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Foaming and chemical foam control of lignin-phenol-formaldehyde (LPF) adhesives

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Abstract

Phenol-formaldehyde resins are a commonly used raw material in plywood adhesives. Lignin is a bio-based polymer that can be used as a partial phenol replacement to create lignin-phenol-formaldehyde (LPF) resins. Foaming is a natural phenomenon caused by continuous formation of bubbles that often negatively affects the quality of the adhesive. The objective of this thesis was to study the mechanism of foam formation and contribution of chemical additives. In the experimental part, efficiency of commercial foam control agents was measured while viscosity development was monitored. Based on the results, an optimal addition point for the chemicals was determined along with evaluation on the defoamers' efficiency and the selected test method.

The efficiency of defoamers in the adhesive was tested in laboratory scale by calculating a volume of air formed during mechanical stirring. The method was described by Evonik Industries AG to evaluate foamability of medium viscosity formulations and compare the performance of individual additives. The trials were conducted in two stages including preliminary and final trials in which the defoamers were added in two variations of addition point and dosage. After that, the best two of the defoamers were chosen based on the preliminary results and further tested in the final trials with one dosage. In both trials the tests were conducted on LPF resin formulated with two different hardeners and with an inclusion of a surface-active agent in the finals. Whilst, the development of viscosity was monitored by Brookfield viscosity in the resin and Flow viscosity in the adhesive, to assess any correlation to the foam volume.

The defoamers showed relatively poor performance as no significant decrease in the volume of air was detected. Visible differences in foam levels were attained by a comparison of the two hardeners as well as between the defoamer additions points. The presence of the surface-active agent expectedly contributed to an overall increase in the foam levels and viscosity by lowering the surface tension and stabilizing the foam. On the contrary, no visible viscosity correlation was detected with the use of defoamers. It was concluded that the test method possessed operational challenges, which contributed to some unexpected results.

Keywords
phenol-formaldehyde resin, lignin, foaming, viscosity, defoamer

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Tiivistelmä

Fenoli-formaldehydihartsit ovat yleisiä vaneriliimojen raaka-aineita. Ligniini on biopolymeeri, jolla voidaan korvata fenolia ligniini-fenoli-formaldehydihartsien (LPF) valmistuksessa. Vaahtoaminen on kaasukuplien nesteeseen muodostama ilmiö, jolla on usein negatiivinen vaikutus liiman laatuun. Tämän opinnäytetyön tavoitteena oli tutkia vaahdon muodostumisen mekanismia ja siihen liittyvien kemiallisten lisäaineiden vaikutusta. Kokeellisessa osiossa mitattiin vaahdonestoaineiden tehokkuutta samalla seuraten viskositeetin kehitystä. Tulosten perusteella voitiin määrittää optimaalinen kohta lisäaineiden lisäykselle liiman valmistuksen aikana sekä arvioida vaahdonestoaineiden tehokkuutta ja testauksiin valitun menetelmän toimivuutta.

Vaahdonestoaineiden tehokkuus määritettiin laboratoriossa laskemalla sekoituksen aikana muodostuneen ilman määrä. Menetelmä oli Evonik Industries AG:n kehittelemä, jolla voitiin arvioida korkea viskositeettisten nesteiden vaahtoamista ja vertailla yksittäisten lisäaineiden vaikutusta. Kokeet suoritettiin kahdessa osassa sisältäen alkutestaukset ja lopputestaukset, joiden aikana vaahdonestoaineet lisättiin kahdessa eri kohdassa ja annostuksessa. Alkutestien jälkeen kaksi parasta vaahdonestoainetta valittiin jatkoon ja kokeet toistettiin yhdellä annostuksella. Molemmissa osissa testit suoritettiin kahdella eri LPF-liimalla, jotka oli valmistettu eri kovetteilla ja lisäksi lopputestauksissa liiman lisättiin pinta-aktiivinen kemikaali. Kokeiden aikana viskositeetin kehitystä seurattiin mittaamalla Brookfield-viskositeettia hartsista ja Flow-viskositeettia liimasta.

Kokeiden aikana vaahdonestoaineiden suoriutuminen oli suhteellisen heikkoa eikä merkittävää vaahdon määrän vähentymistä tapahtunut. Kovetteiden väliset erot vaahtoamisessa olivat huomattavia samoin kuin erot vaahdonestoaineiden lisäyskohtien välillä. Pinta-aktiivinen kemikaali odotetusti nosti kokonaisvaahdon määrää ja viskositeettia alentamalla liiman pintajännitystä ja stabiloimalla vaahtoa. Toisaalta vaahdonestoaineiden korrelaatiota viskositeettiin ei ollut huomattavissa. Kokeiden perusteella voitiin päätellä, että testausmenetelmän operatiiviset ongelmat olivat syynä joihinkin odottamattomiin tuloksiin.

Asiasanat

fenoli-formaldehydihartsi, ligniini, vaahtoaminen, viskositeetti, vaahdonestoaine

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Sanna Laukkanen
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List of symbols and abbreviations

A	area	[m^2]
η	dynamic viscosity	[cP], [mPas]
m	mass	[g]
V	volume	[-], [ml]
D	density	[g/ml]
γ	surface tension	[Nm^{-1}], [Jm^{-2}]
W	The cost of energy	[-]

CMC	Critical micelle concentration
DMC	Dry matter content
F	Formaldehyde
H_2SO_4	Sulfuric acid
LPF	Lignin-phenol-formaldehyde
LVL	Laminated veneer lumber
MDF	Medium density fiberboard
MF	Melamine-formaldehyde
NaOH	Sodium hydroxide
OSB	Oriented strand board
PF	Phenol-formaldehyde
R&D	Research and development
UF	Urea-formaldehyde

1 INTRODUCTION

The increased concern towards environmental challenges and the use of fossil resources has created a strong need for developing new alternative materials and energy solutions. Nowadays many believe that movement to a bio-based production system is a sensible approach for achieving economic and environmental sustainability. As a renewable energy source, biomass does not contribute to carbon dioxide in the atmosphere in contrast to fossil fuels, which means bio-based products have the potential for being more environmentally friendly and less polluting than products made by the petrochemical industry.

Wood-based lignocellulose is a widely available, carbon-neutral, and inedible bioresource that could be regenerated on a world-wide basis in considerable quantities each year. However, most biorefinery processes currently focus on the utilization of the carbohydrate fractions (cellulose and hemicellulose), while underutilizing lignin, the second most abundant terrestrial polymer. Lignin is the only large-volume renewable aromatic feedstock, which is found in most terrestrial plants typically in a range of 15‑30% by dry weight and 40% by energy. (Wang et al., 2018) Traditionally, most large-scale industrial processes that use plant polysaccharides have burned lignin to generate the power needed for biomass conversion.

Research and development of lignin applications has been a very topical issue for years now. Although much of the lignin produced by pulp industry is currently consumed as a fuel, there are other, higher value-added applications, such as carbon material precursor, emulsifier, coating, filler or substitute for metal/inorganic nanoparticles being studied (Figueiredo et al., 2018). Other example of lignin applications which have already been developed further is usage of lignin as a natural adhesive for wood products to replace fossil-based phenol in phenol-formaldehyde (PF) resins. These PF resins are widely used but hold many disadvantages due to their expensive price, toxicity and oncogenic nature (Pizzi, 2016). PF resins modified with lignin are called lignin-phenol-formaldehyde (LPF) resins.

1.1 Objective and scope

The aim of this thesis was to study the foaming phenomenon of plywood adhesives, in this case lignin-phenol-formaldehyde, and the effects it has on plywood manufacturing process. Foaming is the continuous formation of bubbles which often occurs as resin is mixed with fillers and stirred in order to complete the adhesive. The formed air causes technical difficulties with controlling quality of the glue mix and can lead to productional failures during the application. Chemical antifoaming agents that modify the surface tension of a liquid are used either to remove foam or prevent it from generating.

The experimental part of the thesis consists of a comparison between four different antifoaming agents tested with LPF adhesive and an evaluation on the effectiveness of the selected analysis method. The experiment is performed adding certain amounts of additives into the glue mix and stirring it according to instructions of the selected method. The volume of air expresses the quantity of foam and thus allows comparison between the performance of each additive.

1.2 Introduction of the target company

UPM-Kymmene Oyj (UPM) was formed in 1996 as a Finnish forest industry company that has since extended its business to Bioeconomy products such as biofuels, biocomposites and biochemicals. Nowadays UPM consists of six separate business areas; UPM Biorefining, UPM Energy, UPM Raflatac, UPM Specialty Papers, UPM Communication Papers and UPM Plywood. The company currently employs over 19,000 people in 46 countries including production in 12 countries. In 2017, UPM reached its record sales of over 10 billion euros. (UPM, 2018)

UPM’s Northern Europe Research Center (NERC) in Lappeenranta focuses mostly on research of fiber materials, pulp & paper and development of biofuel and biochemical production processes. This thesis was conducted for Lignin team in the UPM Biochemicals unit. (UPM Kaukas, 2018)

LITERATURE REVIEW

The first part of the thesis covers the main points of veneer and plywood manufacturing, glue applications and wood adhesives theoretically. Principals of phenol-formaldehyde resins and lignin application are also determined. Basics of foaming phenomenon and its effects on plywood production are reviewed along with theory of selected chemicals used to control the foam.

2 MANUFACTURING PROCESS OF VENEER AND PLYWOOD

Plywood is an engineered wood product made of three or more thin layers of wood (veneer) bonded together with an adhesive. There are two types of plywood; softwood plywood and hardwood plywood, made from a variety of wood sources. Plywood is used in many applications such as home construction, packaging, furniture and in many kinds of equipment that require high-strength and rigidity, are easy to handle and have shock- and weather-resistant qualities.

Plywood manufacturing process consists of nine main processes presented in Figure 1: log storing, log conditioning, log debarking and bucking, peeling the logs into veneers, drying the veneers, gluing the veneers together, pressing the veneers, plywood cutting, and other finishing processes such as sanding. (EPA, 2002)

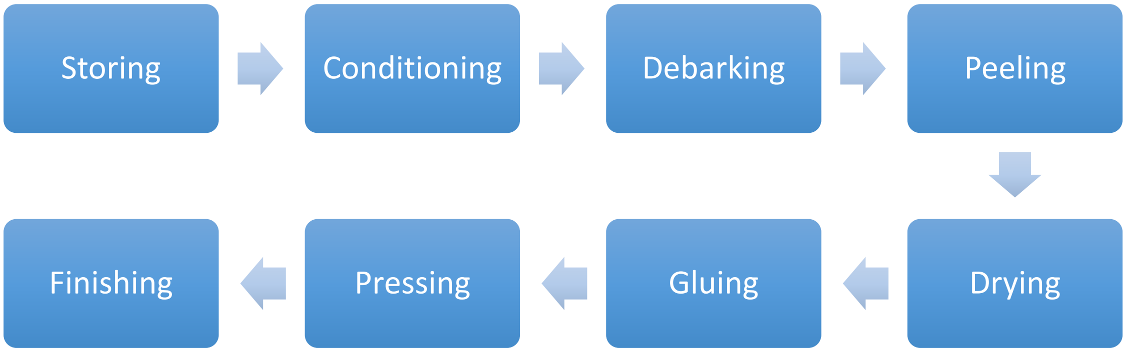


Figure 1. The nine main stages of plywood manufacturing process.

The process begins with logs arriving at the mill, storing them and eventually moving them into a location where the blocks may be steamed or immersed in hot water in order to improve peel ability. This process takes usually 12-40 hours depending on the type of wood, the diameter of the block, and other factors. Once removed from the heat source, the logs are measured and mechanically stripped of their bark. The initial step of debarking is accomplished by feeding logs through one of several types of debarking machines. The purpose of this operation is to remove the outer bark of the tree without substantially damaging the wood. After debarking the blocks are cut to length and divided according to quality. The size that the logs are cut to is usually dependent on the production at the time of cutting; finished panel size and grain direction play a part in the cutting of logs. (Koponen, 2002).

Next, logs are transported to the peeler lathe, where they are automatically aligned and fed into the lathe one at a time. As the lathe rotates the block rapidly about its long axis, a full-length knife blade peels a continuous sheet of veneer from the surface of the spinning block. The veneer knife cuts the blocks into veneers that are typically 3 mm thick. The veneer pieces are then clipped to a usable width to allow shrinkage and trim. Peeling can also be done after the drying phase. (Schramm, 2003)

Veneers are taken to a veneer dryer either before or after the clipper where they are dried to moisture contents appropriate for plywood gluing which normally ranges from around 1 to 15 percent, dry basis (EPA, 2002). Target moisture content depends on the wanted application of the product and type of resin used in subsequent gluing steps. Average moisture contents vary somewhat regarding thickness of the veneers and wood species (Table 1). (Koponen, 2002)

Table 1. Appropriate range and average of veneer moisture content (Koponen, 2002)

	Range %	**Average %**
Birch veneer 1,5mm	0-10	6
Spruce veneer 1,5mm	0-6	3
Spruce veneer over 2mm	0-8	4

When the veneers have been dried to their specified moisture content, they are conveyed to a layup operation, where a thermosetting resin is spread on the veneers. The resins are applied by glue spreaders, curtain coaters, or spray systems. Spreaders have a series of rubber-covered grooved application rolls that apply the resin to the sheet of veneer. Generally, resin is spread on two sides of one ply of veneer, which is then placed between two plies of veneer that are not coated with resin. Assembly of the plywood panels must be symmetrical on either side in order to avoid excessive warpage (Schramm, 2003) Adhesive applying is studied more specifically later in this thesis.

The laid-up assembly of veneers is transferred to a staging point in front of the cold press. Before pressing, the bundle must be allowed to stand for a period of time. This so called “open time” in necessary for the adhesive to give off moisture and convert to a semi-solid state. The amount of time ranges from 5 to 20 minutes depending on glue spread, substrate conditions and mill conditions. (Schramm, 2003) Cold pressing is conducted at room temperature prior the hot-press. (Koponen, 2002) One function of the cold press is to transfer the adhesive from the wet surfaces to the dry surfaces in a way that glue is able to penetrate the pores of each sheet without forced all the way through it. Another objective of the cold press is to sufficiently facilitate loading into the hot press and even the moisture content between the components. Pressure of the cold press is usually set to 1,0 MPa (10 bar) and pressing time from 5 to 10 minutes (Varis, 2017). Once the allotted time has expired, the unit is moved and staged in front of the hot press for final bonding into a plywood panel.

Hot pressing has two main objectives; to activate the thermosetting resins and to press the glue into a thin layer in order to finish the panel. Typical press temperatures range from 100° to 170°C for phenolic adhesives, and 100° to 125°C for urea adhesives (Varis, 2017). Press times generally range from 2 to 7 minutes. The time and temperature vary depending on the wood species used, the resin used, and the press design (Koponen, 2002). Once pressed, panels are discharged onto racks on the outfeed side of the press until being transferred to the sawing area. Thickness of the panels is routinely checked at this point. (Schramm, 2003)

At the finish end, the panels are trimmed to the proper dimensions and its' surfaces sanded smooth before leaving the mill (Schramm, 2003). The further type of finishing depends on the end product desired.

2.1 Glue application systems

Gluing is one of the most important phases of plywood manufacturing. It is crucial considering the product's strength and resistance qualities are, for the most part, dependent on the successfulness of the gluing. (Koponen, 2002)
Four types of basic means are used to apply the adhesive to plywood components (Baldwin, 1995);

- glue spreaders (hard-roll, sponge-roll)
- curtain coaters
- extruders
- sprays

Glue spreaders (Figure 2) or hard rolls are the most common glue applicator and for a long time they were nearly universal. Nowadays other application systems have increased their popularity and hard rolls are now only of many options. (Baldwin, 1995). A hard-roll glue applicator consists of two grooved pairs of rollers, one for the top of the component passing through the machine, and one for the bottom. Each pair of the rollers consists of a larger applicator roll and smaller doctor roll. It is covered with a rubber material with an embossed groove pattern designed to uniformly apply the adhesive over the surface of the substrate. Also, the glue spread is set by adjusting the distance between the two rolls to correspond with the thickness of the substrate (Schramm, 2003).

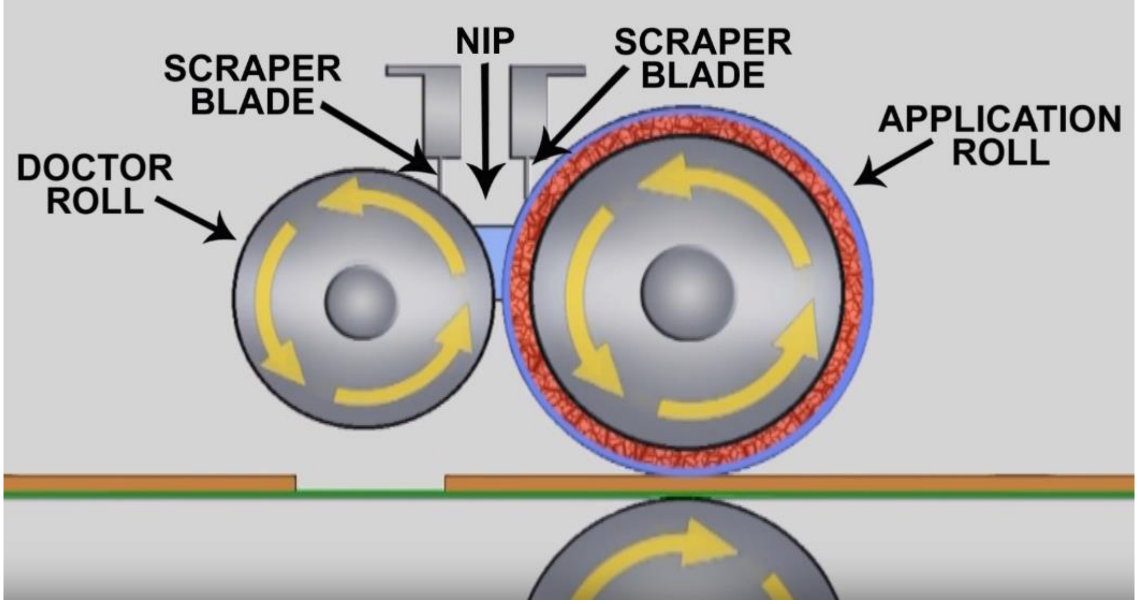


Figure 2. Mechanism of a roller coater glue spreader. (Stanza Machinery, 2017)

There are two types of hard rolls available; 2-roll spreaders and 4-roll spreaders from which the 4-rollers are more common. Factors effecting the quantity of spread glue are:

- pattern and frequency of the surface grooves
- pressure between the rolls
- the space between the rolls
- viscosity of the adhesive

Quantity of glue is dependent of the size and the groove on the rolls' surface thus having an effect on the results of the spreading. Also, increased pressure between the rolls decreases the spread area, which is why the pressure must be adjusted to appropriate level in order to allow the adhesive spread evenly. Similar adjustments are done to optimize the space between the rolls and viscosity of the glue. The viscosity affects the spreading itself but also the formation of glue joint. (Koponen, 2002)

There is also one different type of glue spreader to be mentioned, so called sponge rolls which is ungrooved and close-celled and is most frequently used in automated layup machines. (Baldwin, 1995)

Curtain coating (Figure 3) is one of the latest application systems and it can be divided into two types; (Baldwin, 1995)

- pressure head
- gravity head

Figure 3. Basic curtain coater with a pressure head. (UPM, 2018)

According to Baldwin (1995), a V-shaped pressure head is essentially reservoir made airtight by a removable cover and fitted across the bottom with an adjustable gap. Adhesive is sent into the reservoir by positive-displacement pump with a variable speed. Spread control is determined by the viscosity of the glue, width of the knife gap and the pump speed. Curtain of adhesive is passed onto veneer sheets as an individual plies are conveyed under the head. A part called trough is designed to eliminate entrapment of air, catching the curtain and directing the adhesive back to the reservoir that supplies the pump. Waste is minimum in curtain coating because only the material intercepted by the veneer as it passed through the pressure curtain is used and the unused glue is recirculated. Curtain coating has also a second variation in which the application method is quite similar, but the feeding is functioned by gravity. (Baldwin, 1995)

Spray systems consist of a fixed-head applicator capable of a wide spray with a nozzle pressure of 300 psi or more. These systems operate in one of the two ways:

i. The adhesive is mixed with atomized air
ii. Or the adhesive is atomized by high pressure forcing the glue through a small spray orifice.

