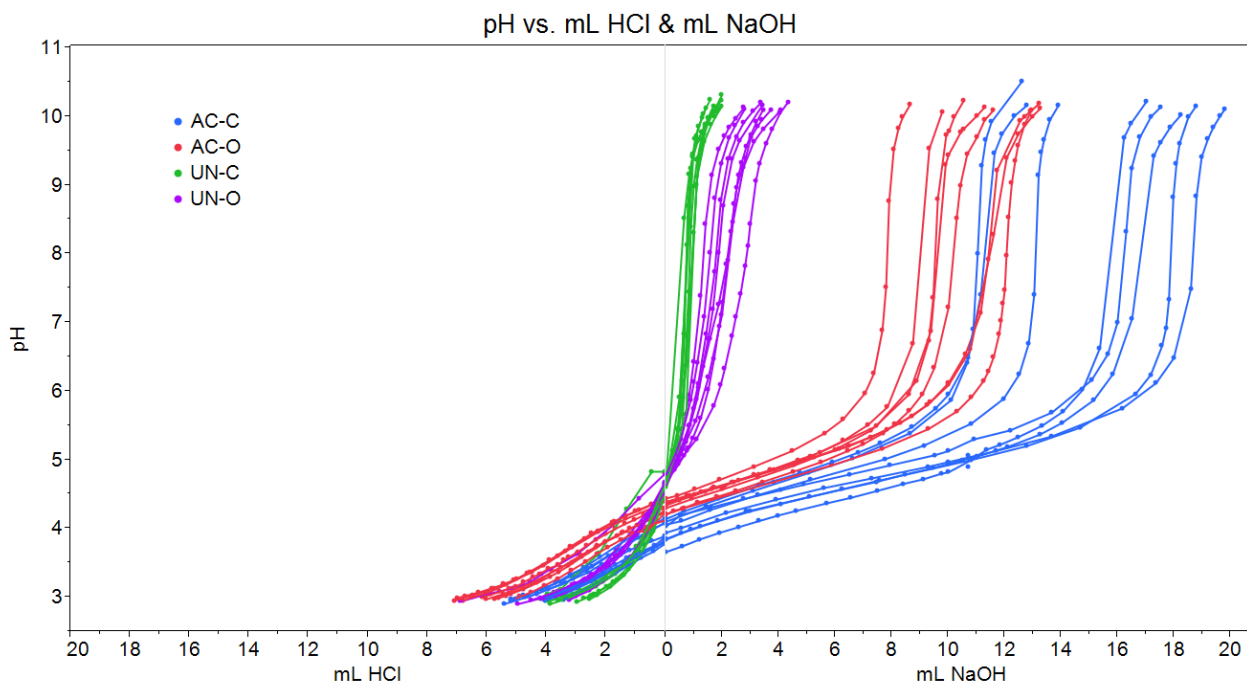
FIGURE 26: THE PLOTTED RESULTS FORM TITRATION WITH HCL (LEFT SIDE) AND NAOH (RIGHT SIDE), BLUE DOTS AND LINE: ACETYLATED CORE, RED DOTS AND LINE: ACETYLATED OUTER PART, GREEN DOTS AND LINE: UNTREATED CORE AND PURPLE: UNTREATED OUTER PART. IT MUST BE NOTED THAT ON THE X-AXIS DIFFERS FOR HCL AND NAOH AND THAT IT IS POSITIVE INCREASING FROM THE RIGHT TO LEFT FOR THE HCL. THE LINES ARE CONNECTIONS BETWEEN THE MEASURED RESULTS RESULTS. EACH LINE IS REPRESENTING ONE PLANK, EIGHT PLANKS IN TOTAL.

The core of the untreated wood makes a significant change in the pH after adding 0.5-1 mL 0.025 M NaOH and reaches pH 10 after adding 1-2 mL 0.025 M NaOH. The core of the acetylated wood has a significant change in the pH after adding 11-19 mL 0.025 M NaOH and reaches pH 10 after adding 11.5-19.5 mL of 0.025 M NaOH. This means (depending on the definition) that the buffer capacity of the water containing extractives from the acetylated wood core is around 10-20 times higher than that of the water with the untreated wood core extractives (see Figure 27).
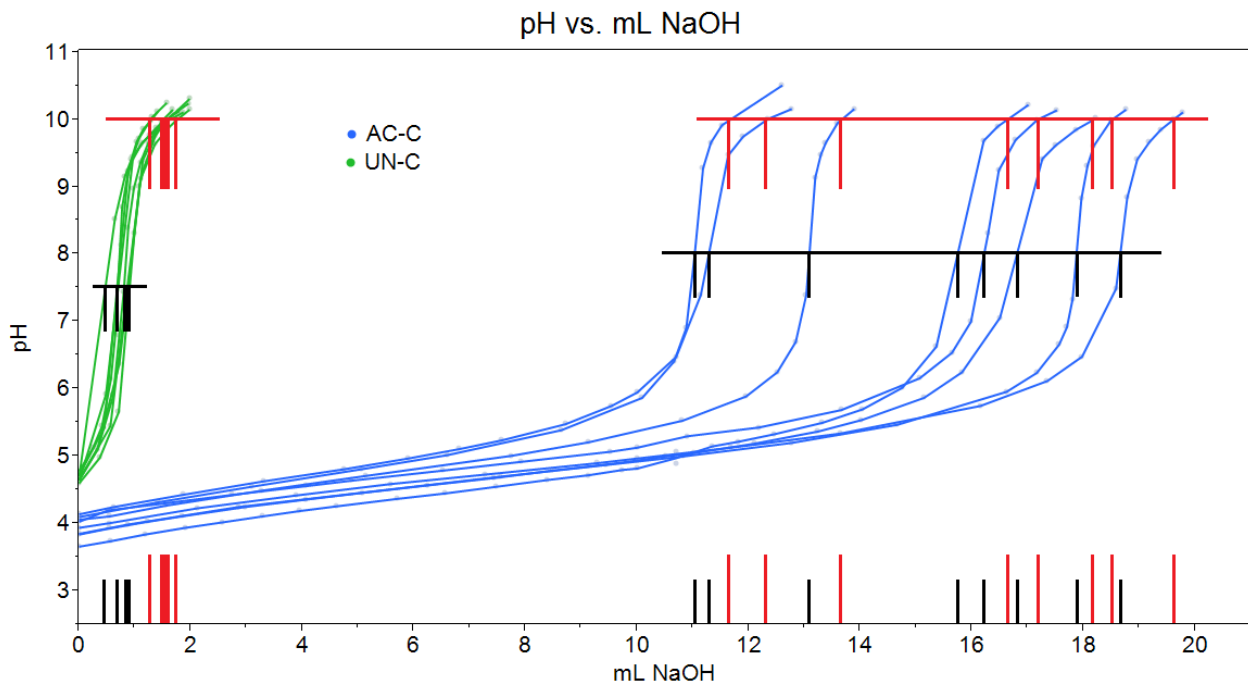
FIGURE 27: TITRATIONS RESULT FOR CORE OF ACETYLATED (BLUE) AND UNTREATED (GREEN) WOOD. PH 10 IS MARKED WITH RED AND THE ESTIMATED EQUIVALENCE POINT (SIGNIFICANT CHANGE IN PH) IS MARKED WITH BLACK. LINES ARE COMING FROM CONNECTION OF THE MEASURED RESULT POINTS.
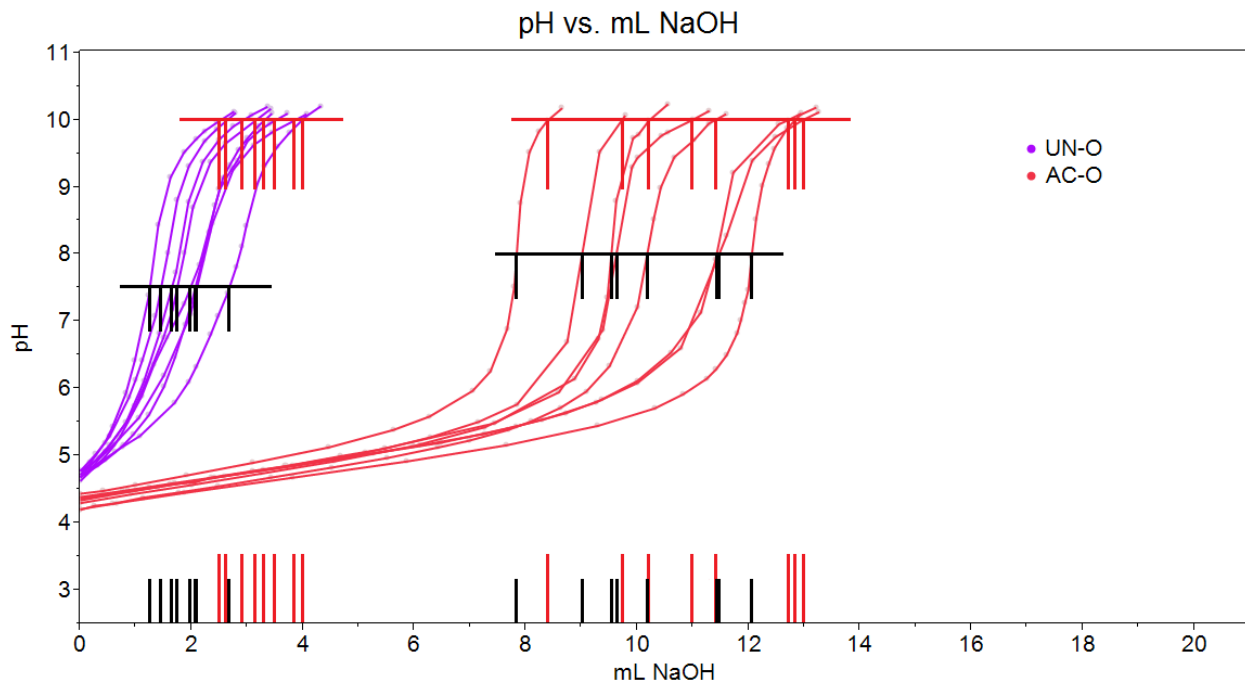
FIGURE 28: TITRATIONS RESULT FOR OUTER PART OF ACETYLATED (RED) AND UNTREATED (PURPLE) WOOD PLANKS. PH 10 IS MARKED WITH RED AND THE ESTIMATED EQUIVALENCE POINT (SIGNIFICANT CHANGE IN PH) IS MARKED WITH BLACK. LINES ARE COMING FROM CONNECTION OF THE MEASURED RESULT POINTS.

