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TANNINS AS SUSTAINABLE TACKIFIERS IN HOT MELT ADHESIVES

Master of Science Thesis

Examiner: University Lecturer, Docent Terttu Hukka
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ABSTRACT

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There is an increasing interest in renewable raw materials in all industries and adhesive industry is no exception. With the continuous development of biorefineries, the selection of bio-based materials is growing. The objective of this Thesis was to determine whether tannins from the bark of Finnish softwood could be added to that selection in regards to hot melt adhesive formulation. More precisely, whether tannins would be compatible with established materials, and whether tannins would be compatible with cellulose derivatives. This work functions as a laboratory scale proof of concept.

The theoretical part of this Thesis introduces how adhesives work, what are hot melt adhesives and how adhesives are tested, before presenting some sustainable materials and tannins in particular. Hot melt adhesives have three primary components, polymer, tackifier and wax, and the properties of the adhesive can be adjusted by component selection and ratio. Hot melt adhesives are mostly used in packaging industry and thus this Thesis focuses on using folding boxboard. Phenolic tackifiers are industrially available and lignin has been proven to function as tackifier with cellulose derivatives. Due to these facts, hypothesis was that tannins should function as tackifiers due to their phenolic nature, especially with cellulose derivatives. Tannins used in this Thesis are extracted from the bark of Finnish softwood.

It was discovered that mixture of tannins and poly(DL-lactide-*co*-ε-caprolactone) was a potential hot melt adhesive. This formulation was developed by screening mixtures of crude spruce tannin with 7 different polymers and 5 different waxes. Screening of the adhesive capabilities of different combinations was done by manual testing, and the peel strength of the most promising formulations was measured. The copolymer can be used as a hot melt adhesive by itself, but the processability and adhesion towards uncoated boxboard increased with tannins. In contrast to expectations, adhesive capabilities with the tested cellulose esters were weak. Next steps should be development of a better mixing mechanism as the tannin-copolymer mixture was not fully homogenous. There should also be research into how the parameters of the copolymer affect the adhesive capabilities of the hot melt adhesive, and whether changing these parameters could be used to enhance the adhesive. Compatibility with other materials should still also be tested with tannins.

TIIVISTELMÄ

VEIKKO HALKOSAARI: Tanniinit kestävinä tarra-aineina kuumaliimoissa
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Teollisuuden kiinnostus siirtyä kestävän kehityksen mukaisiin raaka-aineisiin kasvaa jatkuvasti, eikä liimateollisuus ole poikkeus. Biojalostamoiden kehitys on johtanut biomateriaalien määrän kasvamiseen. Tämän diplomityön tarkoitus oli määrittää, voisiko suomalaisen havupuun kuoresta saatava tanniini toimia biopohjaisena materiaalina kuumaliimassa. Tarkennettuna, toimisiko tanniini vakiintuneiden materiaalien tai selluloosaesterien kanssa. Työ toimi laboratoriomittakaavan perustutkimuksena.

Työn teoriaosuudessa käydään läpi liiman toimintaperiaate ja testaus sekä kuumaliiman ominaisuuksia. Lisäksi esitellään valittuja biopohjaisia materiaaleja ennen tanniineihin syventymistä. Kuumaliimassa on kolme pääkomponenttia, polymeeri, tarra-aine ja vaha. Näitä komponentteja ja niiden määräsuhdetta vaihtamalla voidaan vaikuttaa liiman ominaisuuksiin. Kuumaliimoja käytetään pääosin pakkausteollisuudessa, ja siksi tässä työssä liiman testaus keskittyy pakkauspahviin. Teollisessa käytössä on fenolisia tarra-aineita, ja ligniinin on todettu toimivan tarra-aineena selluloosaesterien kanssa. Näistä johtuen hypoteesi oli, että tanniinit voisivat fenolisen luonteensa ansiosta toimia tarra-aineena etenkin selluloosaesterien kanssa. Työn tanniinit on uutettu suomalaisen havupuun kuoresta.

Työn aikana havaittiin, että tanniinin ja DL-maitohappo/ε-kaprolaktonikopolymeerin sekoitus vaikutti potentiaaliselta kuumaliimalta. Materiaalien valinta tehtiin seulomalla raakakuusitanniinin seoksia 7 eri polymeerin ja 5 eri vahan kanssa. Seulonta tehtiin testaamalla käsin seosten liimautuvuutta, minkä jälkeen lupaavimpien seosten kuorintakestävyys mitattiin. Kopolymeeria voidaan käyttää kuumaliimassa myös ilman tanniinia, mutta käsiteltävyys ja liimautuvuus käsittelemättömään pahviin paranivat tanniinin lisäyksen myötä. Odotuksien vastaisesti tanniinin ja testattujen selluloosaesterien seokset olivat liimausteholtaan heikkoja. Tanniinin ja kopolymeerin seos ei ollut täysin homogeeninen, joten seostuksen parantamisen tulisi olla seuraava askel. Lisäksi tulisi tutkia, miten kyseisen kopolymeerin ominaisuudet vaikuttavat kuumaliiman tehoon, ja voisiko näiden ominaisuuksien muuttaminen vahvistaa liimaa. Tanniinien yhteensopivuutta erilaisten materiaalien kanssa tulisi edelleen myös tutkia.

PREFACE

This Thesis work was performed in the facilities of VTT Technical Research Centre of Finland Ltd in Otaniemi, Espoo under the supervision of Christiane Laine. First of all I would like to thank her for all the invaluable guidance throughout this project. Also thank you Terttu Hukka for your time and help as the examiner.

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And yet above others I owe thanks to my wife Elisa for standing by me, believing in me when I didn’t myself and helping me carry on.

Espoo, 19.12.2018

Veikko Halkosaari

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LIST OF SYMBOLS AND ABBREVIATIONS

CA	cellulose acetate
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
CR1	commercial resin 1
CR2	commercial resin 2
CT1	commercial tannin 1
CT2	commercial tannin 2
CPT	Crude Pine Tannin
CST	Crude Spruce Tannin
DSC	Differential Scanning Calorimetry
FBB	folding boxboard
T_g	glass transition temperature
HMA	hot melt adhesive
MAS	magic angle spinning
MW	molecular weight
NMR	Nuclear Magnetic Resonance
PF	phenol-formaldehyde resin
PCL	poly(ε-caprolactone)
EVA	poly(ethylene-*co*-vinyl acetate)
PLA	polylactide
PDLA	poly(D-lactide)
PDLLA	poly(D,L-lactide)
P(DLLA-CL)	poly(D,L-lactide-*co*-ε-caprolactone)
Co1	poly(D,L-lactide-*co*-ε-caprolactone) formulation 1
Co2	poly(D,L-lactide-*co*-ε-caprolactone) formulation 2
PLLA	poly(L-lactide)
P(LLA-CL)	poly(L-lactide-*co*-ε-caprolactone)
PPT	Pure Pine Tannin
PST	Pure Spruce Tannin
RH	relative humidity
VTT	VTT Technical Research Centre of Finland Ltd
TEC	triethyl citrate

1. INTRODUCTION

Adhesives are used everywhere from milk cartons to cars and walls to secure two surfaces together. In layman's terms, adhesive means any material that is capable of holding substances together by attaching to both surfaces. Adhesives are not a new invention; a 5000 year old corpse found in the Italian mountains wielded an axe that had its blade attached with birch tar [1]. Adhesives as a group are hard to define, as there are numerous different adhesives for numerous different uses. Thus this Thesis focuses on one type of adhesives, hot melt adhesives (HMAs). HMAs are a subgroup of adhesives that are used in their molten state. Global HMA market revenue was 3.6 billion USD in 2012 with 820 kilotons of materials. Packaging industry is by far the largest user of HMAs, using 56.5% of all HMAs in 2012. [2, p. 33,44] At the end of 2017 packaging industry itself was globally worth 851 billion USD and it is projected to grow steadily by 2.9% yearly [3], so HMAs will remain essential in the future.

Present HMAs are mostly synthetic. There is an increasing interest in renewable raw materials in all industries and adhesive industry is no exception. New alternative materials, mostly plant-based, are constantly being researched. One subject of interest as a potential renewable material for HMAs are tannins, which are a group of phenolic compounds present in a large variety of plants. They are being used in several ways in different industries, but they are best known for their traditional use of turning animal hide into leather in the act of tanning.

This Thesis work was performed as a part of a larger project SusBinders, short for Sustainable Binders from bark [4]. SusBinders is a collaboration between VTT Technical Research Centre of Finland Ltd (VTT), Natural Resources Institute Finland, South-Eastern Finland University of Applied Sciences and commercial partners. The overall goal of the project is to refine the tannin extraction technology and evaluate whether tannins from spruce and pine bark could be used in adhesive formulations.

The objective of this Thesis is to evaluate tannins from Finnish softwood as a major component of HMAs for cardboard. More specifically, could tannins be used as sustainable 'drop-in' tackifiers with established HMA materials and whether they could be used with cellulose derivatives.

The hypothesis is that tannins should indeed be usable as tackifiers in HMA formulation, especially with cellulose derivatives. Some phenolic compounds are in use industrially as tackifiers [5] and previous VTT projects have proven lignin to function as tackifier with cellulose derivatives [6]. Thus phenolic tannins, which are relatively similar to lignin, are expected to also function in this role. This expectation is challenged in this Thesis by testing mixtures of tannins and different polymers and waxes for adhesive capabilities on cardboard. This experimental work is mostly focused on crude spruce tannin. This testing aims to function as a laboratory scale proof of concept on the usage of tannins in HMA formulation.

The next chapter will introduce the basic knowledge on adhesion, HMAs and tannins. This will include the phenomena behind adhesion, how adhesives are tested and what kind of sustainable materials there currently are. The components, advantages and usage of HMAs are also presented. Finally the nature and composition, sources and potential uses of tannins are discussed. The third chapter of this Thesis describes the materials as well as the methods used in this research. Most notably these methods include the procedures of manufacturing and testing of the HMA formulations. The results of the research are then presented and discussed in detail in chapter four, before the final conclusions.

2. ADHESIVES AND TACKIFIERS

In the theoretical part the basic knowledge behind sustainable HMAs and tannins will be presented. Firstly the thesis introduces the theories of adhesion and how adhesives work. Then HMAs and their difference from other adhesives, both regarding components and usage will be presented. Testing of adhesives will be briefly noted and background of sustainable adhesives will discussed. Lastly the thesis will focus on tannins; what they are, how can they be produced, what are they used for and what can they be used for.

Both Merriam-Webster and Oxford Dictionaries define ‘*adhesion*’ by the action, state or process of adhering, which is in the same dictionaries defined as sticking fast to a surface. The Adhesive and Sealant Council, Inc. on the other hand gives us the more scientific definition of “[adhesion is] the stage in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking addition, or both” [7, p. 1]. Materials used in adhering, *adhesives*, have long been used; for example gluing feathers onto arrow shaft stabilized its flight. The items bonded together by adhesive are called *adherends*. This is visualized in Figure 1.

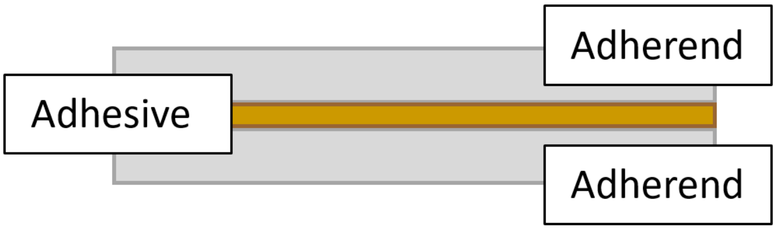


Figure 1. *Visualization of important vocabulary.*

The beginning of modern adhesives technology can be claimed to be when Charles Goodyear, an American engineer, discovered the process that would later be termed ‘vulcanization’. Goodyear noticed in 1839 that heating a mixture of rubber and sulfur changed it from plastic to elastic state. Another major leap happened hundred years later when several synthetic plastic resins, including neoprene rubber, poly(vinyl acetate) and urea-formaldehyde, were commercialized in the United States during 1930s. In the early days of adhesives, a single handbook could include all known raw material options, but by 1960s the amount of alternative materials had grown too large to be collected in a single book. [8, pp. 12–20]

Even though there are numerous different types of adhesives, there is not one universally recognized way to classify them. Instead there are several different ways to classify adhesives. One such way is by chemical composition, where adhesives can be divided into thermosetting, thermoplastic, elastomeric and alloy adhesives. Thermosetting adhesives cure by cross-linking caused by chemical reactions. Thermoplastics harden when the solvent evaporates or when they are cooled from molten state. Elastomerics do not have a set type of curing, but are characterized by their low strength and great flexibility. Alloys are combinations of other groups. Adhesives can also be classified by their physical form, e.g. liquid, film, granule, or end use, e.g. wood adhesives or acid-resistant adhesives. [9, pp. 47–55]

Adhesives are usually not the only option for attaching objects to another. For example welding, screws or simple interlocking may also be applied, depending on the materials and the situation. There are several advantages and disadvantages to note when deciding whether adhesives are the choice to form a certain bond. These are presented in Table 1.

Table 1. *Advantages and disadvantages of adhesive bonding in general. Adapted from* [10, pp. 398–401]

Advantages	**Disadvantages**
Stress is divided on a large area.	Surfaces must be clean, any dirt will weaken the bond.
Cycles of low and high load do not usually weaken the bond.	Long cure times are sometimes necessary.
Acts as shock absorber and vibration damper.	Finished joint is not visible, so inspection is difficult. Process must be well controlled.
Protects metals from galvanic corrosion.	Heat or pressure may be needed to set the adhesive.
Shape and thickness does not prevent joining.	If setting time is long, assembly jigs and fixtures may be needed.
Provides smooth contours.	Cleanup may be expensive.
Can be used to seal joints.	Limitations in operating temperature.
Variety of different materials possible.	Usage environment (e.g. moisture, chemicals) affects how long the bond will hold.
Often cheaper and faster than mechanical fastening.	Commonly compose of hazardous materials so environmental, health and safety considerations are necessary.
Even if heat is required, usually too low to have an effect on metal parts.	Product appearance may be ruined by misapplied adhesive.
Can be made with special properties; insulative or thermally and electrically conductive.	Bonded joints cannot be disassembled. Faulty joints may lead to scrapping the product.
Good strength-to-weight ratio.	

There are a few distinct basic requirements for a good adhesive bond; cleanliness, wetting, solidification, joint design and proper selection of adhesive. Cleanliness means removing foreign materials such as moisture and dirt from the surface, so that they do not form a weak boundary layer. This can also mean a more sophisticated physical or chemical process to prepare the surface. Wetting means the ability of the adhesive to flow into the crevices and pores of the surface. Good wetting increases contact area for the adhesion. Solidification is the process where the adhesive solidifies from its liquid state. Different adhesives employ different methods to achieve that; solvent evaporation, cooling from molten state, chemical reaction due to pressure or cooling agents, to name a few. Joint design means designing the joint so that the forces of adhesion are optimized. The adhesive selection is an integral part; material to be bonded, service and production requirements (temperature, moisture, biological factors etc.) and overall budget should all be considered when selecting adhesives. [10, pp. 404–405].

2.1 Theories of adhesion

The basic principle of adhesion is relatively simple - interfacial forces hold two surfaces together. However, there are several different theories that try to explain the phenomenon. They are each valid to some extent and their importance depends on the materials of the bond. Oftentimes in reality several of them might be simultaneously working together [9, p. 6]. Most of these theories have short-comings and only work in certain cases, but still they give perspective on what might be happening in the interface.

It is important to note that surfaces are different from bulk material. A unit - be it atom or molecule - within the bulk phase is surrounded by similar units and attracted in all directions. The molecules on the surface are not surrounded, so they have different attraction to different directions; usually they are more strongly attracted towards the bulk. This may lead to increased density of molecules on the surface. Interfaces are also rarely sharp planes; not only liquids but even solids utilize vapor pressure which leads to a concentration gradient at the interface. [8, p. 80]

The six different theories of adhesion which are presented in more detail next are

- Adsorption theory
- Mechanical interlocking theory
- Electrostatic theory
- Weak-boundary layer theory
- Diffusion theory
- Chemical bonding theory

Adsorption theory - also sometimes referred to as wetting or thermodynamic theory - is the widely used approach in adhesion at the present. It proposes that adhesion is caused by surface forces developed by molecular contact between the adhesive and the adherend. These forces are thought to primarily be van der Waals forces and hydrogen bonds. For these molecular forces to happen, the materials must have intimate contact. The process of establishing this contact is called wetting. For wetting to happen on a solid surface, the surface tension of the adhesive should be lower than the critical surface tension of the solid. This leads to the adhesive flowing into the irregularities of the surface and thus maximizes the contact surface; poor wetting is the result of adhesive flowing over such irregularities. [8, p. 65][9, pp. 9–10] For example, aluminium has a critical surface tension of 500 mN/m while cellulose has 45 mN/m [10, p. 402]; this means that adhesive that flows readily on aluminium may not do so on cellulose.

Mechanical interlocking theory states that adhesion occurs when the adhesive penetrates into the crevices on the surface of the adherend. Solid surfaces are seldom completely smooth, but consist of pores, peaks and valleys. Bonds are indeed frequently stronger between porous surfaces than smooth surfaces, which supports this claim. However, this interlocking also has the effect of increasing interfacial area between the adhesive and the adherend. So it can be debated whether mechanical interlocking itself is what makes bonds stronger or if it enhances other mechanisms by increasing the contact area. [8, pp. 62–65][9, pp. 6–7][10, pp. 401–404] This mechanical adhesion was regarded as common sense in the 1920s, but the theory was largely rejected by 1950s and 1960s. In 1970s the theory garnered new trust again with new research. [8, p. 77]

Electrostatic theory suggests that the cause of adhesion is electrostatic effect between the materials. Dissimilar electronic band structures between the adhesive and the adherend lead to electron transfer and form an electrical double layer between the materials. Electrostatic forces caused by this double layer would cause the resistance of separation and thus adhesive strength. [8, p. 62][9, p. 8] This theory is supported by evidence of electrical discharges when peeling adhesive [10, p. 403].

Weak-boundary layer theory states that even when the adhesive bond seems to break at the interface of the adhesive and the adherend, the bond between the materials is usually not the reason of failure. The failure is argued to be cohesive within the interfacial zone of one of the substrates, caused by a weak boundary layer. These layers can occur if an impurity, such as dirt or air, concentrates near the bonding surface. This will lead to a weak adhesive bonding and cause failure at lower stress than usual. The failure appears to have happened at the interface, but is in fact really caused by the weak boundary layer. These layers can often be removed or altered by surface treatment. An easy example of a weak boundary layer is an air bubble trapped between the surface and the adhesive due to poor wetting. Also a weaker-bond-forming compound within the material itself, such as shorter polymer chains, can be the cause of weak boundary layers. [8, p. 64][9, pp. 13–14][10, p. 404]

Diffusion theory, on the other hand, suggests that adhesion is caused by molecules diffusing between the adhesive and the adherend and forming an interfacial interphase layer, which consists of molecules of both materials. It implies that macromolecular chains are mobile and soluble in one another. This is primarily applicable when both materials are polymeric and their molecules are capable of movement. While these demands are not always met, they do contribute to the adhesive strength when that happens. [8, p. 69][9, p. 8]

There is also the **chemical bonding theory**, which is relatively simple; chemical bonds between the materials have a profound effect on the adhesion strength. These bonds can be covalent, ion and hydrogen bonds, van der Waals forces or acid-base interactions. Covalent and ion bonds are strong and durable, but require mutually reactive chemical groups. For this reason surfaces can be pre-treated to enable covalent bonding. It is also possible that the chemical bonding is not directly between the adhesive and the adherend, but there might be a so called coupling agent in between, forming a chemical bridge between those two. [8, pp. 71–72][9, pp. 11–12]

2.1.1 Modes of failure in adhesives

Failure of an adhesive bond may occur by three different ways, as depicted in Figure 2; adhesive failure, cohesive failure in adherend or cohesive failure in adhesive. Adhesive failure means that the interfacial bond between the adhesive and the adherend was broken. Cohesive failure in the adherend on the other hand means that the adherend breaks; this is often called *fiber tear* when the adherend is paper or boxboard. Cohesive failure inside the adhesive means that some of the adhesive remains on both adherends. Of course the adhesive bond might not break cleanly in only one way, but show both cohesive and adhesive failure. [9, p. 14] What type of failure mode is deemed desirable depends on the use of the adhesive.

Figure 2. *Examples of modes of failure. From left to right: adhesive failure, cohesive failure in adherend, cohesive failure in adhesive.*

Failure mode can be useful in determining the reason to the bond failure. For example, one reason for adhesive failure can be poor wetting. [9, p. 17] Cohesive failure within the adhesive may be avoided if the adhesive itself is robust enough that high levels of work are needed to cause cohesive failure within the adhesive [11, p. 440].

2.2 Hot melt adhesives

HMAs are generally thermoplastic compounds which are solid in room temperature and used in molten liquid state in elevated temperature. They set up an adhesive bond by solidifying upon cooling. The preferred materials “are usually solid up to 79.4 °C or higher, then melt sharply to give a low-viscosity fluid that is easily applied and is capable of wetting the substrate to be bonded, followed by rapid setting upon cooling" [9, p. 88]; these characteristics make it suited to industrial high-speed use. [8, p. 730] HMAs are generally appreciated for their ease and rate of use, while their most noted drawbacks are low heat resistance and slowly giving in under prolonged load. Thus they are primarily recommended for hold-in-place operations in packaging. [8, pp. 907–908][9, p. 89]

There are subcategories in HMAs; pressure-sensitive and reactive HMAs, the latter which is also called curing HMAs. Pressure-sensitive HMAs are permanently tacky in room temperature [2, p. 18], but they are thermoplastic in nature and as such can be heated to mold them better. Reactive HMAs are for example polyurethane prepolymers, which react with the water content of the wood to create a crosslinked polyurethane network. This leads to them being thermosetting adhesives instead of thermoplastic like most HMAs. Reactive HMAs have higher temperature and moisture resistance and greater strength than conventional HMAs, but they are more expensive and have higher curing times. [8, p. 909]

HMAs have two distinct and important parameters: open time and set time, sometimes called setting speed. Open time is the maximum amount of time between setting the adhesive and applying the second substrate that leads to an acceptable bond. Set time is defined as the minimum length of time needed to wait after applying the second substrate to obtain sufficient bond strength. Both times are oftentimes in the seconds range, though open time can be almost infinite for pressure-sensitive HMAs. [11, p. 440][12, p. 301] Narrow molecular-weight distribution is also quite critical parameter for HMAs, as it minimizes melt elasticity [13, p. 48]. This elasticity leads to poor application patterns, which can occur as long thin tails when the adhesive is handled [11, p. 440].

2.2.1 Components

Adhesives in general are quite diverse component-wise; they all have the adhesive base, sometimes referred to as the binder, but the other components all depend on the kind of adhesive. Binder is indeed the primary component and is responsible for forming a strong bond between the substrates, keeping them together. Adhesives are also generally named after the binder.

In addition to binder, there are several basic components that are commonly used in adhesives. Hardeners are used in thermosetting adhesives to act as catalyst for the curing reaction or to cross-link with the binder to create more robust adhesive. Solvents can be used to reduce the viscosity so that the adhesive can more easily be spread on a surface, and usually evaporate readily. Diluents serve the same purpose as solvents, but differ in the sense that they do not evaporate but stay incorporated in the adhesive. Fillers are usually neutral, non-reactive substances that are added to improve some properties of the adhesive, such as heat resistance or electrical conductivity. They also often reduce materials costs. Carriers or reinforcements are usually thin materials like films or papers, which can serve as support for the adhesive or a release media. In addition to these basic components - all of which are again not found in every adhesive - there are also a number of other additives used to achieve certain characteristics. These include plasticizers, antioxidants, thickeners, inhibitors and surfactants. [9, pp. 47–48]

In HMAs, there are commonly three primary components: binder (usually in HMAs referred to as simply polymer), tackifier (also known as resin) and wax. Tackifiers and waxes are notably missing from the previous paragraph, as they seem to be only found in HMAs. In addition to these, all kinds of previously mentioned different additives can be used to further enhance the adhesive's service properties. [14, p. 106] The properties and functions of the three primary components are collected in Table 2.

The main component is the polymer, which mostly determines the properties. It gives the HMA strength, cohesion and mechanical properties. The molecular mass of the polymer has a high impact on the properties of the HMA. Higher average molecular mass means higher viscosity and therefore worse wetting, but better heat resistance and cohesion [8, p. 908]. As mentioned earlier, the molecular mass distribution affects processing the material, as wide distribution may cause strings or thin filaments coming from the end of the adhesive bead. These are not wanted as they will gradually mess the equipment. For processing of the adhesive to be clean, the adhesive should behave more like liquid and less like rubber, and this is accomplished by narrow molecular mass distribution. [11, p. 443]

Poly(ethylene-*co*-vinyl acetate) - or EVA as it is usually called - is the most used polymer for HMAs with an approximate share of 43%. Polyolefins and polyurethanes have market shares of 31% and 11%, respectively. [2, p. 13] Other common polymers are polyamides and styrene block copolymers [15, p. 3]. Advantages of these different common base polymers have been collected in Table 3.

Table 2. *Primary components of HMAs, revised from* [11, pp. 440–441] *and* [14, p. 106].