Controlling viscosity and temperature are important particularly with the latter system because the atomized spray pattern is dependent upon uniform viscosity and temperature. Viscosity is, for the most part, is determined by the glue mixing procedures and further controlled by keeping glue temperature preferably around 32-37°C at the spray tip. (Baldwin, 1995)

Finally, the extrusion method of glue application in which the plywood adhesive flows through a metering pump at a constant rate, passing to a foamer and growing to about five times its original volume. After that the glue is extruded onto the veneer as glue “rods” which is often described as “spaghetti” glue.
The extrusion system has gained commercial acceptance due to reducing spreads and increasing dry-out resistance. (Baldwin, 1995)

2.2 Plywood adhesives

Plywood adhesives can be defined into two main categories i) synthetic adhesives and ii) natural adhesives. The two main types of synthetic resins used in plywood adhesives are phenol-formaldehyde, which is used for softwood plywood and exterior grades of hardwood plywood, and urea-formaldehyde, which is used to glue interior grades of hardwood plywood. Other available synthetic resins include melamine-formaldehyde adhesives, tannin-formaldehyde adhesives, resorcinol and diisocyanate adhesives and also lignin-based phenolic adhesives. (Pizzi, 1994) Phenol-formaldehyde and lignin-based adhesives are studied later in this thesis.

General requirements for wood adhesives and typical properties of resins are defined below by Dunky, 2003 and listed more detailed by Pizzi (1994) and Koponen (2002) in Table 2:

- Easy application
- Composition (solid content, viscosity, purity)
- Climate resistance
- Compatibility for additives
- Ecological behavior and low emissions
- Hardening characteristics (reactivity, crosslinking)
- Color and smell

Table 2. Properties of a typical PF resin in plywood production (Pizzi, 1994; Koponen, 2002)

Property	Value
pH	11-12,5
Solids content	55-60 %
Storage time (25°C)	3 months
Open time in production	30 min
Cold press time	0,5-1,0 Mpa
Cold press pressure	5-10 min
Hot press temperature	125-130 ºC
Hot press pressure	Birch: 1,7-1,8 MPa Softwood: 1,1-1,3 MPa Mixed: 1,3-1,5 MPa

Urea-formaldehyde (UF) resins are a type of adhesives known as aminoplastic synthetic resins that are polymeric condensation products of the reaction of formaldehyde with urea. Urea-formaldehyde resin was developed in the 1930s and is one of the most important resins used in the manufacture of hardwood and softwood panels and other veneer-based products. (Pizzi, 1994)

The advantages of UF resins were listed by Pizzi (1994a,b) as follows:

- Hardness of the resin
- Low flammability
- Good thermal properties of the resin

- Absence of color in the cured polymer
- Adaptability of the resin to a variety of curing conditions

Weaknesses of UF resins include lack of long-term moisture and temperature resistance, which is why the panels are not applicable in exterior conditions with elevated temperatures and constant cycles of wetting and drying. There is also a concern with free formaldehyde emission originated from either UF resin itself or panel products bonded by UF resins, that have lead to worldwide regulations by World Health Organization (WHO). (A Nuryawan *et al*, 2017; Baldwin, 1995)

Melamine-formaldehyde (MF) resins are quite similar to urea-formaldehyde resins. They are fully compatible and, therefore, are often co-reacted together. MF is made from melamine and formaldehyde by condensation of the two monomers. MF has much higher resistancy to water attacks compared to UF resins but is however very expensive and therefore much less used. The resin blend with melamine, urea and formaldehyde is called melamine–urea–formaldehyde (MUF). One of the most important applications of MF resins are exterior- and semi-exterior plywood and particleboard, where it is often blended with UF resins to improve the scratch and flame resistance and also acts as a flame retardant. (Pizzi, 1994; Baldwin, 1995)

Synthetical isocyanate adhesives are based on polyethylene polyphenyl isocyanate and methylene bisphenyl diisocyanate. They are formaldehyde free adhesives with high bonding strength and tolerance to elevated temperatures. They are used as a combination of isocyanate and phenol-formaldehyde in softwood plywood industry. Benefits of isocyanate adhesives include variety of choices in durability, color and moisture tolerances. However, high cost of ingredients, health hazard concerns and gluing problems have discouraged wide usage. (Baldwin, 1995)

Natural adhesives based on animal products include blood, casein and also organic products such as soybeans and starch. Blood glues have been know since the ancient times and were commonly used for plywood until development of PF resins. Blood adhesives are usually made from soluble dried beef blood, which is a byproduct of meat packaging operation. Currently, blood glues are of little commercial importance in most countries, but they are still used in certain regions for the manufacture of interior grade plywood. Similar traditional adhesive is dairy-based casein, made from acidified milk. Casein glue has been used extensively for heavy timber laminated beams but the synthetic resins have gradually reduced its use. Along with blood glues, soybean is a protein type adhesive discovered in the 1920s. Its use for plywood has not been popular due to availability of more durable adhesives in the market. Compared to other adhesives, soybean glue is more durable and moisture-resistant than starch glues but less durable than casein glue. Durability is defined as ability to withstand wear and tear or decay and for plywood it basically means properties of strength, water, chemical or biological susceptibilities along with long-term glue line degradation. (Sellers, 1985)

Plywood adhesives are formulated by adding water, fillers and possible additives into liquid, water-soluble resin. Extenders are added into resin as a powder, which along hardening components adjust the properties of the glue mix. Extender substances generally have some minor adhesive action and are used to reduce the amount of the primary binder required per unit area. A filler, such as water, is a relatively non-adhesive substance which improves working properties, performance, strength and other qualities of the adhesive. (Sellers, 1985) A typical composition of plywood adhesive is presented in Table 3.

Table 3. Typical composition of plywood adhesive. (Varis, 2017)

Ingredient	**wt% per hundred resin**
PF-resin	100
Hardener	20
Water	25

There are several factors affecting the recipe of the adhesive. Its viscosity, absorbency, solid content, open time and other specific parameters in plywood manufacturing are considered when tailoring the desired formulation. Proper mixing of the adhesive is also important to ensure homogenous composition.

Manufacturing the adhesive usually takes place in plywood mills where the resin is pumped into a large container to which the ingredients are automatically dosed, and the formulation is mixed. (Varis, 2017)

3 PHENOL-FORMALDEHYDE RESIN

Phenol-formaldehyde (PF) resins are the principle resins used for bonding structural plywood and also to bond dense hardwood plywood and waferboard. (Baldwin, 1995) As the first true synthetic polymers to be developed commercially, phenolic resins are still the most common adhesive used in plywood manufacturing (Pizzi, 1994; Koponen, 2002). Formed from a condensation reaction of phenol and formaldehyde, phenolic resin was invented by Belgian-American chemist Dr. Leo Baekeland in 1907 when it was originally named Bakelite (The Chemical Company, 2018).

3.1 Production

The production of phenolic resins is an old but still very active industry. Phenol-formaldehyde resins are fossil-based products meaning its' raw materials are nonrenewable. Formaldehyde is produced from natural gas and crude oil is the source of phenol. The raw material ladder for PF resin is presented in Figure 4.

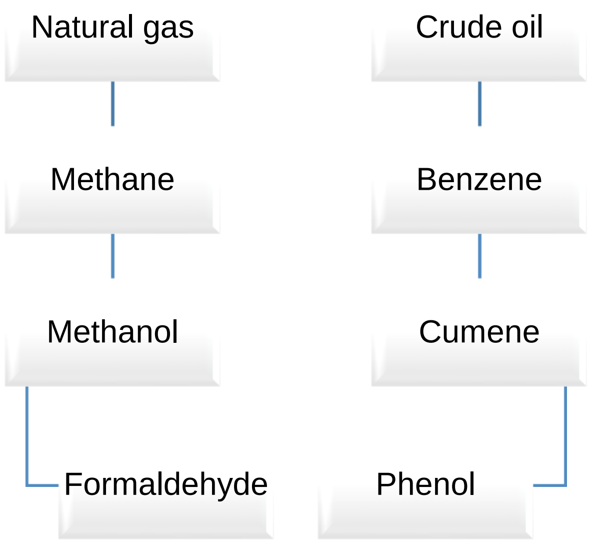


Figure 4. Raw material ladder for PF resins. (Baldwin, 1995; Sellers, 1985)

In formation of phenol-formaldehyde adhesive, formaldehyde reacts with phenol (Figure 5) and water is cleaved via thermal condensation reaction. Because of water-vapour originating from the condensation reaction, the adhesives need high temperature and high pressure for curing in order to avoid volume increase caused by water. (Habenicht, 2009)

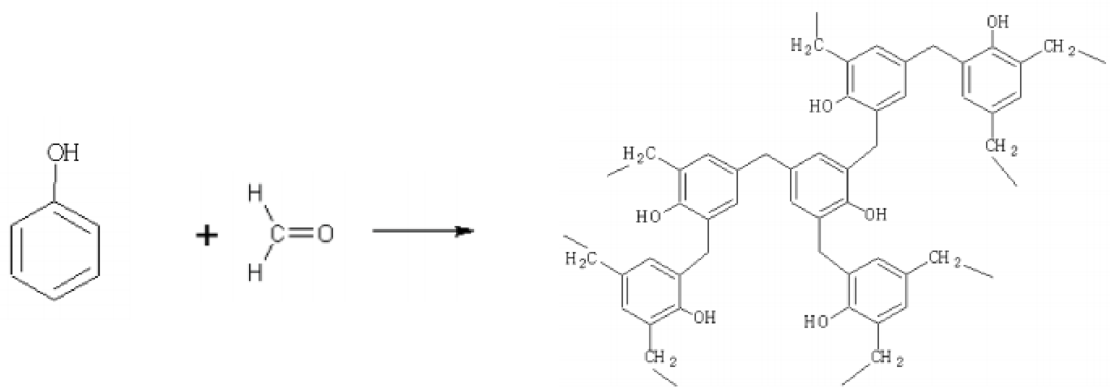


Figure 5. Phenol reaction with formaldehyde forming PF resin. (Habenicht, 2009)

There are two types of phenol-formaldehyde resins, namely Novolac and Resol, that can be formed depending on the formaldehyde to phenol ratio and the type of catalyst involved in the synthesis of the resin (Figure 6). The production of resols is done under alkaline conditions (pH > 7) using an excess of formaldehyde that facilitates a cross-linking density that results in an excellent moisture resistance, low flammability and high tensile strengths in a cured state. A resol molecule contains reactive methyl groups, which under heat cause the reactive resol molecules to condense to form large molecules. With resols, the molar ratio of formaldehyde to phenol can be 1.6-1 to 2.5-1, resulting better gluing qualities with wood applications. (Baldwin, 1995; Pizzi, 1994; Sellers, 1985)

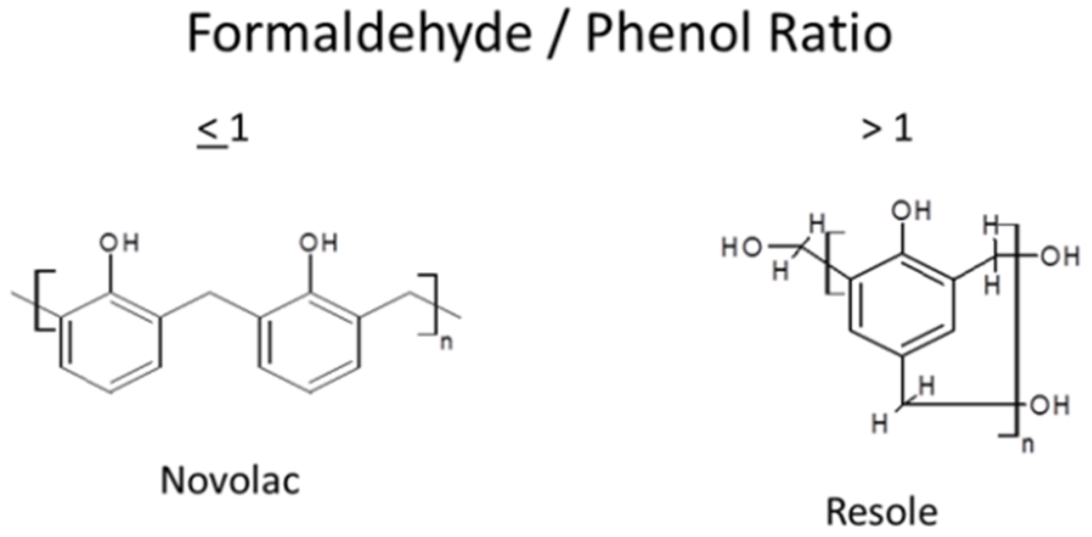


Figure 6. The chemical structures of resin types according to P/F ratio. (Institution of Chemical Engineers, 2015)

The second type of PF resins are thermoplastic Novolacs which melt and flow upon heating, are soluble in various organic solvents and maintain these properties even during prolonged heating (Sellers, 1985). The Novolac resin reactions are acid (pH < 7) catalyzed with a deficiency of formaldehyde, forming the resin under formaldehyde to phenol ratio of less than 1. Due to its' acidity and thermoplastic factors, Novolacs are rarely used in plywood manufacture. (Sellers, 1985; Pizzi, 1994)

The polymerization process for the manufacture of phenol formaldehyde is typically made in batches in a jacketed, stainless steel reactor. The raw materials phenol, formaldehyde and the catalyst are mixed and heated to 80-100C. Water cooling and refluxing remove the excess heat of the exothermic reaction. During the batch, temperatures are kept under 95 to 100°C by applying vacuum to the reactor or by cooling water in the reactor. Reactions times vary depending on pH, the phenol-formaldehyde ratio, the presence or absence of reaction retarders (i.e. alcohols) and the reaction temperature, but usually end up between 1 to 8 hours. (Pizzi, 1994) The reaction times and temperatures are presented in Table 4.

Table 4. Differences between Novolac and Resol in terms of synthesis process conditions (Huang, 2007).

Type of phenolic resin	P/F ratio	Reaction time h	Reaction temperature ℃
Resol	> 1	1-3	79 - 100
Novolac	< 1	3-6	100

3.2 Properties

Significant properties of resins in terms of gluing are viscosity, dry matter content (DMC), pH and gel time (Sellers, 1985) Typically the DMC of plywood resins range from 40 to 45 % and viscosity from 150 to 600 cP at 25 °C (Pizzi, 2003b). Other properties such as alkalinity, free formaldehyde content, phenol and methanol content, molar mass and conductivity are also determined.

PF resol resins possess several advantages, such as the good mechanical and electrical insulation property and excellent durability (Klempner et al 2004; Pilato, 2010). If properly cured, PF adhesives are waterproof and often more durable than the wood itself. High heat and moisture resistance make PF resol resins ideal for exterior use. Other typical properties of PF resol resins include high modulus of elasticity, tensile strength, dimensional stability and low flammability. (Dunky, 2003)

According to Dunky (2003), another advantage of phenolic resins are its' low formaldehyde emissions compared to the widely used UF resins. These lower emissions of PF resins than UF resins are due to the fact that PF resins are resistant to hydrolysis and therefore have stable C-C bonds between aromatic ring and methylene bridges. On the other hand, disadvantages of PF resins include longer pressing times for hardening compared to UF resins, dark color of the glue line and higher equilibrium moisture content of the boards. The synthetization of PF resins from fossil fuel resources also poses two major concerns; sustainability issues and environmental ones. The sustainability issues arise from the inevitable depletion of fossil fuel resources while the environmental concerns relate to the emission of volatile organic compounds. Other concerns include price pressure as demand of other petroleum-based products increases. (Akude, 2017; Baldwin, 1995).

3.3 Applications

Wood adhesives represent the largest market for phenol-formaldehyde polymers where they are used as binders for exterior-grade wood-based composite products. Phenolic resins are widely used glues for construction grade wood panels, that require water-resistance abilities, such as plywood and oriented strand board (OSB). Other wood composites in which PF resins may be used, are structural laminated veneer lumber (LVL), particleboard and medium density fiberboard (MDF), each having different manufacturing processes and methods for glue application (Akude, 2017). The polymers of phenol-formaldehyde are dark in colour as a result of side reactions during polymerization (Pizzi, 1994), making phenolic resins unsuitable for interior decorative paneling (Dunky, 2003). Examples of different wood-based composites are presented in the following Table 5.

Table 5. Classification of composites (Stark et al., 2010)

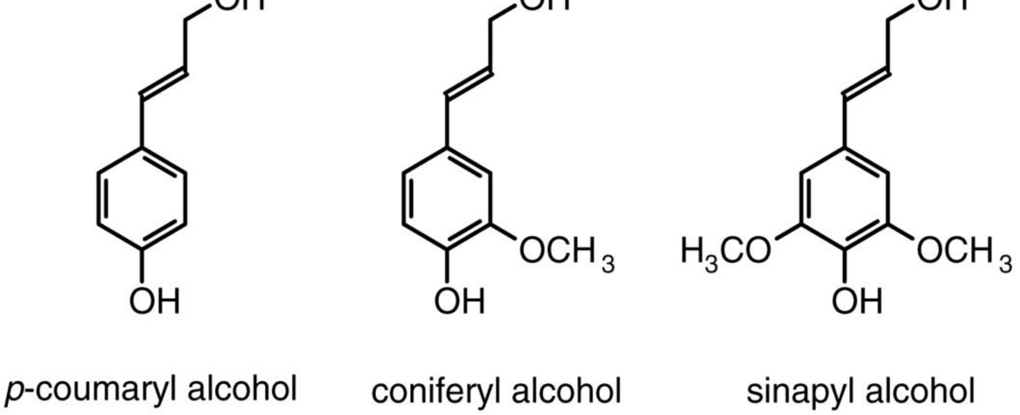
Classes of wood-based composites	**Examples of wood-based composites**
Veneer-based materials	Plywood, laminated veneer lumber (LVL), parallel-laminated veneer (PVL)
Composite materials	Particleboard, waferboard, Oriented strand board (OSB), laminated strand lumber (LSL), oriented strand lumber (OSL)
Laminates	Glue-laminated timbers, overlayed materials, laminated wood-nonwood composites
Wood-nonwood composites	Wood fiber-polymer composites and inorganic-bonded composites

Commercially, the only type of phenolic resins used are Resols which in case of particleboard, are hardened by heating after addition of small amounts of wax emulsion and insecticide solution. In case of plywood, the resin is added with vegetable or mineral filler and tackifiers. (Pizzi, 1994)

4 LIGNIN

Wood is essentially composed of cellulose, hemicelluloses, lignin, and extractives. However, their relative composition varies in different wood species and the contents of cellulose and hemicelluloses are relatively higher than that of lignin. The function of lignin is to contribute to the mechanical strength of the wood by giving stiffness to cell wall. Lignin acts as a barrier and contributes to fluid transport system by making the cell wall hydrophobic in order to protect the wood against microbial degradation. (Alekhina et al., 2015)

Lignin is defined as cross-linked high molecular mass polyphenol that consists of phenylpropane units that are irregularly linked to each other. The exact structure of native lignin is still unclear, as studies have determined that when lignin is isolated from wood it undergoes degradation depending on the extraction method, changing both its structure and molecular weight. (Hatakeyama, 2010) The complex structure of the lignin polymer always differs by its origin, but native lignins can be classified into softwood, hardwood and grass lignins that are formed mainly from three types of monolignols; coniferyl alcohol units, sinapyl alcohol units and p-coumaryl alcohol units (Figure 7). (Stenius, 2000)



p-coumaryl alcohol coniferyl alcohol sinapyl alcohol

Figure 7. Structures of three major monolignols. (Hatfield and Vermerris, 2001)

Coniferyl alcohol units are mainly found in softwood lignin, whereas, hardwood lignin contains both coniferyl and sinapyl alcohol units. The third monolignolic unit, p-coumaryl alcohol, is more commonly found in annual plants. (Nordberg, 2012) The proportion of each monolignol according to plant species is listed in Table 6.

Table 6. Percentage (%) of monolignols in plants. (Gellerstedt, 2008)

	p-Coumaryl alcohol	**Coniferyl alcohol**	**Sinapyl alcohol**
Softwoods	<5[a]	>95	0[a]
Hardwoods	0-8	25-50	45-75
Grasses	5-35	35-80	20-55

[a] Some exceptions exist.

Different types of lignin can be extracted through various extraction methods. In the industry, these methods are conducted in order to obtain the cellulose needed for paper or bioethanol production. Pulping, for instance, is a significant part of the papermaking process in which lignin is near-totally dissolved from cellulose by cooking wood in alkaline solution with sodium hydroxide (soda process) or in a further developed process that also includes sodium sulfide to accelerate the degradation of lignin further (kraft process). Nowadays, kraft process is the most often used pulping method, but instead the main source for commercially available lignin is sulfite process, which is an acidic pulping process, and exists in contrast to the alkaline ones. Sulfite pulping is an acidic process that has a greater percentage of lignin removed with either calcium, ammonium, magnesium or sodium as a base. (Kun et al.,2017; Sjöström, 1993)

As a major component of all plants, lignin represents an enormous renewable raw material source. It is mainly produced by the bioethanol and paper industry as a side product in a form of black liquor that forms during the extraction of the targeted valuable product of cellulose. Approximately 98% of the world-wide black liquor (as well as lignin) production is burnt immediately to provide heat and power for cellulose production. The availability of lignin in large quantities has made its price relatively low meaning that the utilization of lignin in any value-added application would result in considerable economical gain.(Kun et al.,2017) Many possible applications have been studied since a market for lignin-based products could replace fossil derived raw materials at the same time as improve energy efficiency when an excess of energy is taken out from the mills as lignin (Lignimatch, 2007-2009). The difficulty of utilization lies in the complexity of lignin structure, which effects its valorization not only scientifically, technologically, but also economically (Kun et al.,2017).