The outer-part of the untreated wood (UN-O) makes a significant change in the pH after adding 1-3 mL of 0.025 M NaOH and reaches pH 10 after 2.5-4 mL of 0.025 M NaOH. The outer-part of the acetylated wood has a significant change in pH after adding 8-12 mL of 0.025 M NaOH and reaches pH 10 after adding 8.5-13 mL 0.025 M NaOH (see Figure 28).

The significant changes in pH, also known as equivalence point when applying NaOH, are happening at a lower pH for untreated wood (pH 7.5) than for acetylated wood (pH 8). Furthermore, the equivalence point seems not to be related to the location (core or outer-part) in the plank. These differences indicate that different acids are present in the acetylated and untreated wood, but it is the same acid in the outer-part as well as in the core, when the treatment is the same.

The greatest variation between the acetylated planks exists in the core part, while the untreated planks have the greatest variation within the outerpart of the planks. This could be due to the properties of the wood and location of the plank during the acetylation process. Zimmer et al. (2014) have shown a large variation of treatability with furfuryl alcohol in Scots pine (*Pinus sylvestris* L.) between stands. The same situation could easily be the case with acetylation and Radiata pine. Especially when Hernandez (2013) already have showed variations in pH and buffer capacity within the stems of Radiata pine. It would therefore be reasonable to believe that the greater variation in acetylated wood is due to variations in the modification, which might be caused by the properties of the wood influenced by location and conditions during growth.

It is difficult to make comparisons with others results since they don't follow the same method. Both the wood-water ratio, amount of solution for titration and concentration of the acid/alkaline used for titration vary. A standard method would therefore be recommended.

5.4.2. pH

One pH measurement was made before each titration, which means that each water solution with extractives was measured two times. In this way, the following results are based on 16 measurements for each treatment-location combination. The result for each measurement is plotted in Figure 29, where treatment-location combinations can be viewed as well.
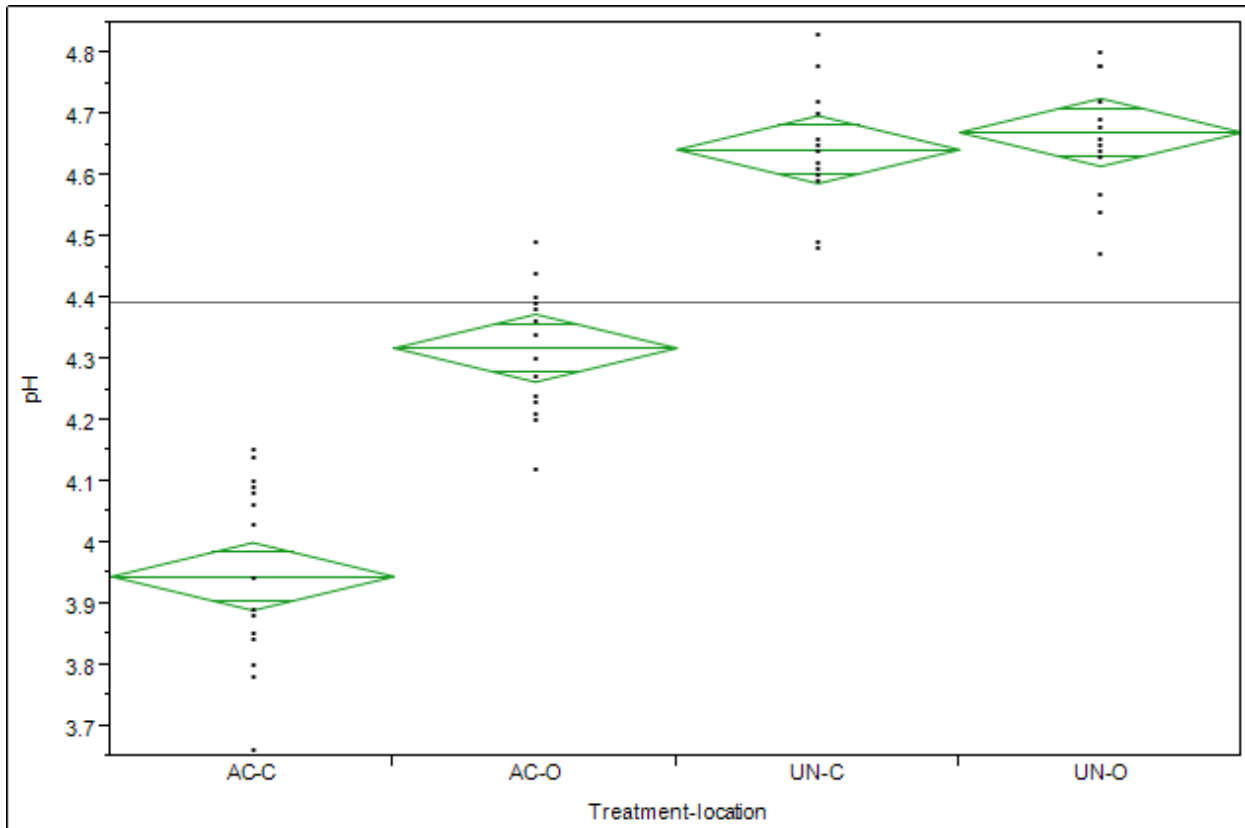
FIGURE 29: FROM THE LEFT ACETYLATED CORE (AC-C), ACETYLATED OUTER PART (AC-O), UNTREATED CORE (UN-C) AND UNTREATED OUTER PART (UN-O). GREEN DIAMONDS SHOWING THE MEAN AND 95 % CONFIDENCE INTERVAL FOR THE MEAN PH FOR THE TESTED PLANKS.