Component	**Properties**	**Functions**
Polymer	• High molecular weight (MW): >10 kg/mol • Glass transition temperature (T_g) usually < room temperature • Physically cross-links on cooling • Strong	• Responsible for the strength of the adhesive bond by forming a hard polymer network • Ability to stick to adherends
Tackifier	• Low MW, <5 kg/mol • T_g usually > room temperature • Amorphous	• Lowers viscosity for better machinability • Improves wetting (contact of adhesive and substrate) • Adjusts T_g to optimize strength at service temperature [15, p. 2] • Dilutes polymer entanglement network to soften the adhesive • Enhances adhesion [8, p. 908]
Wax	• Low MW, <2 kg/mol • T_g < room temperature • Crystalline	• Lowers viscosity • Provides heat resistance • Increases setting speed to enable faster development of strong adhesive bond • Some form crystallites that reinforce the hot melt by resisting deformation under load • Reduces the surface tension of the liquid adhesive, enhance wetting properties • Increases water resistance [8, p. 908]

Table 3. *Common base polymers and their advantages, revised from* [2, p. 21]

Base polymer	**Advantages**
EVA	Low cost, short to moderate open time, compatible with many substrates
Polyolefins	Good barrier against moisture, excellent chemical resistance, low cost, long open time, higher temperature resistance
Polyurethanes	Excellent solvent and chemical resistance, strong bonds, usable with thermally sensitive substrates, long open time
Polyamide	Stable at high temperatures, good chemical resistance, compatible with many substrates, strong bonds
Styrene block copolymers	Optimal low temperature properties, good stability, compatible with most tackifying resins

As shown in the Table 3, EVA and polyolefins have the advantage of low cost. This also explains their popularity. They are primarily used in packaging [2, p. 21]. According to Dreger as cited by Ebnesajjad, polyamide and polyester based HMAs are sometimes referred to as “high-performance” HMAs and are used with a larger variety of adherends, including glass, leather and some metals. Some HMAs of these materials can be used as holding adhesives at even 150 °C. [9, p. 90] According to an article “Thermal cycling makes strong adhesive stronger” as cited by Ebnessajjad, polyesters have a distinct advantage of having sharp melting points, which makes high-speed manufacturing easier. Yet according to same article, both polyamides and polyesters suffer from being susceptible to moisture. [9, p. 90] EVA is often added to polyamide to adjust its’ viscosity and lower the overall cost [8, p. 733].

Being a copolymer, EVA’s properties can be adjusted by changing the vinyl acetate amount. The vinyl acetate levels used in adhesives vary in the range of 6-40 % [11, p. 442]. Usually EVAs used in HMAs include 28% vinyl acetate [8, p. 731]. Increasing the vinyl acetate content increases the adhesion ability, wetting and flexibility, but also price and setting time while heat resistance and cohesion become worse [8, p. 908]. Around 40% of the total mass of EVA-based HMAs consists of the polymer [8, p. 731].

The purpose of the tackifier is to adjust viscosity and service temperature and enhance adhesion. Some renewable tackifiers are already seeing use, such as rosin esters and polyterpenes. More common materials are derivatives of tall oil resin and synthetic hydrocarbon resin. [15, pp. 3–4] Tackifier constitutes usually 10-25% of the total mass of the HMAs [8, p. 908]. The role of tackifier is to act as a solid solvent for the other ingredients in the adhesive. As such, they should not be able to pack too well with itself, since then it will be less prone to dissolve other materials. Low MW also increases the entropy of mixing with other ingredients which leads to stronger solvency power. Phenolic tackifiers are common in HMAs due to their chemical resistance and ability to form hydrogen bonds, which improves the adhesion to substrates capable of hydrogen bonding. [11, p. 442]

Waxes lower the viscosity of the HMA and improve its flow, making it easier to apply. They are also sometimes used to increase water resistance [8, p. 908]. The ones used in HMAs are typically petroleum fraction waxes such as paraffin wax [15, p. 5]. Fischer-Tropsch waxes produces from synthesis gas are also commonly used [11, p. 443].

Antioxidants are often added to adhesives to protect them from free radicals, which can be formed from the polymer by heat or shear, among other things. One of the major groups of primary or free-radical scavenging antioxidants are hindered phenols, which form stable radicals due to electron resonance. In HMA manufacturing, it is typical to use antioxidants to stabilize all of the components (polymer, resin, wax) to ensure no changes to their properties. Especially tackifier resins are susceptible to thermooxidative degradation. [8, pp. 440–454] Antioxidants usually consist of 0.2-0.5 % of the total mass of the HMA [8, p. 732].

2.2.2 Advantages and disadvantages of hot melt adhesives

HMAs are in many ways different from the adhesives used more commonly in everyday lives, such as tape and paper glue. HMAs are distinctively characterized by their high application temperature, lack of solvent and compatibility for high speed application. Some of the most prominent advantages and disadvantages of HMAs have been collected from the literature in Table 4.

Table 4. *Advantages and disadvantages of non-reactive HMAs compared to other adhesives.*

Advantages	**Disadvantages**
No water or organic solvents to be evaporated [8, p. 907]; so no need to invest in solvent recovery equipment [2, p. 17]	Poor creep resistance: slowly creep under low load at far below the softening point [8, p. 907][9, p. 112][11, p. 440]
Formulation can be varied to achieve individual requirements, e.g. melt viscosity, application temperature [8, p. 907]	Low service temperature and heat resistance due to low softening point [8, p. 908][9, p. 112]
Low safety requirements [8, p. 907]: non-volatile [8, p. 730] and chemically nonreactive [11, p. 440]	Certain substrates can be sensitive to the elevated application temperature [8, p. 908]
High-speed application: low set times, rapid curing by cooling, usually seconds [8, p. 730][2, p. 17][11, p. 440]	No solvent and cooling causes quick thickening, so limited ability to properly wet rough or porous surfaces and thermally conductive materials [11, p. 440]
Broad adhesion; good bonding with wide variety of surfaces [2, p. 17][8, p. 907]	
Long shelf life [8, p. 907]	
High bond strength [8, p. 907]	
Generally high water resistance [2, p. 17]	

While the list of advantages does seem longer, hot melt adhesives are by no means the final solution of adhesives. For example, HMAs are used for metal gluing but there a different approach must be taken than when gluing wood or cardboard. With wood it is possible to simply apply molten HMA and press the pieces together. With metals having high thermal conductivity, the HMA might cool and set too fast.

2.2.3 Industrial use of hot melt adhesives

As mentioned earlier, packaging industry is the largest user of HMAs with over 50% share. Paper and board packaging represent 34% of the whole packaging market [16, p. 1], and the experimental focus of this Thesis is particularly in cardboard. In Finland packaging production was valued over 1.6 billion euros in 2012, and 75% of this was exported abroad. There is a long-term project 'Packaging Valley', the aim of which is to help Finnish packaging industry to rise to the top of the world. [17, pp. 2–5]

Due to the high temperatures needed to work with HMAs, special application equipment is required. While there are variations in equipment, by basic principle there are two types of systems for applying HMAs: melt-reservoir and pressure-feed systems. [9, p. 189]

In melt-reservoir system the HMA is loaded into a tank where it is melted. This melt is then pumped through an extrusion gun or application wheel to apply to the adherend. Its biggest advantage is its ability to hold large amounts of adhesive ready for use, while its drawbacks feature difficulties maintaining uniform temperature, especially when more adhesive is added, and the bond degrading due to too high temperature of the adhesive at the nozzle. [9, p. 190]

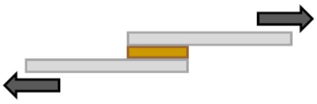
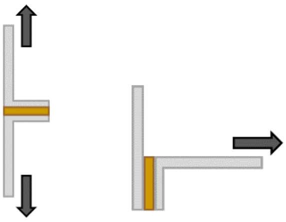
Pressure-feed systems, also known as progressive-feed systems, operate with smaller amounts in a "first in, first out" method. In them adhesives are melted and immediately transferred under pressure or mechanical force to the nozzle. A portable hot-melt gun sometimes used in crafting is an example of this. Pressure-feed systems bolster advantages of minimizing adhesive degradation due to their "first in, first out" system and they are more portable, especially in the case of a personal hot-melt gun. Their disadvantages are lower delivery rates and need of special arrangements to allow use for tacky or soft adhesives. [9, pp. 190–191]

EVA-based hot melts tend to have relatively high melt viscosities and need special manufacturing equipment. A Z-blade mixer with oil-heated jacketing is one way to work around this problem; this kneading action allows copolymers, resin and fillers to be rapidly dispersed even in a viscous compound. Once the product is homogenous, it is extruded into ropes. These ropes can then be supplied into the next application equipment for use, or allowed to cool and be granulated into pellet form. Cooling is commonly achieved by water, so moisture must be eliminated before packing with an air-drying cyclone, for example. [8, p. 732]

2.3 Testing of adhesives

Since the effectiveness of an adhesive bond is quite straight-forwardly examined - the stronger the bond, the larger amount of force it takes to break it - testing is quite an essential part of adhesive manufacturing. There are several different ways to test adhesive bond strength which are listed in Table 5. The figures in the table represent the basic ideas of these bond test types: tensile, shear, peel and cleavage. There are of course more ways to design these tests, such as depicted in [8, pp. 228–237]. In addition to these tests, there are also other properties of the bond that are frequently tested. Those properties include creep, which means weakening of the bond due to static load; fatigue, weakening of the bond due to cycling of low and high load; impact, effect of sudden load; and durability, which contains all kinds of environmental effects. [9, pp. 276–278]

Table 5. *Adhesive test types, gathered from* [9, pp. 273–276]

Bond test type	Figure	Properties
Tensile		Among the most common tests, even though other modes of load are preferred when designing the joint.
Shear		Very common due to simple manufacturing and testing of samples.
Peel		Intended for flexible adhesives and at least one flexible adherend, measures highly localized stress. 180° peel on the left, 90° peel on the right.
Cleavage		Variation of peel where adherends are rigid.

Viscosity of adhesives is also an important parameter that has a major impact on the bond; with too low viscosity, the adhesive might too readily penetrate into the adherend and thus leave too little adhesive to form the actual bond. Yet with too high viscosity proper wetting will not happen, which will lead into low penetration into the adherend and consequently into low or no mechanical interlocking. [8, p. 911] Poor penetration will lead into decreased bond area and this way into decreased bond strength. With hot melts, altering the temperature might change the viscosity, so viscosity can theoretically be played around with.

Durability contains environmental effects. These can range from temperature to humidity and chemicals. In the case of packaging, the major application for HMAs, adhesives might experience some temperature and humidity variety during transfer and possible outside storage. As mentioned earlier in chapter 2.2.2., one major drawback of HMAs is their low service temperature. One could argue that precisely for this reason knowledge of the heat resistance of a certain HMA can be very important.

For some adhesive uses, water resistance can be of importance, especially if the adhesive can be expected to be used outdoors. There are several different ways to measure this and literature of the field sees varied measurements. Frequently used test conditions were soaking at room temperature and boiling, as in literature examples [18, p. 329][19, pp. 2–3]. In these literature examples, two different tests were conducted. Water-soaking-and-drying test saw specimens soaking and drying under fume hood in room temperature. Boiling-water test saw specimens undergo a cycle of boiling, drying, boiling and water cooling, before being tested both wet and after fume hood drying. Also long drying in standard atmosphere after soaking can be utilized [20, p. 38] as well as soaking in elevated temperature [21, p. 3]. A European Union standard for non-structural thermoplastic wood adhesives classifies adhesive durability by its ability to retain a satisfying degree of bond strength after certain conditions. For example holding fast after seven days in standard atmosphere, six hours in boiling water and two hours in room temperature water is one of the requirements for achieving durability class D4. [22]

Heat resistance is in its heart a simpler measurement. To measure that, adhesive bond strength is simply measured at an elevated temperature. In practice this measurement requires a bit more sophisticated measurement devices to ensure the correct temperature. Test specimens simply taken from an oven and tested in room temperature offer merely a crude estimate. ASTM standard D 2295 [23] suggests using heat lamps or other uniform heat source. Other good alternative is to have an environmental chamber in your testing machine as seen here [24, p. 945].

2.4 Sustainable adhesives

Before the era of petroleum, natural raw materials were used out of necessity. For example, according to Delmonte as cited by Pizzi, a protein found in milk called casein, animal bones and starch were all used for adhesives in the 1800s [8, pp. 12–13] As with many other natural materials, soy was industrially used in 1930s and 1940s, but the advantages of petroleum - cheaper cost and biochemical inertness of petroleum-based hydrocarbons - took over and caused industrial use of soy to collapse [25, p. 156].

Renewables gained more interest during the oil crisis in 1970s, but once the cost of oil decreased again, the interest decreased as well. Adhesives from renewable materials have been garnering interest for several years now, when concern for the environment has increased. Then again, the rise of renewable resources has not been only because of environmental issues, but also partly because of economic issues, as new regulations are being put in motion regarding synthetic adhesives. [26, pp. 829–830] Rising and unstable prices of petroleum have caused a switch of attention to other raw materials. This is especially true for renewable materials, where environmental changes are encouraged by offering discounts and subsidies. [14, p. 105]

This switch from petroleum to renewable materials should be easy in theory, since the technology to turn biomass into specific chemicals already exists. However, renewable polymers still only had 5% market share in 2016. This slow change can be attributed mainly to two reasons; renewable polymers often have inferior properties in lower mechanical properties and high hydrophilicity and they are still quite expensive to use in production compared to petroleum based polymers. [14, p. 105] The advantages of renewable materials - lower toxicity, biodegradability, ease of recycling - are drawn back by these weaknesses. There are also some risks in bio-based raw materials having different yield when harvested in different locations and at a different time of year, creating potential instability in the material supply. [8, p. 901]

If general change into renewable materials has been slow, it has been even slower in the adhesives industry. This is partly due to the fact that adhesives industry uses smaller volume of polymers compared to for example packaging industry. [14, p. 105] But with the renewed appreciation for renewable materials, the term ‘bio-based adhesive’ has come to only include “materials of natural, non-mineral, origin which can be used as such or after small modifications to reproduce the behaviour and performance of synthetic resins” [26, p. 830]. While these bio-based adhesives have been researched for quite some time now, major industrial use has not broken through yet in Europe - however, in southern hemisphere plant-based phenols, tannins, are seeing industrial use in wood gluing [8, p. 903].

There is interest in bio-based adhesives, but in general they are regarded as demanding novel technologies and methods to implement [8, p. 901]. There are already several renewable options for HMA’s main components commercially available today. Their relatively small industrial use is caused mainly by lack of suppliers, high introductory prices and difficulties in reformulating, meaning they might have to be chemically altered before using as alternative to the original. [15, p. 3] Depending on the scale of these alterations, adhesives manufactured this way might not be bio-based adhesives as per the earlier definition of ‘bio-based adhesive’, but they would still be a step in the right direction. Several times in literature the properties of an ideal bio-based adhesive are listed, and according to Petrie [15, p. 3] the list is originally from “a specification developed by The Procter & Gamble Company for a sustainable hot melt packaging adhesive”. These properties of ideal bio-based adhesive are listed below:

- 100% renewable raw materials
- Thermoplastic and elastic
- T_g less than -10 °C
- Low or no crystallinity (amorphous)
- Is not stiff, stretches before breaking
- Relatively low melt viscosity
- Stable in molten form
- Must meet all regulatory requirements depending on the application

- Price preferably lower than $5 per kilogram
- Production scalable to 5 000 - 10 000 tons per year in 5 years

As mentioned in chapter 2.2.2, HMAs already have some environmental benefits over other adhesives, namely the low energy consumption and absence of solvents. These benefits continue as regarding renewable resources for adhesives, HMAs are on the front line. One of the big points of using sustainable adhesives is not only reducing the reliance on petroleum, but also making recycling easier. This forces us to consider one important parameter for bio-based HMAs; they should be "stable during storage, processing and application but should degrade rapidly once their purpose is served" [14, p. 108]. Largest problem in creating 100% renewable HMAs is that in general, biodegradable tackifiers and renewable polymers are not compatible [15, p. 5].

Some natural tackifiers are already in use, which includes rosin derivatives and terpenes. They can both be produced from pine stumps and from Kraft process of pulping pine trees [27][28]. They are both compatible with some synthetic polymers such as EVA and acrylics. Pine rosin can adhere to several different kinds of substrates while terpenes are approved for food contact and are very tacky when hot. Natural waxes are often based on plants, which use waxes to reduce the evaporation of water. While natural waxes exist and some HMAs using natural waxes were patented as early as 1975, they often struggle with having too low melting points. [15, pp. 4–5]

Biopolymers used in HMAs today are primarily based on soy, starch, polylactide and polyamide. However, typically biopolymers from renewable sources lack elastomeric character. As a result those biopolymers require toughening agents or plasticizers to achieve greater flexibility. [15, pp. 5–6]

Modified starch shows promise as a biopolymer for HMAs. Starch adhesives provide good adhesion to paper and wood due to starch's similarity to cellulose and ability to form hydrogen bonds. Conventionally starch adhesives are not thermoplastic and suffer starch's poor water and mold resistance, but there is research being made into circumventing these problems by chemical alteration. [14, pp. 113–115][15, pp. 6–7] One possible way is transglycosylation reaction between starch derivatives and alkanols as in this process patented by VTT [29].

Cellulose, polymer consisting of glucose units, is extremely common material, being found in the cell wall of plant cells. Due to the number of hydroxyl groups, cellulose molecules tend to form hydrogen bonds between one another. This leads to crystalline structures, which do not dissolve in most common solvents. However, esterification and etherification of cellulose leads to compounds that can be dissolved. Some of these derivatives are thermoplastic and have seen use in plastic and HMAs. Cellulose acetate butyrate (CAB) for example is reported to be usable in HMAs and also solvent-based adhesives. [8, pp. 492–496] Again, transglycosylation of cellulose derivatives has been found to increase processibility and biodegradability, and be usable for HMAs [30].

Aliphatic polyesters are a group that suits the need for easy recycling, as they have robust mechanical properties but are susceptible to degrade by hydrolysis. One such polyester is polylactide (PLA). Lactic acid, the monomer of PLA, can be produced by fermentation or by chemical synthesis. Lactic acid is a chiral molecule, and fermentation produces selectively either one of the isomers, while chemical synthesis produces a mixture of both [14, pp. 107–108]. Poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are isotactic polymers where all monomers have the same tacticity, and poly(D,L-lactide) (PDLLA) is composed of both types of monomers. Chirality does not affect chemical properties, but can affect how biological systems handle the molecule.

PLA can be degraded by composting which would mean easier recycling and potentially CO_2-neutral life cycle. Melting point of PLA is quite high with 170 °C and it is fairly inflexible, which limit its use in adhesives. [31, p. 220] One way to combat these problems is copolymerizing lactic acid with ε-caprolactone [14, p. 108][15, p. 7]. Poly(ε-caprolactone) (PCL) melts at around 61 °C and is very flexible [32], so it balances the disadvantages of PLA. Both polymers are biodegradable [33, p. 805], so the copolymer should be as well. At the moment PCL is mostly produced from petrochemicals, but since the technology exists to manufacture benzene from biomass [34] and ethylene can be produced from bioethanol [35, p. 1], PCL too can be completely bio-based. Poly(L-lactide-*co*-ε-caprolactone) (P(LLA-CL)) with 81:19 molar ratio is reported to show excellent hot tack, long open time and moderate setting time when it was tested for usability in HMAs [31].

Regarding the natural raw materials for adhesives lignin is one of the most researched, especially concerning wood adhesives [26, p. 835]. Lignin is a class of large cross-linked phenolic polymers abundant in plants, second only to cellulose. Lignins are a large variation of different complex substances which presents us with a conundrum; there are no individual molecules that can be fixed to particular structures, ergo a generic lignin molecule for softwood or hardwood cannot be identified. The attractiveness of lignin is its abundance and cheap price - it is mostly produced as a by-product in wood pulping, estimated 75 million tons per year. [8, pp. 904–906] The International Lignin Institute however estimates the production to be between 40 and 50 million tons per year, and this is mostly uncommercialized waste product. Industrially usable lignosulphonates and Kraft lignins are produced 500 000 tons and 100 000 tons per year, respectively. [36]

Due to this vast supply, there is a lot of interest towards using lignin as raw material. It has not found large scale industrial usage yet, and most lignin-rich wastes are still burned for energy [8, p. 583]. Research has found, however, that it could be used to replace phenols in phenol-formaldehyde resins [8, p. 588]. There has been research conducted in

VTT about using lignin as tackifier in HMAs, and it has been proven as a potential material, especially with cellulose derivatives [6].

2.5 Tannins as sustainable tackifiers

Tannins are a group of phenolic molecules that are present in a large variety of different plants. As such, they could be playfully described as cousins of lignin; they both are a class of plant-based phenolic compounds. However, there are differences, as tannins' historical capability of tanning leather, for example. What follows is a brief explanation on what tannins are, where they are found and what they can be used for.

First mentions of vegetable tannins, as they were known earlier, are credited to a plant encyclopedia by Greek botanist Theophrastus of Eressus around 300 BC [37, p. 587]. When searching for a definition of tannins, one notices that definitions vary. Dictionaries of Oxford, Collins, Cambridge, MacMillan and Merriam-Webster all give different definitions for the word 'tannin'. Oxford's Dictionary of Chemistry defines tannins as a "group of complex organic chemicals -- commonly found in leaves, unripe fruits, and the bark of trees. -- Some tannins have commercial uses, notably in the production of leather and ink." [38, p. 517] In literature, tannins are usually recognized as vegetable water soluble polyhydroxyphenols which can coagulate proteins [8, p. 901]. A prime example of this coagulation, the act of tanning, happens by tannins "forming hydrogen-bonded cross-linked structures with collagen molecules" [37, p. 588]. This widely accepted quality is quite problematic, however, since some compounds without this quality are nevertheless commonly accepted as tannins due to their molecular composition. At the moment, the most explicit way to define tannins seems to be in fact through molecular structure.

2.5.1 Molecular composition

Tannins are commonly divided into three distinctive classes of phenolic compounds: hydrolysable tannins, condensed tannins and phlorotannins. Sometimes phlorotannins, the most recently identified class, are omitted from the list; this might be caused by the fact that the ability of phlorotannins to tan animal skins into leather has not been proven [37, pp. 590–591]. Phlorotannins are present in marine brown algae [39, p. 1927] and are structurally easily defined: they are comprised of phloroglucinol units which are attached to each other by carbon or ether bonds. Some variations with additional bonds or hydroxyl groups are possible. [40, p. 327] Figures 3 and 4 show a phloroglucinol and tetrameric phlorotannin, respectively.