However, one quite recently developed method of commercial lignin extraction has received much attention. This so called LignoBoost process consists of taking black liquor from the evaporation plant and lowering its pH with carbon dioxide. The precipitated lignin is then dewatered by filtration, conditioned with acidified wash water and dewatered again to produce virtually pure lignin cakes. The LignoBoost method makes it possible to extract lignin efficiently from the black liquor in kraft mills and thus enables to expand the capacity of a pulp mill at a lower cost compared to what building extensions to recovery boiler would incur. The first LignoBoost plant in Finland, Stora Enso Sunila mill, was started up in 2015 with a capacity of 50 000 tons of dry (95% dry content) lignin per year. (Valmet, 2018)

5 LIGNIN-PHENOL-FORMALDEHYDE RESIN

Lignin has a similar structure to phenol which means it can be used as a substitute of it (Turunen et al.,2003; Tejado et al.,2007). Lignin polymer’s backbone of phenyl propane units make it an exceptionally comparable to phenol in the production of phenolic resin (Calvo-Flores et al., 2010). Currently, nearly most of the phenol has been able to replace by unmodified and modified lignin in an adhesive formulation of wood composite products without having negative effects on the mechanical properties of the panels. (Khan and Ashraf, 2007; Wang et al., 2009)

5.1 Production

Biomass is the most promising alternative for phenol replacement because it is readily available renewable resource. Lignin can be used with or without chemical modification, depending on the target application. In the early studies on the lignin-phenol-formaldehyde resin, lignin was directly incorporated to phenolic resins and applied as wood adhesives, in which it served both as a filler and a phenol substitute (Hu et al., 2011). Nowadays, chemical modification has enabled preparation of lignin to a large range of chemicals, building blocks and polymers (Laurichesse and Avérous, 2013). Modification increases the chemical reactivity of lignin's hydroxyl groups and the number of reactive sites in lignin towards formaldehyde, while also improving strength properties of the final adhesive. (Hu et al., 2011; Laurichesse and Avérous, 2014) Lignin reaction with phenolic resin is conducted during the cooking procedures of the resin. (Pizzi and Ibeh, 2014)

There are several chemical modification methods to produce phenolic compounds from lignin, of which well-known are (Hu et al., 2011; Laurichesse and Avérous, 2014):

- methylolation (hydroxymethylation)
- demethylaton
- phenolysis (phenolation)
- hydrolysis

The trend is to modify the chemical structure of lignin to increase its reactivity meaning its potential reactive sites toward formaldehyde. In case of lignin-phenol-formaldehyde resins, there are two different options to synthesize them: i) crude lignin reaction with formaldehyde in which the condensation reaction with lignin and with PF resins is rather limited. ii) To modify lignin with methods such as methylolation, demethylation and phenolysis. (Mankar et al., 2012)

In phenolysis, the reaction of lignin with phenol, lignins are usually modified in the presence of ethanol or methanol (Effendi et al., 2008). During the process, lignin is thermal treated with phenol in an acidic medium, leading to the condensation of phenol with lignin aromatic ring and side chain. In addition, ether bonds are also cleaved, which decreased the molecular weight of lignin molecules. In phenolysis, the resulting materials can react with formaldehyde under either alkaline or acid conditions to synthetize novolac or resol resins. (Ysbrandy et al.1992; Cetin et al. 2002)

Lignin methylation is dominantly carried out via The Lederer-Manasse reaction in an alkaline medium with formaldehyde (Zhao, 1994). Methylation increases lignin's reactivity by incorporating hydroxymethyl groups in the aromatic rings of lignin. On the contrary, the principal of demethylation is to partially remove methyl groups that are known to block lignin's reactive aromatic hydroxyl groups, resulting the lignin to have much more free phenolic groups and therefore more reactivity (Okamoto et al. 1996).

The other methods for lignin modification included hydrolysis that depolymerizes lignin by tearing off the ether and C-C bonds which bind the phenyl-propane units together. These units in lignin are the sources of phenolic compounds. Hydrolysis can be carried out in alkaline conditions for example with sodium hydroxide (NaOH) or in acid conditions using sulfuric acid (H_2SO_4). (Hu et al., 2011) In addition, another recently developed method for lignin modification is alkalation in which the lignin is first treated with hydroxide of an alkali metal (i.e. NaOH), and heated. Alkalation increases the reactivity of lignin, making it more suitable for further applications, such as plywood adhesive production (Pietarinen et al., 2014) Furthermore, there are also studies that have focused on the conversion of lignin to syngas by gasification (Yoshida.2004; Osada 2006) and others such as the production of bio-oil from lignin through pyrolysis (Petrocelli, 1985).

5.2 Properties

As previously explained, the phenolic nature of lignin enables replacement of phenol with lignin derivatives in PF resins to formulate wood composite adhesives suitable for plywood, particleboard and other similar kind of composites, replacing current synthetic PF resins based on petrochemical, non-renewable materials. A variety of different lignins have been used in PF resin preparation, such as kraft lignin, organosolv lignin, soda lignin and lignosulfonates. Also, black liquor has been applied directly (Ghaffar and Fan, 2014)

According to UPM, kraft lignin, meaning lignin extracted from kraft pulping process, has been successfully used as a phenol replacement up to 50-60% in PF resins. These adhesives have previously not been acceptable in gluing applications due to unsatisfying properties of the glue joints caused by lignin’s low reactivity during the production of resin composition. (Pietarinen et al., 2014) Until now, the properties of lignin-based PF resins had been equal with those of commercial resins up to 30-35 wt% partial replacement but development to achieve higher substitutions has been successful. (Ghaffar and Fan, 2014; Pietarinen et al., 2014)

The substitution of phenol with lignin also contributes to rapid increase in viscosity during resin cooking and thus affects the polymerization process. Viscosity development is controlled by lower cooking temperature and longer cooking time to reach the desired polymerization degree and suitable curing time of the resin. Due to their differences in performance, LPF resins generally require longer pressing times and higher pressing temperatures for curing than commercial PF resins when used in plywood applications. (Effendi, 2008; Pizzi 1994; 2003a)

6 FOAMING

A general definition of foam is described as a dispersion in which a large proportion of gas by volume in the form of bubbles is dispersed in a liquid, solid or gel, hence forming closed cell structures. Foams are proved to exhibit both solid and liquid like behavior, which among other useful properties, has allowed them to be used in many aqueous applications such as fire-fighting, mineral flotation and detergents. (Cantat et al., 2013) Foaming as a phenomenon is mostly based on differences in the surface activity and it is often considered either desirable or undesirable phenomenon (Ullmann’s Encyclopedia, 1986).

The process of foam formation begins with dispersion of gaseous material (e.g. air) under the surface of (foamable) liquid. It occurs as dissolved surfactant molecules diffuse out of the bulk phase toward the gas/liquid interfaces and form reversibly adsorbed monolayers. (Weaire and Hutzler, 1999; Saint-Jalmes at al., 2005)

Foams can be divided into two categories of transient (wet) foam and metastable (dry) foam (Tan, 2005). Structure of chemically metastable foam is determined by the minimisation of interfacial area for a given liquid volume fraction, and by simple geometric rules at the scale of a film and a few bubbles (Drenckhan and Hutzler, 2015). A key parameter used to describe the amount of liquid contained within a foam is liquid volume fraction φ (Equation 1), which also explains the effect of gravity on the metastable foam seen in Figure 8 (Hill and Eastoe, 2017). The effect is also called drainage and it is studied later in this paragraph.

$$\emptyset = \frac{Vliquid}{Vfoam} \tag{1}$$

When

V_{liquid}	the volume ratio of the liquid content	[-]
V_{foam}	the foam volume	[-]

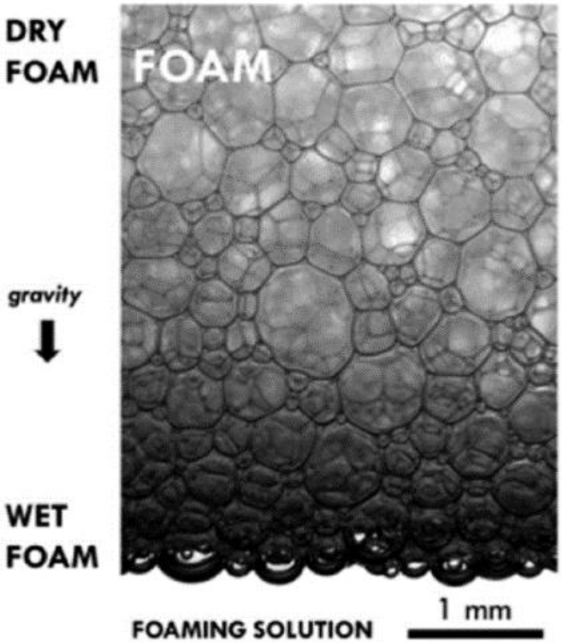


Figure 8. Demonstrating effects of liquid drainage in wet foam/dry foam solution. (Drenchkan, 2015) Copyright 2015 Elsevier.

The liquid volume fraction affects various physical and mechanical properties including thermodynamic, acoustic, and rheological. The foams with a liquid volume fraction over 0,1 are defined as wet foams, which are located around the air/water interface as a random close packing of solid spheres. When the volume fraction becomes less than 0.05, the foam can be referred to as dry foam that consist of well-defined edges at the top of the foam. (Weaire and Hutzler, 1999; Saint-Jalmes, 2006) Wet foams are of spherical-bubble type and dissolve quickly when fresh. The amount of liquid in the wet foam causes individual bubbles to have little influence upon one another. This however changes after drainage as it causes the distance between bubbles to diminish, resulting in dry foam with polyhedral shape. (Weaire and Hutzler, 1999; Ullmann’s Encyclopedia, 1986)

Foams do not form spontaneously, because they require energy to disperse the gas in the liquid to create bubble surfaces. The cost of energy (W) can be broadly described as the product of the surface tension γ and of the created area A.

$$W = \gamma \Delta A \tag{2}$$

When	γ	the surface tension	[Nm^{-1}]
	A	the created area	[m^2]

Thermodynamic instability causes foams to separate with time under the influence of van der Waals forces and gravity (Fameau et al., 2015). Lifetime of foams is what describes the division of wet and dry foams. It can vary from few seconds, with transit foams, to minutes and even up to years with metastable foams (Pugh, 1996). A way to produce the metastable foams successfully, is by using stabilizing agents, such as surfactants, polymers, proteins or particles to modify the surface properties and to stabilize the foam (Hill and Eastoe, 2017).

Foams can be generated with many techniques that are usually divided into two main mechanistic categories i) dispersion methods and ii) condensation methods. The first one occurs as mechanical action increases the surface area that separates liquid and gas. Foaming establishes as the two phases are exposed to flow velocities in a turbulent range. These types of methods are applied in foam generators and dispersion turbines. Condensation methods rely on spontaneous degassing of supersaturated, continuous liquid phases. This can be establishes by either pressure reduction or temperature increase. Known example of condensations method is the carbon dioxide foam at the surface of carbonated soft drinks or alcoholic beverages. (Ullmann’s Encyclopedia, 1986)

A large number of foaming techniques exist in the industry and they all seek to control the varying physical properties of foam. Unfortunately, each individual technique typically covers only a relatively small range of these parameters. The difference between foaming techniques is how exactly they choose to put the required energy into liquid to create foam. It can be done by physical, chemical or even biological means. These options and their differences are presented in Table 7. (Drenckhan and Saint-Jalmes, 2015)

Table 7. Classification of different foaming techniques. (Drenckhan and Saint-Jalmes, 2015)

Global mechanism	Sub-mechanism	Examples
Physical foaming	Mechanical foaming	Bubbling, sparging, foam generation in porous media, wave breaking, shaking, rotor-stator mixers
	Phase transition	Champagne, beer, extrusion, cream dispenser, shaving foam
Chemical foaming	Chemical reaction	Fizzy drink tablets, baking powder, polyurethane foaming
	Electro-chemical reaction	Microflotation
Biological foaming	Yeast	Baking

6.1 Foam stability

Stability of foams is defined as the foam’s ability to maintain thick lamella that preserve it from external forces and its ability to prevent rupture by fixing potential weak spots on the liquid film. In foam, these thinner spots are repaired via Marangoni effect which is a mechanism that stabilizes foam during mechanical stress. According to Marangoni effect the bubble repairs its random film variations by moving surface active molecules from surrounding regions to cover the thinner spots. The effect is based on Gibb’s elasticity where a high surface tension pulls more strongly on the surrounding liquid than one with a low surface tension. (Ullmann’s Encyclopedia, 1986) Foam stability is also a measure of the life-span of the foam, which can be indicated as the time foam takes to decompose to half its of original volume (Eklund and Lindström, 1991).

Foam stability is mainly influenced by surface tension, viscosity, pH and temperature. Other factors such as concentration of surface active substances and the area of foam also have an effect on it. (Garret, 1992) Destabilization of foam lamellae is caused by liquid drainage or in other words when reduction in lamellar thickness reaches a certain critical value. (Ullmann’s Encyclopedia, 1986) This reaction is found to increase in elevated temperatures. However, in most cases foam rapture is a consequence of external forces instead of liquid draining from the bubble walls (Bendure, 1975)

A presence of surface active molecules enriches the gas/liquid interfaces and thus lowers the surface tension. If surfactant concentration is low, the surface tension is high, and it barely changes during stretching. Hence the solution shows low elasticity and poor foaming tendency. On the contrary, too high surfactant concentration is neither desired. Optimal foaming ability is obtained just below the critical point (critical micelle concentration) where the surface tension is low, but surfactants are not overdosed. (Eklund and Lindström, 1991) The critical micelle concentration is further explained later in this thesis.

Viscosity of the liquid affects the lifetime of foam and therefore its overall stability. Extremely low viscosity liquids only form transient foams that vanish rapidly while high viscosity can cause nearly everlasting solid foams. The influence of viscosity is related to the rate of liquid drainage from the bubble walls and Plateau border (Figure 10) according to time. In case of high viscosity, drainage is slow as the increased viscosity diminishes the rate of escape of interlamellar liquid, thus increasing foam stability and area. However, high viscosity can also slow down the process of foam formation. (Ullmann’s Encyclopedia, 1986) Elevation in liquid temperature decreases viscosity and hence accelerates drainage. Furthermore, surface viscosity can differ from the bulk viscosity, which is affected by accumulation of surface active substances near the liquid/gas interface. It is stated that the easiest way to influence the viscosity of foaming systems is by modifying the surface viscosity instead of the bulk viscosity (Kanner and Glass, 1969).

Another contributor in foam stability is surface elasticity. It strengthens foam’s ability to withstand mechanical stress such as the formation of new foam, hydrostatic pressure of bubble walls and the flow of liquid. Elasticity is crucial in maintaining formed bubbles. When the foam surface extends due external force, the concentration of surface active molecules in that particular spot decreases, resulting to increase in surface tension. To balance that surface tension, surrounding surface active molecules move to cover the spot as described in Marangoni phenomenon. The transport of material takes place in the surface layer, which also draws the underlying liquid, contributing to a reinforcement of the lamella. (Kanner and Glass, 1969; Eklund and Lindström, 1991)

6.2 Foam destabilization

Producing foams with single component liquids is generally not suitable as their stability is easily ruptured due to vulnerability of thermal or mechanical perturbations (Figure 9). Hence, soluble surfactants or impurities are needed to stabilize the foam by hindering the rapid coalescence of bubbles. (Ullmann's Encyclopedia, 1986)

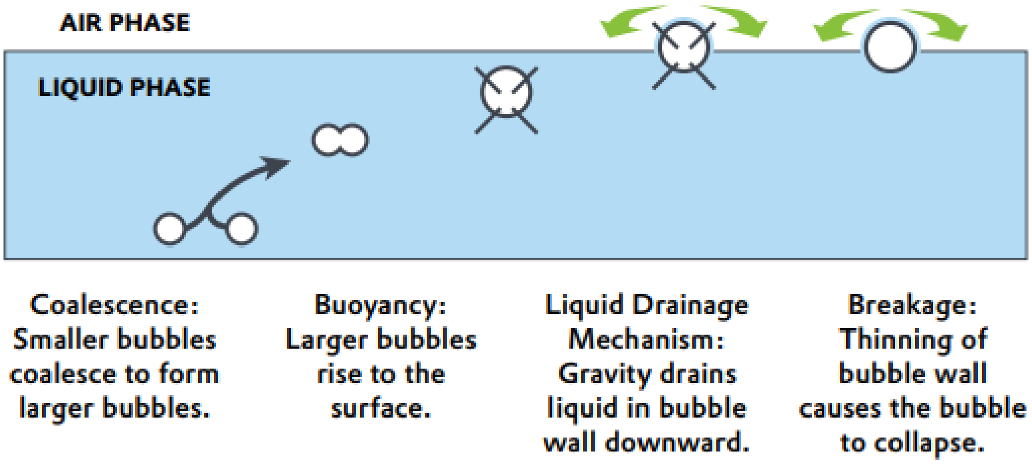


Figure 9. Unstabilized air bubbles in pure liquids burst quickly (Evonik, 2015)

As explained, there are several factors that affect the stability of foams. However, three main factors govern the decay processes of foams (Hill and Eastoe, 2017);

- drainage
- coarsening
- bubble coalescence

Drainage describes the irreversible flow of liquid caused by gravity and capillary forces between fragile film membranes and Plateau borders (Figure 10). Practically, drainage can be seen as water begins to drain leaving the top of the foam dry (<1% liquid), while the bottom remains wet. The mechanism causes the shape of bubbles to change from somewhat spherical shape into polyhedral shapes and leads to gas bubbles becoming less stable, and increasingly susceptible to bursting. (Saint-Jalmes, 2006) Hindering drainage significantly improves the foam stability and it can be achieved by ensuring higher liquid bulk viscosity and by enabling the surface-active material to rigidify the film surfaces by formation of stable monolayer. (Monnereau et al., 1999; Hill and Eastoe, 2017)

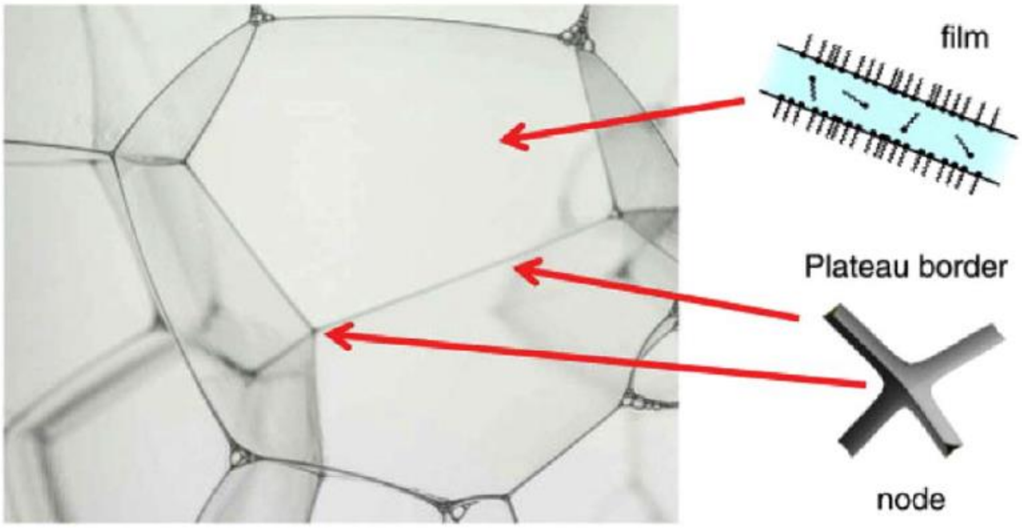


Figure 10. Demonstration of Plateau border and surfactant molecules packed on a foam film surface. (Rio et al.,2014) Copyright 2014 Elsevier

Coarsening (Figure 11) is defined as process of growth and shrinkage of bubbles within a foam due to inter-bubble gas diffusion (Hill and Eastoe, 2017). The driving force for the diffusion is the difference in pressure between the inside and the outside of a curved surface between gas and liquid that causes volume of some bubbles to increase at the expense of others. This can be measured as an average growth of mean bubble diameter in time. Moreover, there are many other features that determine the rate of coarsening including liquid fraction, the average bubble size to the physical chemistry of the gas and the liquid. (Saint-Jalmes, 2006) A term of characteristic coarsening time of foam is a combination of several properties such as gas diffusivity and solubility constants, the bubble deformation, the liquid volume fraction content, thickness of the thin film, the initial diameter of the bubble and the solution surface tension (Rio et al., 2014; Hilgenfeldt et al., 2001). The gas employed also plays an important role meaning water-soluble gases such as carbon dioxide give less stable foams by being able to transport across water film much more readily than not so water-soluble gases such as nitrogen (Hill and Eastoe, 2017).

