THE EFFECT OF PRE-DRYING TO THE QUALITY OF ADHESIVE LAMINATE FOR MEDICAL APPLICATIONS

Lappeenranta–Lahti University of Technology LUT

Master's Programme in Chemical Engineering, Master's Thesis

Chemical and Process Engineering

2025

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TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT

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Esikuivauksen Vaikutus Lääketieteellisiin Sovellutuksiin Käytetyn Liimalaminaatin Laatuominaisuuksiin

Diplomityö

2025

112 sivua, 49 kuvaa, 11 taulukkoa ja 0 liitettä

Tarkastaja(t): Dosentti Rama Layek ja Antti Holopainen, Master of Science

Avainsanat: Akryyli, akrylaatti, adheesio, liima, laminaatti, lääketiede

Opinnäytetyö keskittyi määrittämään esikuivauksen lisäyksen vaikutusta lääketieteellisiin tarkoituksiin käytetyn liimalaminaatin laatuun. Tutkimus tehtiin, koska laminaatin toinen lisätty liimakerros oli havaittu kärsivän laatuongelmista.

Kirjallisuusosa laadittiin tukemaan ymmärrystä liimojen ja liimautumisen periaatteista, sekä auttamaan kokeellisen osan suunnittelua.

Työn kokeellisessa osassa tutkittiin infrapunalamppujen esikuivauksen vaikutusta liimalaminaatin ominaisuuksiin. Tuotannosta tuotettiin kahdeksan erilaista näytettä erilaisista prosessin olosuhteista ja eri prosessivaiheista. Termogravimetrinen analyysi, Fourier-infrapunaspektroskopia, alkuaineanalyysi, pyyhkäisyelektronimikroskopia ja kuorintatesti valittiin näytteiden analysointiin.

Tulokset osoittavat, että esikuivauksella ei ollut selkeää positiivista, tai negatiivista vaikutusta lopputuotteen laatuominaisuuksiin. Sitä voidaan käyttää prosessissa 70 ˚C lämpöasetuksella, koska korkeammat lämpötilat eivät eroa vaikutukseltaan pienemmästä lämpötilasta.

ABSTRACT

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The Effect of Pre-Drying to the Quality of Adhesive Laminate for Medical Applications

Master's thesis

2025

112 pages, 49 figures, 11 tables and 0 appendices

Examiner(s): Docent Rama Layek and Antti Holopainen, Master of Science

Keywords: Acrylic, acrylate, adhesion, adhesive, laminate, medical

This thesis focused on determining the effects of an addition of pre-drying to the quality of an adhesive laminate that is utilized for medical applications. This was done because the product had been observed to suffer an adhesive failure occasionally after the addition of the secondary adhesive.

The literature review focused on acrylic adhesives, adhesion, lamination and drying methods as well as analysis methods for adhesive laminates and ammonia. It was constructed to provide support in understanding adhesion and aid in the planning of the experimental part of the thesis.

The experimental part studied the effects of the addition of infrared pre-drying on the final product of the production process of the adhesive laminate. Eight different samples were provided from different conditions and parts of the production process. Thermogravimetric analysis, Fourier infrared spectroscopy, elemental analysis, scanning elemental microscopy and peel tests were performed on the samples to observe any differences between samples.

The results show that there was no clear benefit to the final product when pre-dried. On contrary the addition of the pre-drying did not cause any negative effects to the product and could be used in the process at 70 ˚C setting, because higher temperatures do not change either adhesive properties.