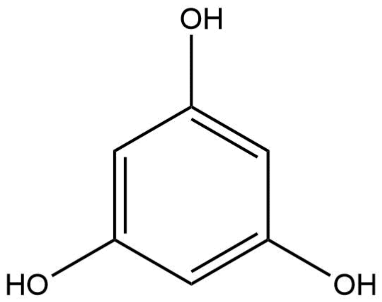


Figure 3. *Phloroglucinol.*

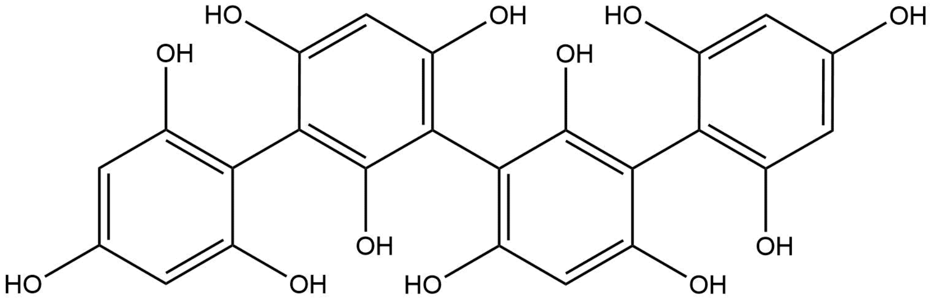


Figure 4. *Tetrameric phlorotannin.*

Condensed tannins are more prevalent and constitute around 90% of total world production of commercial tannins with 200 000 tons per year [8, p. 569]. Condensed tannins consist of at least two subgroups, procyanidins and prodelphinidins, though also a third group, profisetinidins, have been mentioned [41]. Procyanidins consist of stereoisomers (+)-catechin and (−)-epicatechin, the structures of which are depicted in Figure 5. The structure of prodelphinidins' stereoisomeric main units, (+)-gallocatechin and (−)-epigallocatechin is shown in Figure 6. There are also other, smaller groups of condensed tannins where the main units may be missing one or more hydroxyl groups. Example of procyanidin polymer is given in Figure 7. [40, p. 328]

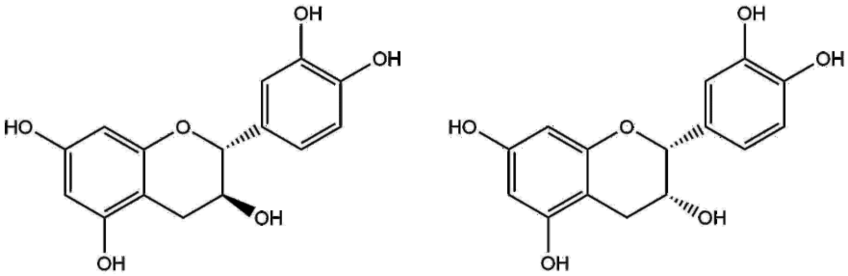


Figure 5. *Molecular structures of (+)-catechin (left) and (−)-epicatechin (right).*

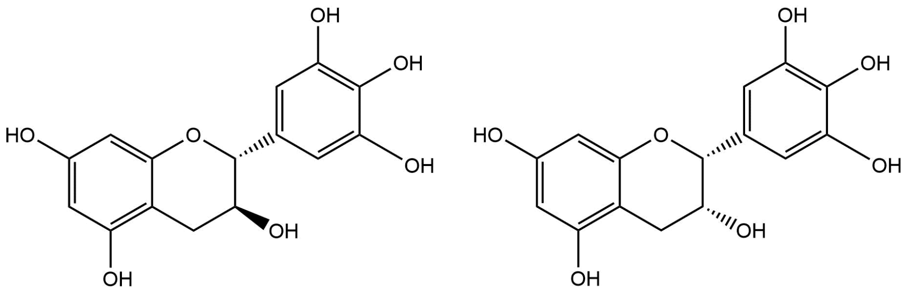


Figure 6. *Molecular structures of (+)-gallocatechin (left) and (−)-epigallocatechin (right).*

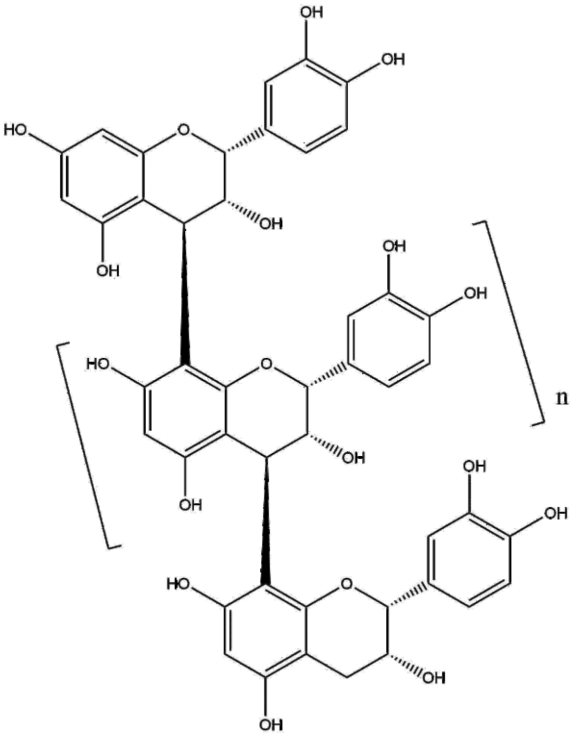


Figure 7. *Example of procyanidin polymer consisting of (−)-epicatechin monomers.*

Arguably the most complex group of tannins are the hydrolysable tannins, which are divided into gallotannins, ellagitannins and simple gallic acid derivatives. Simple gallic acid derivatives contain up to five galloyl groups which are usually esterified to glucose or quinic acid. If there are six or more galloyl groups, they are defined as gallotannins. Figure 8 depicts gallic acid, esterified group of which is called galloyl group. Figure 9 presents heptagalloyl glucose, a simple gallotannin. [40, pp. 328–329]

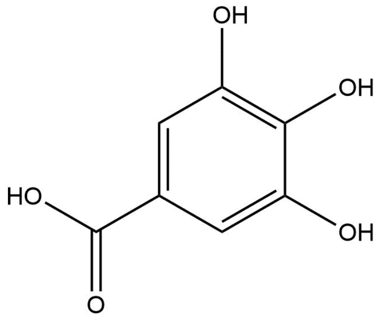


Figure 8. *Gallic acid.*

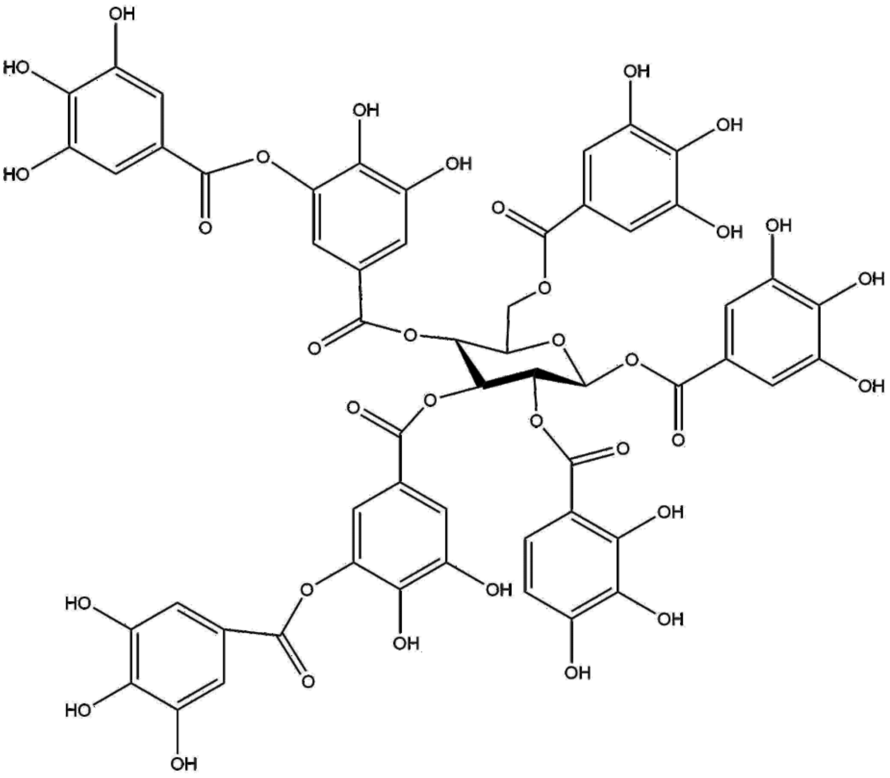


Figure 9. *Heptagalloyl glucose.*

Ellagitannins are much more common in plants than gallic acid derivatives and gallotannins. They are also very diverse; over 500 ellagitannin structures have been reported, which can be divided into six slightly different subgroups. The basic common building blocks in ellagitannins are glucose, galloyl group and hexahydroxydiphenyl group, which is the bonded form of ellagic acid. [40, pp. 329–330] Ellagic acid and an example ellagitannin in corilagin are depicted in Figures 10 and 11, respectively. Some ellagitannins have trouble binding proteins at low or neutral pH, and are therefore problematic regarding the common definition of tannins [40, p. 327].

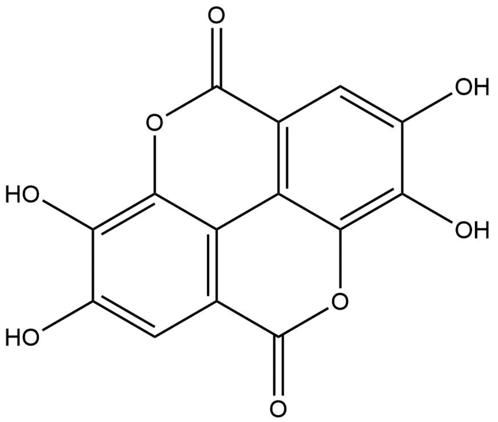


Figure 10. *Ellagic acid.*

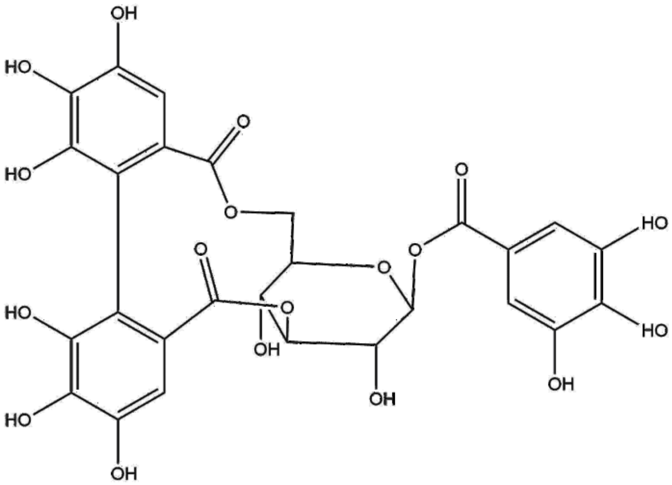


Figure 11. *Corilagin.*

As shown, tannins compose of a myriad of different compounds. Fortunately the compounds are chemically quite similar in regards to their functional groups. This means it is possible to relatively reliably know what kind of reactions they will undergo, even if the exact molecular composition is unknown.

2.5.2 Sources

Tannins can be found in a plethora of plants, both flowering and seed-producing, and in lesser extent in fungi, algae and mosses. They are found in all types of plant tissues serving different causes; in the roots tannins are found under the epidermal layer and act as a protection against pathogens; in the trunk tannins are found in the areas of active growth where they regulate said growth; inside the seeds tannins contribute to the maintenance of dormancy; in the fruits and leaves tannins serve as a natural line of defense by providing an astringent flavor to reduce animals' appetites. [41] However, largest sources of commercial tannins are barks of various trees, which are rich in condensed tannins [8, p. 569].

In January of 2018, a Finnish magazine reported that annually Finnish forest industries produce 3 000 000 tons of softwood bark, and at the moment they are mostly burned for energy [42]. In year 2016 77 million cubic meters of wood was used in Finland, 88% of it in wood industry. Of the wood industry's by-products, 12 million cubic meters are used in energy production. [43] Over 7 million cubic meters of this was bark [44].

Dry matter of spruce bark contains circa 10% tannin [45, p. 70]. In the hypothetical state where this 10% is applicable to all bark, theoretically some 700 000 cubic meters or 300 000 tons of tannins are available from wood industry per year. These tannins would be primarily from Finnish softwood, which means Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). In his 1977 article [46, p. 1425], Bate-Smith concluded that gymnosperms - which include both spruce and pine - produce only condensed tannins. This is quite fortunate, because hydrolysable tannins have several disadvantages; "lack of macromolecular structure in their natural state, the low level of phenol substitution they allow, their low nucleophilicity, limited worldwide production, and higher price" all severely limit their chemical and economical potential [26, p. 830].

Commercial tannin extracts are produced from bark of various tree species, including several from *Acacia*, *Schinopsis*, and *Pinus* families. [8, p. 569] Extraction can be done in a reactor where hot water with a small amount of extraction chemicals is circulated through the bark. Water temperature is in the 55-90 °C range, and sodium bisulfite and sodium carbonate can be utilized as extraction chemicals. [47, p. 159] This extraction solution also includes sugars, pectins, amino acids and other substances. [8, pp. 901–902]. As an example, usually circa 75 % of commercial wattle bark extracts are active phenolic ingredients. The rest is mostly simple sugars and hydrocolloid gums. These impurities are of course unwanted and pure tannins would be preferred, but industrial fractionation of tannin and the nontannin fraction has proven to be difficult. [8, p. 573]

Synthesis of tannins has been widely researched as well. Condensed tannins consist of many oligomeric products formed from flavanol units by condensation reactions through a biomechanism that is not yet fully understood. Controlling the degree of polymerization and the regio- and stereochemical features prove to be difficult, however. This has been approached by several stepwise-condensation processes, most of which are based on an alkylation process to connect a flavan-3-ol derivative to a nucleophilic flavan-3-ol unit. Of hydrolysable tannins' sub-group gallotannins, only 'simple' gallotannins are reported to be able to be synthetized. Ellagitannins, another sub-group of hydrolyzed tannins, are reported to be readily synthetized using esterification of gallic acid or hexahydroxydiphenoic acid and diol derivative of glucose.[37, pp. 607–611]

2.5.3 Properties and usage

As mentioned earlier in chapter 2.5.2, bark from wood industry and tannins within are burned for energy in Finland. However, while the heating value of bark is on the same level as the rest of the tree, it is weakened as fuel due to heterogeneity and high amounts of water and ash [48, p. 83]. Worldwide tannins are still mainly used for leather tanning [8, p. 569].

Tannins function as antioxidants. This ability is caused by several different mechanics; they can chelate metal ions that are involved in producing OH• radicals or they can inhibit enzymes that generate reactive non-radical oxygen compounds such as O_2^{-}•, but the major way for phenolic compounds to quench radicals is electronic delocalization throughout the molecule. This stabilizes the phenolic radicals so that they are mostly unreactive and as such terminate the radical chain reaction. The strength of polyphenols' antioxidant abilities depend on the atomic structure of the molecule and its ability to stabilize by resonance. [37, pp. 596–597] This ability is simplified and portrayed in Figure 12. However, polyphenols are also reported to have prooxidant properties under certain circumstances [49].

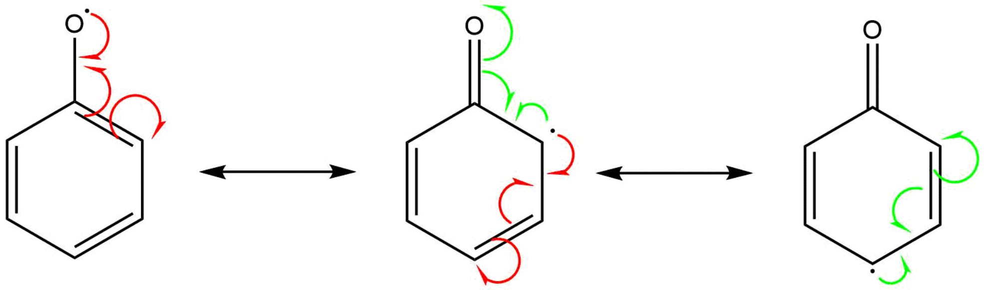


Figure 12. *Resonance stability of phenolic radical.*

Tannins have been reported to have both carcinogenic and anticarcinogenic properties, and some tannins have also been reported to have antimutagenic properties. Both anticarcinogenic and antimutagenic properties may be related to tannins' antioxidative property and ability to protect cellular components from oxidative damage. Different tannins have been reported to inhibit a large variety of bacteria, fungi and yeast. These antimicrobial properties may be caused tannins' tendency to inhibit certain enzymes and impair absorption of vitamins and minerals. [50, pp. 426–443]

These attributes have lead tannins to also be widely used in oenology to increase the longevity of red wine, protect vineyards from fungi, precipitate metals from wines and inhibit micro-organismic growth by enhancing the antimicrobial properties of sulfur dioxide. Tannins are also used in cosmetics and pharmaceutical industries for their antioxidant and anticarcinogenic properties. [41]

There have been also other interesting possibilities for the use of tannins. Research has suggested it could be used to recover uranium from seawater due to immobilized tannin having high selective adsorption ability to uranium [51]. There has also been a suggestion of investigating the use of tannin and other polyphenols as “prodrugs” against diseases such as cancer due to their ability to act as pro-oxidants under certain conditions. Cancer cells in general are characterized by a higher level of reactive oxygen species which could potentially be taken advantage of to preferentially kill cancer cells [52, p. 105]. Tannins could theoretically be developed for this purpose. [37, p. 614]

In chapter 2.4 it was mentioned that lignin could be used to replace synthetic phenols in phenol-formaldehyde (PF) resins. Tannins possess the same ability due to their phenolic nature, which allows cross-linking by formaldehyde in a polycondensation reaction [53, p. 186]. There are several mentions in literature about partially substituting phenols in PF with tannins. But unlike lignin, tannin can also be used alone with formaldehyde to create PF-like adhesive. [8, pp. 903–906] Another part of the SusBinders project was a proof of concept whether Finnish softwood tannins could be used for these formaldehyde resins, and initial results were promising [54].

Interesting discovery – or lack thereof – regarding this Thesis was that no mention was found about using tannins as major component in HMAs. Considering tannins are used in other kinds of adhesives even on industrial level, this was quite surprising. This Thesis work thus presents for the first time the implementation of tannin as major component in HMAs.

3. MATERIALS AND METHODS

3.1 Materials

Tannins used in this Thesis were extracted at an earlier part of the SusBinders project. Crude Spruce Tannins (CST) and Crude Pine Tannins (CPT) from Finnish spruce (*Picea abies*) and pine (*Pinus sylvestris*) bark were used. CST and CPT composed of 40-45 % and 30-35 % tannins, respectively. Carbohydrate contents were 35-40 % for CST and 40-45 % for CPT. Molecular weight of CST was 3.4 kg/mol compared to 1.9 kg/mol of CPT. [55, p. 11] Thermogravimetric analysis with heating rate of 5 K/min had been conducted on both CST and CPT, and degradation began around 200 °C. Mass losses of 5 % were achieved at temperatures 212 °C and 216 °C, and mass losses of 10 % were achieved at temperatures 237 °C and 244 °C, for CPT and CST respectively. These properties are listed in Table 6 below.

Table 6. *Properties of crude tannins of SusBinders project.*

Property	CST	CPT
Tannins (%)	40-45	30-35
MW (kg/mol)	3.4	1.9
Temperature with 5 % mass loss (°C)	216	212
Temperature with 10 % mass loss (°C)	244	237
Carbohydrates (%)	35-40	40-45

Due to the high amount of sugars, the enzymatic purification of the crude tannins has also been examined as another part of the SusBinders project. The sugars are expected to decrease the efficacy of tannins and thus HMAs with purified tannins instead of crude tannins are expected to be stronger. Purified and ultrafiltered tannins used in this Thesis are Purified Spruce Tannins (PST) and Purified Pine Tannins (PPT).

Two different copolymers (Co1 and Co2) of lactic acid and ε-caprolactone were used in this Thesis. These poly(D,L-lactide-*co*-ε-caprolactone) (P(DLLA-CL)) were polymerized in another VTT project. Their polymerization procedure is confidential and not presented in this Thesis.

Commercial chemicals used are listed in Table 7. Cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) and their oxidized derivatives CA-Ox, CAP-Ox and CAB-Ox were used in material testing as renewable polymers. In cellulose esters cellulose's hydroxyl groups have reacted to form esters. Oxidation reactions were done with hydrogen peroxide before the start of this Thesis. Waxes used belong to one of two categories. Triethyl citrate (TEC), tributyl O-acetylcitrate (CITRO) and Soft-N-Safe acetid acid ester (SNS) were different acid esters while Sasolwax H1 and C80 were used as synthetic Fischer-Tropsch waxes.

Table 7. *Commercial chemicals used.*

Chemical	Product Name	Manufacturer	Product Code
PLA	Polylactide	NatureWorks LLC	Ingeo 4060D
PCL	Poly(ε-caprolactone)	Sigma-Aldrich	Product number 704105
EVA	Poly(ethylene-*co*-vinyl acetate)	Sigma-Aldrich	Product number 437220
TEC	Triethyl citrate	Sigma-Aldrich	Product number 27500
CITRO	Tributyl *O*-acetylcitrate	Sigma-Aldrich	Product number 388378
SNS	GRINDSTED® SOFT-N-SAFE Acetic Acid Ester	DuPont	Material number 175540
H1	Sasolwax® H1	Sasol Limited	
C80	Sasolwax® C80	Sasol Limited	
CA	Cellulose Acetate	Eastman™	CA-398-3
CAP	Cellulose Acetate Propionate	Eastman™	CAP-482-20
CAB	Cellulose Acetate Butyrate	Eastman™	CAB-321-0.1
Palmitic acid chloride	Palmitoyl Chloride 98%	Aldrich	CAS 112-67-4
N,N-dimethylformamide	*N,N*-dimethylformamide >99.8%	Sigma-Aldrich	CAS 68-12-2
Triethylamine	Triethylamine >98%	Fluka	CAS 121-44-8

As reference, a commercial HMA was used. Also two commercial tannins from Silvateam S.p.A., two commercial resins and a reference EVA were later used. These materials are presented in Table 8 below.

Table 8. *Reference materials.*

Material	Abbreviation	Product
Commercial Tannin 1	CT1	Silvateam S.p.A. Fintan OP
Commercial Tannin 2	CT2	Silvateam S.p.A. Fintan Q
Commercial Resin 1	CR1	Ester of hydrogenated rosin
Commercial Resin 2	CR2	Ester of hydrogenated rosin
Reference HMA	REF	EVA-based HMA
Reference EVA	REF-EVA	Commercial EVA with a melt index of 400 and a vinyl acetate content of 28%

Adherend material used in this Thesis was mainly commercial folding boxboard (FBB). FBB had a coated white side and an uncoated light brown side, as seen in Figure 13 below.

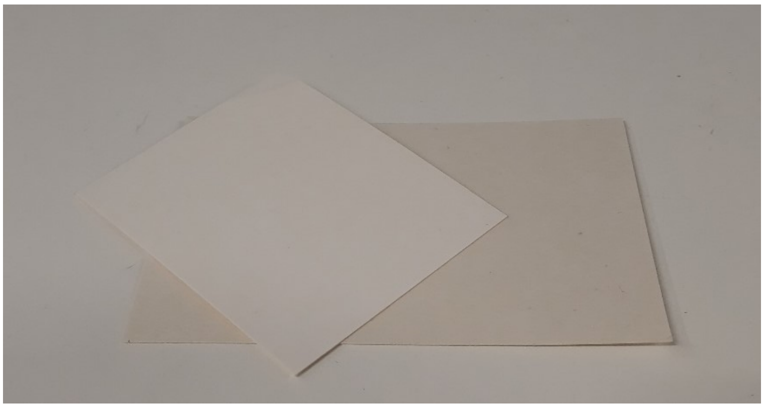


Figure 13. *Commercial FBB used in this Thesis.*

Other materials used as adherends were borosilicate glass, cloth with linen and cotton, aluminum foil, poly(ethylene terephthalate) film and birch veneers.

3.2 Methods

3.2.1 Manufacturing the adhesives

In the so-called try-out phase, adhesive formulations were manufactured by weighing the materials in a small glass vial or a beaker. The mixture was then heated in an oil bath and stirred with a wooden spatula until homogenous melt was achieved. For the strength measurements the formulations were done with a DACA Instruments (USA) microcompounder to ensure homogeneity, if possible. For the microcompounder, mixing time was set to 10 minutes, mixing force was maximum 5 Newtons and mixing speed was 100 rounds per minute. For some materials beakers were still used due to their tendency to aggressively stick to materials.

In the try-out phase small FBB strips of approximately 25 mm x 40 mm were used and adhesive was applied on an area of approximately 25 mm x 10 mm. Three pairs were glued per try-out formulation. For strength measurements, FBB was cut into 70 mm x 15 mm strips. For each separate measurement, ten pairs were cut and numbered. All strips were marked with code to represent the adhesive formulation or test condition. On one strip of each pair a 20 mm area was marked for the adhesive. Diagram of the test strips is seen in Figure 14.

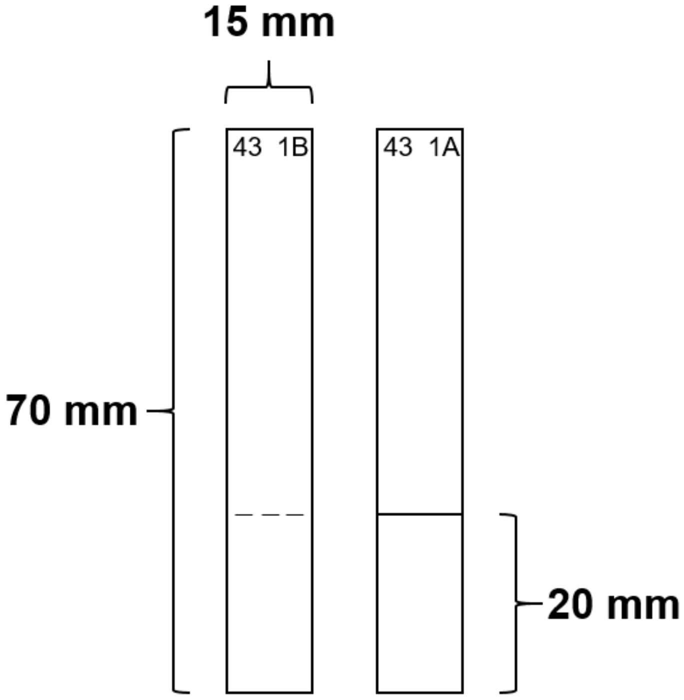


Figure 14. Diagram of test strip pair #1 for adhesive formulation 43.

For gluing, adhesive formulations were heated in oil bath. Once the mixture was molten or at least soft enough, it was spread on the designated area on the FBB strip and another FBB piece was then pressed on top. The glue bond was always formed between coated and uncoated side of the FBB, unless otherwise noted. Glued pieces were briefly pressed against the heat plate to ensure enough bonding that the pieces would not separate while transporting, then set in oven for 10 minutes under weight of 5.3 kg. Oven temperature was set as the same temperature as the oil bath. After this, the glued strips were allowed to set in 23 °C and 50% relative humidity (RH) for several days before conducting strength measurements.

3.2.2 Strength testing

For try-outs, adhesive strength was tested by hand. The glued test specimens were peeled open and the resistance or lack thereof was noted. The formulations that indicated notable resistance were then taken to second round of testing with strength measurements.

The strength measurements of the HMAs were conducted in VTT's standard atmosphere laboratory (23 °C and 50 % RH) using universal testing machine Lloyd Instruments Advanced Materials Testing System LS5 by Ametek (USA) with constant crosshead speed of 100 mm/min. The machine is shown in Figure 15.

Figure 15. *Universal testing machine used in strength measurements.*

Most of the measurements were done using 180° peel and using a 100N sensor. Four sets of measurements were done in shear mode, where a 1000N sensor was used instead. Measurement modes are given in Figure 16. 10 parallel tests were conducted for each experiment, and both average and standard deviation were noted. For all different measurements, REF was also measured. FBB peel strengths with REF showed 100% cohesive failure in the adherend. This is also called fiber tear, as mentioned in chapter 2.1.1.

Figure 16. Strength measurement modes used.