The mixed model with treatment as a fixed factor and plank as random factor showed a significant ($P < 0.0001$; $F = 153.65$) difference between acetylation and untreated planks with respect to their pH. The total unexplained variance by treatment is on 0.030 and 4.4% can be described as differences between the planks. 95.6 % of the unexplained variance is between the samples within the same plank. If the mixed model instead has the combined treatment-location (AC-O, AC-C, UN-O and UN-C) as a fixed factor and plank as random factor, the total unexplained variance will fall to 0.0125. 30.7 % of the total unexplained variance is due to differences between planks and 69.3 % is due to variance between the samples within the same plank. Only plank 30 showed a significant difference from three other planks (98, 87 and 80), see connecting letters report in Table 4. The location had a significant effect on the acetylated wood from the core (AC-C) and form the outer part (AC-O) see connecting letters report Table 5. The untreated wood differed significantly from both the core and outer part of the acetylated wood, but the location in untreated wood does not lead to significant difference (see Table 5).

TABLE 4: CONNECTING LETTERS REPORT FOR EACH PLANK WITH MEAN PH, PLANKS WITH SAME LETTERS DO NOT DIFFER STATISTICALLY.

Planks			Least Sq Mean
30	A		4.50
76	A	B	4.44
66	A	B	4.42
57	A	B	4.38
48	A	B	4.37
98		B	4.37
87		B	4.35
80		B	4.33

TABLE 5: CONNECTING LETTERS REPORT FOR EACH TREATMENT-LOCATION WITH MEAN PH, TREATMENT-LOCATION WITH SAME LETTERS DO NOT DIFFER STATISTICALLY.

Treatment-location				Least Sq Mean
UN-O	A			4.67
UN-C	A			4.64
AC-O		B		4.32
AC-C			C	3.95

Even though, we see differences in the pH between acetylated and untreated wood the extremes are within approx. 1 pH unit. While Hernandez (2013) found pH values from 3.83 to 5.7 for 30 years-old trees, approx. 2 pH units within untreated Radiata pine sapwood. But here must the different extraction methods be taken into consideration.

5.4.3.   FREE ACETIC ACID.

10 cm of each of the eight acetylated planks was also analysed by Accsys Technologies for free acetic acid content. The planks were divided into three sections: the surface (0-5 mm), the intersection (5-10 mm) and the core (10-18 mm). The method was Accsys Technologies' standard method.

A good correlation ($R^2 = 0.76$) was shown in a mixed model using the distance from the surface (middle of each interval: 2.5 mm, 7.5 mm and 14 mm) as a fixed factor, plank as a random factor and the acetic acid content as the variable. If the fixed factor was kept categorical (surface, intersection and core), instead of change it to a continuous factor, was the surface significantly lower in free acetic acid content in relation to the intersection and core (see Table 6).

TABLE 6: CONNECTING LETTERS REPORT FOR EACH LOCATION WITH MEAN % FREE ACETIC ACID, LOCATIONS WITH SAME LETTERS DO NOT DIFFER STATISTICALLY.

Location			Least Sq Mean
Core [10-18 mm]	A		0.600
Intersection [5-10 mm]	A		0.525
Surface [0-5 mm]		B	0.425

An average of the intersection and core corresponds very well to the area described as the core in the pH and buffer capacity measurements. There is a strong correlation ($R^2 = 0.927$) between the mean pH for each location (AC-O and AC-C) as function of the free acetic acid content for the surface and new core (average of core and intersection), when plank is a random factor. As expected, with increasing acetic acid content the pH falls.

Besides free acetic acid measurement did Accsys Technologies also measured the density and MC, which correspond to the expected results and the ones not presented, but measured during the acclimatization period of the wood (see Table 7).

TABLE 7: DENSITY, MC AND ACETIC ACID RESULTS FROM EAIGHT PLANKS BOTH ACETYLATED AND UNTREATED MEASURED BY ACCSYS TECHNOLOGIES AS A PART OF THE GIACEWOOD PROJECT.

Treatment	Sample	Density [kg/m3]	MC [%]	Acetic acid content [%]		
				Surface [0-5 mm]	Intersection [5-10 mm]	Core [10-18 mm]
Untreated	UN80	549	11.5			
	UN87	491	10.6			
	UN48	580	10.5			
	UN30	506	10.6			
	UN66	553	10.6			
	UN57	532				
	UN98	564	11.3			
	UN76	502	10.8			
Acetylated	AC80	587	3	0.4	0.5	0.5
	AC87	568	3.3	0.5	0.6	0.6
	AC48	521	3.5	0.3	0.5	0.7
	AC30	541	3.3	0.4	0.4	0.6
	AC66	593	3.1	0.4	0.5	0.5
	AC57	574	3.6	0.5	0.6	0.7
	AC98	649	3.2	0.5	0.6	0.7
	AC76	556	2.9	0.4	0.5	0.5

5.5. RHEOLOGY – RESULTS AND DISCUSSION

When analysing the complex viscosity curves a trend supporting our theories seemed to exist. In the first couple of minutes, a slope difference between the acetylated planks and the untreated seemed to be present. This was tested by calculating the slope for the complex viscosity in the first three minutes between time 0.1 and 3 minutes.