The process of bubble coalescence is not as understood compared to drainage and coarsening. However, the overall result of coalescence is similar to coarsening including an overall decrease in the number of bubbles. (Hill and Eastoe, 2017) Coalescence is enabled by drainage which causes the films between bubbles to eventually become very thin (5–20 nm) making them more likely to rupture (Rio et al., 2014). However, unlike in coarsening where the gas diffuses from one bubble to another, coalescence causes rupturing of the bubble films leading to a decrease in gas volume within the foam until it completely disappears (Cantat, 2013). According to studies of Carrier and Colin (2003), coalescence was found to be dramatically enhanced below a critical liquid fraction of the meaning the events do not directly depend on the size of the bubbles. Both coarsening and coalescence are presented in Figure 11.

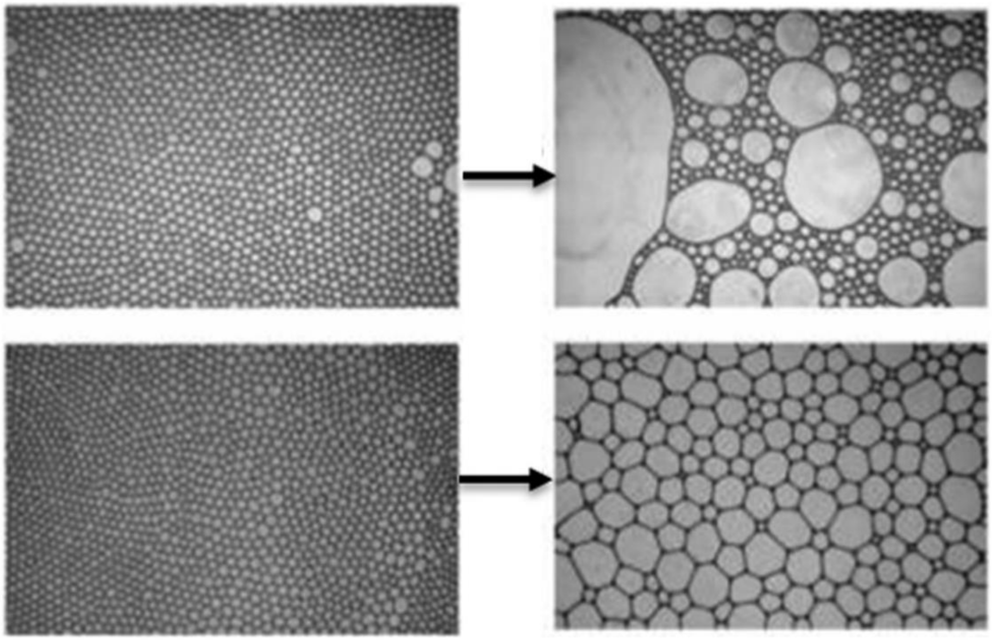


Figure 11. Top images show coalescence and lower images show coarsening. (Hill and Eastoe, 2017)

In order to attain further knowledge on behavior of foaming, more research is required. One perpetual problem in foam studies is the absence of so-called standard foam. Its materials; liquid, surfactant and gas are relatively easily defined unlike such important quantities as average bubble size, bubble size distribution that are practically unmeasurable. Also, foam behavior is often dependent on the type of generator, which makes comparing difficult as one is often identifying the properties of the foam generator as much as of the foam.

6.3 Foaming of adhesives

Unlike non-foaming pure liquids, adhesives include surface active substances that promote formation and stabilization of foam. These surfactants including wetting agents and emulsifiers lower the surface tension of the adhesive resulting in bubble formation. They also prevent small bubbles beneath the air-liquid interface from coalescing and increase the surface viscosity making the foam more stable (Figure 12). Due to their tendency to create foam, adhesives require defoamers to restrain that bubble formation. (Evonik, 2015) Surface active chemicals and defoamers are further reviewed later in this thesis.

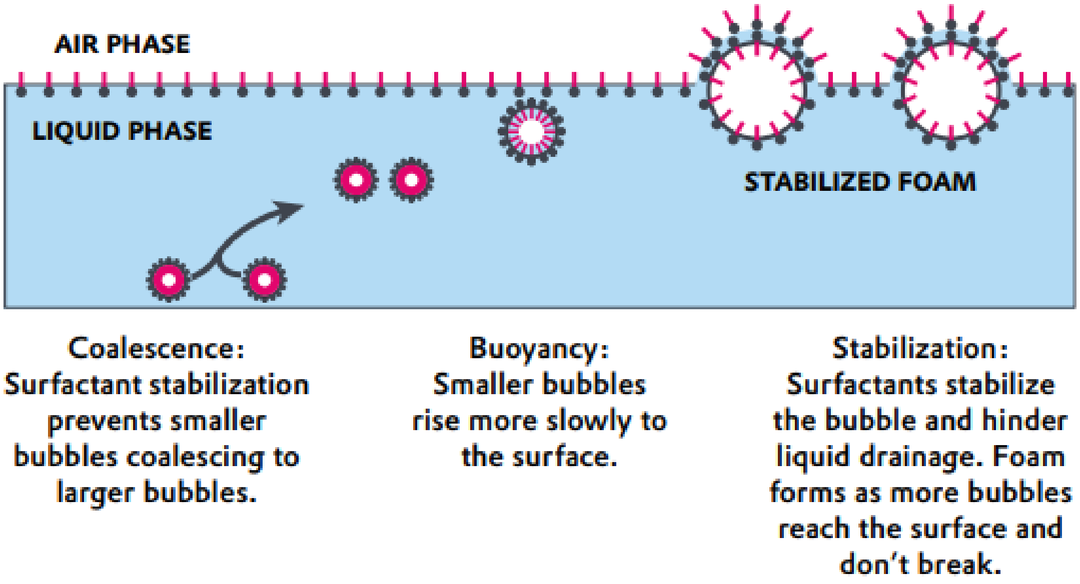


Figure 12. Surfactants stabilizing air bubbles, inhibiting coalescence of smaller bubbles, slowing bubble rise and preventing foam collapse (Evonik, 2015)

In terms of industrial foaming, it is important to distinguish the difference between intentional foaming done in order to increase the performance of the target process from unwanted foaming that happens as a side reaction of particular operation such as mechanical stirring. In some cases foaming is desired, for example in methods based on foaming the adhesive prior application in order to achieve efficiency with lower glue spread.

Foam extrusion is a plywood glue application method where the glue is intentionally foamed with air and then extruded into long strands to cover the entire veneer surface when pressed. The nature of foam extrusion requires not only foaming capability for the glue but also foam stability. The foamed-adhesive bubbles must be the proper size, uniform and stable in order to bond plywood. The mixing and foaming is carried out in a mixer with a compressed-air supply, until the adhesive is mixed and foamed to about one-fifth of its original specific gravity. (Sellers, 1985) Proteins (e.g. animal blood or soy protein) are often added to the glue as an extender to act as a foaming agent (Hojilla-Evangelista and Dunn, 2001) Advantages of foam extrusion include low glue spread required, ease of control, and the ability to glue rough veneer (Sellers, 1985).

6.4 Problems caused by foaming

Unwanted foaming may often occur as a side-effect during mixing of the adhesive and therefore create operational challenges during plywood manufacturing. Glue mixing is carried out according to recipe and maintaining critical viscosity level is a priority. In most plywood mills, the glue mixing happens on elevated platforms in large vats, or mixers that have motorized agitators to blend the components as they are added. The foam formation method in the case of mixing is referred to as dispersion, meaning that in order the gas to disperse into liquid, energy must be brought into the system as a form of mechanical action. Mixing devices and pumps create strong liquid velocities that generate that needed energy to create foam. (Ullmann’s Encyclopedia, 1986) In a plywood mill, the formation of foam is practically unavoidable, especially as these mechanical procedures are a necessary part of adhesive production.

In application of curtain coating, the formation of foam can have significant negative effects on stability of the glue spread. Curtain coaters, as well as spray-lines, require precise viscosity control in the adhesive in order to spread evenly and form homogenous glue lines (Baldwin, 1995). As foaming occurs, the air increases the glue viscosity, which results in higher foamability and deterioration in quality of the curtain. High viscosity systems are also more difficult to defoam and require stronger and more expensive defoamers to destabilize foam (Evonik, 2015). Increased viscosity and large amounts of foam in the adhesive also lead to practical difficulties in pumping of the glue between mixers and applicators.

7 CHEMICAL FOAM CONTROL

Foam control is an essential part of numerous technological processes and it is well known in many industries such as pulp and paper, fermentation, oil and gas recovery, froth flotation, wastewater treatment, textile dyeing, phosphoric acid production, food and beverages production, and chemical processing. Also many consumer products from pharmaceuticals to paints and adhesives often rely on foam control during application. (Denkov et al., 2013)

The most common foam control method is application of chemical additives to prevent or reduce the formation of undesired foam. Depending on their properties, these chemicals are correctly referred to either antifoamers (to prevent) or defoamers (to reduce). Third kind of application type can be described as a compromise of the two, where a limited amount of foam with a limited lifetime is found beneficial to the product (e.g. machine-washing detergents). In the later type, the most appropriate term for the used chemicals is “foam control agents”. However, it must be noted that in many references all these three types of chemicals may simply be referred to as only one of the terms (antifoamer, defoamer or foam control agent). The average dosing of chemical foam control additives is small (usually between 0,01 and 0,5 wt.%) due to their expensive prices and lack of efficiency in high concentrations. (Garret, 1993; Denkov, 2004; Wasan et al., 1994)

Various chemical substances exist as additives to control foaming and in many cases similar substances can be used for all three explained functions. Examples of these substances include (Denkov et al., 2014):

- oils; silicone and mineral
- fats; vegetable and animal
- mixtures of oils and particles of so-called antifoam “compounds”
- various amphiphilic molecules; alcohols, fatty acids, fatty esters
- specific polymers with partial solubility in water such as polymers based on oxyethylene, oxypropylene and oxybutylene units

Despite them all being applicable with the same intention, there are some subtle differences between the substances meaning that a substance with good defoaming properties does not necessarily function well as an antifoamer etc. These subtle effects and divergences can be clarified by analyzing the mechanisms of action of the substances and the main controlling factors. However, the mechanism of why a certain substance can be very efficient in some applications, while being very inefficient in others, has been often difficult to clarify due to the complex chemistry of the substances and their diverse range of applications (Denkov et al., 2014). Studies conducted in order to achieve better understanding on antifoaming systems, suggested that the physicochemical analysis of the mode of antifoam action could be a rather useful approach. The main goal of the approach is to converge a variety of compositions into a limited number of mechanistic scenarios and define the mechanism of antifoam action. This would then enable rationalization of the efforts to optimize the antifoam by varying systematically only those critical physicochemical parameters needed to control the mechanism (Denkov et al., 2014), including:

- contact angles
- interfacial tensions
- rheological properties
- size of antifoam globules etc.

Unfortunately, most of the usual physicochemical measurement techniques are not suitable for directly studying complicated agglomerates of draining gas bubbles in a moving, foaming liquid. More legitimate approach on understanding the fundamentals of foam stability have been reached with studies conducted on isolated foam lamellae. This makes sense as foam degradation is in the end, a process consisting of the rupture of many individual lamellae (Ullmann’s Encyclopedia, 1986).

7.1 Foam control agents

Development of foam controllers (i.e. antifoamers) began in the early 20th century with mechanical devices such as air jets, special still heads, paddle wheels, perforated spiral canals, centrifuges etc. However, these methods were soon found too expensive due to their energy consumption, which started the development of chemical antifoaming methods. In the first decades (1940s-1970s) market was dominated by “oil” antifoam products before “oil + hydrophobic particles” antifoam products were found more efficient. (Karakashev and Grozdanova, 2012)

Antifoams are defined as emulsions containing hydrophobic particles that interact with foam (Karakashev and Grozdanova, 2012). Theoretically, defoaming (antifoaming) occurs as the stable lamella of bubble is interfered and ruptured. This occurs as insoluble droplets spread on the lamella and push water away creating weak spots on the film that eventually cause the bubble to break (Wamsley and Gammon, 1994). According to Evonik (2015) the oil is typically considered as a carrier of the particles.

As explained, the function of chemical antifoams base on destabilizing the liquid film by surrounding the air bubbles inside the foam with the hydrophobic particles (Prins and van’t Riet, 1987; Karakashev and Grozdanova, 2012). The process itself is relatively complex with variable durations but can be divided into three following mechanisms by which antifoam agents work (Wacker Chemie, 2018);

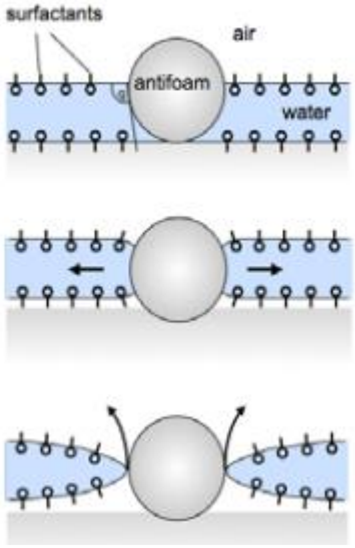


Figure 13. Mechanism of dewetting created by “bridging” of antifoam droplets. (Wacker Chemie, 2018)

i. In Figure 13, the antifoam droplet penetrates the foam lamella while displacing surface-active compounds from the interface. The antifoam droplets thereby begin to “dewet” their vicinity leading to thinning of the lamella and eventually rupture of the bubble.

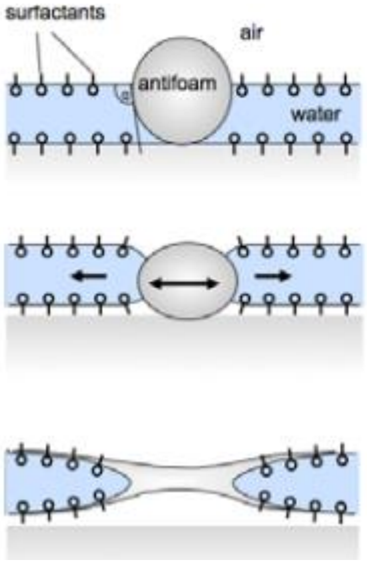


Figure 14. Mechanism of stretching created by ”bridging” of antifoam droplets. (Wacker Chemie, 2018)

ii. In Figure 14, the antifoam droplets penetrate the foam lamella and form hydrophobic “bridges” between interfaces that stretch due to uncompensated capillary pressured at the particle-water interfaces. As the stretching increases, the lamella begins to rupture at the thinnest part of the stretched antifoam fluid droplet.

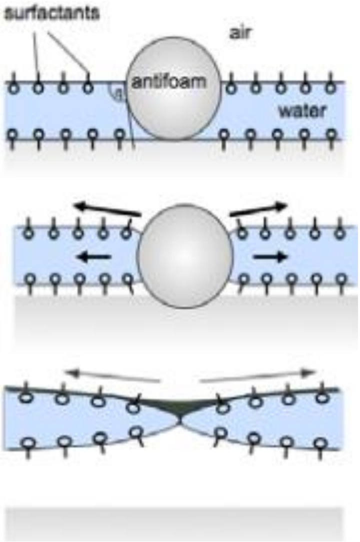


Figure 15. Mechanism of fluid entrainment created by spreading of antifoam droplet. (Wacker Chemie, 2018)

iii. In Figure 15, the antifoam droplets spread through the liquid film and penetrate the foam lamella. The Marangoni effect causes water to drain away from the fluid droplets until the lamellas become thinner and more easily ruptured, leading to bubble coalescence as presented in Figure 11.

The film breaking ability of the particle is dependent on various subtle factors such as the critical receding contact angle between the foam film and the particle and emerging of convex flow driven by the local capillary forces near the spot of the particle (Karakashev and Grozdanova, 2012). Although, it is extremely difficult to experimentally determine which antifoamer would be most effective for given situation, there are several key physical properties important to take into account when selecting antifoamer components and considering the final formulations (Wamsley and Gammon, 1994):

- Lower surface tension than the foaming medium.

- Spreading and solubility, meaning performance of the chemical dispersion, speed of the reaction and persistency of the formulation in order to remain cost-effective
- Viscosity of the final product, because low viscosity oils spread out much faster which is important in a continuously foaming phase.
- Optimum average particle size distribution of hydrophobic particles, meaning the importance of correct particle size for the ”bridging” mechanism. Too large average particle size lowers efficiency of the reaction and too small disables the bridge forming of the particles
- Optimum molecular weight distribution of components, meaning the importance of optimizing the molecular weight distribution of chemical species such as mineral oils, fatty amides, silicone compounds in order to make them more suitable for antifoaming applications and to improve their cost-efficiency

Addition of antifoams can also have disadvantages, one of which is a significant reduction in the oxygen transfer rate (OTR). It is defined as the steady state rate at which oxygen gas can permeate through a film and the reduction of OTR is commonly attributed to the accumulation of the antifoam at the gas-liquid interface where it creates an additional barrier for oxygen transfer. Although there are different kinds of antifoamers, it suggested by numerous studies that all of them behave in a similar way at the interface, leading to the observed reductions in oxygen transfer. (McClure et al., 2017)

7.2 Surface active agents

Surface active agents, shortened as surfactants are widely used chemicals in reducing surface tension of liquids or the interfacial tension of two-phase systems (Kruss, 2018). Particularly applications that involve contact or mixing between different phases used in cleaning, wetting, coating or emulsification, utilize surface active chemicals for their ability to mobilize and combine materials, typically water, oils, fats and solvents, that otherwise would not mix due to their incompatible molecular properties. (Cesio, 2017)

Surfactants are also responsible for the formation of foam and their presence has stabilizing effects that increase the lifetime of foam. This happens as surfactants' amphiphilic nature causes preferential adsorption of the surfactants at the air-liquid interface, resulting in a reduction of the interfacial tension that enables foam formation. Surfactants also prevent the gas bubbles from collapsing as they accumulate to the Plateau border (Figure 10) of the bubbles making them more stable. (Ullmann's Encyclopedia, 1986)

The amphiphilic surfactant molecules are organized according to its' structure of polar groups directed toward the water and hydrophobic chains toward the air as shown in section B of (Figure 16) Only at very low concentrations do hydrophobic groups lie flat on the surface and even a relatively low surfactant concentration is enough to erect the hydrophobic chains by inducing the formation of densely packed aggregates. (Ullmann's Encyclopedia, 1986)

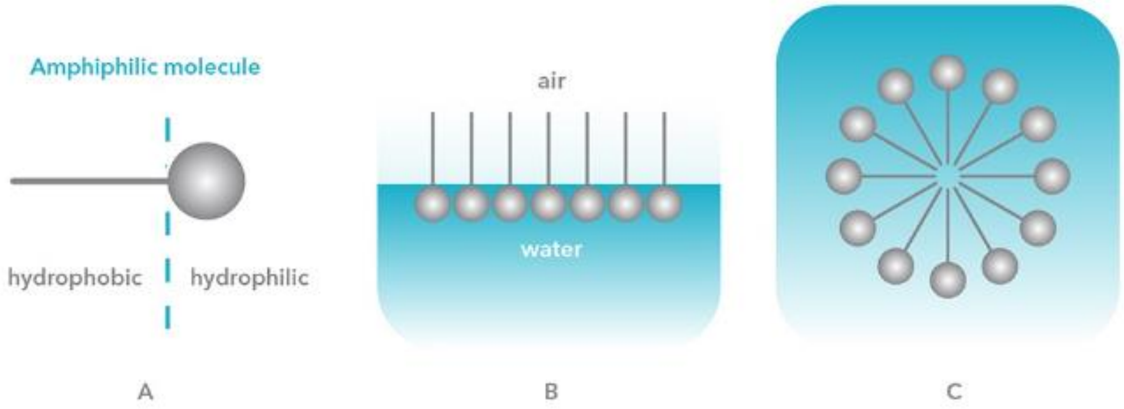


Figure 16. Polar orientation of surfactant molecules. (Biolin Scientific, 2018)

Most surfactant have fairly similar "tails" but divide into four different types based on their composition of polar head groups (Wacker Chemie, 2018; Hirsch, 2015);

- Non-ionic surfactants have no charged head groups. They foam extensively at low temperatures but stop foaming and may even exhibit defoaming properties when properly heated

- Anionic surfactants such as sulfonates and phosphates have a negative charge. They are mainly used in detergents and have a high tendency to foam, especially at low temperatures
- Cationic surfactants consist of positively charged head and are mostly used as anti-mircobials or anti-fungals etc.
- Amphoteric (also zwitterionic) include both cationic and anionic centers attached to the same molecule. They have low toxicity and can be used in shampoo-purpose foaming agents

A spreading pressure characterizes the surface activity of a given surfactant or surfactant mixture at a particular concentration. A dynamic equilibrium between the surfactant dissolved in the bulk phase and the surfactant absorbed at the boundary surface can be reached in a stable temperature. At low concentrations, the amount of adsorbed surfactant increases with increasing concentration and at the same time, the increasing spreading pressure reduces the surface tension. The adsorption capacity of the surface is completely utilized when the maximum spreading pressure is reached, meaning when the number of adsorbed molecules remain constant despite further concentration increase. (Ullmann’s Encyclopedia, 1986)

The critical micelle concentration (CMC) is described as the concentration of surfactants above which so-called micelles form and all additional surfactants added to the system transfer into micelles (shown in section C of Figure 16). The surface tension reduces linearly with increase of surfactant concentration until CMC is reached and stays constant after that. Above the CMC, the spreading pressure of given pure surfactant is also constant. Typical CMC values vary considerably as a function of molecular structure of the surfactant. (Ullmann’s Encyclopedia, 1986)

EXPERIMENTAL PART

The experimental part of the thesis consists of an introduction of the materials and methods selected for the case. The aim of the experiment is to determine a volume of foam generation in formulated lignin-phenol-formaldehyde (LPF) adhesive during a process of stirring. Furthermore, selected commercial defoaming agents are added into the adhesive in which their individual efficiency is determined, and the results are compared. Functionality of the selected method is also evaluated and discussed in light of previous tests, including some conducted in pilot scale. Prior the experiment, the selected LPF resin is mixed with two different hardeners to formulate two slightly different adhesives to define their variations in performance with the selected additives.