Peel testing measures the ability to resist localized stress. So comparing maximum measured peel load to the total mass of the adhesive gives accurate information only if the adhesive layer is assumed to be uniformly thick. This assumption cannot be done due to the hand-made nature of these test specimens. Mass-related strength does, however, allow quantifying how easy the adhesive is to spread. High viscosity and difficult to spread means more mass.

It was discovered that some adhesives showed pressure-sensitive properties, ergo they had the ability to be re-glued simply by pressing. This pressure-sensitivity or re-adhesion phenomenon was first tested by simply pressing them in hand and measuring the opening again. Later on this was standardized into holding them under weight of 2,5kg for one minute.

Nearly all the tests in this Thesis have been done on commercial FBB. It was decided to briefly test the adhesion properties to some other materials as well. Borosilicate glass, poly(ethylene terephthalate), aluminium foil and linen-cotton cloth were tested by hand. Birch veneers were cut into suitable pieces, glued and their shear strength was measured.

3.2.3 Viscosity

Viscosity was measured with Cone & Plate Viscometer by Research Equipment (London) Ltd using temperature of 150 °C. Measurement was allowed to run for at least 20 seconds or until the value had stabilized. Some specimens were aged in a oven for 24 hours in their given temperature.

3.2.4 Characterization

For characterization, differential scanning calorimetry (DSC) measurements were conducted on several different materials and compounds. Measurements were done on Mettler-Toledo (USA) DSC 2, using 2-10 mg of material and 40 µl aluminium crucibles. Method is depicted in Figure 17.

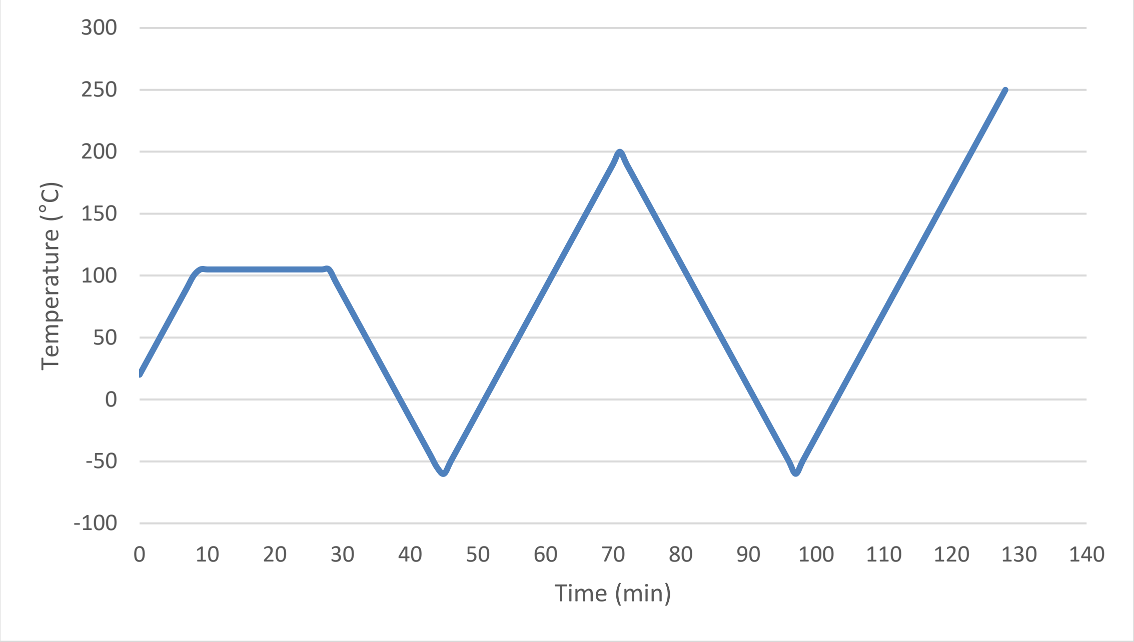


Figure 17. *DSC method.*

The method consisted of a 20 minute drying and a heating-cooling-heating curve. The drying temperature was 105 °C and the temperature change rate was 10 K/min. DSC measurement was done in nitrogen gas flow of 80.0 ml/min.

3.2.5 Esterification of Tannin

For the esterification reaction, a two litre glass reactor was set up with mixer and cooling. Spruce tannin, N,N-dimethylformamide and trimethylamine were added to the reactor. Once the mixture was cooled to 0 °C, palmitic acid chloride was slowly added through a dropping funnel. After this the cooling was stopped and the mixture was allowed to react overnight. In the morning the mixture was moved to a large decanter glass and sediment was allowed to descend. Mixture was centrifuged for 10 minutes at 4500 rpm and washed four times, until it no longer smelled like organic solvent and left very little color in the water. It was then allowed to dry in a hot air oven in 38 °C for 72 hours before it was ground with a mortar.

Tannin ester was measured by DSC, using the same method as described earlier, and by solid state ^{13}C Nuclear Magnetic Resonance (NMR) using an Agilent (USA) DD2 600 NMR spectrometer. The ^{13}C cross polarization magic angle spinning (MAS) NMR measurements were performed with magnetic flux density of 14.1 T. The spectrometer was equipped with a 3.2 mm T3 MAS NMR probe operating in a double resonance mode. The samples were packed in ZrO_2 rotors and the MAS rate in experiments was 10 kHz. Using a 1.3 ms contact time and a 6.0 s delay between scans, the samples were scanned 8000 times. SPINAL-64 proton decoupling with a field strength of 80 kHz was used to decouple protons during acquisition. α-glycine was used to calibrate Hartmann-Hahn match for cross polarization and 90 degree pulse durations. The spectra were processed using TopSpin 3.5 software.

3.2.6 Water resistance

Test conditions for water resistance were taken from European Standard EN 204:2001 [22]. Conditioning sequences 2 and 4 were used to test the effect of room temperature water. Sequence 2 consists of 7 days in standard atmosphere (23 °C and 50% RH), 3 hours in water at (20±5) °C and another 7 days in standard atmosphere before measurement. Sequence 4 consists of 7 days in standard atmosphere, 4 days in water at (20±5) °C and again another 7 days in standard atmosphere before measurement.

3.2.7 Folding boxboard properties

Hydrophobicity of FBB was measured with Attension Theta by Biolin Scientific (Finland) using Contact Angle (Young-Laplace) Analysis and 4.000 ul drop size. Hydrophobicity was determined by measuring contact angle of water. FBB was allowed to gain balance in 23 °C and 50% RH overnight before it was measured in the same conditions. Contact angle was first measured once for 100s for both coated and uncoated sides of the FBB, after which it could be seen that no change happened after first ten seconds. Thus contact angle measurements for 10s were made for both sides.

Thickness of FBB was measured with Micrometer 51 by L&W (Sweden). Measurement was repeated for three different A4 sized FBB pieces, five measurements each.

Roughness of FBB was measured with Bendtsen Tester by L&W (Sweden). Measurement was done using four different A4 sized FBB pieces, totalling 10 measurements per side.

4. RESULTS AND DISCUSSION

4.1 Phase 1: Screening of cohesive polymers and waxes

The purpose of the first phase was to test formulations with different polymers and waxes with SusBinders tannins to determine which material combinations could potentially work as a HMA. For this, commercial FBB was used as a standard adherend. The properties of FBB are presented below in Table 9. The contact angle with water shows that FBB is hydrophobic.

Table 9. *Commercial FBB properties.*

Measurement	Average	Standard deviation (%)
Thickness	343 µm	5.8
Roughness - uncoated side	434 ml/min	8.1
Roughness - coated side	19 ml/min	26.0
Contact angle with water - uncoated side	100°	5.6
Contact angle with water - coated side	86°	1.7
Mass per area	200 g/m^2	(value from manufacturer)

The method of manufacturing the adhesives have been introduced earlier in this Thesis. The 7 different polymers and 5 different waxes used in the phase 1 are listed in Table 10 below. Motivation for the polymer selections are discussed below in separate subchapters. The tannin was standardized to be CST throughout the phase 1. This decision was based on CST having higher tannin content than CPT, as seen in Table 6 in chapter 3.1. Thus adhesives with CST were assumed to have better properties and were regarded as a better starting point.

Table 10. *Materials used in screening phase.*

Polymer	Wax
poly(ethylene-*co*-vinyl acetate) (EVA)	triethyl citrate (TEC)
oxidiced cellulose acetate (CA-Ox)	tributyl *O*-acetylcitrate (CITRO)
cellulose acetate butyrate (CAB)	acetic acid ester (SNS)
oxidized cellulose acetate butyrate (CAB-Ox)	Fischer-Tropsch hard wax #1 (C80)
poly(D,L-lactide-*co*-ε-caprolactone) formulation 1 (Co1)	Fischer-Tropsch hard wax #2 (H1)
poly(D,L-lactide-*co*-ε-caprolactone) formulation 2 (Co2)	
50:50 mixture of polylactide (PLA) and poly(ε-caprolactone) (PCL)	

Before the start of this Thesis, there had already been some manual testing of different materials. As per those tests, six different formulations had been manufactured with a microcompounder in temperature of 140 °C. These formulations are depicted in Appendix A, noted as P-1 through P-6. The peel strength measurement for these formulations was conducted before the screening, and the results were used as a basis for the new formulations. The results of these preliminary tests and the phase 1 are depicted and discussed together, divided according to the polymers used in the formulations.

During the phase 1 a total of 40 different formulations were mixed and heated, and of those 19 showed potential and were applied to small FBB strips. This first round delivered non-quantitative results as all adhesive formulations were tested for resistance simply by tearing by hand. The formulations and notes can be seen in Appendix A.

After this first round of manual testing, six most promising formulations were selected for quantitative testing as will be discussed in chapters 4.1.1-4.1.3. Larger batches of these adhesives were produced with a microcompounder when possible to assure homogeneity. Mixing settings were introduced in chapter 3.2.1, and the melt temperature was used both as mixing temperature and as gluing temperature. This temperature is noted as “Temperature” in Appendix A and following tables.

4.1.1 Poly(ethylene-*co*-vinyl acetate)

Formulations based on EVA, the most prominent polymer in HMA industry, are discussed in this chapter. EVA with synthetic Fischer-Tropsch waxes H1 and C80 proved to be a potential formulation, especially with a higher wax content. The formulations with the other three of the selected waxes did not function as HMAs. Formulation with TEC was impossible to spread and formulations with CITRO and SNS showed no adhesive properties. In Appendix A, EVA-based formulations can be seen with IDs 1-3, 7-8 and 16-17.

Formulations 16 and 17 utilizing H1 and C80 with EVA were selected for quantitative analysis due to being notably strong in the manual testing. These formulations were composed of 22% EVA, 28% CST and 50% wax, and were melted and glued in 160 °C. These properties and the results of the peel strength measurements are shown in Table 11 and Figure 18, respectively. In the column ‘Fiber tear’ is marked the amount of specimens, where fiber tear was observed. The vertical axis of Figure 18 and other such Figures in this Thesis depict the measured peel strengths of the HMA formulations in Newtons. REF of Figure 18 was a commercial HMA for packaging applications, which was used as a reference point for the measurements in this Thesis. REF-EVA of Figure 18 was a pure EVA copolymer with different properties than what was used in formulations. This was done because the EVA used for compounding did not melt in suitable temperature for gluing.

Table 11. *Properties of EVA-based HMAs.*

ID	Materials used	Mass ratio	Temperature	Fiber tear
16	EVA - CST - H1	22 : 28 : 50	160 °C	No
17	EVA - CST - C80	22 : 28 : 50	160 °C	1 of 9

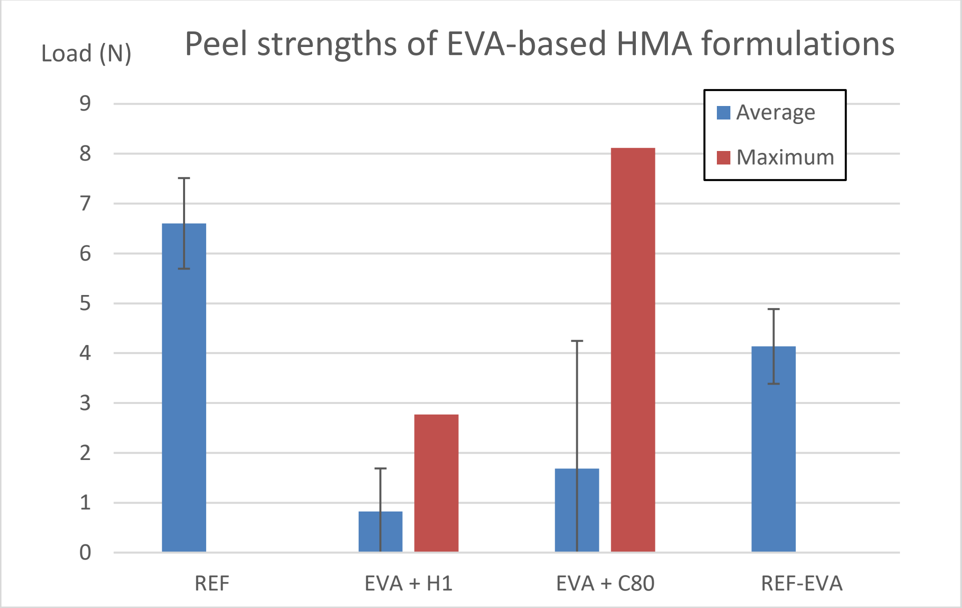


Figure 18. *Peel strengths of EVA-based HMA formulations. Due to high variation, maximum strengths of the formulations are also shown.*

While the measurements showed that formulation 17 was stronger than 16, the measurements showed high variation in maximum load. For formulation 17, there was a single very strong measurement but others were considerably weaker. This strong measurements was also the only fiber tear of these formulations. Due to the strength in the manual testing, it was believed that these low results were caused simply by suboptimal gluing conditions leading to poor wetting between adhesive and adherend. As mentioned in chapter 2, good wetting increases the contact area and thus enables stronger adhesion. Thus it was believed that small corrections in the gluing conditions could lead to proper wetting and reliable adhesion.

Therefore formulation 17 was tested several times with different gluing conditions in an attempt to find the optimal conditions. All the measurements run only ever had one or zero strong specimens, however. There does seem to be potential to use tannin as a drop-in tackifier in synthetic HMAs, but this potential could not be realized in this Thesis. Due to this low reproducibility, it was decided to abandon work on formulation 17 and move forward with other materials.

4.1.2 Cellulose esters

In this chapter, the formulations with cellulose derivatives as polymers are presented. Oxidized cellulose acetate had proven to work in HMA formulations with lignin [6], so similar results were expected also with tannins. In the pre-Thesis testing cellulose esters CA, CAP and CAB and their oxidized versions were all used with TEC as wax. These are noted in Appendix A with IDs P-2 to P-6. This was continued in phase 1 by using the most promising ones, CA-Ox, CAB and CAB-Ox, with new waxes.

Formulations with CA-Ox are numbered 11-14 and 40 in Appendix A. Formulation 40 with TEC as wax was re-testing of formulation P-4, and it was also the only formulation utilizing CA-Ox to melt. Formulations with CAB are numbered 20-24. The ones with synthetic waxes H1 and C80 did not lead to a homogenous melt and had no adhesion ability. The others could be glued, and formulations 21 and 22 did exhibit a notable level of adhesion. Formulations with CAB-Ox are numbered 25-29 and behaved similarly to CAB. Synthetic waxes did not work but also other waxes lead to very weak adhesion. As such, formulations 21 and 22 were selected for further quantitative analysis. The properties and peel strength measurements of selected formulations and earlier formulations P-2 to P-6 are shown in Table 12 and Figure 19, respectively. As can be seen, TEC caused the formulations to melt in a lower temperature than the other waxes.

Table 12. *Properties of cellulose ester based HMAs.*

ID	Materials used	Mass ratio	Temperature	Fiber tear
P-2	CAP - CST - TEC	26 / 34 / 40	160 °C	No
P-3	CAB - CST - TEC	21 / 29 / 50	160 °C	No
P-4	CA-Ox - CST - TEC	26 / 34 / 40	160 °C	No
P-5	CAP-Ox - CST - TEC	21 / 29 / 50	160 °C	No
P-6	CAB-Ox - CST - TEC	21 / 29 / 50	160 °C	No
21	CAB - CST - CITRO	22 / 28 / 50	180 °C	No
22	CAB - CST - SNS	22 / 28 / 50	180 °C	No

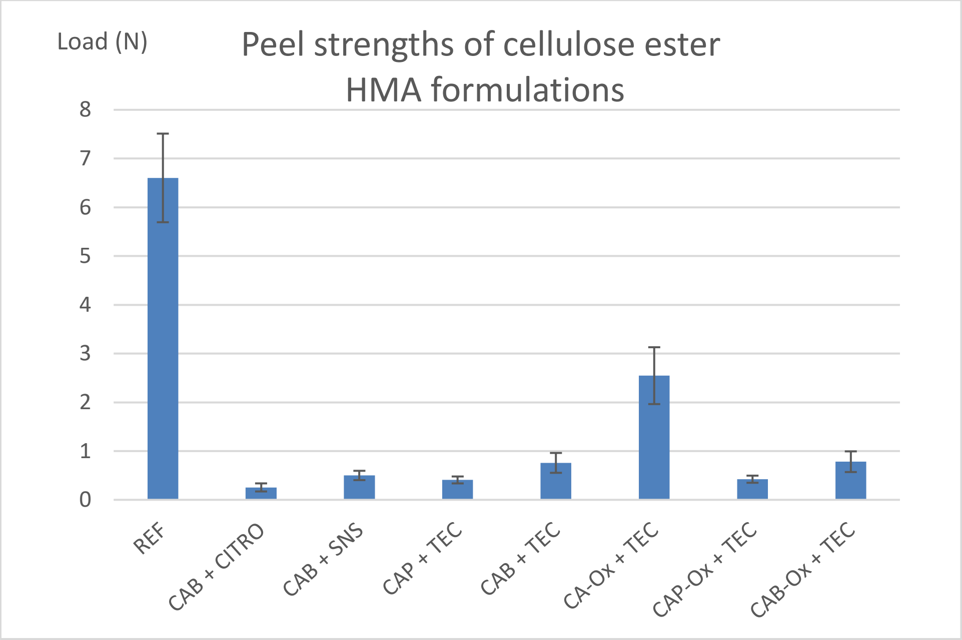


Figure 19. *Peel strengths of cellulose ester HMA formulations.*

Two interesting discoveries were done. Formulations 21 and 22 experienced a clean adhesive failure and the adhesive could be peeled off the FBB as a solid brown film. Also formulation P-6 was noted to be able to readhere when pressed together after opening. While this pressure sensitivity or readhesion was fairly weak, it could hold on to a variety of different materials: FBB, wooden office desk, denim jeans, cotton shirt and even metal. It could also adhere to a concrete wall, where the adhesion was relatively strong. This led to keeping an eye out for other adhesives with similar ability.

The results of these peel strength measurements were quite clear, however. Formulation P-4 with CA-Ox and TEC proved multiple times stronger than the others, but even it achieved no fiber tears. The others all showed relatively similar weak strengths. Formulations with CAB and CAB-Ox had shown potential in the manual testing before this Thesis and therefore their weakness was relatively surprising. While formulation P-4 was strongest of the cellulose ester HMAs, it was overshadowed by other, more promising formulations and as such studying it was not continued.

As tannins did not achieve proper adhesion with cellulose derivatives, one part of the original hypothesis was rebutted. This was quite surprising because as previously mentioned, lignins had worked quite well with cellulose derivatives. Formulations with lignin and cellulose derivatives had reached strengths over twice of that of formulation P-4’s. [6, pp. 17–20]

4.1.3 Polylactide and poly(ε-caprolactone)

This chapter presents the formulations including PLA and PCL. Before the start of this Thesis, both PLA and PCL were inspected for possible use as polymers. PLA's melting point was considered too high for formulations, but PCL was tested and measured as formulation P-1. As mentioned in chapter 2.4, P(LLA-CL), a copolymer of these two, is reported to have shown promise for use in HMAs. Two different copolymers produced in another project in VTT were tested. These poly(D,L-lactide-*co*-ε-caprolactone) compounds were coded Co1 and Co2. Co1 was hard and sticky in room temperature and aggressively tacky when heated; Co2 had cohesion similar to honey in room temperature and as such was not expected to work well in HMAs. Formulations with these are numbers 30-39 and 41-44 in Appendix A.

Formulations with Co1 seemed to follow the same pattern as cellulose esters; Fischer-Tropsch waxes did not produce a homogenous melt while the other waxes did. Even the formulations with the other waxes had low adhesion, however, with some breaking off even before testing. Co2 was only tested with the one wax that seemed to work best with Co-1, but it showed no adhesive strength.

After this it was decided to test these copolymers and tannins without adding wax. Formulations with 60% copolymer and 40% tannins melted at suitable temperature. Formulation with Co2 showed no adhesive strength, but formulation with Co1 showed strength similar to pure Co1. As an added bonus adding tannin made the handling enormously easier; pure Co1 was aggressively tacky when heated while mixture with tannin was much easier to handle and clean.

It was also tested whether simply melting the polymers together would cause them to bond and cause a sort of "pseudo-copolymer". For this, 0.5 g of both PLA and PCL was melted in a glass vial in oil bath, let cool and melted again. Melting the combined system did not happen in a lower temperature, however.

The effect of adding wax to the PLA-PCL mixture for reducing its melting point was tested by adding 0.5 g of TEC. The mixture started releasing vapour at around 180 °C, and investigating literature [56] revealed that PLA starts to deteriorate at lower temperatures in presence of TEC. Thus it was concluded that the vapour was lactic acid which has boiling point of 122 °C. Hence the PLA-PCL mixture was used with other waxes. This 50:50 mixture of the polymers was tested in formulations 4-6 and 9-10. Mixtures with Fischer-Tropsch waxes H1 and C80 did not melt at suitable temperatures. The other waxes CITRO and SNS did allow gluing, but the adhesive strength was deemed too weak.

As such, formulation 43 with Co1 and CST was selected for quantitative analysis with pure Co1 as reference. The properties of formulations P-1, 43 and pure Co1 are shown in Table 13 and the peel strengths are shown in Figure 20.

Table 13. *Properties of polylactide or poly(ε-caprolactone) based HMAs.*

ID	Materials used	Mass ratio	Temperature	Fiber tear
P-1	PCL - CPT - TEC	26 : 34 : 40	160 °C	No
43	P(DLLA-CL) - CST	60 : 40	150 °C	3 of 10
Co1	P(DLLA-CL)	100	140°C	3 of 7

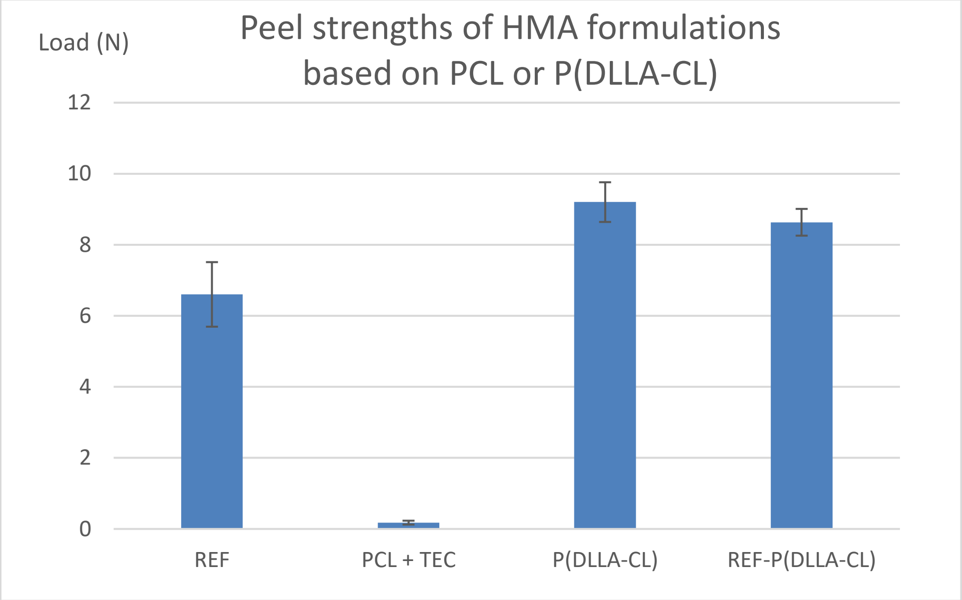


Figure 20. *Peel strengths of HMA formulations based on PCL or P(DLLA-CL).*

The results of the quantitative measurements were promising. Co1 and Co1-CST HMA both achieved higher maximum loads than the reference HMA, REF. To keep in mind is the fact that all specimens with REF opened with fiber tear, while only part Co1 and Co1-CST HMA did so; mostly they opened with cohesive failure in adhesive. It is believed that REF achieved fiber tear faster due to more rigid form; the more elastic copolymer absorbed some of the force to elongate the adhesive. And while both pure copolymer and copolymer-tannin mixture achieved similar strengths, adding tannin caused a notable difference in handling. Co1 in itself was difficult to handle due to its aggressive tackiness and its tendency to leave fine tails and filaments. After adding tannins the mixture was significantly easier to handle due to the fact that it turned into a paste that left no tails or filaments when handled.