Comparing the slopes for each disc, grouped by treatment, it is possible to see a trend of lower slopes for acetylated (AC) planks than untreated planks (UN) (see Figure 30 and Figure 31).
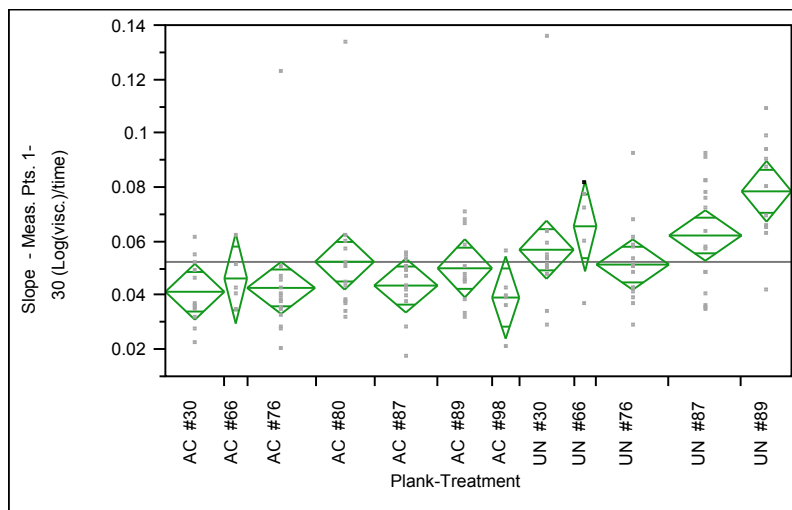
FIGURE 30: MEAN SLOPE FOR THE COMPLEX VISCOSITY ON ACETYLATED (AC) AND UNTREATED (UN) WOOD SURFACES IN THE FIRST 3 MINUTES AFTER APPLICATION BY PLANK WITH MUF ADHESIVE PREFERE 4546/5022 RATIO 100:20 FROM DYNEA AS
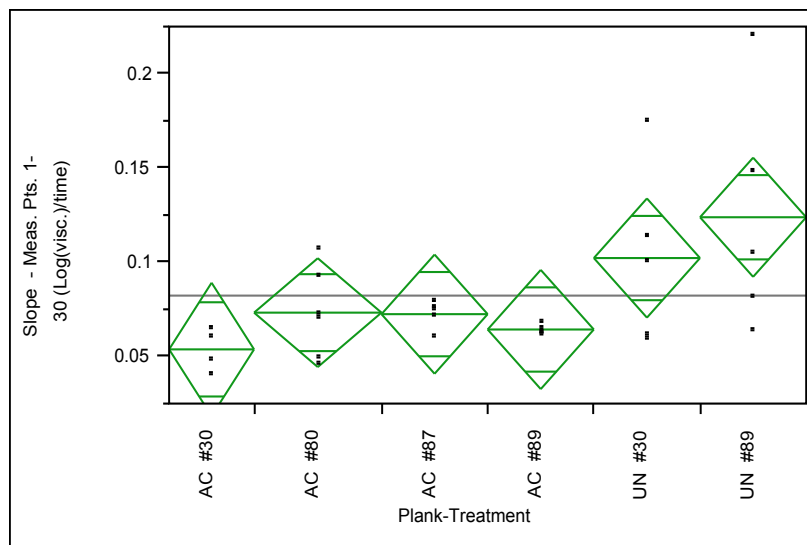
FIGURE 31: MEAN SLOPE FOR THE COMPLEX VISCOSITY ON ACETYLATED (AC) AND UNTREATED (UN) WOOD SURFACES IN THE FIRST 3 MINUTES AFTER APPLICATION BY PLANK WITH MUF ADHESIVE PREFERE 4546/5022 RATIO 100:50 FROM DYNEA AS

The planks and number of measurements showed in Table 8 were used in the Variance component model (mixed model) for Prefere 4546/5022 ratio 100:20.

TABLE 8: PLANKS AND NUMBER OF DISCS USED IN THE VARIANCE COMPONENT MODEL

Rheology test with Prefere 4546/5022, ratio 100:20					
Plank	**30**	**66**	**76**	**87**	**89**
AC	13	5	15	14	12
UN	12	5	16	16	11

No outliers have been removed, only planks AC-80 (13) and AC-98 (6) have been removed.

The mixed model shows the treatment has a significant effect ($P < 0.0001$; $F = 26.939$) on the slope for the complex viscosity.

REML[2] Variance Component Estimates the total unexplained variance is 0.0003607 and 9 % of this can be explained by variance from the planks and 91 % is variance between samples within same plank. If factors such as fibre angle, latewood proportion, annual ring angle and perhaps even time since planing were measured on each disc and put in as fixed factors, probably a lot more of the total unexplained variance would be explained. Compared to the contact angle measurement, the variance between the planks is lower here. A possible explanation for this is that the rheology method is less sensitive due to the fact that these measurements cover a bigger surface area. A droplet's contact angle is more sensitive for variations at the wood surface, than the complex viscosity development of MUF adhesive. Rheology measurements give an average for a bigger area, than the smaller area covered by a water droplet.

The predicted slope for acetylated wood in the first 3 minutes is 0.0449 with a 95% confidence interval of [0.0364;0.0533]. Untreated wood has a predicted slope for the first 3 min on 0.0621 with a 95% confidence interval on [0.0537;0.0705] on the mean response. It must be noted that the slope is calculated for a straight line in a semi-logarithmic graph (see Equation 2).

TABLE 9: NUMBER OF DISCS USED PER PLANK AND TREATMENT IN THE VARIANCE COMPONENT MODEL

Rheology test with Prefere 4546/5022, ratio 100:50		
Plank number	**30**	**89**
AC	4	5
UN	5	5

No outliers have been removed, only planks AC-80 (6) and AC-87 (5) have been removed.

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[2] Restricted Maximum Likelihood (REML) Method

The planks and number of measurements showed in Table 9 was used in the Variance component model (mixed model) for Prefere 4546/5022 ratio 100:50.

The mixed model shows a significant difference ($P < 0.0106$; $F = 8.36$) between the slopes for the complex viscosity on acetylated and untreated wood for Prefere 4546/5022 ratio 100:50.

In contrast to the 100:20 ratio, with the 100:50 ratio is it not possible to explain any of the total unexplained variance of 0.00167 with variance between the planks (100 % of the unexplained variance is therefore between the measurements within the plank). This is probably due to the few observations and planks in the model. Another reason could be domination of the curing effect above the plank effect, due to the faster curing when hardener amount is increased from 20 pbw to 50 pbw. In spite of a difference between the AC and UN, there is not a significant difference between the individual planks when comparing AC and UN.

The predicted slope for Prefere 4546/5022 ratio 100:50 in the first 3 minutes is 0.0598 with a confidence interval of [0.0265;0.0931] for acetylated wood and 0.1130 with a confidence interval of [0.0803;01457] for untreated wood.

The method is very sensitive and during the pre-tests it became clear that the variables of temperature and MC of the wood were important for reliability, as well as thickness of the discs. Even after a lot of work with making the measurement more reproducible and reliable, unexplainable variations were observed. With increasing test durations, the variations became bigger and the ability to reproduce the results declined. In this way the variation in development of the complex viscosity increased with time. This could tell us that some of the variables are still not controlled. Known uncontrolled variables are the RH under the temperature hood, the proportion of late- and earlywood under the spindler, the location in the trunk from where the disc are taken (besides in the sapwood), fibre direction, density and exact wood MC among others. This can explain some of the variations in the complex viscosity development. In addition, some variations can also be explained by the smaller variations in the adhesive. The adhesives are not fully filtered and it is possible that polymers above the theoretical size occur; furthermore, in the adhesive there are fillers to increase the gap-filing effect and curing. A gap between the two surfaces of 0.2 mm have been used in other rheology experiments (Kariz et al. 2013; Schmidt et al. 2010), but, depending on swelling behaviour of the wood and amount of fillers in the adhesive, disturbances in the measurements can in theory occur. Furthermore, small variations in the ratios of the glue and

hardener mixture can occur, but all weightings should be within ±0.05 g.[3] Finally, the time after mixing to beginning of the measurement have been notated not to differ more than ± 40 seconds.