Overall, the experimental part is conducted in two stages. Between the stages the results up to that point are reviewed and the most efficient defoamers are selected for further testing. In the second stage, a commercial surfactant is also added into the resin to study its effects on foam formation and to create similar conditions of LPF adhesive used in industrial scale curtain coating. Also, viscosity development of the adhesive is determined to review its variations during the experiment.

8 MATERIALS

Next, the introduction of used materials including resin, hardeners, surfactant and defoamers is reviewed.

8.1 Resin

The experiment is conducted using Lignin-phenol formaldehyde (LPF) resin with 50% of phenol substituted with softwood lignin. The LPF resin is produced by UPM according to following Figure 17.

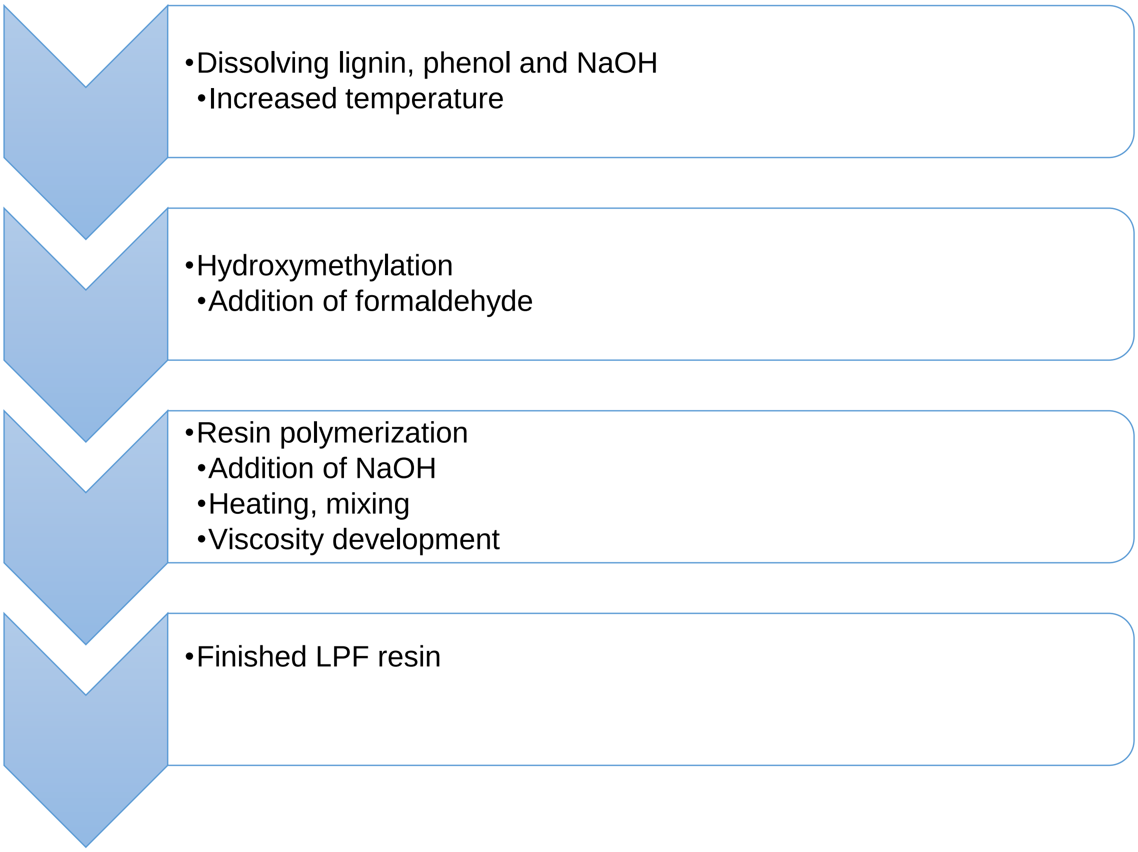


Figure 17. Preparation of Lignin-phenol-formaldehyde resin. (Pietarinen et al., 2014)

Resin used in this experiment is stored frozen in a -19°C freezer and melted before using. Liquid resin is then stored in a +5-7°C fridge where it is usable for a week at longest. Before using, the resin is calmly mixed to ensure homogenous composition and its Brookfield viscosity is measured. The resin is then formulated into adhesive by adding of hardener and water according to appropriate recipe and mixed. Adhesive production is reviewed in Plywood adhesives and a typical adhesive recipe is presented in Table 3.

8.2 Hardeners

Hardeners are added to liquid resin as extender substances to adjust the properties of the resin. In this work, two different hardeners were used to formulate two slightly different adhesive mixtures.

Hardeners are:

- Hardener 1 is a white solid powder. Applicable as a hardener in wood industry. Produced by Prefere Resins Finland Oy.
    - Contains: limestone and sodium carbonate
- Hardener 2 is a white solid powder. Applicable as a hardener in wood industry. Produced by Hexion Inc.
    - Contains: limestone, sodium carbonate and organic fillers

8.3 Additives

Additives used in this work including one surfactant and three defoamers are presented in Table 8. One defoamer is produced by Dow Chemical and other additives are produced by Evonik Industries AG.

Table 8. The used chemicals.

Name	Producer	Discription	Applicability	Content
Defoamer 1	Evonik Industries AG	An organic oil defoamer with abilities to control and eliminate foam	In water-based systems and adhesives	Unknown
Defoamer 2	Evonik Industries AG	A vegetable oil defoamer	Especially in water-based polymerization of rubber materials	Unknown
Defoamer 3	Evonik Industries AG	A non-ionic dynamic wetting agent and a surfactant	In water-based coatings and adhesives	2,4,7,9 tetramethyldec-5-yne-4,7-diol and ethane-1,2-diol
Defoamer 4	Dow Chemical	A water-soluble non-ionic surfactant and a defoamer	In paper processing	Alcohol alkoxylate
Surfactant 1	Evonik Industries AG	A non-ionic dynamic wetting agent with low foamability	In water-based coatings and adhesives	Ethoxylated 2,4,7,9-tetramethyl 5 decyn-4,7-diol

Surfactant 1 was chosen based on success in previous trials and it is considered a good additive for achieving a stable curtain for curtain coating of veneer. Defoamer 3 is also a surfactant but desirable performance has not been reached with a typical surfactant dosage. However, defoamer 3 has shown defoaming abilities at lower dosages. Defoamers 1, 2 and 4 have been tested before in a previous laboratory foaming tests with satisfactory results. Research on coinfluence of surfactant and defoamers has been previously conducted somewhat but not from a defoaming point of view.

A typical defoamer dosage varies between 0,01% to 0,5% of the weight of resin, but 0,03% and 0,05% are considered relevant for industrial scale production process. Defoamer dosage of 0,1% of the weight of resin is also applicable and was chosen for this thesis along with 0,05%. Surfactant are generally added at dosages of 0,1-0,6% of the weight of resin. Amount of 0,6% is considered maximum dosage from an economic point on view and 0,1% minimum to achieve desired properties of the adhesive. For this trial, 0,4% of the weight of resin was chosen for surfactant dosing.

Addition of defoamers in this work was conducted in two different variations: i) into resin prior mixing of the hardener and ii) into finished adhesive prior the experiment. The objective of the variations is to study the additives’ defoaming performance and its relation to the point of the addition. In previous pilot trials, defoamers have been added into resin before mixing of the hardener to provide influence time for the defoamer to affect the adhesive. Adding defoamer in the beginning of the adhesive production process is also practically easier to execute. In the second stage of the experiments, Surfactant 1 was added into resin and stored 24h before mixing of the hardener to allow influence time. Addition points of all the additives is presented in Figure 18. Differences in performance between the variations and coinfluence of surfactant and defoamers are reviewed in the results of this thesis.

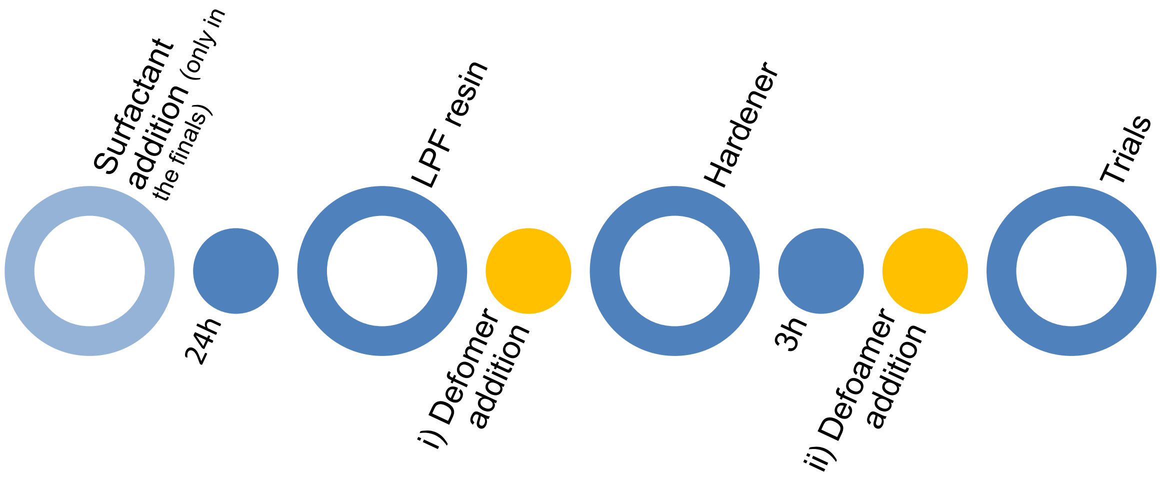


Figure 18. Timeline presenting the **two variations** of defoamer addition points (as previously explained) and that of surfactant in the final trials.

9 METHODS

Next, the analytical methods and used devices of the experiment are reviewed.

9.1 Resin/Adhesive viscosity

Viscosity defines as one of the general properties of resin. In this experiment resin viscosity was determined by:

- Brookfield DV1 digital viscometer with a plate spindle (number 02) set for speed of 50rpm (Figure 19)

Figure 19. Brookfield DV1 viscometer with a 02-spindle attached.

Brookfield viscosity was determined for resin before mixing of the hardener and water. Tests were conducted at a resin temperature of 25°C according to standard mod. SCAN-P 50:84. The results were expressed in unit of Millipascal-second (mPas) or Centipoise (cP).

After resin was formulated into adhesive, its viscosity was determined by:

- Flow viscosity cup (FC) DIN53211 with a 6mm hole (Figure 20).

Figure 20. Flow viscosity cup with a 6mm hole.

Viscosity of the formulated adhesive was determined in four stages according to time; 0h, 3h and 24h starting from mixing of the hardener into resin. 0h indicates the viscosity of a finished adhesive and 3h the beginning of the trials after required three-hour swelling time for adhesive to reach final composition. Later, the viscosity of the adhesive was also determined after the trials to affirm the viscosity variations during the testing. The 24h viscosity indicates the viscosity development after the adhesive is stored in a room temperature for 24 hours from mixing of the hardener. Flow viscosity was conducted in an adhesive temperature of 25°C according to standard SFS-EN ISO 2431:2011 and the results were expressed in unit of Second (s).

9.2 Volume of foam

Volume of foam in a formulated adhesive was determined by stirring test described by Evonik Industries AG. The test was conducted to entrain air into the system and measure the influence of additives by density. In the beginning of the test, a 100g of adhesive was poured into a 250ml beaker (6cm diameter) and stirred with a turbine stirrer (Figure 21) for 30s at a speed of 500rpm. A stirrer head with a diameter of 3,5cm (Figure 22) was used for the trials. Immediately after the 30s, the stirring was continued for 2 minutes at a speed of 2000rpm and the sample was then poured into a 50ml measuring flask up to calibration mark. Its weight was then determined by a scale with an accuracy of 0,01g. The weight of the sample depends on the amount of air generated by the mechanical action of stirring. Consequently, it is also a measure of the efficiency of the additive (surfactant, defoamer) in the solution. For each trial point, 4 replicates were conducted with a ± 2 g margin of error of the weight of the stirred sample to determine an average foam volume as precisely as possible.

Figure 21. The laboratory stirrer used for conducting the stirring tests.

Figure 22. The stirrer head used in the trials.

The addition of additives was conducted before beginning of the experiment. In the first variation, defoamer and/or surfactant was already added into resin before adhesive preparation so no additional procedures were done before starting of the stirring. For the second variation, defoamer was added into adhesive and the stirring was initiated within 1 minute from that. Dosing of additives was conducted with a 1ml pipette. Before that, the average weight of a drop was determined by weighing 10 separate drops of an additive formed with the 1 ml pipette.

To calculate results, density of LPF adhesive was determined by areometer (hydrometer) used for measuring the relative density of liquids based on the concept of buoyancy (Figure 23). Areometer consist of a sealed hollow glass tube with a wider bottom, a ballast for stability and a narrow stem for graduations. Density was measured as the areometer was gently lowered into liquid inside a tall container (i.e. measuring glass) to float and allowing the surface of the liquid to stop. The value of density was then estimated visibly from the graduations with and at least 1-2 replicates were done for each sample. Repeatability of the measurements was good, and the average relative density was calculated for each sample. The accuracy of the device was 0,001g/ml. All measurements were performed in a laboratory environment in a temperature of 23 ± 2 ºC and the results were expressed in a unit of g/ml.

Figure 23. Areometer for measuring relative density of liquids.

Finally, the volume of foam was calculated by the following formula:

$$Volume\ of\ air\% = 100\% - ((m2 * 2)/D) \tag{3}$$

When	*m2*	weight of 50ml stirred emulsion	[g]
	D	density of unstirred emulsion	[g/ml]

10 TRIAL POINTS

Experiments of this work were conducted in two variations of defoamer addition as reference (Figure 24). Presentation of preliminary trial points is presented in Figure 25 and following that, the final trial points based on the preliminary results are presented in Figure 26.

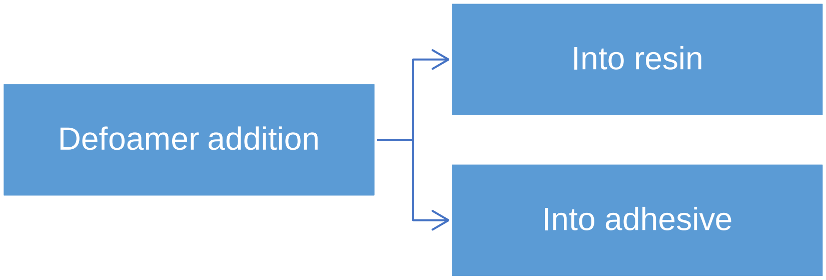


Figure 24. Basis of the experiments concerning the addition point of defoamers. All trials were conducted in both variations. Addition points are explained in Additives and presented in Figure 18.

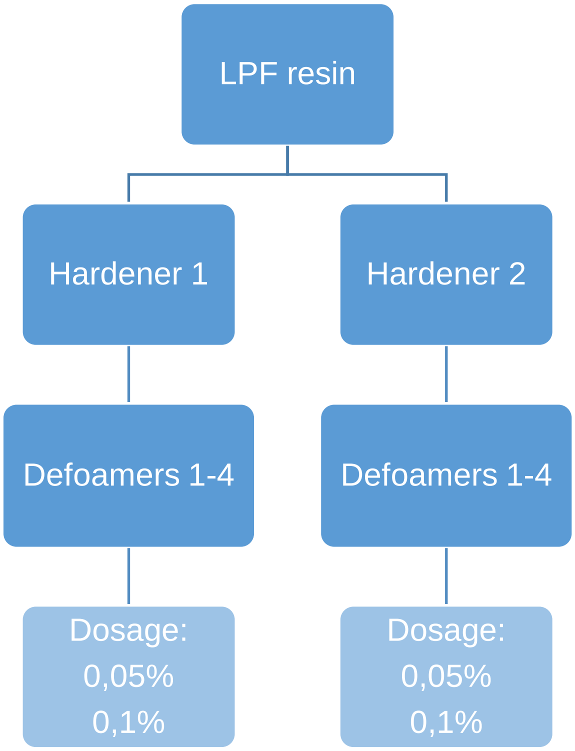


Figure 25. Preliminary trials of the experiment. LPF resin was formulated with hardeners 1 and 2 to prepare two different adhesives. All 4 defoamers were added at dosages of 0,05% and 0,1%.

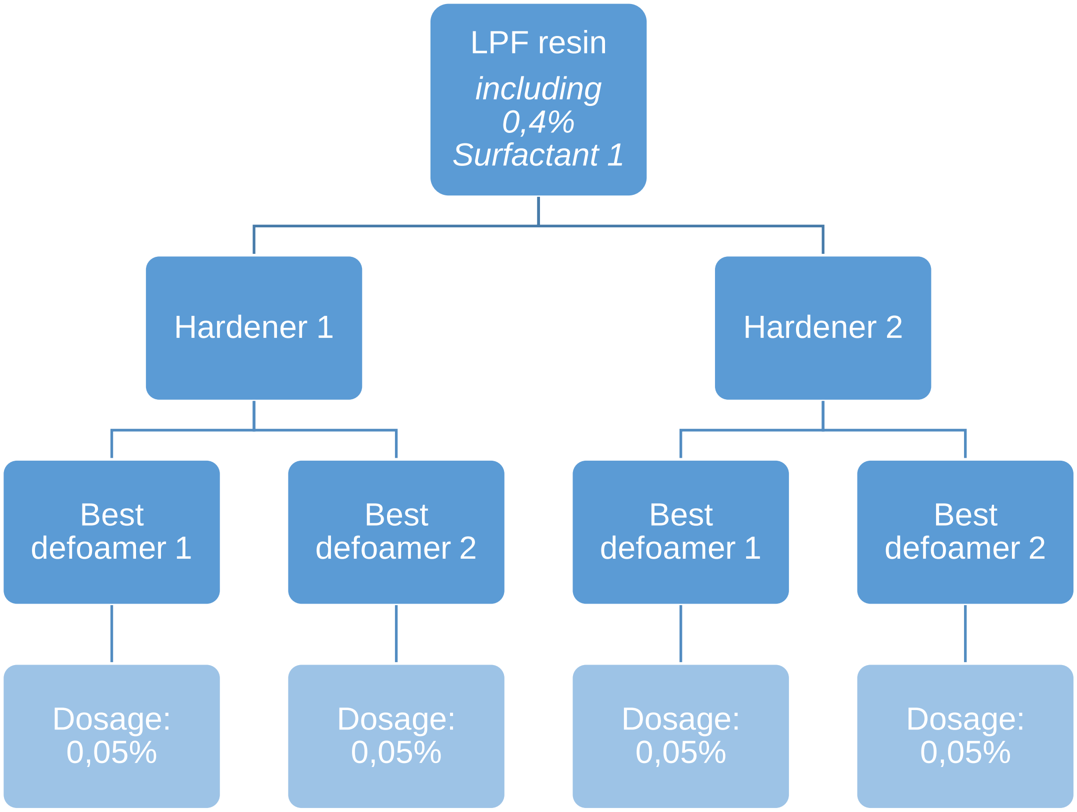


Figure 26. Final tests of the experiment. Surfactant 1 is included in LPF resin (dosage 0,4%). Two best defoamers are selected based on results of the preliminary trials. Dosage 0,05% is chosen for both defoamers as more economically feasible in larger scale.