Notable were also the pressure-sensitive properties of Co1 and Co1-CST HMA; those test specimens that did not result in fiber tear could be reattached by pressing them together. This phenomenon was tested only manually in this phase, but it was considerably strong. More detailed studies were performed later on as reported in chapter 4.6. There was also no major difference detected between the peel strengths of Co1 and Co1-CST HMA. Another point of interest in this formulation is its probable biodegradability; as mentioned in chapter 2.4, P(DLLA-CL) is believed to be biodegradable, and tannin as biomaterial is. Thus Co1-CST HMA as their combination is believed to be a biodegradable HMA. Due to strong adhesion and interesting properties, Co1-CST HMA was selected for further studying.

4.2 Phase 2: Mass ratio and aging

After the quantitative results were promising with formulation 43, the biodegradable two-component adhesive, this formulation was taken into more serious consideration and variation of mass ratio was tested. Different mass ratios were compared; mixtures with 50%, 60%, 70%, 80% and 90% Co1. Of these, only 50% did not melt but all others seemed to be nearly equally strong, as is seen below in Figure 21.

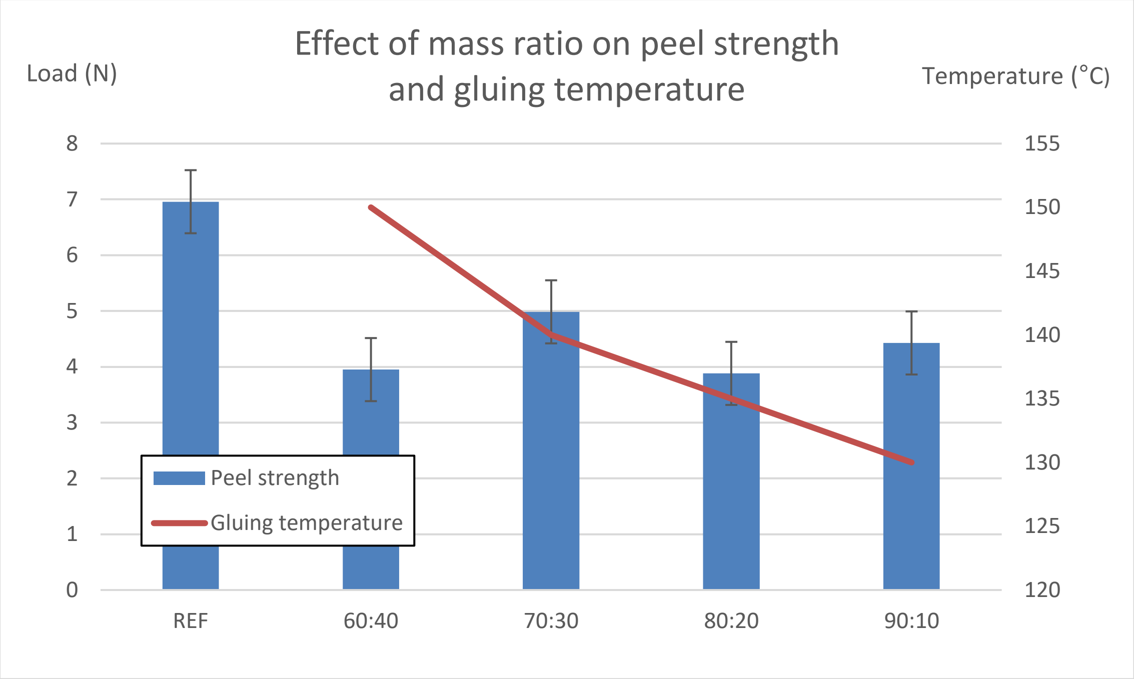


Figure 21. *Peel strengths of Co1-CST HMAs using aged copolymer. Mass ratios are noted Co1:CST.*

As seen from the graphs, all the formulations are relatively close to each other strength-wise. The temperature needed to achieve a homogenous melt decreased as amount of copolymer increased. The level of peel strength was notably less than what formulation 43 achieved in phase 1, however. The explanation for that was that the Co1 sample was stored at room temperature for several weeks. This had caused it to deteriorate; this is widely reported in literature to be caused by hydrolysis of the ester group in the copolymer. This deteriorating has been earlier observed and methods for tackling this issue have been suggested [31, p. 220]. As 70:30 seemed like the best mass ratio, it and the original 60:40 were then mixed again, this time using copolymer that was stored in the freezer. The results of that experiment are given below in Figure 22.

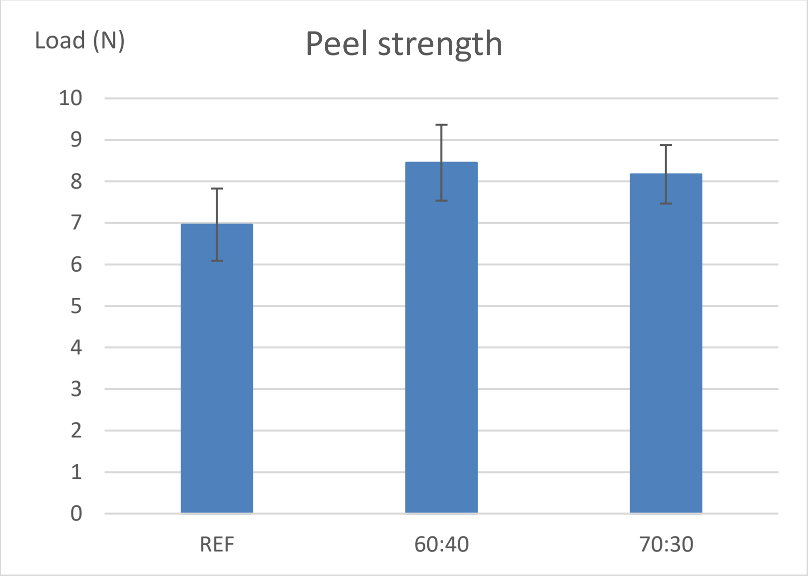


Figure 22. *Peel strengths of two Co1-CST HMAs. Mass ratios are noted Co1:CST.*

Now the strength of the glue bond is again on the level it was earlier in Phase 1. 60:40 and 70:30 are still relatively even. However, formulation with 70% copolymer had some advantages; it was notably less viscous and as such was much easier to handle. This lead to thinner, lighter and more uniform layer of adhesive. Gluing conditions were also 10 °C lower for the HMA with 70% copolymer. An interesting note in this test is that all specimes in this measurement suffered fiber tear compared to 3/10 in the first quantitative measurement for Co1-CST, as noted in Table 13 in chapter 4.1.3. This reinforces the notion that the copolymer deteriorates quite fast in room temperature. Based on the results more detailed studies were conducted on Co1-CST HMA with 70% copolymer.

4.3 Variation of adhesive amounts and adherend surfaces

The effect of amount of HMA and cardboard coating was studied. It has been suggested that smaller amounts of adhesive are stronger [57], and this interesting notion was decided to be tested. The amount of adhesive was tested with three stages; first it was spread like in previous measurements, and in later measurements it was deliberately tried to use a smaller and even smaller amount. These test specimens are noted below as ‘Normal’, ‘Less’ and ‘Least’. The results of these measurements are given in Figures 23 and 24.

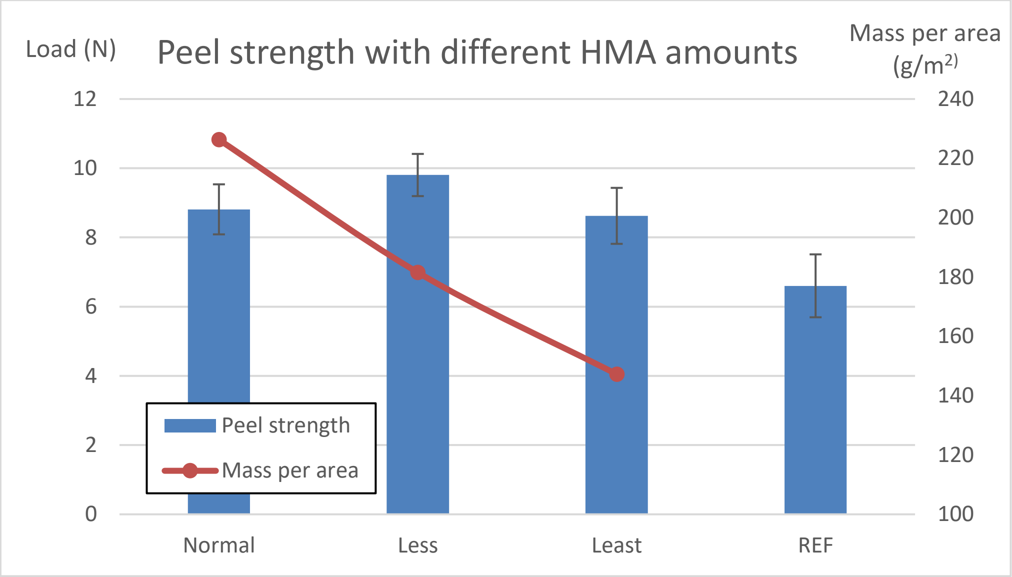


Figure 23. *Peel strengths with different amounts of Co1-CST HMA.*

It can be clearly seen that first decreasing the amount of glue had a positive impact on the bond strength, but further decreasing returned it to its original state. This is backed by the load per weight results presented below in Figure 24; first decrease had considerably stronger effect than second decrease. In this Figure the vertical axis depicts the measured peel strengths per mass in Newtons per gram. The methods of bond failure changed according to the HMA amount; originally there were 9/10 cohesive failures in adherend, but that amount decreased to 7/10 and finally to 5/10 when HMA amount decreased. This is an interesting result, as with higher peel strength it would have been logical to also have a higher degree of fiber tear.

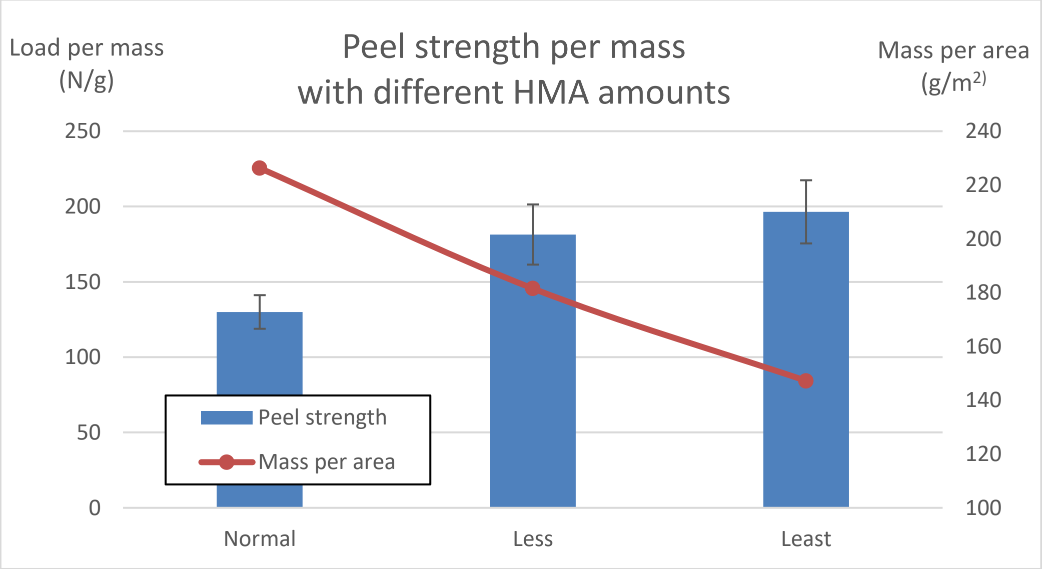


Figure 24. *Peel strengths per mass with different amounts of Co1-CST HMA.*

These numbers are quite different compared to the reference HMA REF, however; REF measured at over 700 N/g and averaged approximately 31 g/m^2. This is partly because compared to tannin HMAs, REF is extremely easy to spread very thinly and extra adhesive tended to be forced out in the gluing process. Tannin HMAs, however, resembled a thick paste and thus naturally accrued a thicker layer than REF. And while some extra adhesive was forced out in the case of tannin HMAs as well, it is evident that a larger amount was left in the adhesive layer. This is most likely caused by the thicker nature of the tannin HMAs. It should be remembered that the developed HMA with Co1 and CST was rather a HMA prototype compared to commercial HMA. It is expected that the spreadability can be improved by further development and additives.

FBB used in this Thesis had different surfaces on its sides as earlier noted. White coated sides and natural coloured uncoated sides. As all earlier testing had been between coated and uncoated sides of the FBB, measurements were now done between two similar sides. Results are seen in Figure 25.

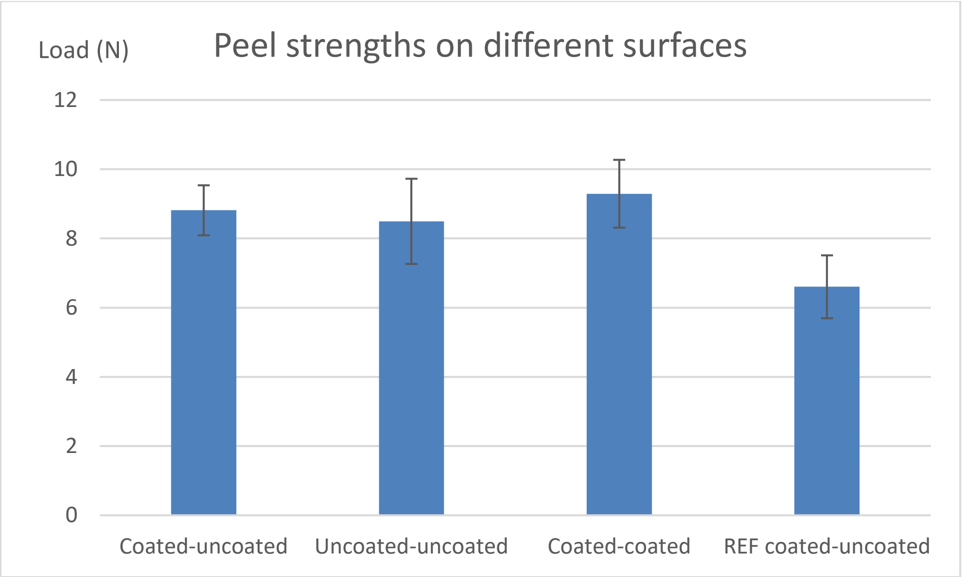


Figure 25. *Peel strengths on different surfaces.*

The results of this experiment are quite interesting. It is clear that the different surfaces behave differently, with coated sides having slightly stronger bonds. What cannot be seen from the figure is the effect the coating had on the opening itself. In the coated measurement, all specimens but one opened with fiber tear. Yet in the uncoated measurement not a single specimen opened with fiber tear; all suffered cohesive failure in adhesive. This indicates that the adhesive experiences stronger adhesion to the coating layer than the coating does to the cardboard itself. Figure 26 shows a close-up picture of a fiber tear.

The thin coating layer can clearly be seen on the left, while clear FBB is visible on the right.

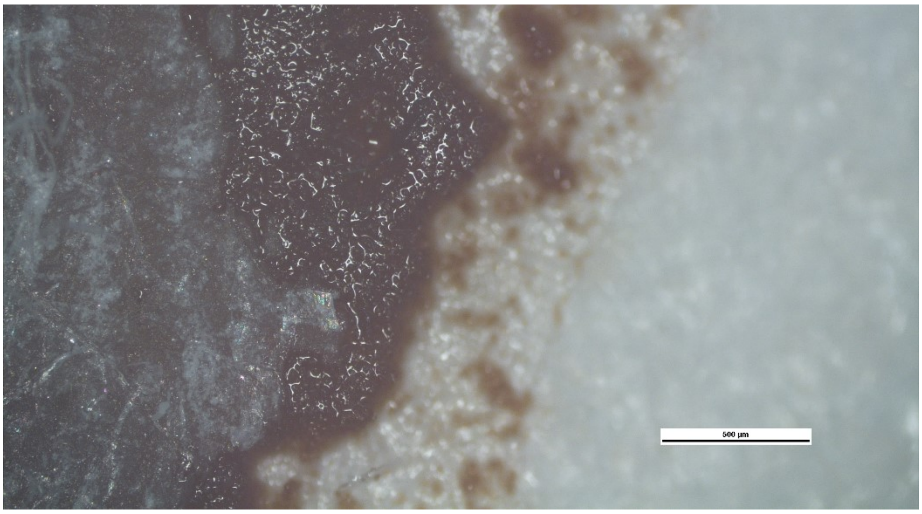


Figure 26. *Picture of fiber tear on Co1-CST HMA with 40x zoom.*

It was also decided to measure the shear strength of the adhesive and the reference HMA to further see how well they compare. This experiment was done between coated and uncoated surfaces. Both adhesives were strong enough to cause the FBB to break at approximately 100 N.

4.4 Stability and water resistance

Due to Co1 degrading by hydrolysis and tannins being water-soluble, the water resistance of the Co1-CST HMA was measured. As mentioned earlier, the degradation of the copolymer of lactic acid and caprolactone is widely reported in literature to be caused by hydrolysis of the ester group. This hydrolysis can be catalysed by the carboxylic acid end groups [58, p. 640]. In literature it is also mentioned that ε-caprolactone and DL-lactide have been copolymerized to achieve faster degradation rates [59, p. 770]. There are some ways to stabilize the polymers; hydrophobic aliphatic end-capping groups seem to have an effect by decreasing the polymer’s ability to absorb water [60, p. 442], while at the same time also preventing the carboxylic acid end groups from catalysing the hydrolysis. Peroxides have also been reported to stabilize PLLA [61], so this could also be tested for the copolymer.

The test specimens were held in room temperature water for 3 hours or 4 days as per the methods described in chapter 3.2.6. The results are given in Figure 27 below.

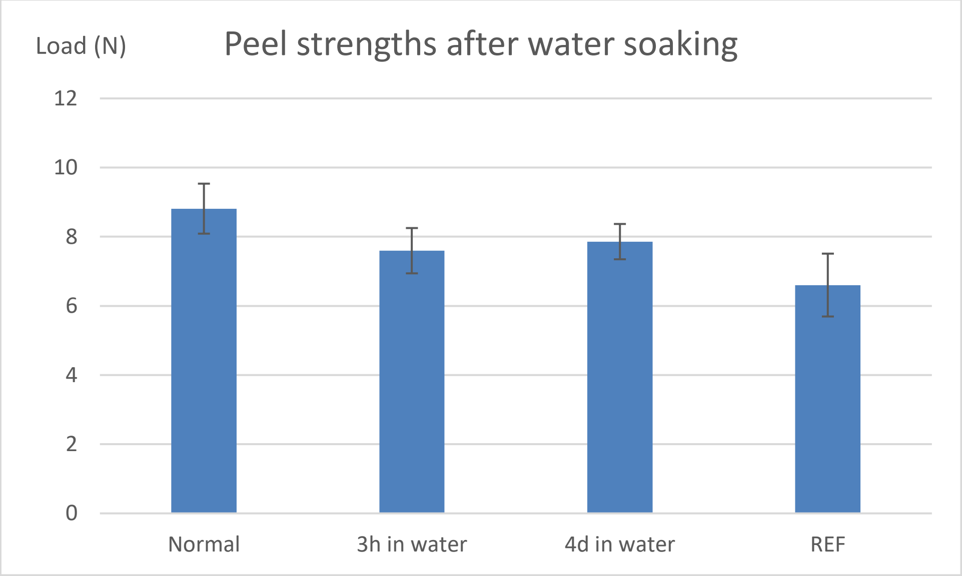


Figure 27. *Peel strengths after soaking the specimens in room temperature water.*

As seen from above, only a small difference was observed in the peel strengths of soaked specimens. Even though Co1 was not protected against hydrolysis, the HMA held well. This leads to two questions; does water soaking hasten the rate of hydrolysis and does the HMA degrade at the same rate as pure Co1? As from this experiment it is unclear, whether the decrease in peel strength is due to a change in the adhesive or in the FBB, as all the test specimens ended in fiber tear. The water used in the measurement gained a strong brown hue which leads to believe that at least some tannins were dissolved.

While tannins may or may not affect the hydrolysis degrading Co1, they should have other properties affecting the stability. Tannins function as antioxidants by having stabile phenolic radicals as mentioned in chapter 2.5.3. Antioxidants are often added to adhesives for stability. Tannins could potentially function as both components at the same time. This would however require more research.

4.5 Comparison of tackifiers

The formulation with 70:30 Co1-tackifier was tested with other project tannins, reference tannins and reference resins. Using the same 70:30 mass ratio, eight different mixtures were manufactured using eight different materials, listed below:

- Crude Spruce Tannin (CST)
- Crude Pine Tannin (CPT)
- Purified Spruce Tannin (PPT)
- Purified Pine Tannin (PST)
- Commercial Tannin 1 (CT1)

- Commercial Tannin 2 (CT2)
- Commercial Resin 1 (CR1)
- Commercial Resin 2 (CR2)

In Figure 28 below, pictures of different mixtures can be seen. Leftmost picture is of pure Co1 which is transparent. Second is the light grey mixture with CR2; the mixtures with commercial resins had the advantage of being easier to spread than any mixture with tannin. The middle picture shows mixture with CT1 and the one to its right is the Co1-CST HMA. Both of these seem dark brown, even black in the pictures. In reality, CT1 gave the compound a reddish brown color while Co1-CST HMA is indeed dark brown. Later the light brown color of Co1-CPT HMA will be seen. The last picture on the right is the reference HMA, REF. As can be seen, all other pictures show droplets; REF started solidifying faster than others which led to it leaving thin filaments and not forming a round droplet.

Figure 28. *Examples of HMA appearance. From left to right: Co1, Co1 + CR2, Co1 + CT1, Co1 + CST, REF.*

All mixtures were tested both between coated and uncoated and between two uncoated sides. This latter was done due to the fact that coated-uncoated measurements tended to end in fiber tear; uncoated-uncoated measurements, as seen earlier, ended in cohesive failure in the adhesive and as such could potentially better show improvements in the adhesives. Results of testing on coated-uncoated surfaces are shown in Figure 29, and results from two uncoated surfaces are shown in Figure 30. The results for REF and Co1 from earlier testing were included to the graphs for reference.

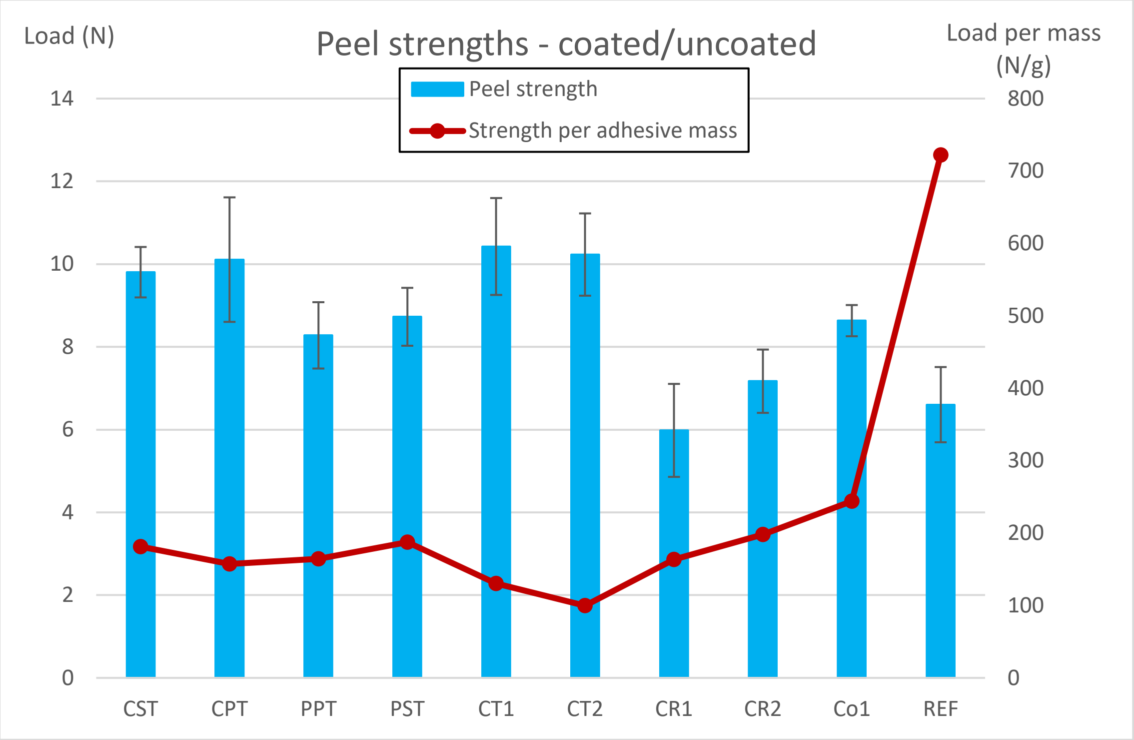


Figure 29. *Peel strengths and peel strength per adhesive mass of Co1 HMAs with different tackifiers between coated and uncoated sides of FBB.*

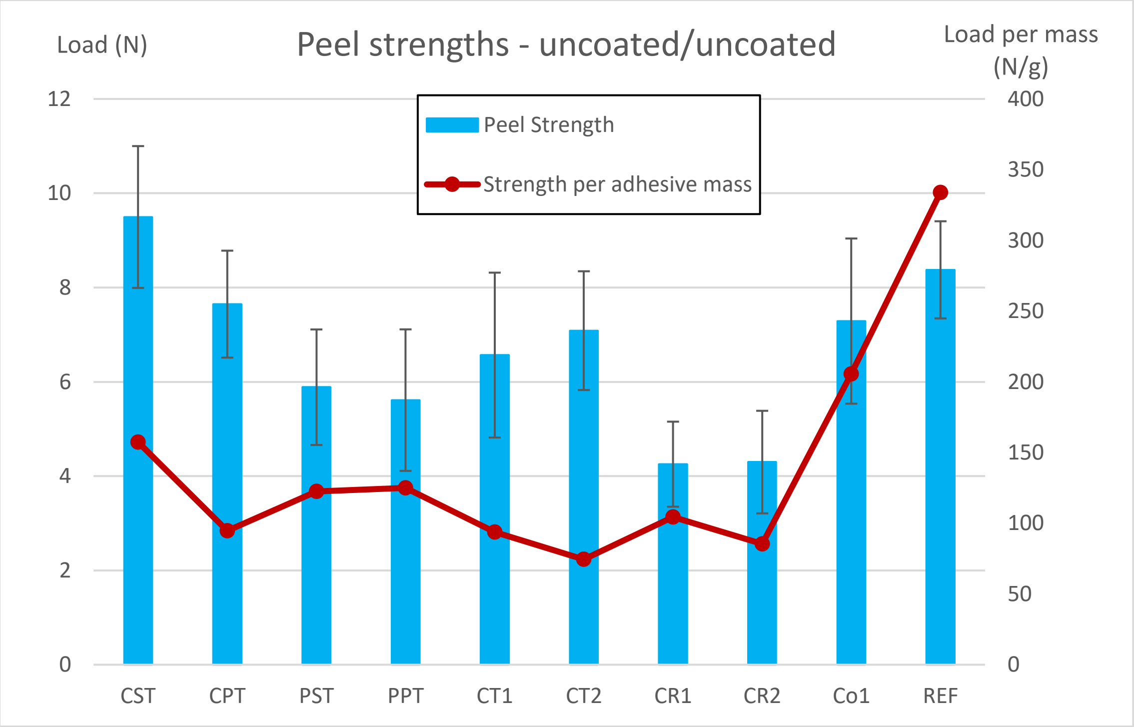


Figure 30. *Peel strengths and peel strength per adhesive mass of Co1 HMAs with different tackifiers, measured between two uncoated sides of FBB.*

In general it is quite clear that stronger adhesion happens when at least one of the surfaces is coated, as was previously noted. From the results it is also evident that tannins are more compatible with Co1 than the commercial resins used in this Thesis. The peel strengths of all formulations with tannins are relatively close to each other in the measurement between coated and uncoated surfaces. But when the adhesion was measured between two uncoated surfaces, this changed. Formulation with CST is the only formulation that shows the same level of peel strength on both occasions. Also commercial tannins' decrease of peel strength is larger than that of CPT. This is an interesting notion. As mentioned in chapter 3.1, crude tannins were expected to form weaker HMAs than pure tannins due to their carbohydrate content. Yet here the effect seems to be reverse. A possible explanation is that the carbohydrates in fact contribute to the adhesion capabilities due to their ability to form hydrogen bonds. These bonds would then positively contribute to the adhesion.