The change in gap thickness as the adhesive or some of its components are penetrating into the wood has not been measured. Schmidt et al. (2010) investigated the changing gap thickness for MUF on different wood species between two wooden surfaces, but not on acetylated wood. An investigation of this might answer the question; what makes the viscosity of the adhesive increase faster on untreated wood compared with acetylated? The faster increase of the complex viscosity in the untreated samples could be caused by penetration of water from the adhesive into the wood. This would increase the slope of viscosity, since the amount of dry matter would increase, as long as the penetration of water has a stronger affect than the chemical curing. The slopes for the measured viscosities are in this way an expression for the penetration of water. Schmidt et al. (2010) assumed that faster penetration of adhesive or water from the adhesive, does not necessarily lead to faster curing. Following this assumption, we cannot conclude that the MUF is curing faster or slower on untreated wood compared to acetylated wood. This could also explain that no obvious difference was noted with increasing test time.

When wood is acetylated, the density will increase and the moisture content will be much lower (see 5.4.3. Free acetic acid.) (Hill 2006). Since the gap development during the curing hasn't been noted, one could think that this might affected the penetration and thereby the complex viscosity. This could theoretically make sense, but Schmidt et al. (2010) notated on untreated wood that the decrease in the gap with adhesive was reduced with increasing amount of latewood on the surface, while they didn't see any influence by the density or moisture content of the plank.

During the method development, it was noted that the oil, to avoid skin creation on the excess adhesive pressed out under the spindler, was quit important, and not only the oil itself, but also the viscosity of the oil (see 3.1.2. Experiences from rheology pre-tests). Therefore, this must be taken into account when comparing rheology measurements of adhesives on wood across different experiments. Schmidt et al. (2010) performed rheology studies using two wooden surfaces where the excess adhesive was removed to avoid a bonding on the edge of the upper wooden part, but their study does not mention anything about applying oil or grease on the edge. Kariz et al. (2013) point out specifically that the edges of discs were not covered with silicone grease. Witt (2004) also notes

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[3] Correspond to a variation of 0.25% for the glue and 1.25 % for the hardener in a 100:20 mixture.

the problem with skin formation but in relation to PRF and suggests that the edges should be covered with silicone oil or a solvent trap. A disadvantage in using oil is that the oil might affect the measurement since it penetrates into the wood. If the oil penetrates into the wood and under the area covered by the spindler, it can in theory affect the penetration of the adhesive and swelling of the wood. Some of the increasing variation between the samples in the complex viscosity during long time runs could be explained by this or by skin formation due to a slower run off of oil as it was observed with low viscosity oil.

In the future, when similar experiments are carried out, a much better experimental design can be proposed. It would be recommended to use more planks with less samples coming from each plank. However, each plank should provide enough samples to represent variation in the plank and the same number of samples should come from every plank. Control of the sample location in relation to the root-top of each trunk should be preferred, as well as more specific knowledge about factors such as density, fibre direction, MC, annual ring angle, early-/latewood amount and surface pH.

Measuring more than the complex viscosity, such as the gel-point and creep or penetration of the adhesive could be interesting for analysis. Kariz et al. (2013) tested gel-point of MUF on heat treated spruce. The gel-point could be interesting to test, to see if the untreated wood reaches this before the acetylated wood. On the other hand, measuring the gel-point would demand much more time for each measurement. Use of two wooden surfaces in the measurements will give a more realistic picture of the adhesive behaviour. However, using two wooden surfaces would increase the complexity since the many variables related to wood would be increased. The wood specimens' shape complexity is increased and precision must be high when producing specimens for testing rheology with two wood surfaces. It can therefore be demanding to produce several freshly planed specimens from the same plank, if access to a CNC wood router or similar does not exist. Under all circumstances, the thickness of the wood must be considered. It was observed that the applied oil could penetrate through the disc in less than a half an hour. The 3 mm thickness corresponds to the thickness of beech veneer used by Witt (2004), while Schmidt et al. (2010) used a 10 mm thick wood specimen for at least the upper part and Kariz et al. (2013) 8 mm discs.

It has not been possible to prove from the rheology results that free acid and lower pH in the acetylated wood speeds up the curing. If the free acid and lower pH would speed up the curing, the opposite result would be expected – lower slope for untreated (UN) than for acetylated (AC) wood.

On the other hand, this does not prove that the theory is wrong since other factors such as low wettability might have a stronger effect then the free acid and pH.

5.6. MICROSCOPY

Microscopy is a well-known method and widely used for determination of the adhesive penetration into the wood cells (Adamopoulos et al. 2012; Chandler et al. 2005; Frihart 2013; Stoeckel et al. 2013). An obvious difference in the penetration between the acetylated and untreated wood could partly explain the adhesion problem MUF has on acetylated wood, since the importance of penetration and mechanical interlocking are still under debate (Chandler et al. 2005; Frihart 2013; Nardin & Schultz 2003; Pizzi 1994). Furthermore, it is important to know where a failure occurs, since the knowledge can help to improve the adhesive (Frihart 2013).

Two obvious differences were already noted during the preparation of the thin slices on the microtome. The first one being, that the acetylated wood split in the interface between the bulk adhesive and interphase (see Figure 2, Figure 32 and Figure 34). Sometimes the bulk adhesive attached to one of the lamella and other times it splits into three with the two lamellas and the bulk adhesive separated. The other difference was the increased hardness of the acetylated wood and therefore the shorter service life of the microtome blade when cutting the acetylated wood. Making thin cross sections of the acetylated wood with an unbroken glue line was not possible. The bonding of the acetylated wood is so poor that it splits up on the microtome blade (see Figure 32). Before cutting the thin sections, the wood samples were boiled in water so they were fully soaked, in order to soften the samples. This could perhaps have had an effect on the bond line. But the same problem more or less was present before boiling. Without boiling the samples hardness made it almost impossible to make any good cuts from the acetylated samples.

Distinguishing the wood from the adhesive was much easier under a fluorescence microscope, than a normal light microscope due to the stronger colour difference. No clear differences in the depth of penetration were observed, with both the treated and untreated wood showing MUF adhesive penetration of a 0-4 cells wide interphase. On the other hand, the acetylated wood surface, with the interphase, and the cured bulk adhesive were almost fitting together like a puzzle or cogwheel, where the adhesive had separated from the wood (see Figure 32). The very variating interphase (depth of adhesive penetration) from zero to four axial tracheid cells was found in both acetylated and untreated wood, and the penetration in the rays was found to be more than 200 μm in many

cases. In cross section areas were found without penetration of adhesive into one of the lamellas (no interphase observed, from bulk wood to bulk adhesive). On one side of glue line, penetration could be present in the lamella, while the other lamella was without penetration. Shifting of this effect from side to side along the glue line was observed some places. This indicates that the interphase is not due to a penetration but rather due to the applied pressure during gluing. To investigate this further, thin sections were made along the grain (fibre direction) in the direction of the glue line. From the radial/tangential view it became clear that the adhesive was present in the tracheids which had an opening towards the glue line. Cells with a closed end towards the glue line didn't contain adhesive, and penetration of adhesive in cells parallel with the glue line was observed rarely (see Figure 33).

145 measurements from the acetylated delamination block and 95 measurements on the untreated delamination block gave an average thickness of the glue line of 38.7 µm for acetylated wood and 38.6 µm for untreated wood. No significant difference between acetylated and untreated wood.