11 RESULTS AND DISCUSSION

Next, the results of the analyses and test trials are presented and discussed. Commercial additives were used to modify properties of LPF resin. Viscosity of resin and adhesive was determined during the trials by Brookfield viscometer and Flow viscosity cup (6mm). In the results, development of viscosity is presented in line charts to visualize the viscosity trends over time. Volume of foam in LPF adhesive was determined by Evonik stirring test to calculate an average formation of foam per each additive. The results are presented in column charts of preliminary and final trials.

11.1 Volume of foam

Next, the results of Evonik stirring test are presented and discussed. The columns visualize the amount of foam (%) formed during the trials per each additive. A volume of foam without defoamer is also presented as a reference. In the final trials, a surfactant is included in the adhesive. Circulations in the charts stand for most efficient results on average.

11.1.1 Preliminary trials

The results of the preliminary trials are presented in following figures 27-30.

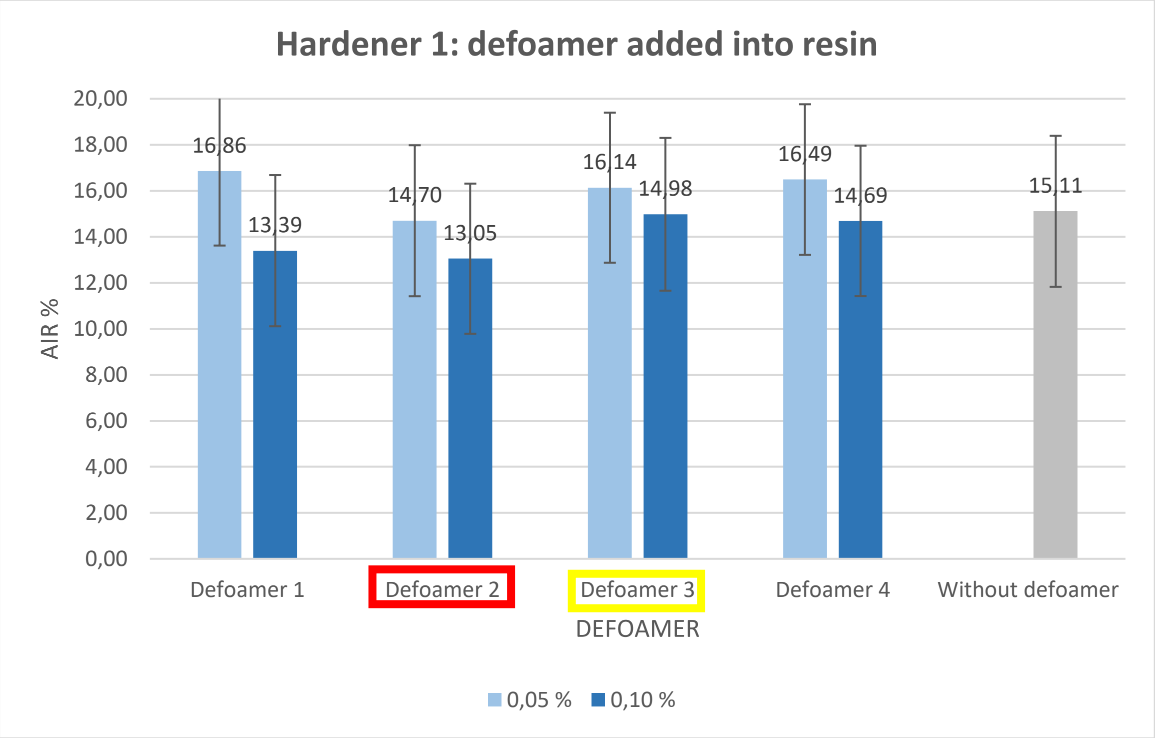


Figure 27. Volume of foam in LPF adhesive formulated by hardener 1. Results of each defoamer added into resin with dosages of 0,05% and 0,1% as a comparison. A volume of foam without defoamer is also presented as a reference. The error bars indicate the uncertainty of the measurements.

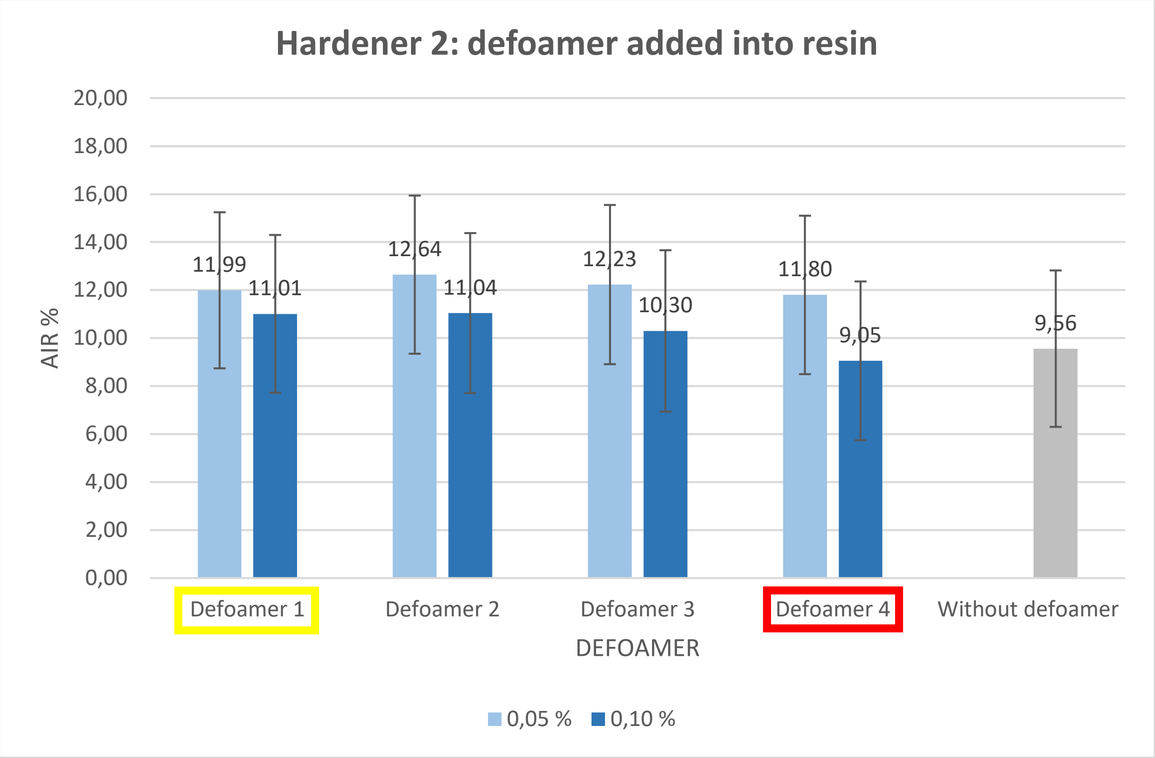


Figure 28. Volume of foam in LPF adhesive formulated by hardener 2. Results of each defoamer added into resin with dosages of 0,05% and 0,1% as a comparison. A volume of foam without defoamer is also presented as a reference. The error bars indicate the uncertainty of the measurements.

As seen from Figure 27 with 0,05% and 0,1% defoamer added into resin with hardener 1, the average level of foam volume modified with defoamers varies between 13-17% while the volume without defoamer is 15%. It can be speculated why the level with some defoamers appears to increase the level of foam, but in this case the results of 0,05% demonstrate at least a very weak performance. The results of dosage 0,1% indicate a relatively good defoaming abilities, especially with defoamers 1 and 2. In Figure 28 with 0,05% and 0,1% defoamer added into resin with hardener 2, the overall level of foam volume is lower compared to previous with hardener 1. The foam volume varies between 9-13%, while the level without defoamer is 9,5%. Remarkable is that the similar effect of some defoamers increasing the foam volume is visible is both cases of defoamer added into resin. With hardener 2, the dosage of 0,1% performs better than 0,05% but barely shows any defoaming abilities. All defoamers appear with similar efficiency, defoamer 4 being the least ineffective.

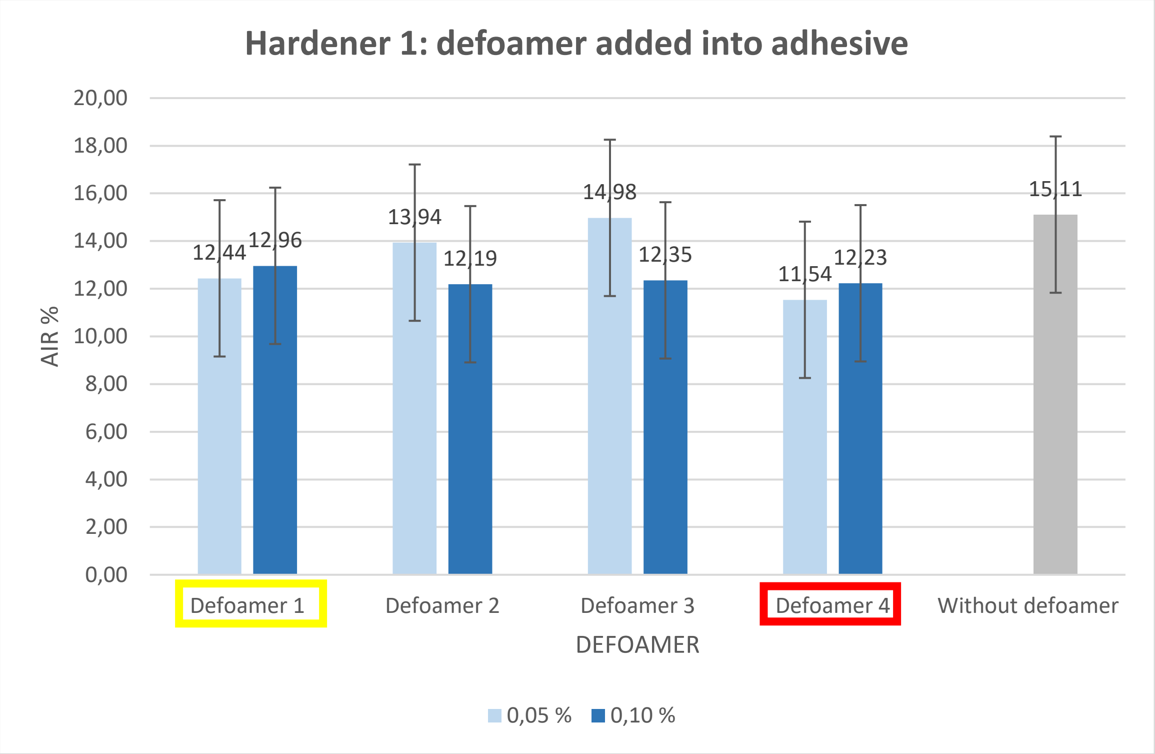


Figure 29. Volume of foam in LPF adhesive formulated by hardener 1. Results of each defoamer added into formulated adhesive with dosages of 0,05% and 0,1% as a comparison. A volume of foam without defoamer is also presented as a reference. The error bars indicate the uncertainty of the measurements.

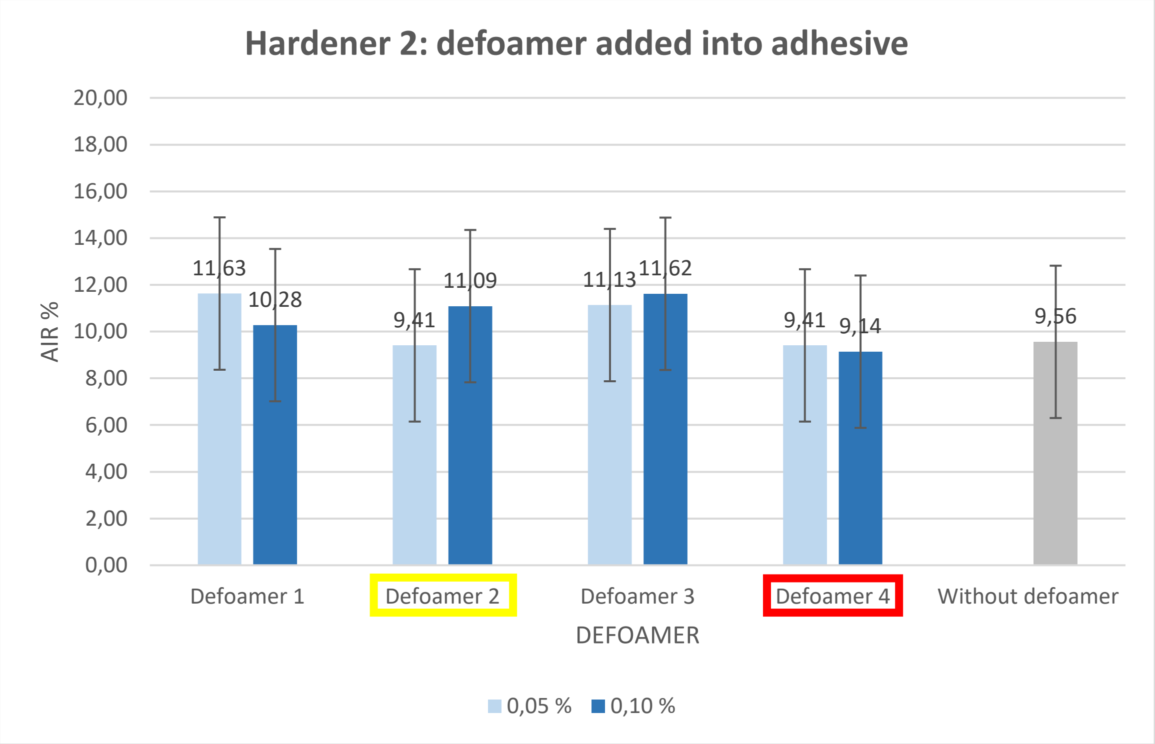


Figure 30. Volume of foam in LPF adhesive formulated by hardener 2. Results of each defoamer added into formulated adhesive with dosages of 0,05% and 0,1% as a comparison. A volume of foam without defoamer is also presented as a reference. The error bars indicate the uncertainty of the measurements.

Figures 29-30 of the preliminary trials present the performance of defoamers when added into formulated adhesive before beginning of the trials. In Figure 29 with hardener 1, the average level of foam volume varies between 11-15% while the volume without defoamer is 15%. Hence, it can be concluded that the defoamers performed well as the volume foam has decreased. Comparison between the dosages of 0,05% and 0,1% show a significant improvement in performance with higher dosage as is expected. All defoamers demonstrated similar qualities with defoamer 4 being the most efficient. In case of hardener 2 in Figure 30, the overall level of foam volume was 9-12% while the volume without defoamer was 9,5%. It is notable that the overall level of foam volume in this case was the lowest compared to rest. However, no significant improvement in the performance of defoamers is visible. The level of the most efficient defoamers 2 and 4 indicates to approximately same level as without defoamer, meaning no remarkable improvement in defoaming has occurred.

In conclusion, the performance of the defoamers proved relatively poor during the preliminary trials since decrease in foam volume was almost non-existent. In comparison between the hardeners, it was clear that the hardener 2 showed significantly less tendency to foam even without defoamers. As of the defoamers, no overall difference in performance between the hardeners was detected. However, it is notable that the defoamers did perform better when added into adhesive compared to resin. The dosages of 0,05% and 0,1% showed expected differences as the higher dosage improved the performance of the defoamer decreasing the foam volume.

Based on the preliminary results, two defoamers were selected for further testing. Defoamer 4 had shown the most efficiency in nearly all cases performing relatively well with both hardeners and dosages. The second-best ones were defoamer 1 and 2 from which defoamer 2 was chosen based on its better performance in previous pilot trials. As for the dosage, the 0,05% is selected as more economically feasible in industrial scale.

11.1.2 Final trials

The results of the final trials are presented in the following figures 31-34.

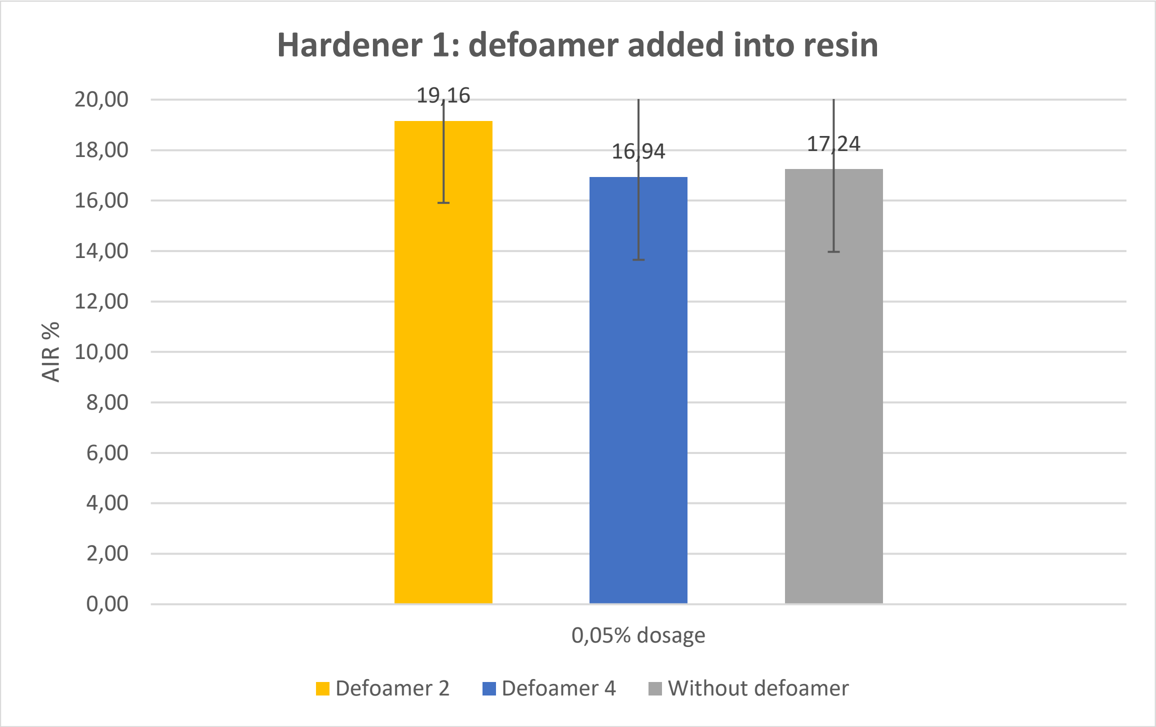


Figure 31. Volume of foam in LPF adhesive formulated by hardener 1. Results of each defoamer added into resin with dosage of 0,05%. Surfactant 1 also included (0,4%). A volume of foam without defoamer is presented as a reference. The error bars indicate the uncertainty of the measurements.

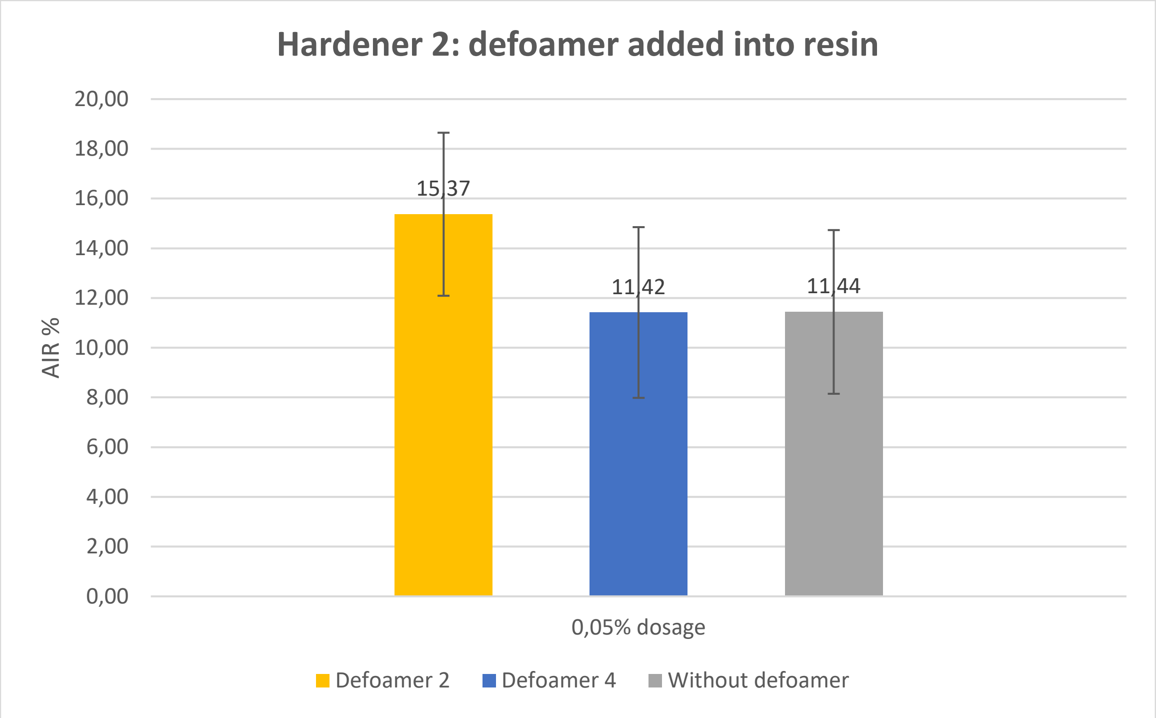


Figure 32. Volume of foam in LPF adhesive formulated by hardener 2. Results of each defoamer added into resin with dosage of 0,05%. Surfactant 1 also included (0,4%). A volume of foam without defoamer is presented as a reference. The error bars indicate the uncertainty of the measurements.