This could partially explain why enzymatically purified tannins did not prove to be stronger in this formulation. Another effect could be caused by freeze-drying of the solutions that caused the solid purified tannins to be considerably less dense than the crude tannins. Due to that the usual 70:30 mass ratio mixture did not melt. To achieve melting, copolymer had to be added until there was 14% and 21% tannins, for Spruce and Pine respectively. They achieved similar properties, especially maximum load per weight, as crude tannins, except between uncoated sides where their peel strength was inferior. As such purifying tannins for this formulation was not beneficial and can be omitted.

There was also quite strong differences in how well the mixtures seemed to blend. This is where the commercial resins had an advantage over tannins; the formation of homogenous mixture between Co1 and commercial resins led to easier spreading. Conversely, commercial tannins were unable to form a homogenous mixture; especially Co1-CT2 HMA looked more like a heterogeneous dispersion. This heterogeneity lead to difficulties in spreading the adhesive which in turn lead to increased mass and thus lower strength per mass. This problem was also visible with CPT. Figures 31 and 32 below show the difference between formulations with CST and CPT.

Figure 31. *Co1-CST HMA on cardboard after opening. Co1-CST created a seemingly homogenous dark brown paste.*

Figure 32. *Co1-CPT HMA on cardboard after opening. Co1-CPT did not achieve homogeneity, and small tannin particles can be seen.*

CST, which had been used so far, created a visually homogenous dark brown paste. CPT, however, did not achieve the same level of homogeneity, but was quite "crunchy" and it appeared as if some tannin particles did not mix with the copolymer. These particles are notably visible in the figures above, and even better visible in the microscope pictures in Figures 33-35 below. These pictures show HMA formulations with CST, CPT and PPT and show the level of homogeneity of Co1-tannin HMA.

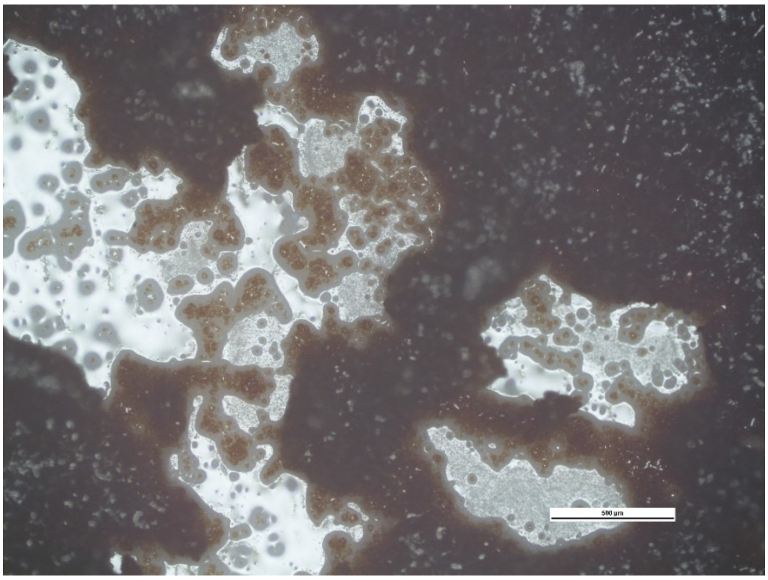


Figure 33. Picture of Co1-CST HMA with 40x zoom.

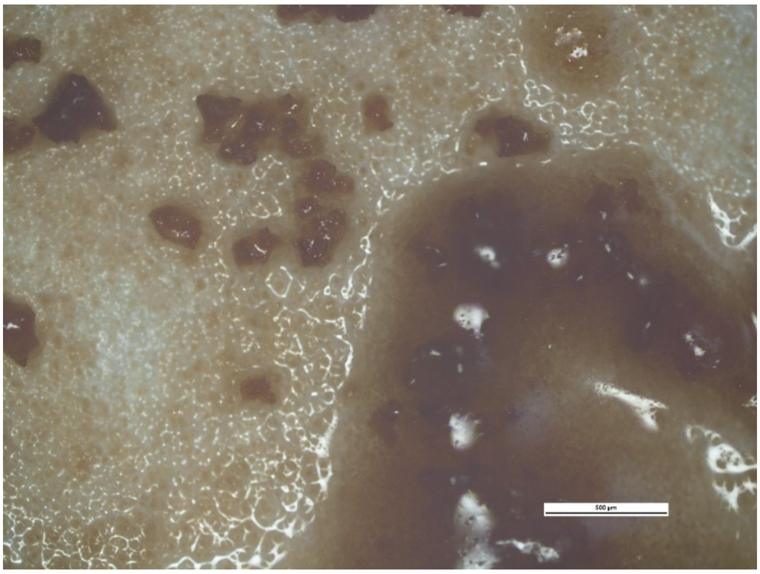


Figure 34. Picture of Co1-CPT HMA with 40x zoom.

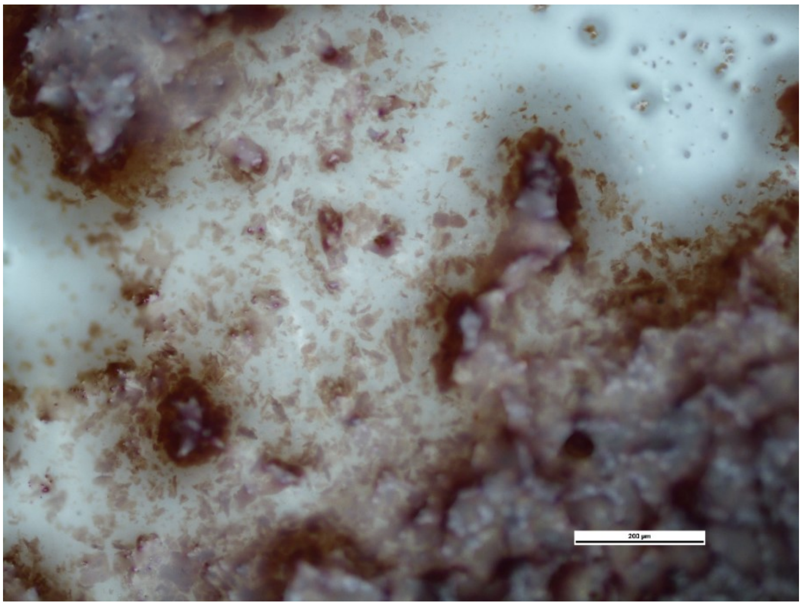


Figure 35. *Picture of Co1-PPT HMA with 100x zoom.*

In Figure 33 the dark brown paste of Co1-CST HMA that appeared homogenous to human eye is revealed to be heterogenous in the micrometer scale. The paste is lumpy and small particles can be seen throughout the picture. These same particles can be assumed to be the cause of the lumps in the paste. Co1-CPT HMA depicted in Figure 34 shows comparably larger particles as could be expected based on Figures 31 and 32. While the bulk in bottom right seems quite homogenous, even there very small particles can be seen. In Figure 35 the picture of Co1-PPT HMA shows small flakes of purified tannins within the copolymer, and here the heterogeneity is very strongly visible.

4.6 Pressure sensitivity in readhesion

The pressure sensitivity observed earlier in Co1-tannin HMAs was investigated by measuring the peel strength of repeatedly opened and closed bond. While the phenomenon was weak in formulation P-6 with which it was first observed, it did lead to testing all future formulations of this same affinity. The adhesive bond was closed after each measurement by keeping it under a weight of 2.5 kg for one minute in room temperature. Pressure sensitivity was measured between uncoated surfaces to prevent fiber tear on opening. Measurements of Co1-CST HMA, Co1-CPT HMA and pure Co1 are depicted below in Figures 36 and 37.

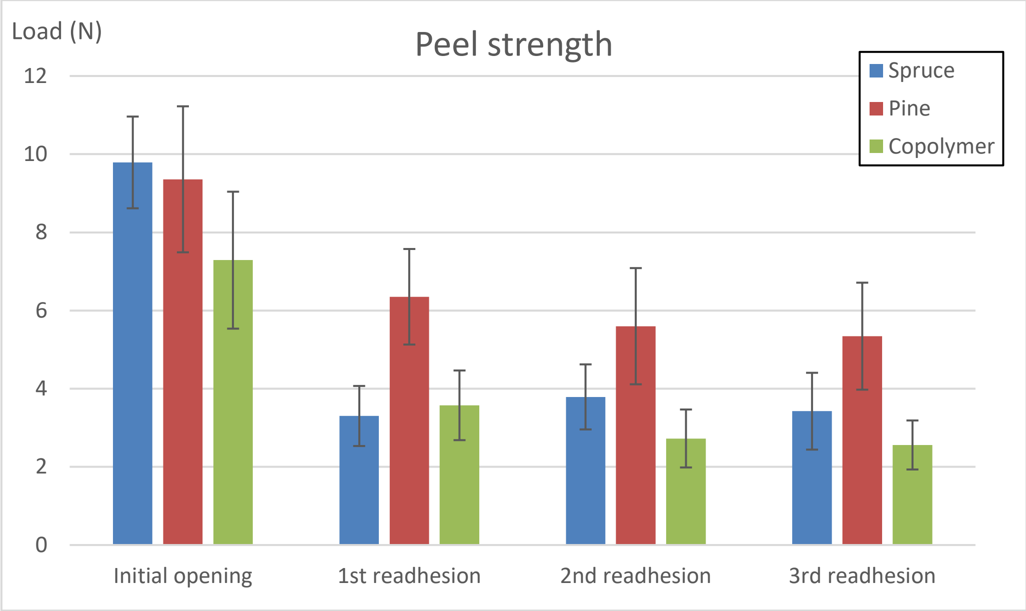


Figure 36. *Peel strengths of repeated closing and opening of tannin HMAs and pure copolymer between uncoated surfaces.*

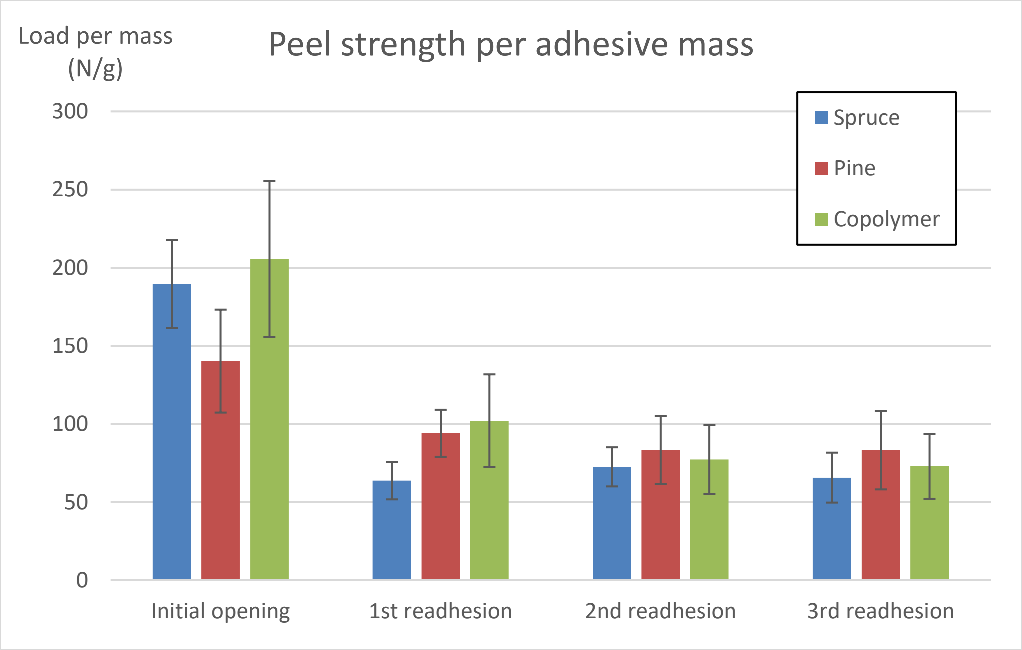


Figure 37. *Peel strengths per adhesive mass of repeated closing and opening of tannin HMAs and pure copolymer between uncoated surfaces.*

These results suggest that tannins enhance the adhesive ability of Co1 against uncoated FBB surface. This could be partially caused by the carbohydrates in crude tannins, as discussed earlier. More drastic difference is the effect on pressure sensitivity caused by adding pine tannins. Co1-CPT HMA had approximately twice as strong adhesive ability after re-closing the bond compared to Co1-CST HMA or pure Co1. In the loads per weight figure, again the homogeneity and the ability to be spread can be seen; Co1-CST HMA was easier to spread than Co1-CPT HMA. This could be seen in the opened specimens in Figures 31 and 32. While Co1-CST HMA was quite uniformly spread on the surface, Co1-CPT HMA seemed to have a tendency to clump a bit more, creating an uneven layer of adhesive. Whether this tendency is related to pine tannins' superior capability to readhere after opening, is an interesting question and could potentially be studied.

4.7 Viscosity

Viscosity for selected materials was measured to gain better knowledge on how viscosity of HMA affects its spreadability. Measurements were also done for aged HMAs to evaluate HMA stability. Viscosity was measured for materials listed below:

- REF
- Co1-CST HMA
- Co1-CST HMA, aged 24 hours in 60 °C
- Co1-CST HMA, aged 24 hours in 140 °C
- Co1-CT1 HMA
- Co1-CR2 HMA
- Co1

Results are presented in Table 14.

Table 14. *Viscosity measurements.*

Material	**Viscosity (g cm^{-1} s^{-1} (poise))**
REF	6,2 ± 0,1
Co1-CST HMA	3,9 ± 0,6
Co1-CST HMA, aged in 60 °C	4,3 ± 1,4
Co1-CST HMA, aged in 140 °C	3,3 ± 0,6
Co1-CT1 HMA	Could not be measured.
Co1-CR2 HMA	4,3 ± 1,8
Co-1	1,7 ± 0,3

HMA with commercial tannin could not be measured, as it did not melt homogenously on the measurement device and remained as a layer on the top part of the device. It was observed that reference HMA was quite uniform, as expected, and also very viscous. Pure copolymer was quite fluid and the viscosity increased rapidly when adding other materials. Some of these results were unexpected. The reference HMA was so easy to spread that it was expected to have low viscosity. Likewise the disparity of the spruce tannin HMAs were surprising. A possible explanation is that unaged HMA and the one aged in melt temperature remain quite homogenous, and aging in 60 °C makes the HMA lose its homogeneity and thus increases viscosity.

The developed HMA specimens were in a suitable viscosity range when compared to REF. The HMA viscosity range of 3.9−4.3 g cm^{-1} s^{-1} measured here is also comparable to the reported viscosity of starch-based HMA developed by VTT. HMA with purified transglycosylated starch acetate and TEC measured viscosity range of 3.2−5.2 g cm^{-1} s^{-1} [29, p. 23].

4.8 Alternative adherend materials

In this chapter alternative adherend materials, birch veneer, cotton-linen cloth, borosilicate glass, poly(ethylene terephthalate) and aluminium foil, were evaluated. During the manual testing of these materials, the note of HMAs weak creep resistance became obvious. When materials were glued together in a 180 peel configuration, sharp and strong pulls did not seem to do much. However, constant slow pull opened all the peel configurated bonds quite easily. Adhesion on poly(ethylene terephthalate) and aluminium foil was noted to be on a weak but acceptable level. Adhesion on linen-cotton cloth was quite strong and especially the shear mode held well.

Adhesion on borosilicate glass could not be tested, as the glass proved to be too fragile and was broken too easily. However, during a viscosity testing a piece of adhesive had become stuck in the bottom of a glass vial, and the vial was shattered in the attempt to wrangle it free. This incident does suggest that the adhesive does indeed adhere to glass quite well.

Birch veneers were glued with REF and Co1-CST HMA in shear configuration and the bond strength was measured. Results for Co1-CST HMA are presented in Figure 38. REF held until the machine's safety limit of 900 Newtons and as such no data is available. This showed that Co1-CST had weaker adhesive strength than REF.

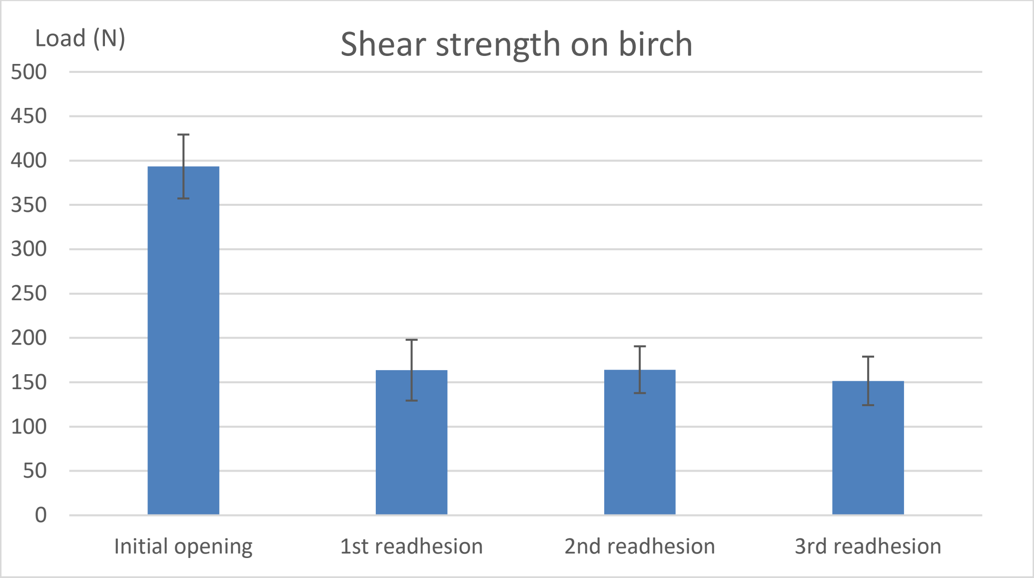


Figure 38. *Shear strength on birch veneer. Adhesive bond was re-closed by keeping it under 2.5 kg for one minute.*

As the adhesive suffered a cohesive failure, it was pressed again under 2.5kg for one minute before measuring the shear strength again. The results seen above match the results of pressure sensitivity testing for Co1-CST HMA. With uncoated FBB, the readhesion loads were approximately 35% of the initial load while here the later loads were approximately 40%.

4.9 Esterification of Tannin

Esterification of lignin with tall oil fatty acids has been researched at VTT. The esterified lignin together with oxidized cellulose acetate achieved peel strengths comparable to other formulations, without needing a wax component. [6, pp. 22–23] This so called internal plasticizing was a matter of interest for tannins as well, so spruce tannin was esterified with palmitic acid, saturated fatty acid with 16 carbons.

The esterified tannin powder was tested with several formulations. Using it in tannins' place in formulation 43 did not create a plausible mixture; esterified tannins remained on the surface of the molten copolymer. Also mixtures of 50:50 and 20:80 of EVA and esterified tannin were tested; these formulations did mix together but had no adhesive strength. And upon testing formulation 17 with EVA, esterified tannin and C80, it was noted that the mixture formed bubbles. This is assumed to be caused by ester degrading, because the esterified tannin was dried for 72 hours and as such should not contain water. Due to the results of these tests, work with esterified tannins was not continued. The DSC and NMR measurements of esterified spruce tannin are given in Figures 39 and 40, respectively.

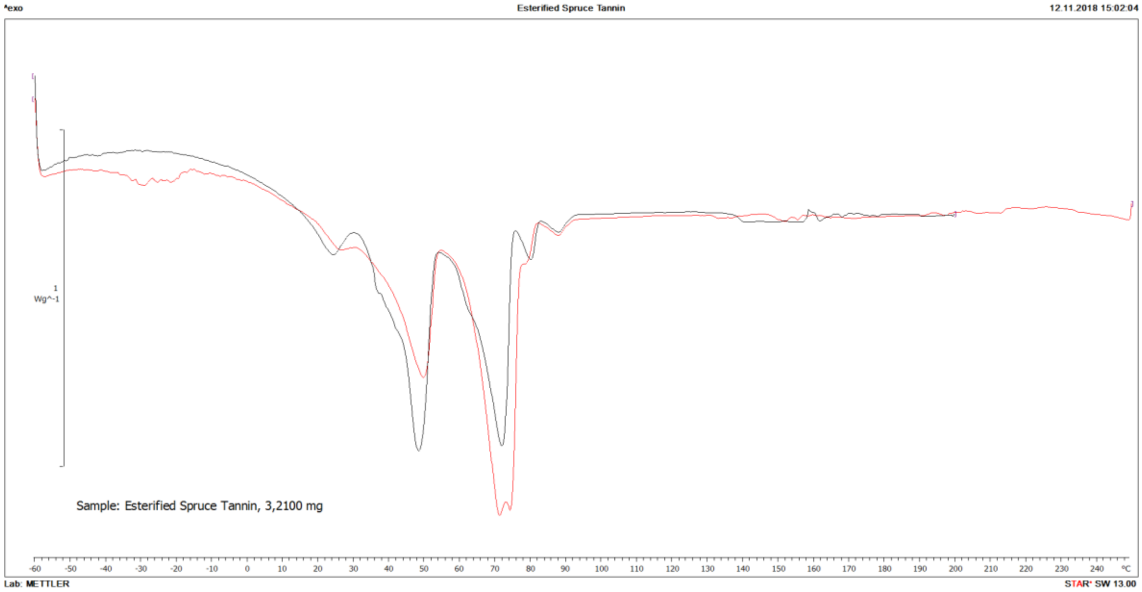


Figure 39. *DSC measurement of esterified spruce tannin. Black line represents the first heating run and the red line represents the second heating run.*

Esterified spruce tannin shows two melting points around temperatures 50 and 75 °C. Due to the change of intensities between heating runs, it is assumed that there were different forms of crystallization in the sample, and during cooling one form is preferred. There can also be different esters present, as condensed tannins have several hydroxyl groups where the ester bond can be formed. These different esters would explain the shoulders of the melting peaks.