When investigating the bulk adhesive in fluorescent light, an edge on the adhesive where it has been in contact with the wood surface seemed to exist. The edge or darker coloured line (see Figure 32 and Figure 34 pointed out with red arrows) can be due to refraction of light in the glue or due to another chemical composition. If it's another chemical composition of the adhesive, the theory about a thin pre-cured layer, created when the adhesive gets in contact with the wood might true. If the observed line is this layer, it also confirms that rheology measurement will not be sensitive enough to be influenced by a very thin layer of pre-cured adhesive.
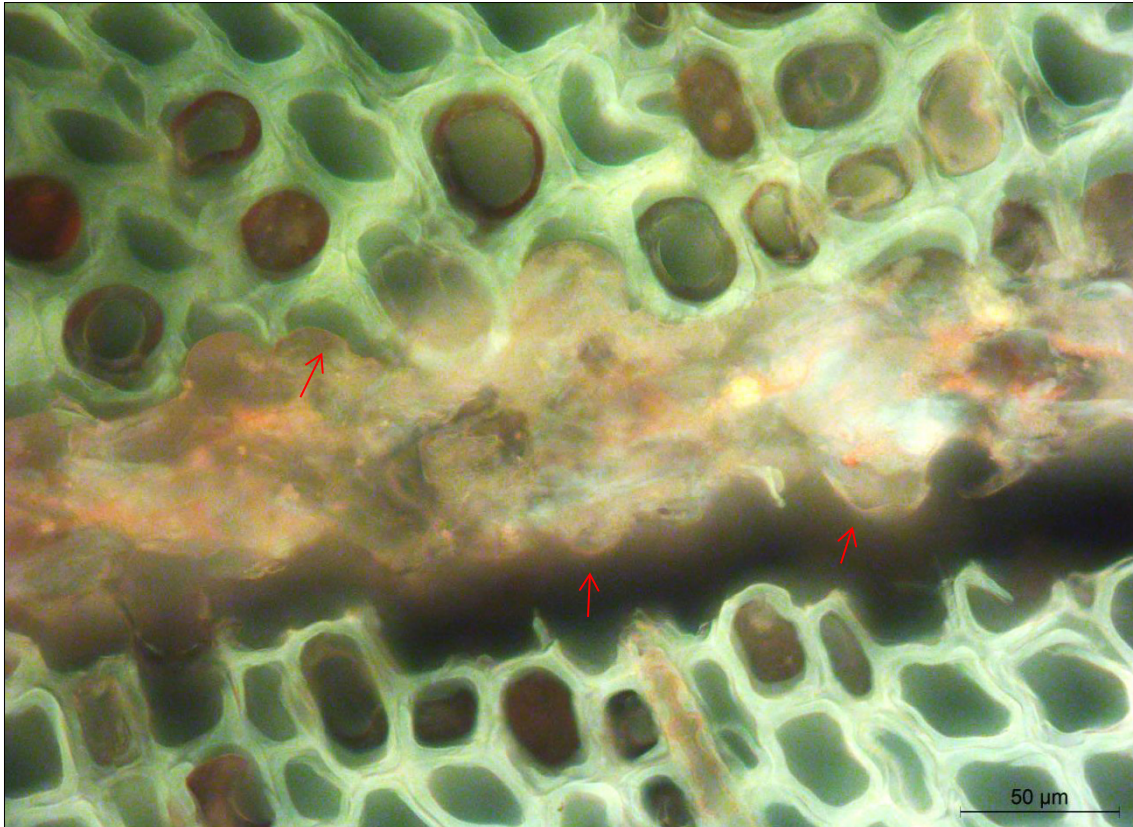
FIGURE 32: MUF GLUE LINE IN ACETYLATED WOOD UNDER FLUORESCENT LIGHT. RED ARROWS POINT OUT WHAT MIGHT ARE A PRE-CURING.
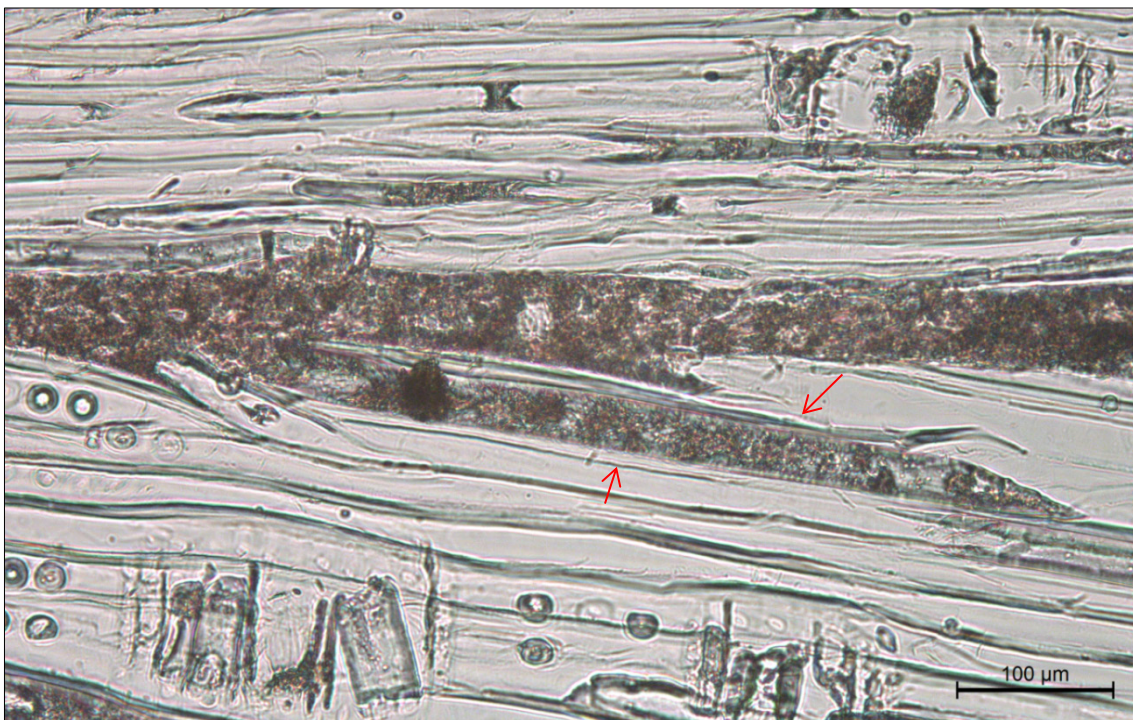
FIGURE 33: MUF GLUE LINE IN ACETYLATED WOOD CUT IN THE GRAIN DIRECTION AND VIEWED UNDER A NORMAL LIGHT MICROSCOPE. RED ARROWS POINT OUT TRACHEID CONTANING ADHESIVE IN THE LUMEN.
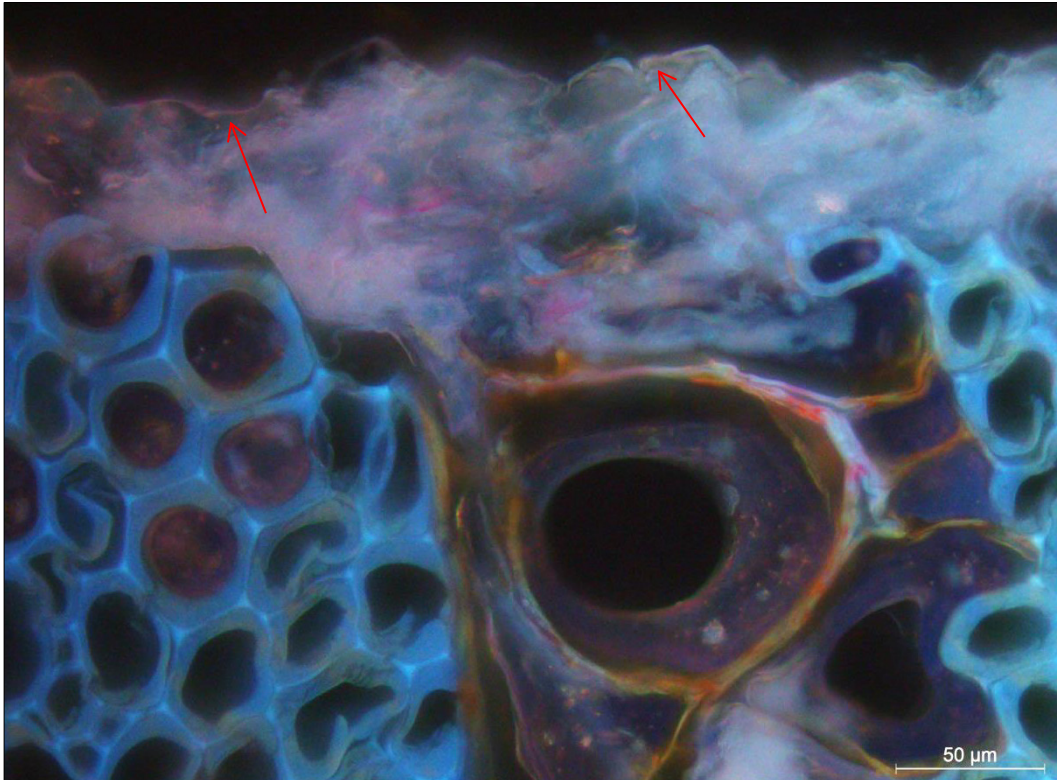
FIGURE 34: MUF GLUE LINE IN ACETYLATED WOOD UNDER FLUORESCENT LIGHT. RED ARROWS POINT OUT WHAT MIGHT ARE A PRE-CURING.
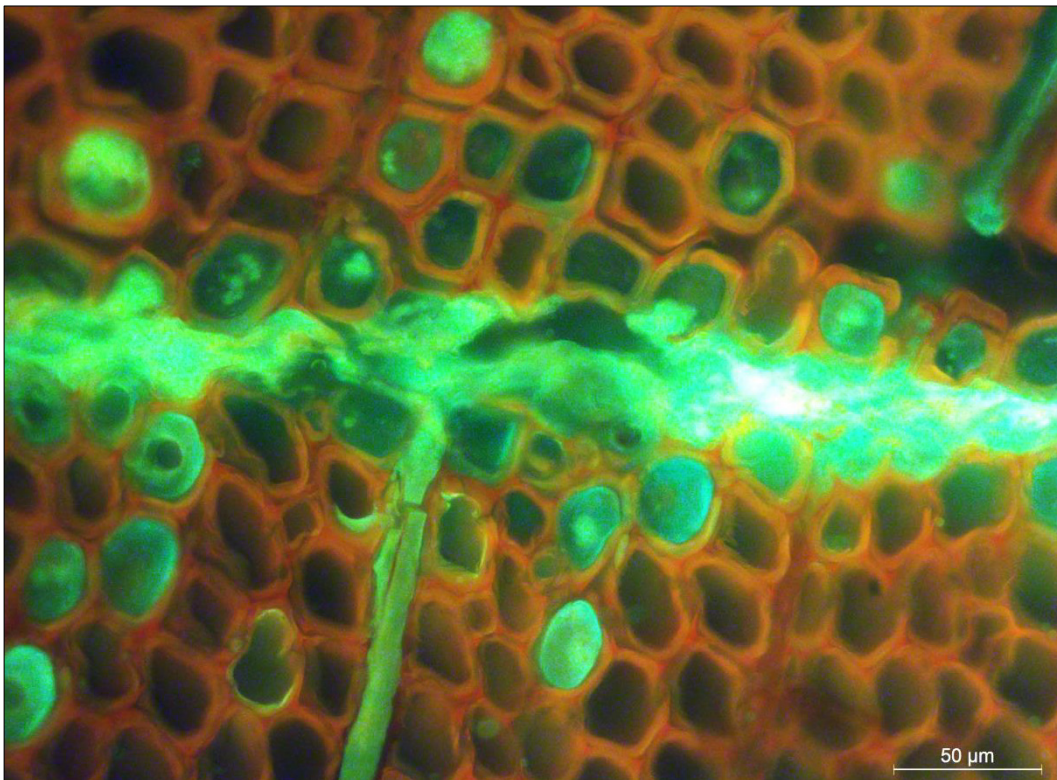
FIGURE 35: MUF GLUE LINE IN UNTREATED WOOD UNDER FLUORESCENT LIGHT.