As seen from Figure 31 with the defoamers added into resin formulated by hardener 1, the overall level of foam volume varies between 17-20%, the level without defoamer being 17,2%. The defoamers show similar level of efficiency with barely affecting the volume of foam. Defoamer 4 demonstrates better efficiency compared to defoamer 2 but no significant difference to one without defoamer. In case of hardener 2 with defoamer added into resin (Figure 32), the overall level is 11-16% with clear difference between the defoamers. The level of defoamer 2 is remarkably high meaning an increase in foaming compared to level of 11,4% without defoamer. Defoamer 4 has not increased foaming but demonstrates no effectiveness compared to without defoamer.

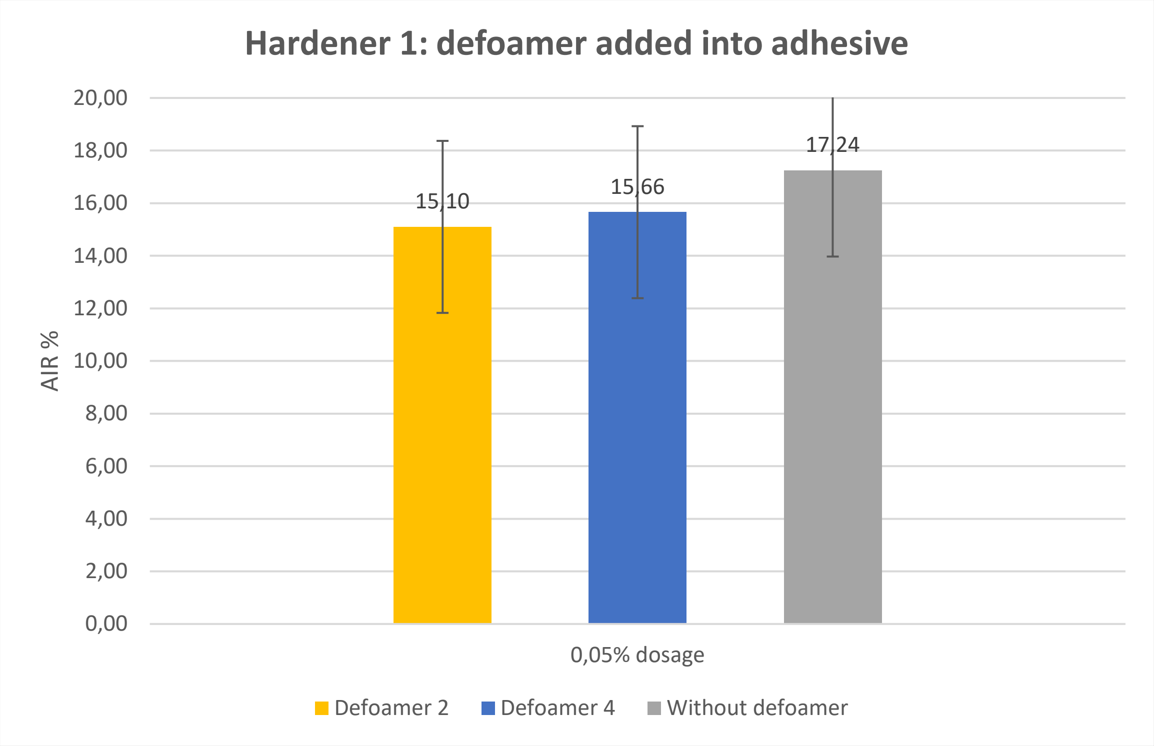


Figure 33. Volume of foam in LPF adhesive formulated by hardener 1. Results of each defoamer added into resin with dosage of 0,05%. Surfactant 1 also included (0,4%). A volume of foam without defoamer is presented as a reference. The error bars indicate the uncertainty of the measurements.

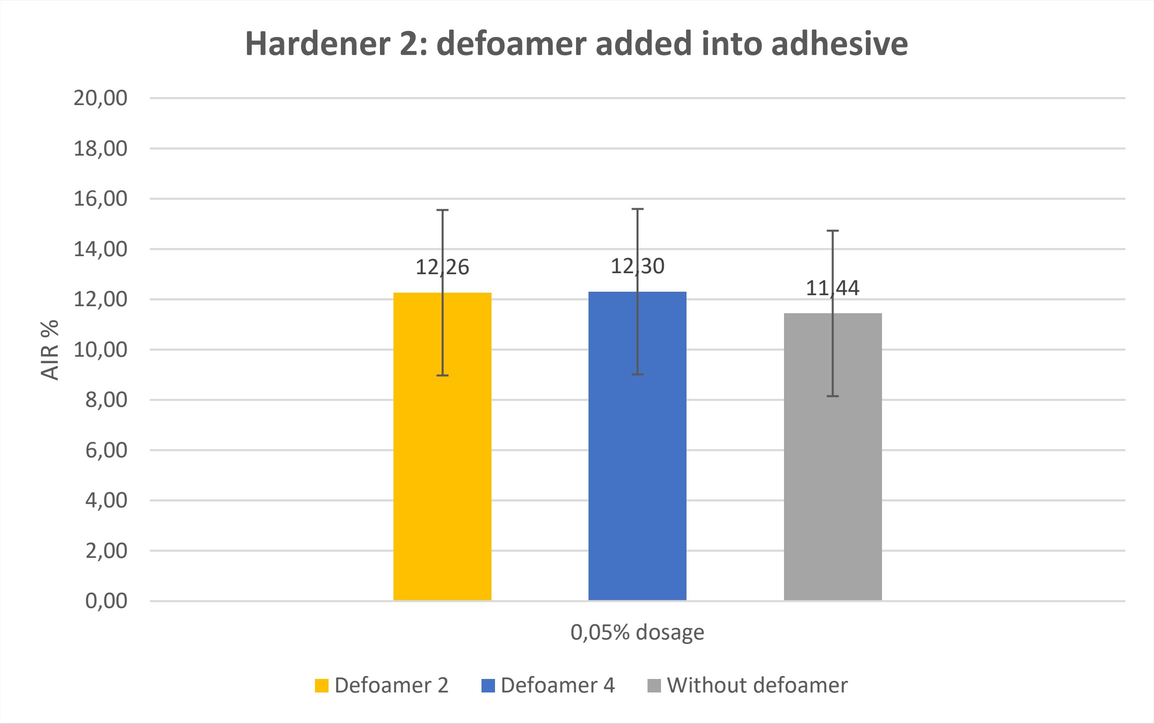


Figure 34. Volume of foam in LPF adhesive formulated by hardener 2. Results of each defoamer added into resin with dosage of 0,05%. Surfactant 1 also included (0,4%). A volume of foam without defoamer is presented as a reference. The error bars indicate the uncertainty of the measurements.

Figures 33-34 of the final trials present the performance of defoamers when added into formulated adhesive prior the experiment. The overall level of foam volume in Figure 33 is 15-18% with level of without defoamer being 17.2%. In this case, both defoamer show a visible efficiency in defoaming with minimal difference between one another. With hardener 2 in Figure 34, no similar was effectiveness was found as the defoamers only settle to approximately same level as the one without defoamer.

In conclusion of the final trials, the defoamers showed similar level of foam volume as ones without defoamer. It is notable that surfactant 1 has increased the overall levels is foam in all cases, indicating to lower surface tension, which provokes the adhesive’s tendency to foam. Due to that, the performance of the defoamers proved weaker compared to preliminary trials. Defoamer 4 demonstrated the best efficiency with small defoaming abilities in nearly all cases, especially the case of defoamer 4 added into adhesive with hardener 1 as seen in Figure 33. As with defoamer 2, the overall performance was weaker than in the preliminaries with barely no defoaming abilities. Overall, the smaller dosage of 0,05% showed no remarkable efficiency but rather a same level as the ones without defoamer.

Despite the defoamers´ poor performance during the trials, it was found that visual observations conducted on the samples did show a significant difference between reference adhesives and adhesives added with a defoamer. As an example, Figure 35 is presented with a comparison of reference adhesive and adhesive + 0,05% defoamer included. Both adhesives were formulated with hardener 2 and in the second picture defoamer 2 was used. Both pictures were taken 3h after mixing of the hardener, which indicates to defoamers ability to hinder the formation of foam during the settling time. The similar effect was visible with both hardeners and defoamers, but individual differences were unclear.

Figure 35. A visual comparison between reference adhesive without additives (left) and adhesive + defoamer 2 (right). The pictures were taken after 3h settling time.

11.2 Resin/adhesive viscosity

Next, the development of viscosities in resin and adhesive is presented and discussed. The results are divided according to preliminary and final trials due to presence of Surfactant 1 modifying the viscosity in the finals.

11.2.1 Preliminary trials

Brookfield viscosities of LPF resin are presented in Appendix 2. Based on the results no remarkable changes in the Brookfield viscosity of the resin were detected. Small increases in viscosity are expected during storage time. An average level of the viscosity for LPF resin varies normally between 300-400 mPas in 25°C with a Brookfield measuring accuracy of ± 20 mPas. Thus, the variations in the results were considered acceptable.

Next, the flow viscosities of preliminary trials are presented.

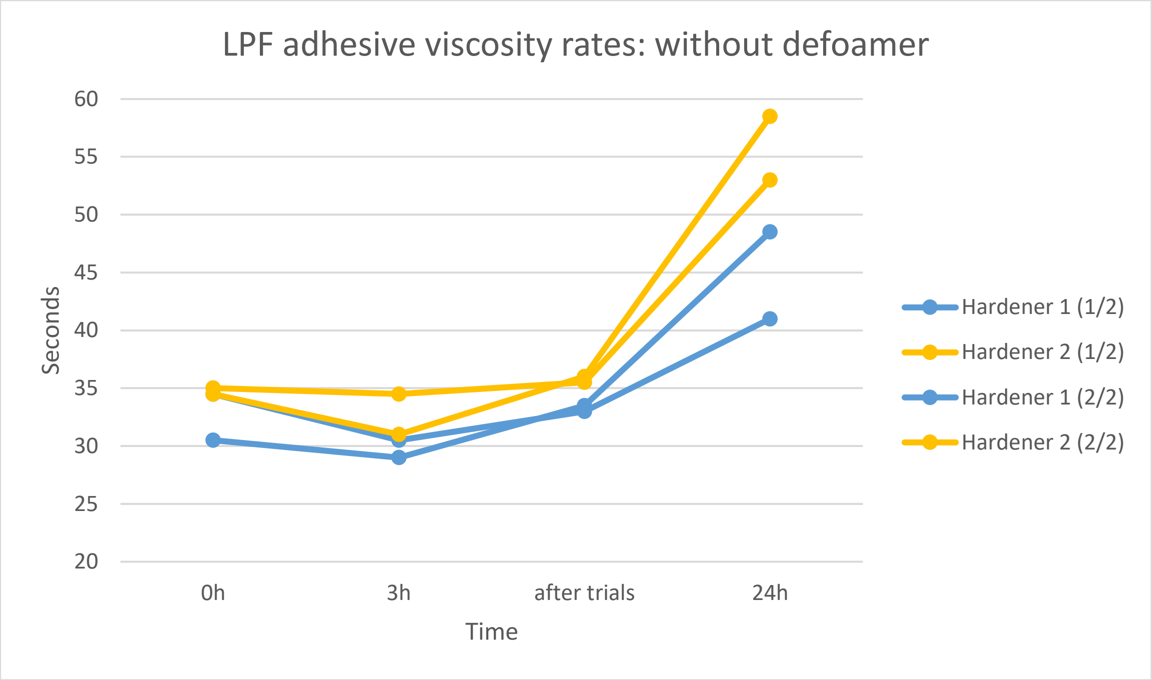


Figure 36. Flow viscosity development of LPF adhesive without additives. The viscosity was determined in temperature of 25°C. The results present an average of 2 replicates.

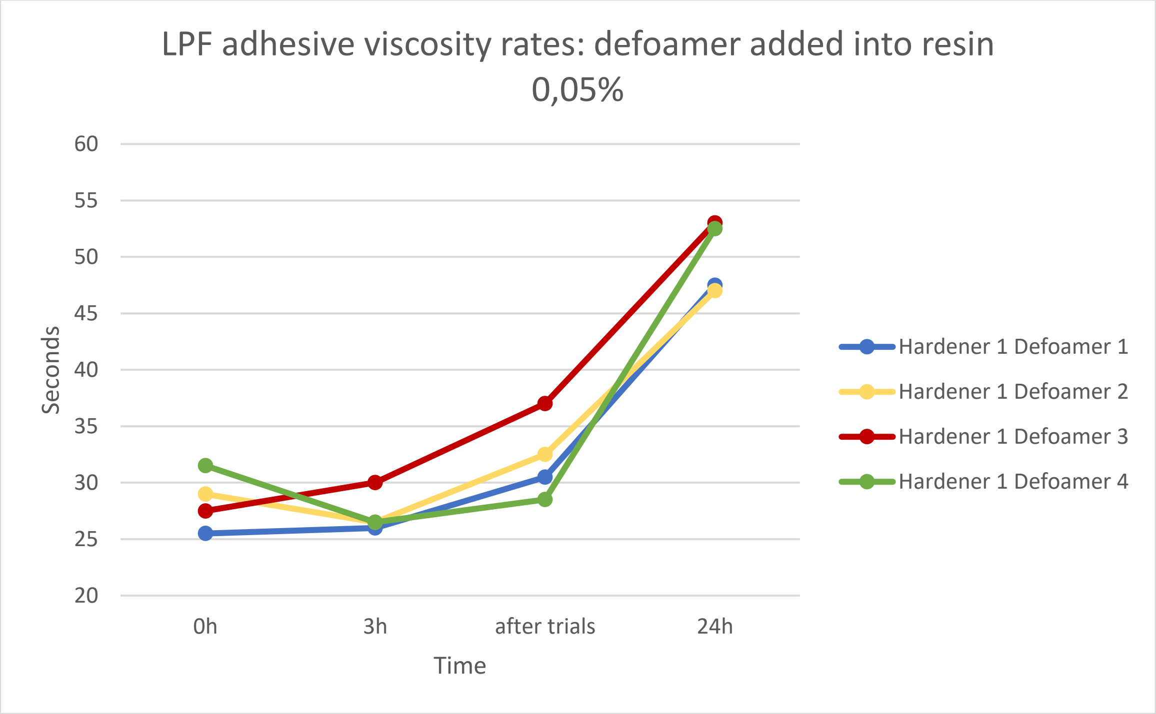


Figure 37. Flow viscosity development of LPF adhesive with 0,05% defoamer added into resin. The viscosity was determined in temperature of 25°C. The results present an average of 2 replicates.

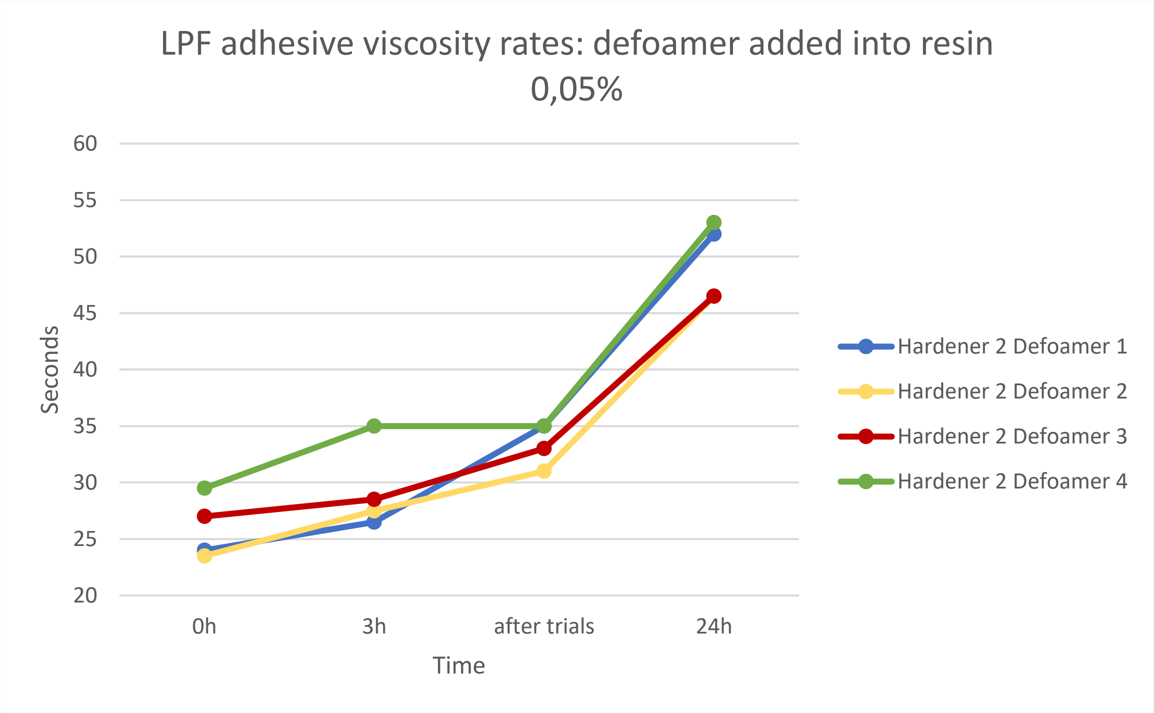


Figure 38. Flow viscosity development of LPF adhesive with 0,05% defoamer added into resin. The viscosity was determined in temperature of 25°C. The results present an average of 2 replicates.

Figure 36 indicates the flow viscosity variations with hardener 1 and 2 without additives. Both lines visualize a similar trend from 30-35s at 0h to (expectedly) 40-60s at 24h. The difference between the two hardeners is notable with hardener 2 clearly showing a higher level of viscosity at all points compared to hardener 1.

As seen from Figure 37 with 0,05% of defoamer added into resin formulated with hardener 1, the overall viscosity level stays lower at all points compared to one without additives. The defoamer 3 is an exception with significantly higher viscosity level compared other defoamers at nearly all points. Defoamer 1 and 2 exhibit a similar trend from 3h to 24h while defoamers 3 and 4 show a significant difference in level from the beginning but end up with the same viscosity in 24h. In case of hardener 2 in Figure 38 with 0,05% defoamer added into resin, all defoamers appear with relatively similar viscosity levels with defoamer 4 making a large increase in 3h. Defoamers 1 and 2 begin with similar viscosity levels but end up with significant difference of defoamer 1 in 52s and defoamer 2 in 46s. The same trend is seen with defoamer 3 and 4 also beginning with similar levels but finishing with a significant difference. Overall between hardeners (Figure 37 and Figure 38), defoamer 2 shows a remarkable difference with the lowest average viscosity with hardener 1 and the highest with hardener 2.