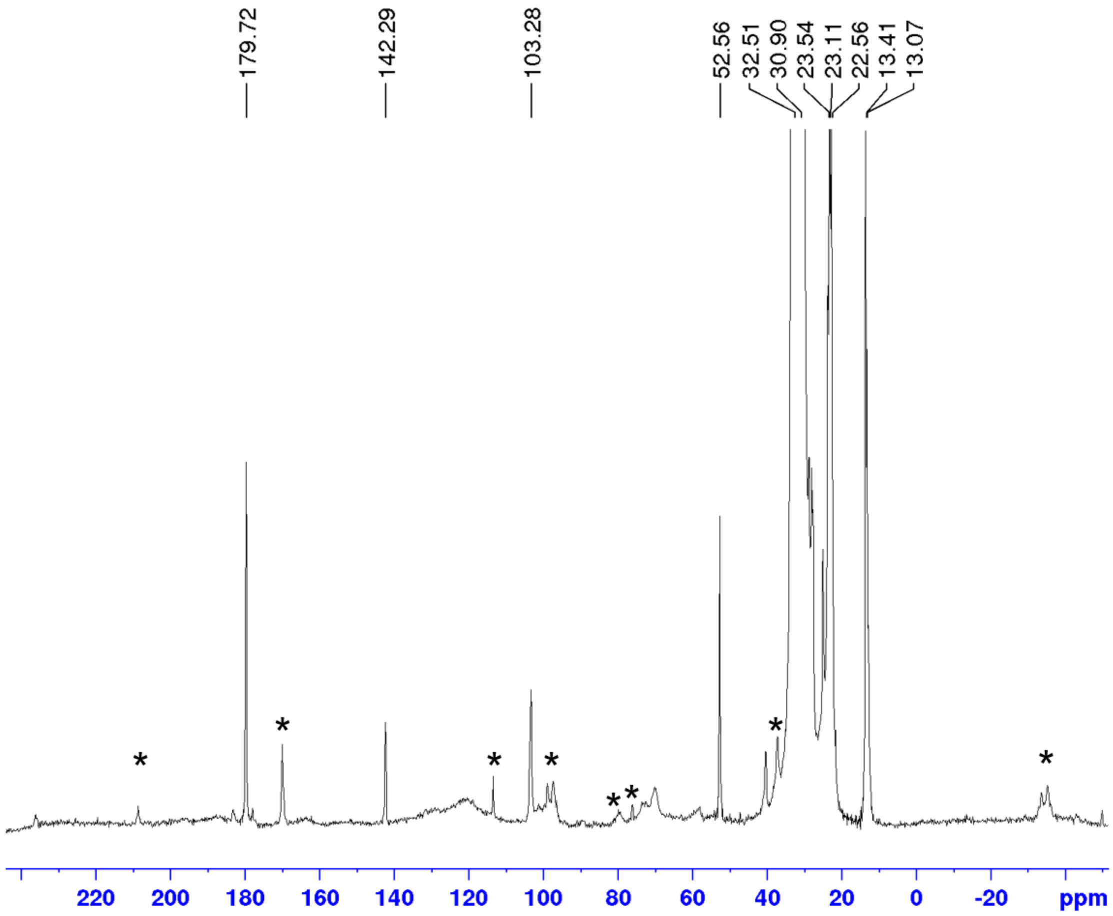


Figure 40. *Solid state ^{13}C NMR measurement of esterified spruce tannin. Peaks marked with asterisks were determined to be spinning sidebands.*

In Figure 40, the peaks marked with an asterisk were determined to be spinning sidebands. These artifacts may appear in solid state ^{13}C NMR at multiples of spinning speed. The strong peaks around 13-33 ppm all correspond to aliphatic C-C bonds of the palmitoyl side group, and peak at 180 ppm corresponds to carbonyl of the ester group. The fact that these are intensive compared to the other peaks of the spectrum suggests that the esterification rate was very high.

Comparing this measurement to a NMR result of condensed tannin from *Picea mariana* bark, some peaks not related to the palmitoyl ester can be assigned. Peak at 142 ppm could be assigned to tannin's aromatic carbon with a hydroxyl group, and peak at 103 ppm to aromatic carbon with hydrogen. [62, p. 4] However, tannins should present several more peaks around 100-160 ppm. It is probable that some of the spinning sidebands are in fact actually measurement peaks that are coincidentally at the locations of spinning sidebands and that the low wide peak around 120 ppm is caused by aromatic carbons. Also no clear cause could be discerned from literature for the peak at 52 ppm; however its intensity suggests that it is common in the structure of the ester.

4.10 Thermal properties

The thermal properties of different materials were evaluated by DSC. The different materials are depicted in Table 15.

Most of the graphs are depicted here and discussed in more detail. Graphs of EVA, C80 and commercial tackifiers are shown in Appendix B. In some measurements there are disturbances below room temperature; these were caused by an unknown problem in the DSC machine but deemed minor enough that repeated measurements were unnecessary.

Table 15. *DSC measurement test subjects.*

Raw materials	**Tannins and reference materials**	**Adhesives**
EVA	PST	REF
C80	PPT	Co1-CST HMA
Co1	CT1	Co1-CT1 HMA
Aged Co1	CT2	Co1-CR2 HMA
CST	CR1	
CPT	CR2	
	Esterified Tannin	

Figures 41-43 depict DSC measurement of both CST and PST, both CPT and PPT, and both commercial tannins, respectively. Figures 44-45 show measurements of P(DLLA-CL) and its aged version, respectively. Figure 46 depicts DSC curves of mixtures of 70% P(DLLA-CL) with CST, CT1 and CR2, and Figure 47 presents the DSC measurement of reference HMA.

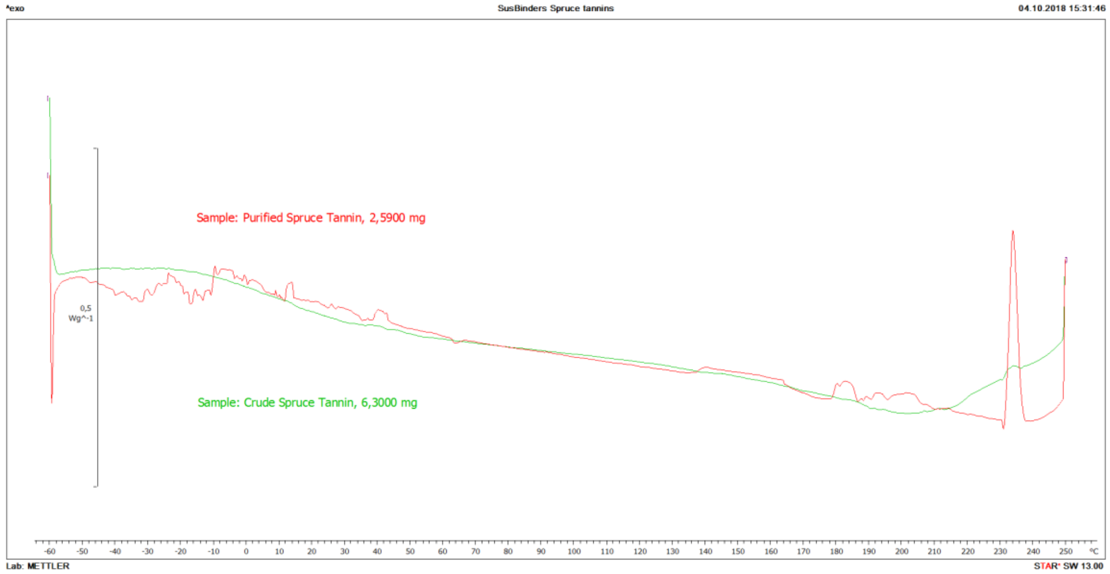


Figure 41. *DSC measurements of spruce tannins.*

Figure 42. *DSC measurements of pine tannins.*

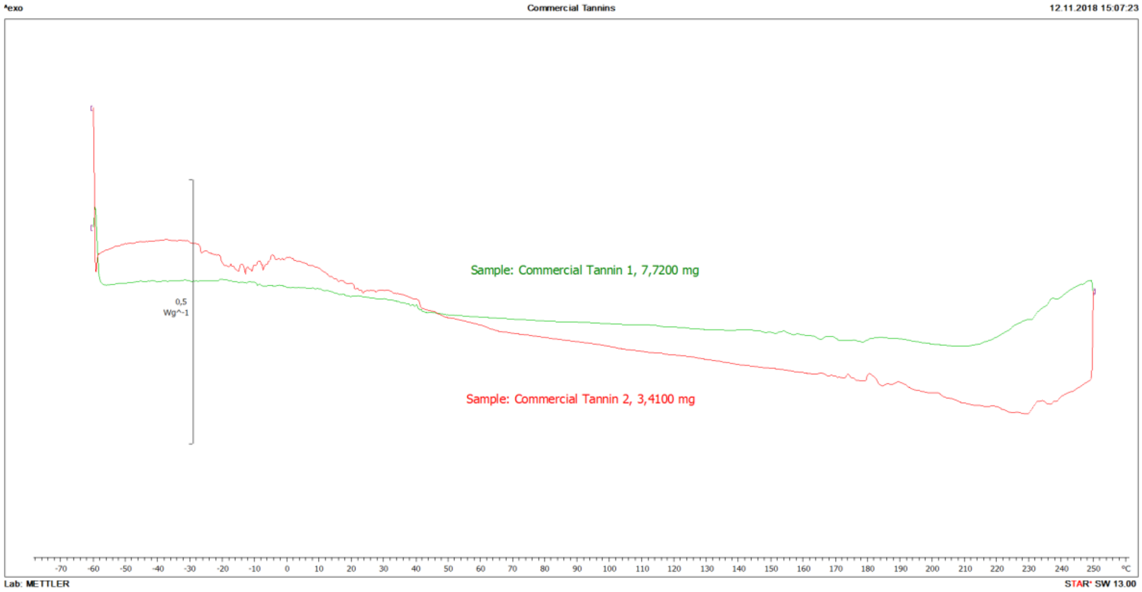


Figure 43. *DSC measurements of commercial tannins.*

These measurements of Figures 41-43 show that tannins lack any distinct features on their DSC curves. The crude tannins' graphs closely resemble the DSC of tannin from *Acacia dealbata* depicted here [63, p. 3189]. Interestingly the PST graph shows a high exothermal peak at 235 °C. This peak could be related to degradation of tannin; as noted in chapter 3.1, CST and CPT started to degrade in temperatures over 200 °C.

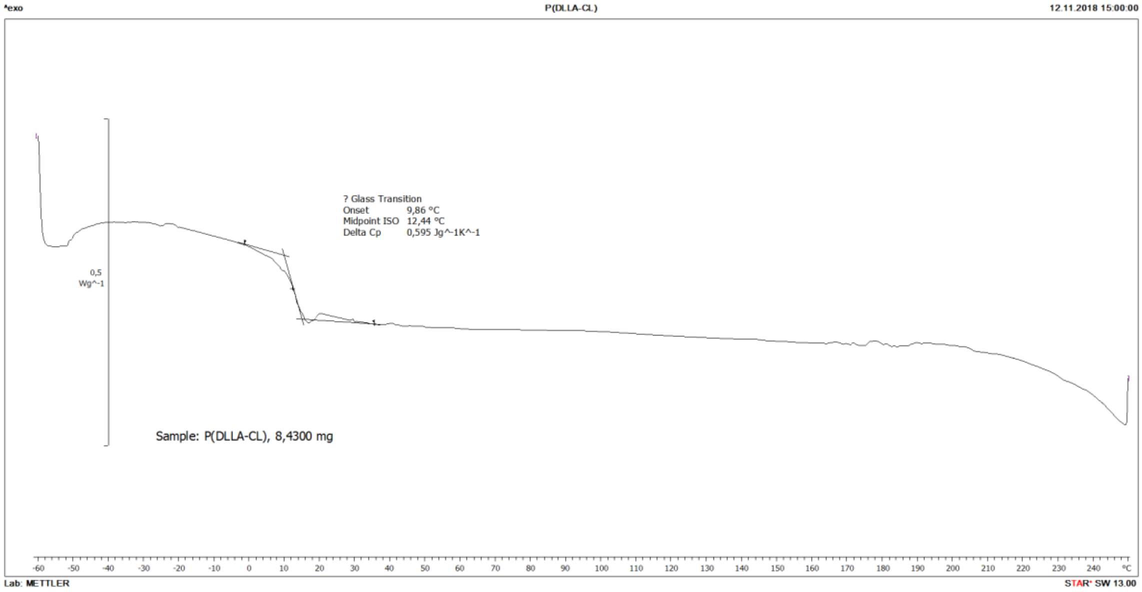


Figure 44. *DSC measurement of Co1.*

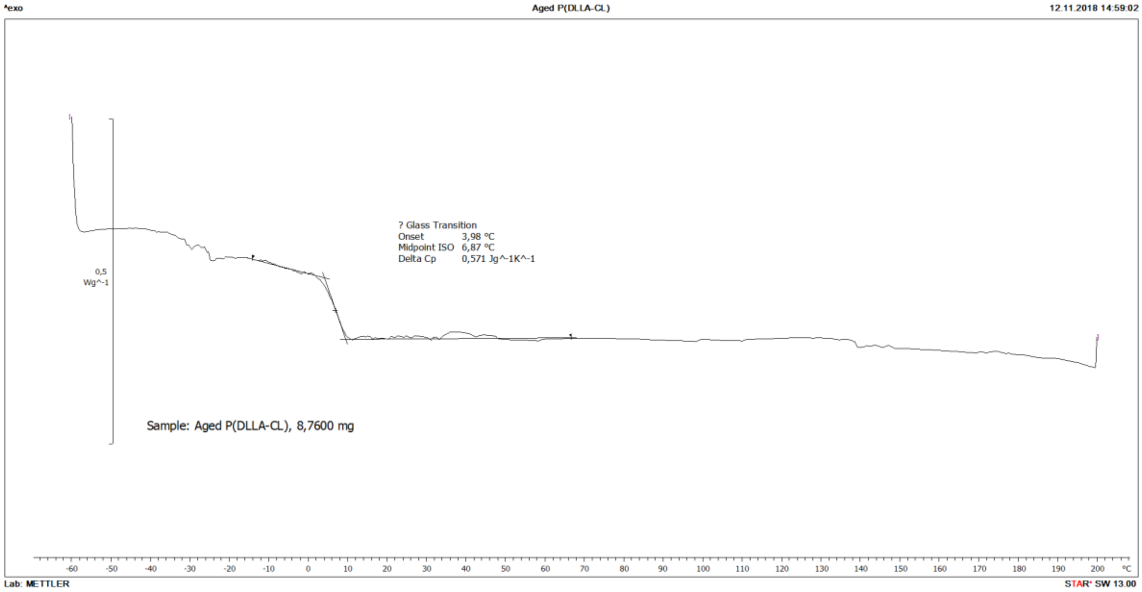


Figure 45. DSC measurement of aged Co1.

The aged Co1 specimen of Figure 45 was stored in the laboratory for several weeks while the temperature was 25-30 °C due to the high summer temperatures. The effect of aging and deteriorating can be seen in the glass transition temperature of the copolymer. The temperature has decreased by several degrees. While this seems like a small change, the effects are evident when comparing Figures 21 and 22 in chapter 4.2. Also evident from these graphs is Co1's thermoplastic nature; there is no clear melting point but instead it softens when heated.

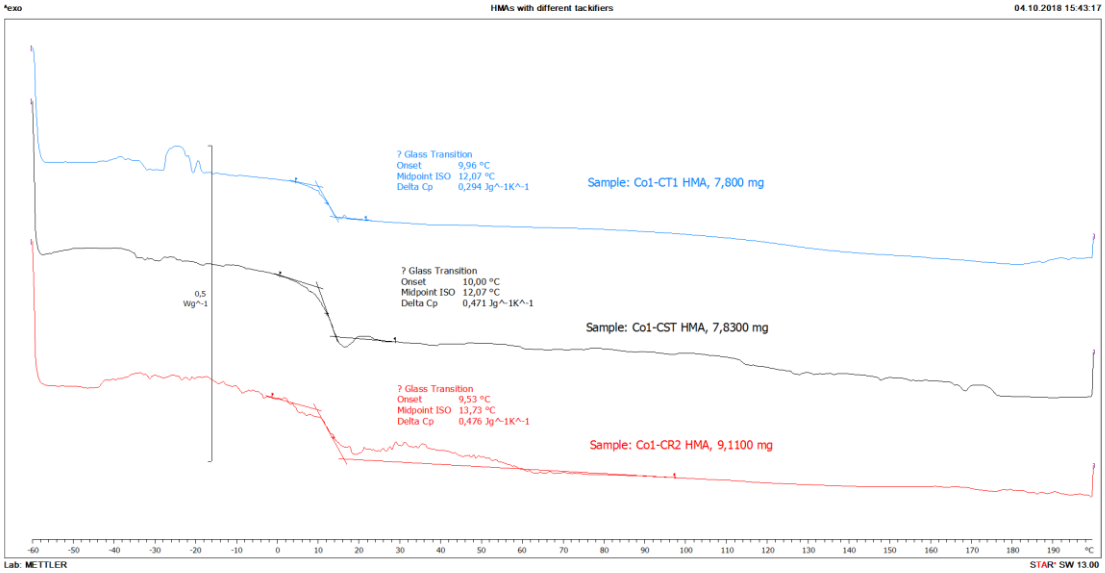


Figure 46. DSC measurements of Co1 HMAs with different tackifiers.

Figure 46 depicts DSC curves of Co1 HMAs with CT1, CST and CR2. It seems that the thermal properties of the Co1 HMAs are mostly those of Co1. Only notable change is the change in heat capacity (noted as ‘Delta Cp’ in the graphs) in the glass transition. It decreased in all mixtures and quite significantly in the case of Co1-CT1 HMA.

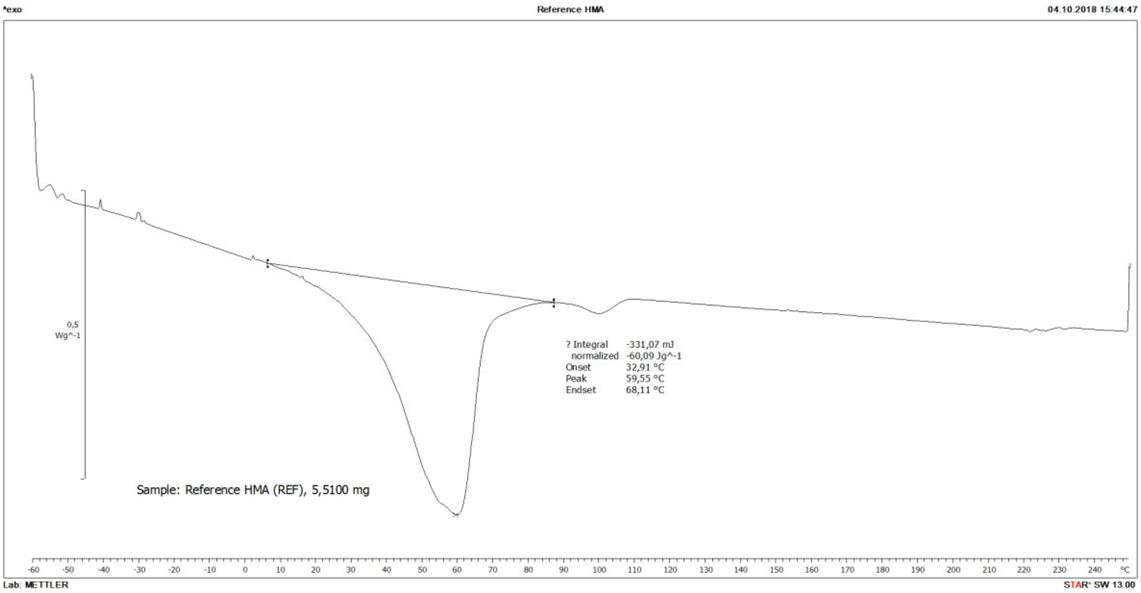


Figure 47. *DSC measurement of REF.*

The melting is clearly visible in the DSC graph of REF in Figure 47. No glass transition could be identified from the graph. The relatively wide melting range explains the forming of long thin filaments as seen in figure 28 in chapter 4.5, as some parts of the melt will solidify at higher temperatures.

5. CONCLUSIONS

The formulation of HMA with tannins as component was experimentally studied by measuring the peel strength of adhesive formulations between commercial cardboard. It was concluded that tannins could be used to affect the properties of poly(D,L-lactide-*co*-ε-caprolactone) (Co1) without decreasing its adhesive capabilities, and that this mixture could be used as a HMA for cardboard. This mixture is believed to be biodegradable. Co1 in itself was difficult to handle due to its aggressive tackiness and its tendency to leave fine tails and filaments. As mentioned in chapter 2.2.1, this tendency can be caused by a wide molecular weight distribution. After adding tannins the mixture was significantly easier to handle due to the fact that it turned into a thick paste that left no tails or filaments when handled. The added tannins also increased the viscosity.

Adding tannins increased the adhesion properties towards uncoated surface of commercial FBB. This could be caused by hydrogen bonding between tannins and the surface of the FBB. The most interesting finding, however, was the effect of tannins in the readhesion properties of the formulation. When an adhesive bond of pure Co1 was opened, it could be closed again by simply applying pressure. Adding pine tannins increased the strength of the reclosed adhesive bond. There was a distinct difference between pine and spruce tannins in this regard, as spruce tannins did not cause such increase. The cause of this effect is unknown. It can be caused by the molecular differences of the tannins due to different origins or the difference in the homogeneity. It was noted that the mixing mechanism used in this Thesis resulted in heterogeneity in the micrometer scale. The effect of homogeneity and heterogeneity should be studied in more detail.

As for the research questions introduced in the beginning of this Thesis, the research concluded that using cellulose derivatives as the base polymer with crude tannins results in weak adhesive properties. The research also suggests that the prospect of using crude tannins as simple ‘drop-in’ alternatives of established tackifiers does not seem probable with the selected materials used in this Thesis. Formulation 17 with EVA and C80 did show potential, however, and was only plagued by reproducibility issues. This potential should be revisited in an attempt to actualize it. Using EVA with different parameters and different mass ratios could be tested as well as purified tannins.

This Thesis was conducted using crude spruce tannins, and other tannins were only used as comparison on the final formulation. Other tannins, crude pine tannins and purified tannins, appear to behave differently. Thus it is recommended that research on the other tannins should include new screening, even if same materials are used. Also research on different adherend surfaces would be interesting for future studies. Most of the experiments in this Thesis were conducted between commercial FBB due to the prevalence of

HMAs in packaging. The adhesive capabilities of Co1-CST HMA between cotton-linen cloth and borosilicate glass were only tested by hand, but they appeared quite strong.

A point of interest is the first formulation where pressure sensitivity was noticed; formulation P-6 with CAB-Ox and TEC showed weak adhesive strength but could adhere to a wide variety of materials. Especially the strength of adhesion towards a concrete wall was an interesting notion.

Sources of potential imprecision in this Thesis must be kept in mind. Firstly, all spreading of adhesives was done by hand due to the lack of small scale adhesive testing equipment. Even though great care was taken in attempts to achieve an adhesive layer as smooth as possible, uneven spreading could not be fully avoided. This means that no adhesive layer tested in this Thesis is uniform and that no two test specimens were exactly alike. As such, adhesives with high viscosity or high heterogeneity were the most affected by this. Most tannin based HMAs had one or both of those disadvantages. This also had the effect of the amounts of adhesive to be quite high. Even when trying to spread as little adhesive as possible, the amount of Co1-CST HMA was almost five times as high as REF. The imprecision of manual work also affected the Co1-based HMA formulations; due to its aggressive and tacky nature, the formulations were not mixed in a microcompounder. Instead they were manually heated and mixed in an oil bath, which by its very nature is more prone to less homogenous mixture. This could be seen in Co1-CPT HMA, for example, as it could have been more homogenous if it had been able to be done in a microcompounder. Another issue to keep in mind is the degradation of the copolymer. While care was taken to minimize the time the copolymer had to degrade before measurements, it is possible to have affected the measurements conducted on the copolymer.

This Thesis aimed to function as a laboratory scale proof of concept of the hypothesis that tannins could be used as tackifiers in HMAs. This hypothesis was proven with the copolymer of lactic acid and caprolactone. The potential of the formulation with EVA and C80 should also be remembered. This Thesis also cannot address the potential of purified tannins in the role of tackifier. Nevertheless, more research must be done before the prospects of tannins in HMAs can be really determined. Further research should include polymers and waxes not tested in this Thesis, such as polyurethanes, and a proper mixing to achieve homogenous compounds.

REFERENCES

[1] Ötzi the Iceman, South Tyrol Museum of Archaeology. (Online). Available: http://www.iceman.it/en/#. (Accessed: 24-10-2018).

[2] Dokos, L., Mondal, S., Global Analysis of the Hot Melt Adhesives Market - Asia-Pacific Market is Likely to Maintain Growth Momentum, Frost & Sullivan, 2013, 129 p.

[3] The Future of Global Packaging to 2022, Smithers Pira, 2017. (Online). Available: https://www.smitherspira.com/industry-market-reports/packaging/the-future-of-global-packaging-to-2022. (Accessed: 09-08-2018).

[4] Sustainable Binders from bark. (Online). Available: https://www.vtt.fi/sites/SusBinders. (Accessed: 22-10-2018).

[5] Kraton Corporation, Tackifiers for adhesives. 2017, 14 p.

[6] Laine, C., Liitiä, T., Ropponen, J., Willberg-Keyriläinen, P., Talja, R., Biobased hot-melt adhesive including lignin as a component, PCT/FI2018/050005, 05.07.2018, 28 p.

[7] Standard Definitions of Terms Relating to ADHESIVES, The Adhesive and Sealant Council, Inc., 2004.

[8] Pizzi, A., Mittal, K. L., Handbook of Adhesive Technology, 2nd ed., Marcel Dekker, Inc., 2003, 999 p.

[9] Ebnesajjad, S., Landrock, A. H., Adhesives Technology Handbook, 2nd ed., William Andrew Inc., 2008, 363 p.