Cyr et al. (2007) have investigated the penetration of UMF (Urea-Melamine-Formaldehyde) in fibres from MDF-boards (Medium Density Fibreboard) with a High Resolution Confocal Laser Scanning Microscope. A similar method could be interesting in this case to take a closer look to see if the adhesive is penetrating the cell wall in the same way as in untreated wood.

6. CONCLUSION

Acetylation of Radiata pine changes the wood properties which are influencing the gluing with MUF adhesive systems. Especially the changed wetting properties and pH seems to carry a big part of the responsibility for the poor bonding properties with the tested MUF system.

- The viscosity of the MUF, analysed in rheology measurements, is increasing slower on acetylated wood than on untreated wood in the first 3 minutes. The opposite effect was expected, due to the lower pH and higher acetic acid content of the acetylated wood. It is assumed that a faster penetration of the water from the adhesive into the untreated wood is resulting in a higher complex viscosity and not necessarily a curing difference. In this way, rheology measurement of adhesives directly on wood surfaces does not seem to be the appropriate method to detect curing differences.

- There is not observed any difference in the penetration or thickness of the glue line between acetylated and untreated wood. This shows that penetration into the cell lumen is not affected by the modification. Further, it can be assumed from microscopy analysis of the glue line in axial direction that penetration into the cell lumen is mainly due to the applied pressure and open tracheids towards the glue line.

- There exists a thin line of what can be assumed to be pre-cured adhesive, where the adhesive has been in contact with the cell wall of acetylated wood.

- The pH of acetylated wood is lower than for untreated and in contrast to untreated wood there exist a buffer capacity for water dissolved extractives from acetylated wood. A lower pH of the wood can contribute to accelerate curing and the buffer capacity shows that it is more difficult to increase the pH in acetylated wood compared to untreated wood.

- A significant difference in pH is found between the core and outer part of the acetylated wood planks. It is assumed that this is mainly due to evaporation of acetic acid from the surface. Removing free acetic acid in an industrial process is not working optimally all the way through the plank.

- The average apparent contact angle is higher for acetylated wood than for untreated wood. This confirms that acetylation decreases the wetting properties of the wood.

- Poorer wetting of acetylated wood affects the gluing properties of the adhesive negatively. The poor wetting properties in combination with a lower pH and free acetic acid in the

acetylated wood, which potentially can speed up the curing, will further reduce the performance of the MUF system.