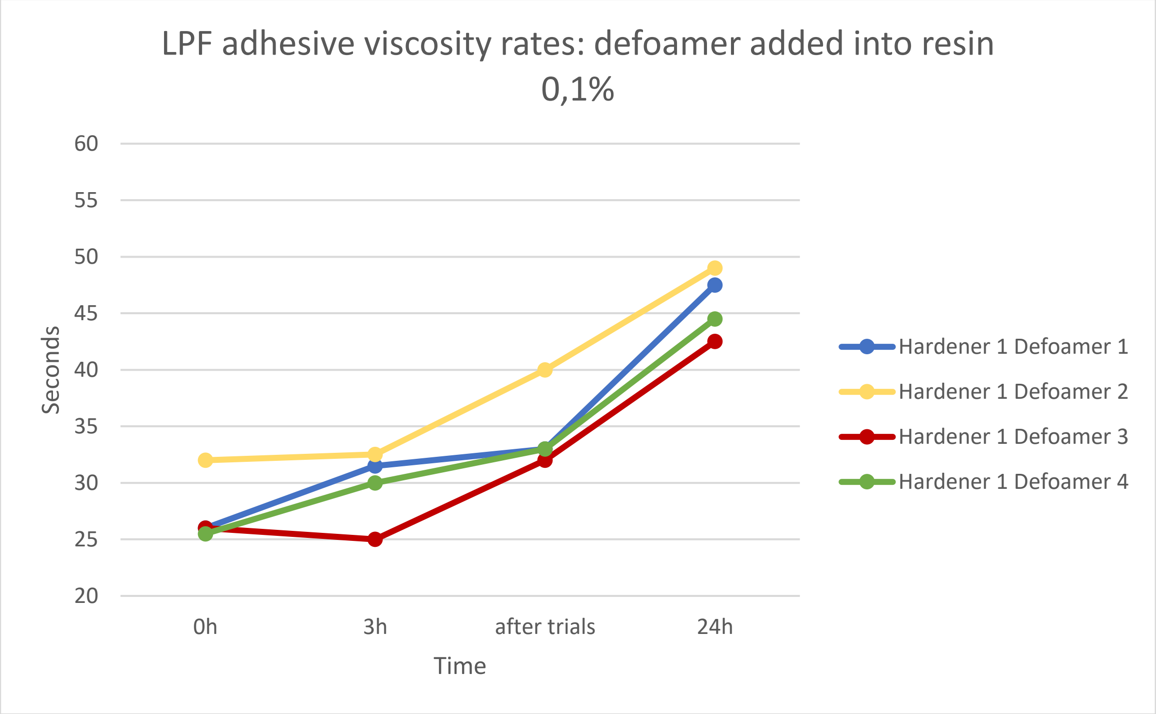


Figure 39. Flow viscosity development of LPF adhesive with 0,1% defoamer added into resin. The viscosity was determined in temperature of 25°C. The results present an average of 2 replicates.

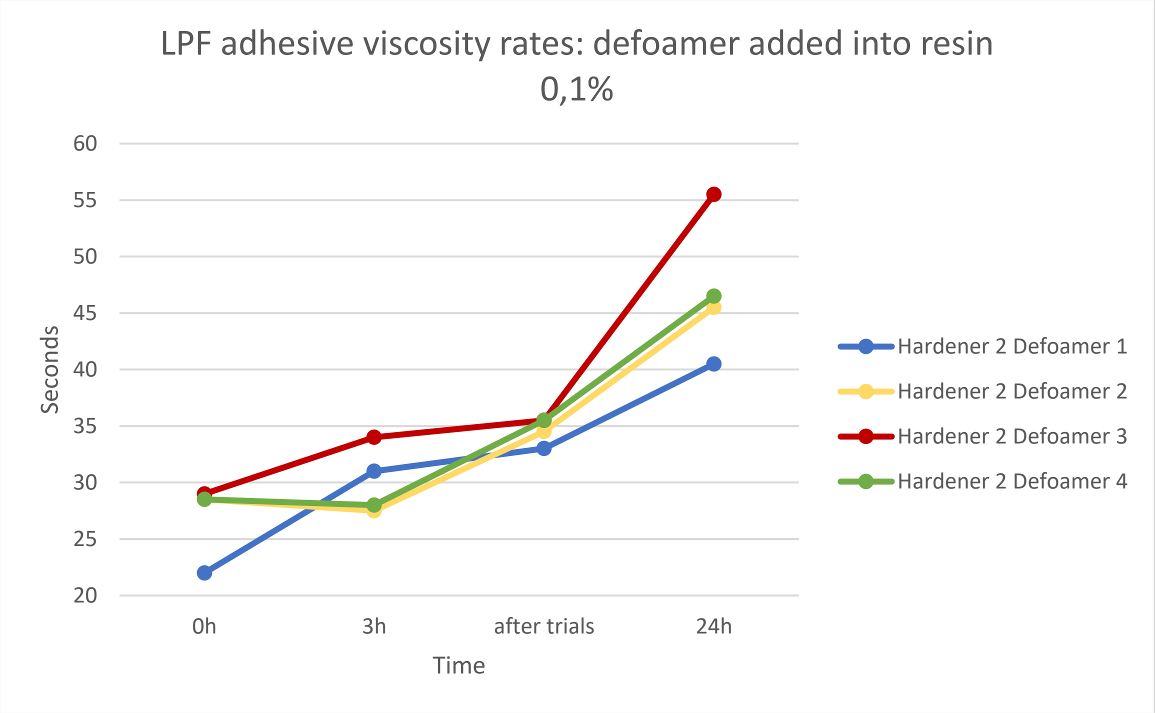


Figure 40. Flow viscosity development of LPF adhesive with 0,1% defoamer added into resin. The viscosity was determined in temperature of 25°C. The results present an average of 2 replicates.

Figures 39-40 present the viscosity with 0,1% defoamer added into resin. In both cases, the defoamers show a significant variation compared to previous figures. With 0,1% dosage in Figure 39 , the overall increase in viscosity is smaller compared to one with 0,05% defoamer (Figure 37), but less stable between the additives. Defoamers 1 and 4 show almost identical trend with hardener 1 while defoamers 2 and 3 show a significant difference with defoamer 2 being the overall highest and defoamer 3 the lowest.

In Figure 40 with 0,1% dosage, the defoamers show a slightly lower 24h viscosity compared to 0,05% (Figure 38) with less uniform trends. It is notable that the defoamers exhibit remarkably different behavior compared to that smaller dosage. Defoamer 2 and 4 show completely identical trends while defoamers 1 and 3 demonstrate a large difference especially in 24h with defoamer 3 being the overall highest and defoamer 1 the lowest.

11.2.2 Final trials

Brookfield viscosities of resin before surfactant are presented in Table 9. In 24h, the viscosity increased from 370 mPas to 387 mPas before the first trials and finally to 410 mPas after 3 days. Small increases in viscosity are expected during storage time, however, the increase in resin viscosity (370-410mPas) with surfactant included appears to escalate faster compared to preliminary results without surfactant (Appendix 2).

Table 9. Brookfield viscosity (mPas) of LPF resin **prior** hardener and additives in 25°C.

	Final trials	
Trial point	Hardener 1	Hardener 2
Before surfactant	370	370
Adhesive, 0,05%	395,2	395,2
Defoamer 2, 0,05%	387,2	410,4
Defoamer 4, 0,05%	387,2	410,4

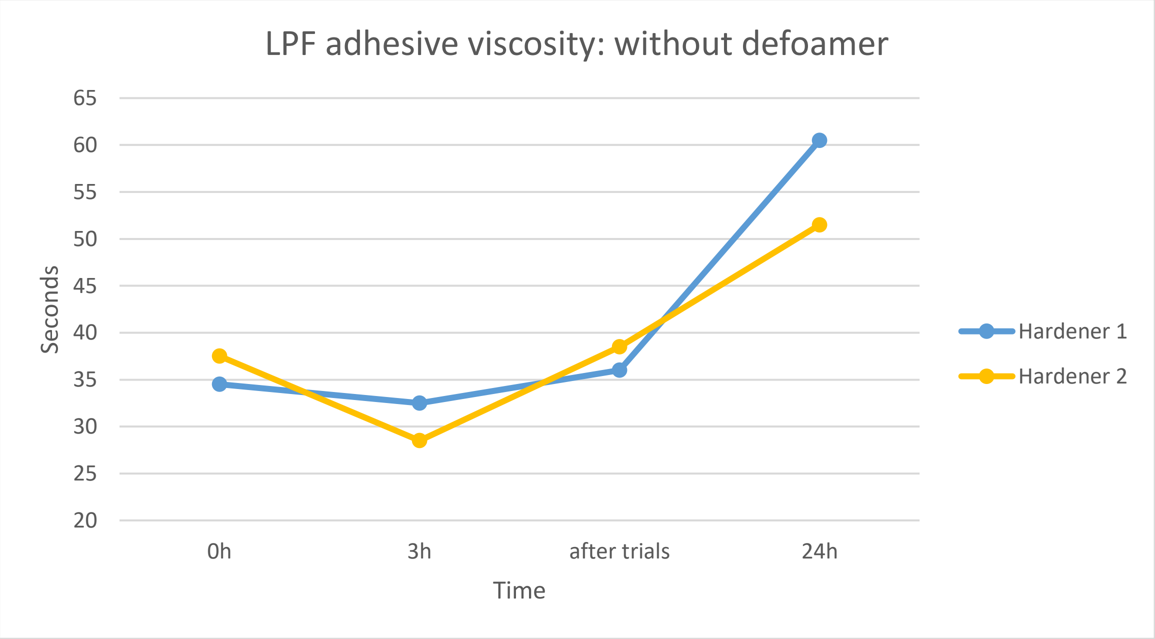


Figure 41. Flow viscosity development of LPF adhesive with 0,05% defoamer **and** 0,4% surfactant added into resin. The viscosity was determined in temperature of 25°C. The results present an average of 2 replicates.

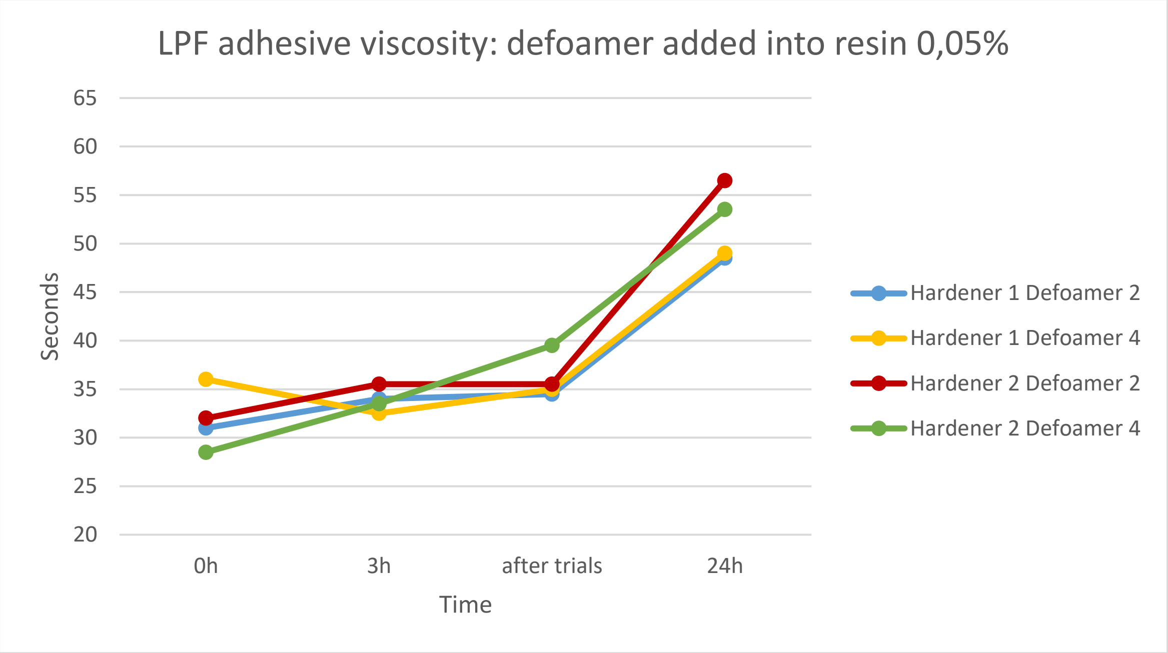


Figure 42. Flow viscosity development of LPF adhesive with 0,05% defoamer **and** 0,4% surfactant added into resin. The viscosity was determined in temperature of 25°C. The results present an average of 2 replicates.

As seen from Figure 41, the level and trend of flow viscosity with surfactant is similar to one without additives Figure 36. However, both hardeners appear to demonstrate higher increase in 24h under the influence of surfactant 1 compared to preliminary results without additives. Overall the difference between the hardeners has decreased as hardener 2 has previously shown significantly higher viscosity levels compared hardener 1.

Figure 42 presents the flow viscosity of LPF adhesive with 0,05% defoamer and surfactant 1 included. Compared to preliminary results (Figure 37 and Figure 38), the overall viscosity level is higher under the influence of surfactant which is potentially caused by lower surface tension and increased foam formation. The viscosity is especially high between 0h to after trials but stabilizes in 24h. In Figure 42, the defoamers also exhibit relatively uniform behavior with much less variation compared to preliminary trials. As for the trends, defoamers with hardener 1 show nearly identical viscosities while defoamers with hardener 2 demonstrate some minor differencies with defoamer 2 reaching slightly higher.

12 EVALUATION ON THE TEST METHOD

In the experimental part, the performance of the defoamers showed occasional inconsistency during the trials. As explained, the principle of defoaming agents is to cause rapture of bubbles and ultimately lead to decrease in foam volume. In this work, that phenomenon was studied by entraining air into adhesive via mechanical agitation of stirring. The aeration causes a particular structure of gas pockets trapped in a network of thin liquid films to form. The stirring test was originally described by Evonik Industries AG. to measure efficiency of commercial defoamers. Broadly, it consisted of adding the chemical into sample and stirring it for a specific period of time at a specific variation of speed. After that, the sample is poured into measuring glass and its weight is measured. Volume of foam is calculated by using a formula which, while considering the sample’s density, determines the increase in sample weight caused by formation of air. The volume of foam allows the results to be compared according to individual chemical.

During this work, several problems arose concerning the method. Firstly, the instructions from Evonik described the testing equipment in general but provided only a little detail on the design of the turbine stirrer and of its required features. Based on the available information, equipment for the trials were purchased and tested to be found applicable according to the method. However, one exception was made concerning the original stirring speed of 2500rpm which was not achievable with the available equipment. Thus, in this work the maximum speed of stirring was set to 2000rpm. Another feature of the available stirrer was its manual adjustment to control the height of the stirrer head and the up & down movement of the stirrer body. These features proved to be surprisingly significant during the experiments as the stirrer occasionally caused undesired agitation to the sample leading to increased levels in the foam volume. During the trials, it was found that those sudden increases in the results were also caused by adjustment of the stirrer head near the liquid surface which ultimately lead to a formation of excess surface foam. The same effect was not found by adjusting the head lower into the sample which made it important finding an appropriate stirring height to be applicable in all occasion and to provide reliable results. Hence, to minimize the possible errors during the experiment, the necessary adjustments were determined, and markings were made ensure setting of the correct stirring height on each trial point. The results were also calculated as an average of 4 replicates with a ± 2g margin of error of the weight of the stirred sample to determine the volume of foam as precisely as possible.

As an overall, the Evonik stirring test provides a capable method to determine a volume of foam in various liquids and to define efficiency of chemicals that contribute to it. As a reference, the chemical company BASF applies a similar stirring test (Figure 43) to evaluate the efficiency and separation tendency of a defoamer in a liquid system.

Figure 43. Stirring test conducted by BASF (2018b).

According to BASF (2018b), the method includes stirring the complete formulation with a toothed dissolver for approximately 3 min at very high speed of 4000rpm as an example. After stirring, the efficiency of the defoamer is determined by density of the formulation measured by a pycnometer. A pycnometer is either a flask or a bottle with a close-fitting stopper to obtain accurate volume, which enables the density of a fluid to be measured accurately, by reference to an appropriate working fluid such as water (Thomas Scientific, 2018). The stirring equipment used by BASF is a high-speed dissolver with clamps for holding the container in place to avoid excess agitation to the sample.

This enables more precise evaluation on the defoamer's performance to be made, since in this work the problems were mostly related to the structure and functions of the used stirring equipment. As a result, achieving stability in stirring was often difficult to reach or required unnecessary attention, which became more challenging as the available stirrers required most of the adjustment to be set manually without possibility to reliably standardize the conditions. Based on the trials, it is recommended that every "manual" stirrer is tested individually to ensure reasonably stable performance and all the trial points are conducted with the same equipment. This, together with sufficient number of stable replicates allows the results, in theory, to become reliable and mutually comparable. However, comparability with results attained by other methods such as stirring tests conducted in pilot scale, cannot be guaranteed without further experiments.

13 CONCLUSIONS

In this thesis, foaming and chemical foam control of lignin-phenol-formaldehyde (LPF) adhesives used in plywood manufacturing was studied. Foaming is a phenomenon which often occurs as an undesired side effect during adhesive mixing that causes weakening of the glue qualities and leads to potential bonding failures in later applications. Foaming is commonly controlled by use of chemical defoaming (antifoaming) agents that contribute to bubble rupture. Several types of defoamers are commercially available for plywood adhesives and they are usually added into resin during preparation of the adhesive before the mixing. The objective of this thesis was to determine efficiency of four selected defoaming agents in two slightly different LPF adhesives and define an optimal point of defoamer addition during the preparation.

Viscosity development of each adhesive was monitored for 24h during the trials to define its potential correlation to foam formation and study the influence of surface active substances. The results showed an overall increasement in flow viscosity levels with the use of surface active agent, which was expected as the non-ionic surfactant forms micelles due to hydrophobic interactions. The same increase was not detected with the sole use of defoamers, but the viscosity development indicated that adhesives formulated with hardener 2 possessed higher flow viscosity levels compared to hardener 1 and the difference was not significantly affected by the presence of surface active agent. Individually the defoamers exhibited no remarkable influence on the adhesive viscosity but more rapid increasement was detected from after trials (approximately 4 hours from mixing) to 24 hours with 0,05% defoamer dosage compared to more stable viscosity development with 0,1%.

The most important laboratory experiments were conducted in two parts to evaluate the efficiency of selected defoamers during adhesive mixing. In the first trials, defoamers exhibited significantly low efficiency on foam volume compared to reference results. Unexpectedly it was also found that stirring tests showed levels of increased foam volumes, indicating to defoamers' ability to rather stabilize foam in some conditions than disrupt it. Although the reliability of these results is questionable due to challenges involving the test method, it was evident that an adhesive formulated with hardener 1 demonstrated significantly higher foam levels than that of hardener 2 but clear correlation to viscosity levels was not visible. In all trial points, individual differences between the defoamers were moderate with larger dosages expectedly showing better efficiency by contributing to occasional decreases in foam volume. This was also supported by visible examinations done after 3h settling time, which showed distinctly lower amounts of surface foam when the defoamer was included in the adhesive. However, it was concluded that based on this experiment the defoamer dosage of 0,05% did not demonstrate defoamability sufficiently enough to be recommended in similar trials.

The second part of the trials included testing the defoamers efficiency in a coinfluence with surface active agent to simulate the same adhesive properties used in curtain coating of veneer. The influence of surfactant was expected to lower the surface tension of the adhesive leading to increased level of foaming. This effect was found clearly visible from the results as the foam levels were higher compared to the preliminary trials. Yet, the performance of the defoamers did not show significant efficiency to restrain additional foaming as some were even shown to increase it.

The defoamers efficiency was also studied by variation of two addition points. Industrially, additives are generally dosed into resin before the adhesive preparation. In this experiment, the results showed that the defoamers' performance was hindered when dosing was conducted into resin, which suggest that the efficiency undergoes a relatively rapid decrease as the higher foam levels later indicated. These results were however not supported by previous knowledge and may only apply to laboratory conditions.

The conclusions of this thesis indicate that the use of defoaming agents will not provide a cost-effective way to reduce foaming in plywood adhesive production. Instead more profitable would be to focus the necessary procedures on choosing the correct hardener compositions to minimize additional foaming and maintaining the appropriate viscosity levels to support foam destabilization. Also, reducing any excess mechanical agitation as much as possible during the production process is crucial. In the future, studies regarding the topic are recommended to further evaluate the reliability of the test method. In a situation where no previous research of similar trials exists, comparability of the results is yet to be confirmed since the properties of foam are often strongly related to the particular generator and since defoaming characteristics are strongly influenced by the conditions of the adhesive during application. Thus, it is recommended that the selected test method permits evaluation under conditions close to those in practice.

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BROOKFIELD VISCOSITIES OF PRELIMINARY TRIALS

Brookfield viscosities of preliminary trials are presented in the following table. The results are organized according to trial points i.e. reference 0,05% meaning the viscosity of the used resin **before** mixing of hardener and additives. In case of i.e. adhesive + defoamer 1, 0,05%, the viscosity is determined prior the adding of 0,05% defoamer into resin and the following adding of hardener. Trial points are named to point out the Brookfield viscosity existing in the resin before the measurements of flow viscosity from the formulated adhesive. Results from the final trials are presented in Table 9 in the thesis.

Table. Brookfield viscosity (mPas) of 25°C LPF resin **prior** hardener and additives.

	Preliminary trials	
Trial point	Hardener 1	Hardener 2
Reference, 0,05%	374	359
Reference, 0,1%	372	379
Adhesive + Defoamer 1, 0,05%	380	369
Adhesive + Defoamer 1, 0,1%	380	380
Adhesive + Defoamer 2, 0,05%	380	380
Adhesive + Defoamer 2, 0,1%	396	380
Adhesive + Defoamer 3, 0,05%	396	380
Adhesive + Defoamer 3, 0,1%	359	372
Adhesive + Defoamer 4, 0,05%	359	372
Adhesive + Defoamer 4, 0,1%	359	372