[10] Petrie, E. M., Plastics and Elastomers in Adhesives, in Handbook of Plastics, Elastomers, & Composites, 4th ed., C. A. Harper, Ed. McGraw-Hill, 2002, pp. 397–505.

[11] Paul, C. W., Hot-Melt Adhesives, MRS Bulletin, Vol. 28, No. 6, 2003, pp. 440–444.

[12] Malysheva, G. V., Bodrykh, N. V., Hot-Melt Adhesives, Polymer Science, Series D. Glues and Sealing Materials, Vol. 4, No. 4, 2011, pp. 301–303.

[13] Georjon, O., Faissat, M., Chambon, F., Understanding the Sprayability of Hot-Melt Adhesives, Adhesives Age, Vol. 42, No. 2, 1999, pp. 44–48.

[14] Utekar, P., Gabale, H., Khandelwal, A., Mhaske, S. T., Hot-Melt Adhesives from Renewable Resources: A Critical Review, Reviews of Adhesion and Adhesives, Vol. 4, No. 1, 2016, pp. 104–118.

[15] Petrie, E. M., Biobased Components in Hot Melt Adhesive Formulation,

SpecialChem, 2012. (Online). Available: http://www.iterg.com/IMG/pdf/biobased_components_in_hot_melt_adhesive_formulation.pdf. (Accessed: 11-05-2018).

[16] Ernst & Young, Unwrapping the packaging industry: Seven factors for success., United Kingdom: EYGM Limited, 2013, 24 p.

[17] Pakkauslaakso, Pöyry Management Consulting Oy, 2016, 11 p.

[18] Li, K., Geng, X., Simonsen, J., Karchesy, J., Novel wood adhesives from condensed tannins and polyethylenimine, International Journal of Adhesion & Adhesives, Vol. 24, 2004, pp. 327–333.

[19] Faris, A. H., Rahim, A. A., Ibrahim, M. N. M., Alkurdi, A. M., Shah, I., Combination of lignin polyol-tannin adhesives and polyethylenimine for the preparation of green water-resistant adhesives, Journal of Applied Polymer Science, Vol. 133, No. 20, May 2016, p. 43437.

[20] Zhong, Z., Susan Sun, X., Fang, X., Ratto, J. A., Adhesion properties of soy protein, Journal of the American Oil Chemists' Society, Vol. 78, No. 1, 2001, pp. 37–41.

[21] Zhao, S., Xing, F., Wang, Z., Kang, H., Zhang, S., Li, J., High bonding strength and boiling water resistance of soy protein-based adhesives via organosilicon–acrylate microemulsion and epoxy synergistic interfacial enhancement, Journal of Applied Polymer Science, Vol. 135, No. 16, 2018, pp. 1–8.

[22] Classification of thermoplastic wood adhesives for non-structural applications, European Standard EN 204, 2001, 9 p.

[23] Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal), ASTM International, 2002, 3 p.

[24] Banea, M. D., Silva, L. F. M. Da, Campilho, R. D. S. G., Effect of Temperature on Tensile Strength and Mode I Fracture Toughness of a High Temperature Epoxy Adhesive, Journal of Adhesion Science and Technology, Vol. 26, No. 7, 2012, pp. 939–953.

[25] Kumar, R., Choudhary, V., Mishra, S., Varma, I. K., Mattiason, B., Adhesives and plastics based on soy protein products, Industrial Crops and Products, Vol. 16, 2002, pp. 155–172.

[26] Pizzi, A., Recent developments in eco-efficient bio-based adhesives for wood bonding: opportunities and issues, Journal of Adhesion Science and Technology, Vol. 20, No. 8, 2006, pp. 829–846.

[27] Isoprenoids (Terpenoids). (Online). Available: https://polymerdatabase.com/polymer classes/Isoprenoids.html. (Accessed: 13-11-2018).

[28] Rosin Esters and Polymers. (Online). Available:

https://polymerdatabase.com/polymer classes/Rosin.html. (Accessed: 13-11-2018).

[29] Mikkonen, H., Valta, K., Sivonen, E., Peltonen, S., New starch-based composition and process for the production thereof, PCT/FI2003/000796, 06.05.2004, 27 p.

[30] Mikkonen, H. *et al.*, New cellulose derivatives, method of producing the same and use thereof, PCT/FI2009/050159, 03.09.2009, 26 p.

[31] Viljanmaa, M., Södergård, A., Törmälä, P., Lactic acid based polymers as hot melt adhesives for packaging applications, International Journal of Adhesion & Adhesives, Vol. 22, 2002, pp. 219–226.

[32] Polycaprolactone (PCL), Polymer Properties Database. (Online). Available: http://polymerdatabase.com/Polymer Brands/PCL.html. (Accessed: 08-08-2018).

[33] Gross, R. A., Kalra, B., Biodegradable polymers for the environment, Science, Vol. 297, No. 5582, 2002, pp. 803–807.

[34] Virent Announces World's First Demonstration of Full Range Bio-Aromatics Production, Virent, Inc., 2014. (Online). Available: http://www.virent.com/news/virent-announces-worlds-first-demonstration-of-full-range-bio-aromatics-production/. (Accessed: 09-08-2018).

[35] Production of Bio-ethylene: Technology Brief, IEA-ETSAP and The International Renewable Energy Agency (IRENA), No. January, 2013, 20 p.

[36] About lignin, The International Lignin Institute. (Online). Available: http://www.ili-lignin.com/aboutlignin.php. (Accessed: 07-11-2018).

[37] Quideau, S., Deffieux, D., Douat-Casassus, C., Pouységu, L., Plant polyphenols: Chemical properties, biological activities, and synthesis, Angewandte Chemie - International Edition, Vol. 50, No. 3, 2011, pp. 586–621.

[38] Daintith, J., Dictionary of Chemistry (6th Edition), Oxford University Press, 2008, 543 p.

[39] Arnold, T. M., Targett, N. M., Marine tannins: The importance of a mechanistic framework for predicting ecological roles, Journal of Chemical Ecology, Vol. 28, No. 10, 2002, pp. 1919–1934.

[40] Salminen, J. P., Karonen, M., Chemical ecology of tannins and other phenolics: We need a change in approach, Functional Ecology, Vol. 25, No. 2, 2011, pp. 325–338.

[41] All about tannins, Silvateam. (Online). Available: https://www.silvateam.com/en/who-we-are/extracts-nature/all-about-tannins.html. (Accessed: 11-06-2018).

[42] Liimojen myrkyt korvataan havupuun kuorella – Suomessa kehitetään täysin uutta tuotantomenetelmää miljardimarkkinoille, Tekniikka & talous. (Online). Available: https://www.tekniikkatalous.fi/tekniikka/metsa/liimojen-myrkyt-

korvataan-havupuun-kuorella-suomessa-kehitetaan-taysin-uutta-tuotantomenetelmaa-miljardimarkkinoille-6696698. (Accessed: 24-05-2018).

[43] Total wood consumption 2016, Natural Resources Institute Finland, 2017. (Online). Available: http://stat.luke.fi/en/total-wood-consumption-2016_en. (Accessed: 26-09-2018).

[44] Wood in energy generation 2016, Natural Resources Institute Finland, 2017. (Online). Available: http://stat.luke.fi/en/wood-energy-generation-2016_en. (Accessed: 26-09-2018).

[45] Kemppainen, K., Production of sugars , ethanol and tannin from spruce bark and recovered fibres, dissertation, Aalto University, VTT Science 76, 2015, 129 p.

[46] Bate-Smith, E. C., Astringent tannins of Acer species, Phytochemistry, Vol. 16, No. 9, 1977, pp. 1421–1426.

[47] Iii, P., Spruce bark as an industrial source of condensed tannins and non-cellulosic sugars, 2014, pp. 158–168.

[48] Alakangas, E., Hurskainen, M., Laatikainen-Luntama, J., Korhonen, J., Suomessa käytettävien polttoaineiden ominaisuuksia, VTT Technology 258, Espoo, 2016, 229 p.

[49] Eghbaliferiz, S., Iranshahi, M., Prooxidant Activity of Polyphenols, Flavonoids, Anthocyanins and Carotenoids: Updated Review of Mechanisms and Catalyzing Metals, Phytotherapy Research, Vol. 1391, No. May, 2016, pp. 1379–1391.

[50] Chung, K. T., Wong, T. Y., Wei, C. I., Huang, Y. W., Lin, Y., Tannins and human health: A review, Critical Reviews in Food Science and Nutrition, Vol. 38, No. 6, 1998, pp. 421–464.

[51] Sakaguchi, T., Nakajima, A., Recovery of Uranium from Seawater by Immobilized Tannin, Separation Science and Technology, Vol. 22, No. 6, Jun. 1987, pp. 1609–1623.

[52] Pelicano, H., Carney, D., Huang, P., ROS stress in cancer cells and therapeutic implications, Drug Resistance Updates, Vol. 7, No. 2, 2004, pp. 97–110.

[53] Pizzi, A., Wood products and green chemistry, Annals of Forest Science, Vol. 73, 2016, pp. 185–203.

[54] Berguis, A., Tannin-based phenolic resins for plywood and laminates, 2018.

[55] Alakurtti, S., Polyphenols from softwood bark in adhesive applications, Nordic Wood Biorefinery Conference, 24.10.2018.

[56] Maiza, M., Benaniba, M. T., Quintard, G., Massardier-Nageotte, V., Biobased additive plasticizing Polylactic acid (PLA), Polimeros, Vol. 25, No. 6, 2015, pp. 581–590.

[57] Gutowski, W., Dealing With Mechanics of Adhesion, European Adhesives &

Sealants Summit 2018, Warsaw, Poland, 23.-24.05.2018.

[58] Siracusa, V., Rocculi, P., Romani, S., Rosa, M. D., Biodegradable polymers for food packaging: a review, Trends in Food Science & Technology, Vol. 19, No. 12, 2008, pp. 634–643.

[59] Nair, L. S., Laurencin, C. T., Biodegradable polymers as biomaterials, Progress in Polymer Science, Vol. 32, 2007, pp. 762–798.

[60] Vert, M., Li, S., Bioresorbability and biocompatibility of aliphatic polyesters, Journal of Materials Science: Materials in Medicine, Vol. 3, 1992, pp. 432–446.

[61] Sodergard, A., Selin, M. N. J., Nasman, J. H., Changes in Peroxide Melt-Modified Poly(L-lactide), Industrial and Engineering Chemistry Research, Vol. 34, 1995, pp. 1203–1207.

[62] Diouf, P. N., Tibirna, C. M., Royer, M., Dubé, P., Stevanovic, T., Structural Elucidation of Condensed Tannin from Picea mariana Bark, Vol. 2013, No. June, 2013, pp. 1–8.

[63] Lisperguer, J., Saravia, Y., Vergara, E., Structure and thermal behavior of tannins from Acacia dealbata bark and their reactivity toward formaldehyde, Vol. 4, 2016, pp. 3188–3190.

APPENDIX A: MATERIAL TESTING NOTES

Table A1. *Material testing notes from screening in phase 1.*

ID	Ratio	Polymer	Tackifier	Wax	Gluing temp	Results	Notes
P-1	26 / 34 / 40	PCL	Pine	TEC	160°C	Extremely weak	
P-2	26 / 34 / 40	CAP	Spruce	TEC	160°C	Weak	
P-3	21.4 / 28.6 / 50	CAB	Spruce	TEC	160°C	Weak	
P-4	26 / 34 / 40	CA-Ox	Spruce	TEC	160°C	Okay	
P-5	21.4 / 28.6 / 50	CAP-Ox	Spruce	TEC	160°C	Very weak	
P-6	21.4 / 28.6 / 50	CAB-Ox	Spruce	TEC	160°C	Weak, readhesion	
1	26/34/40	EVA	Spruce	TEC	-	-	Didn't adhere to cardboard
2	26/34/40	EVA	Spruce	CITRO	180°C	Doesn't hold	
3	26/34/40	EVA	Spruce	SNS	180°C	Doesn't hold	
4	-	PLA/PCL	Spruce	TEC	-	-	TEC causes PLA to deteriorate
5	26/34/40	PLA/PCL	Spruce	CITRO	160°C	Extremely weak	
6	26/34/40	PLA/PCL	Spruce	SNS	160°C	Very weak	
7	26/34/40	EVA	Spruce	H1	160°C	Okay	Same as 16 but 40% wax
8	26/34/40	EVA	Spruce	C80	160°C	Weak	Same as 17 but 40% wax
9	26/34/40	PLA/PCL	Spruce	H1	-	-	
10	26/34/40	PLA/PCL	Spruce	C80	-	-	
11	26/34/40	CA-Ox	Spruce	CITRO	-	-	
12	26/34/40	CA-Ox	Spruce	SNS	-	-	
13	26/34/40	CA-Ox	Spruce	H1	-	-	
14	26/34/40	CA-Ox	Spruce	C80	-	-	
15	21.7/28.3/50	EVA	Spruce	TEC	-	-	
16	21.7/28.3/50	EVA	Spruce	H1	160°C	1/3 fiber tear, 1/3 weak	Same as 7 but 50% wax
17	21.7/28.3/50	EVA	Spruce	C80	160°C	1/3 fiber tear, OK	Same as 8 but 50% wax
18	21.7/28.3/50	PLA/PCL	Spruce	H1	-	-	
19	21.7/28.3/50	PLA/PCL	Spruce	C80	-	-	
20	21.7/28.3/50	CAB	Spruce	TEC	150°C	Weak - okay	
21	21.7/28.3/50	CAB	Spruce	CITRO	180°C	Okay	
22	21.7/28.3/50	CAB	Spruce	SNS	180°C	Okay	
23	21.7/28.3/50	CAB	Spruce	H1	-	-	
24	21.7/28.3/50	CAB	Spruce	C80	-	-	
25	21.7/28.3/50	CAB-Ox	Spruce	TEC	-	-	
26	21.7/28.3/50	CAB-Ox	Spruce	CITRO	150°C	Very weak	
27	21.7/28.3/50	CAB-Ox	Spruce	SNS	170°C	Very weak	
28	21.7/28.3/50	CAB-Ox	Spruce	H1	-	-	
29	21.7/28.3/50	CAB-Ox	Spruce	C80	-	-	
30	30/40/30	co-1 (PLA/PCL)	Spruce	TEC	120°C	-	Broke when taking from oven.
31	30/40/30	co-1 (PLA/PCL)	Spruce	CITRO	120°C	-	Broke when taking from oven.
32	30/40/30	co-1 (PLA/PCL)	Spruce	SNS	130°C	Doesn't hold	
33	30/40/30	co-1 (PLA/PCL)	Spruce	H1	-	-	
34	30/40/30	co-1 (PLA/PCL)	Spruce	C80	-	-	
35	40/60	co-2 (PLA/PCL)	Spruce	-	-	-	
36	-	co-2 (PLA/PCL)	Spruce	CITRO	-	-	Skipped.
37	28.6/42.8/28.6	co-2 (PLA/PCL)	Spruce	SNS	-	-	
38	-	co-2 (PLA/PCL)	Spruce	H1	-	-	Skipped.
39	-	co-2 (PLA/PCL)	Spruce	C80	-	-	Skipped.
40	26/34/40	CA-Ox	Spruce	TEC	170°C	Okay	Best of preliminary testing.
41	40/60	co-1 (PLA/PCL)	Spruce	-	-	-	
42	100	co-1 (PLA/PCL)	-	-	140°C	Good	100% copolymer for reference.
43	60/40	co-1 (PLA/PCL)	Spruce	-	150°C	Good	
44	60/40	co-2 (PLA/PCL)	Spruce	-	-	-	

APPENDIX B: ADDITIONAL DSC GRAPHS

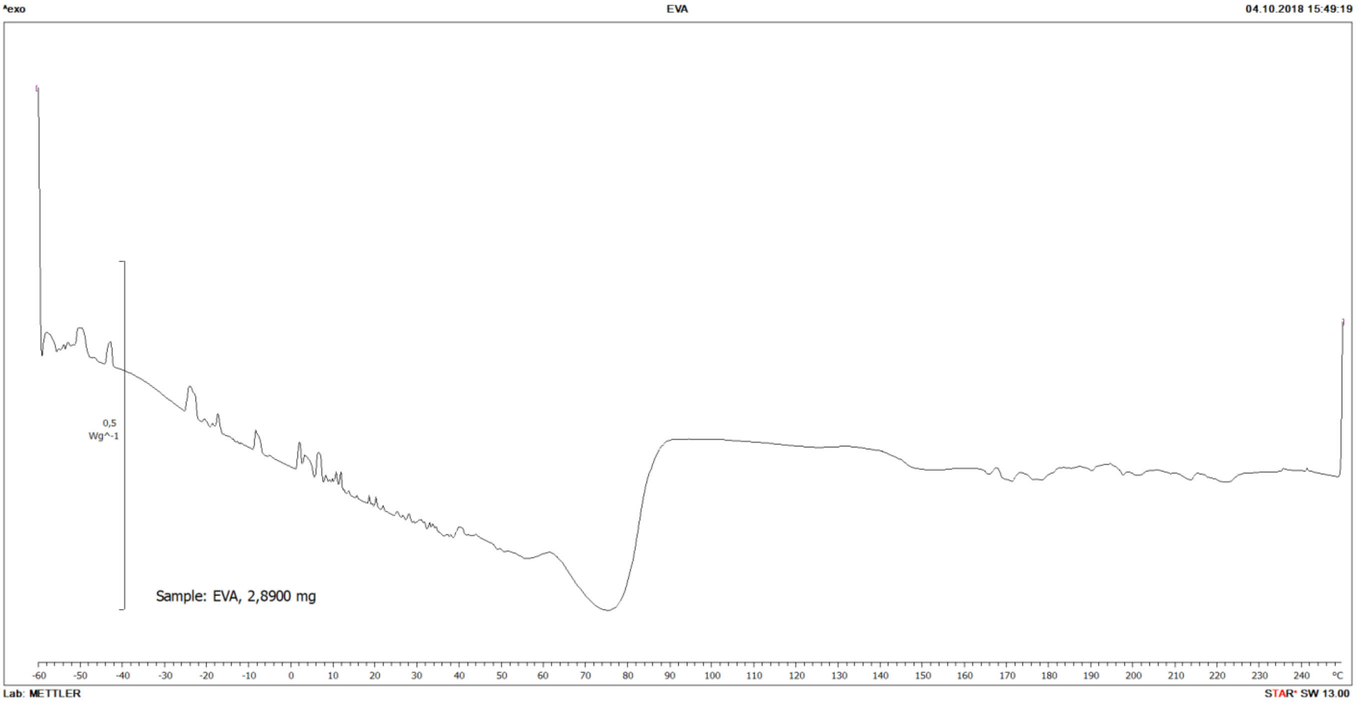


***Figure B1**. DSC measurement of poly(ethylene-*co*-vinyl acetate)* (EVA).

The graph closely resembles that found in "Curing kinetics of EVA using DSC, DMA and model free kinetics", Thermal Analysis Application No. UC 312 by METTLER TOLEDO. Glass transition is not clearly visible, but seems to be at around −40 to −30 °C. Examining the sample after measurement showed that it had not completely melted but instead was a softened granule.

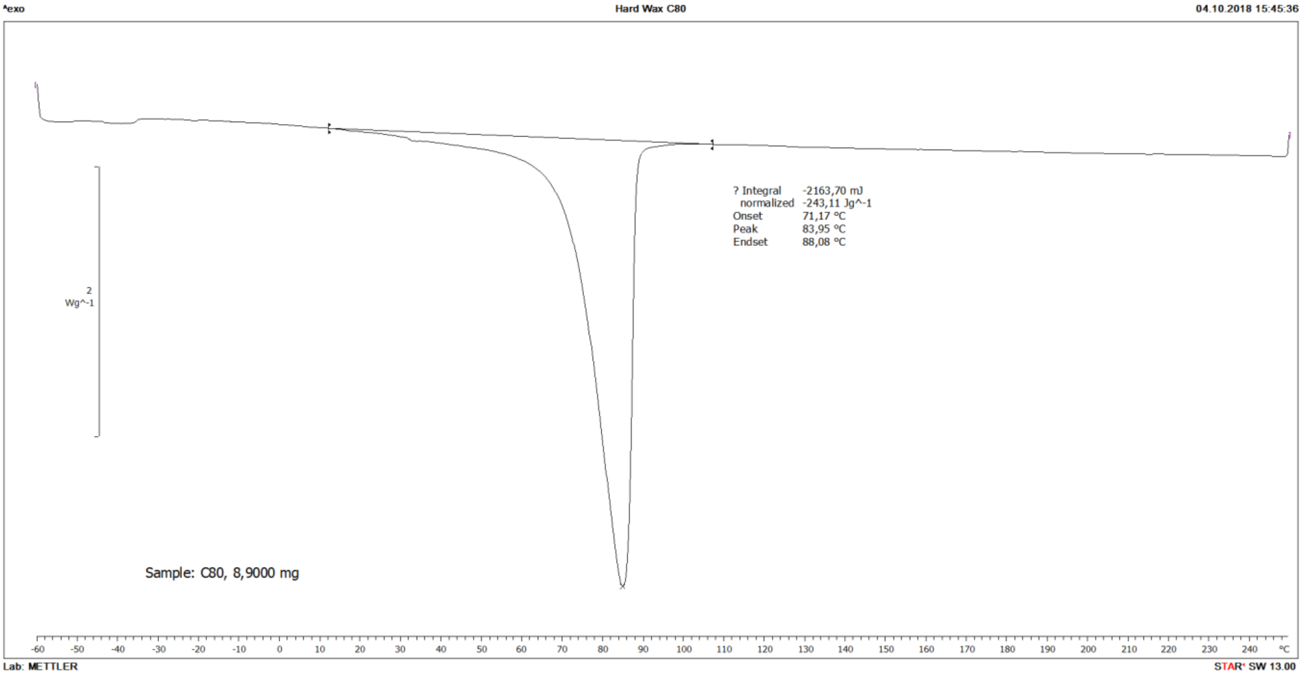


Figure B2. *DSC measurement of hard Fischer-Tropsch wax C80.*

A relatively sharp melting peak is clearly visible at 84 °C.

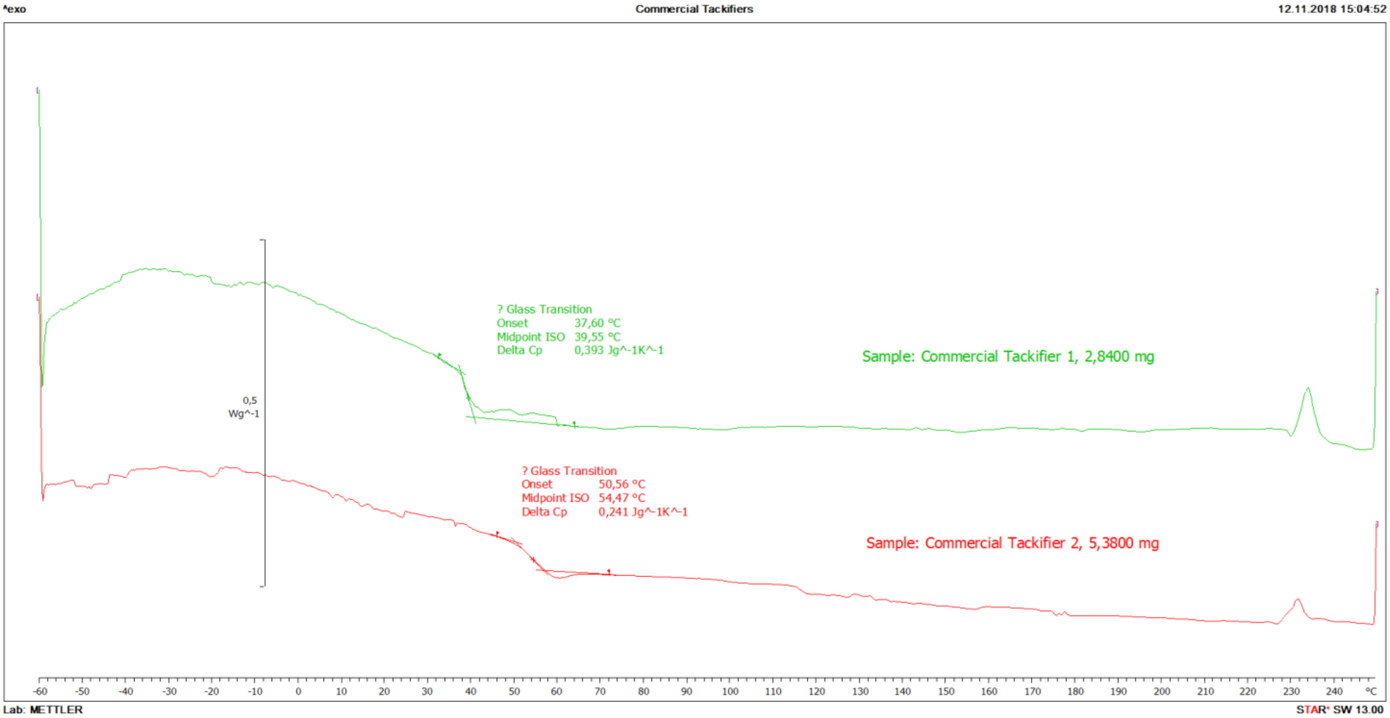


Figure B3. *DSC measurement of commercial tackifiers CT1 and CT2.*

Glass transition temperatures can be seen at around 40 and 55 °C. No melting peak is visible, but sample granules had turned changed into film layer during the measurement.