7. RECOMMENDATIONS

Next step to improve the bonding properties of MUF on acetylated wood can be modifying of the MUF systems or the wood surface. The focus can be divided into three physical areas: the acetylation of the wood, the surface or interaction between the adhesive and wood and finally in the adhesive system itself. In the latter case, it would be obvious to test MUF with more wetting agents and getting the correct interfacial tension between the wood and adhesive. More advanced would be to change the pH range of which the MUF is curing. The tested MUF system is curing with a pH of 3-4 (Ormstad 2007; Viljugrein 2015) and the pH in the water dissolved extractives from untreated wood has a pH close to 4.6 while the acetylated has a pH close to pH 4. Lowering of the pH of which the MUF adhesive is curing could this way maybe improve the bonding of acetylated wood. Changing the ratio between the melamine, urea and formaldehyde could also affect the properties (Zanetti & Pizzi 2003) and probably the penetration as well since the F/U mole ratio effects the penetration in UF adhesives (Nuryawan et al. 2014). In the interaction area between the wood and adhesive coupling agents or promoter molecules might improve the chemical bonding (Nardin & Schultz 2003). Treatment of the wood surface could also be a part of the solution. An increment of the wood surface pH with applying an alkaline before applying the adhesive could theoretically work in the same way as lowering the pH area of where the adhesive is curing. Another method of changing the acetylated wood surface could perhaps be with oxidation activation. Sakata et al. (1993) have shown an increased wetting and glueability with UF on a range of different unmodified wood species after a corona treatment (oxidation activation) of the surfaces. Zanetti and Pizzi (2003) have shown to improved water and weathering resistance and wet internal bond strength of MUF wood adhesives after introducing "hexamine sulfate" to the resin. Most interesting in this case is that Zanetti and Pizzi (2003) also found that hexamine in a MUF resin will increase the buffering action and extend the buffering zone of the resin. This might be interesting in relation to the changed buffer capacity of the wood after acetylation. If choosing to change the chemical structure of the adhesive DSC could then be an alternative or supplement to the rheology. Zhang et al. (2013) have used DSC to study the curing behaviour UF and MUF made from different recipes.

Interesting to test, to see if the main problem is the free acetic acid, is the relative new acetylation method with microwaves developed in Sweden. The method should be able to remove acetic acid completely from both fibres and solid wood (Rowell, R. M. 2012).

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9. WORD-LIST

Adhesion: The interaction between the adhesive and substrate that holds them together, several forces and mechanisms exist here (see 1.4. Adhesives and adhesion).

Adhesive: referrer to the mix of the glue/resin and hardener components and can be both in the cured and fluent state.

ASE (%): Anti-Swelling Efficiency (Anti-Shrink Efficiency) expresses the increase in dimensional stability of modified wood, calculated on the formula:

$$ASE\ (\%) = \left[\frac{S_u - S_m}{S_u}\right] \cdot 100$$

S_u is the S (%) of unmodified wood and S_m is the S (%) of modified wood (the higher ASE % the less swelling or shrinking and more stabile wood) (Hill 2006).

CCA: A conventional wood preservative consisting of Copper Chrome and Arsenic as the active components. The product is widely used worldwide, but environmental restrictions in especially Europe have restricted the use of CCA products.

Cell wall polymers: Mainly Cellulose, hemicellulose and Lignin

Cell wall structure: middle lamella – primary wall – Secondary wall (S1 Outer layer, S2 Middle layer and S3 Inner layer)

Cells in conifers: Tracheids (fibres) more than 90 % of the volume, Parenchyma cells (mainly rays and resin canals) (epithelial cell).

CNC wood router: Computer Numerical Control wood router

Contact angle θ: the angle between the tangent to the liquid surface and the liquid/solid surface at the point of liquid/solid contact (Wålinder 2000).

DSC: Differential Scanning Calorimetry

EPI: Emulsion Polymer Isocyanate, two components wood adhesive with ability to bond plastic and other non-wood substrates, high resistance to moisture, heat and solvents.

Glue line: referrer to the line/layer of adhesive between two pieces of material, which holds them together (see Figure 2 on page 7).

Gluing: Referrer either to the process of applying adhesive or as a synonym to the adhesion.

Green Diamond: The distance between the top and bottom of the green diamond, represents the 95 % confidence interval. The horizontal line in the middle of the green diamond represents the group mean, while the length of this line is proportional to the sample size (Institute Inc. 2012. *JMP® 10 Basic Analysis and Graphing.* Cary, NC: SAS Institute Inc.).

HCl: Hydrochloric acid, a strong acid.

HSD: Honestly Significant Difference (Tukey-Kramer HSD)

Interface: Two-dimensional plane with no thickness - Surface between two liquids, two solids, or a liquid and a solid (Wålinder 2000).

Interphase: Has a certain thickness and is situated between two other phases (see Figure 2 on page 7). Also known as weak boundary layer (equivalent to a weak interphase) (Wålinder 2000).

MC: Moisture content, measured on the formula:

$$MC\ (\%) = \left[\frac{m_{wet} - m_{dry}}{m_{dry}}\right] \cdot 100$$

m_{wet} is the mass of the wood before drying, md_{ry} is the mass of the wood after drying.

MDF-boards: Medium-Density Fibreboards

MF: Melamine Formaldehyde, wood adhesive with high water resistance, light coloured, used with hardeners, hot and could cured.

MOE: Modulus of Elasticity is normally the static bending stiffness tested on small pieces of clear wood.

MOR: Modulus of Rupture is normally the bending strength tested on small pieces of clear wood.

MUF: Melamin Urea Formaldehyd, wood adhesive with high water resistance, light coloured, used together with a hardener.

NaOH: Sodium hydroxide, a strong base

PBW or pbw: Parts By Weight, here used in the glue-hardener ratio. 100:20 can e.g. be 20 grams glue and 4 grams hardener.

PF: Phenol Formaldehyde, wood adhesive cannot cure at room temperature (heat curring needed), high water resistance and good durability, yellow-brown coloured.

PRF: Phenol Resorcinol Formaldehyde, wood adhesive with high water resistance, yellow-brown dark coloured when cured, used together with a hardener, can cure at room temperature.

RF: Resorcinol Formaldehyde, wood adhesive can cure at room temperature, high water resistance, yellow-brown dark coloured when cured.

RH: Relative humidity, the percentage of water vapour in the air relative to the maximum for a given temperature.

S (%): Swelling coefficient expresses the dimensional stability, calculated on the formula:

$$S\ (\%) = \left[\frac{V_{ws} - V_{od}}{V_{od}}\right] \cdot 100$$

V_{ws} is the water-swollen volume of the wood and V_{od} is the oven-dry volume of the wood (Hill 2006)

Service class 1: MC in the materials correspond to a temperature of 20 °C, RH of the surrounding air only exceeding 65 % for a few weeks per year (homes, offices, shops) (DS/EN 1995-1-1 DK NA:2014 2014; EN 1995-1-1 (2004) 2004)

Service class 2: MC in the materials correspond to a temperature of 20 °C, RH of the surrounding air only exceeding 85 % for a few weeks per year (vacation homes, garages, warehouses) (DS/EN 1995-1-1 DK NA:2014 2014; EN 1995-1-1 (2004) 2004).

Service class 3: Climatic conditions leading to higher moisture contents than in service class 2 (constructions in damp arears or exposed to rain or water in general) (DS/EN 1995-1-1 DK NA:2014 2014; EN 1995-1-1 (2004) 2004).
UF: Urea Formaldehyde, wood adhesive with poor water resistance for indoor applications, light colour, used with hardeners.

WPG: Weight Percent Gain, tells the extent to which the wood has been modified and chemically bond been formed, calculated on the formula:

$$WPG\ (\%) = \left[\frac{M_m - M_u}{M_u}\right] \cdot 100$$

M_m is oven-dry mass of the modified wood and M_u is the oven-dry mass of the unmodified wood, often supplemented with the dimension changes (Hill 2006).

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