SYMBOLS AND ABBREVIATIONS

Abbreviations

AFM/SPM	Atomic Force Scanning Microscopy
ATR	Attenuated Total Reflection
CSEM	Cryogenic Scanning Electron Microscopy
DMEA	Dimethylethanolamine
DTA	Differential Thermal Analysis
EA	Elemental Analysis
EDX	Energy Dispersive X-Ray Spectroscopy
ESEM	Environmental Scanning Electron Microscopy
FRET	Fluorescence Resonance Energy Transfer
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gass Chromatography
GMM	Gravimetry Methods
HPLC	High Performance Liquid Chromatography
IR	Infrared Radiation
ISS	Ion Scattering Spectroscopy
LPDE	Low Density Polyethylene
MFFT	Minimum-Film Forming Temperature
MS	Mass Spectrometry
OM	Optical Microscopy
OPA	o-Phtaladehyde
PAA	Polyacrylic Acid
PDA	Photo Diode Array

PE	Polyethylene
PET	Polyethylene Terephthalate
PSA	Pressure Sensitive Adhesive
PUR	Polyurethane
SANS	Small-Angle Neutron Scattering
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectroscopy
SPSA	Acrylic Pressure Sensitive Adhesive
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TXRF	Total Reflection X-Ray Fluorescence
ToF	Time-of-Flight
XPS	X-Ray Photoelectron Spectroscopy

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Literature Review: Adhesive Laminate

1 Introduction

Pressure sensitive acrylic adhesives have many utilizations in different field of industries. They can be divided into different groups depending on the material they are made of. Basic pressure sensitive adhesive formulations are silicones, acrylics and rubbers. In medical and pharmaceutical field, they are used in self-adhesive tapes, dermal dosage systems and protective films as an example. In dressings and tapes, they act as tapes and dressings to create a barrier against bacteria and control permeability of moisture and air. (Zbigniew, Agnieszka, 2011) Many of these adhesive products, like bandages, are adhesive laminates. The performance of the laminate is highly dependent on the adhesion quality of the adhesives.

When applied, adhesives have two types of failures. Adhesive failure occurs between the substrate and adhesive interface. Cohesive failure occurs within the adhesive. (Houtman, et. al., 2007) Failures in adhesion and within the adhesive are rarely caused by a single factor and can be caused by various factors such as incomplete curing, substrate surface preparation or moisture. (Ebnesajjad S., Ebnesajjad C., 2013) For example, adhesive curing process is sensitive to contaminants that can occur in the substrate surface. It can cause both adhesive and cohesive failures within the laminate. (Borges, et al., 2023) In medical application of adhesive laminates this can cause issues in product utility such as leave traces of uncured adhesive on customer's skin.

Good and safe performance of the adhesive and customer satisfaction is important, especially when medical applications are in question. This is why recognizing, preventing and minimising the failures in the adhesive performance is crucial. A challenge has been identified in production of adhesive laminate that is used in would dressing products. The secondary adhesive in the laminate has been observed to suffer an occasional adhesive failure. This failure causes the secondary adhesive to detach itself from the substrate and leave traces on the process machinery and sometimes customer skin. A probable cause for this adhesive failure is thought to be incomplete curing of the secondary adhesive caused by

contaminants on the substrate that remain after drying from earlier in the process. Main identities of these contaminants are thought to be water and ammonia. The goal of this research is to study if an addition of infrared pre-drying before the application of the secondary adhesive would be effective to remove the possible ammonia and water contaminants and this way improve the success of the curing and quality of the finished adhesive laminate product.

This work consists of two parts. The first part is a literature review about adhesives, adhesion, lamination methods, laminate drying methods and analysis methods for laminates. It is constructed to support the understanding and planning of the second part of the work. The second part is an experimental part where the pre-drying is trialled in the actual production process of the laminate. Samples are produced with and without pre-drying and analysed with various techniques to see if there is difference in amount of possible contaminants, appearance, properties or quality between samples.

2 Polymers

The produced adhesive laminate that is used to manufacture the wound care products uses acrylate waterborne dispersion, pressure sensitive adhesive that consists mainly of poly(butyl acrylate) polymer. This chapter discusses about polymers, polymerization and different types of free radical polymerizations.

2.1 Polymer Definition

Polymers are substances that consist of very large macromolecules that have molecular weights ranging from couple of thousand to millions of grams per mole. Polymers can be natural, such as proteins, cellulose or DNA. They can also be synthetic which constitute one of the most useful classes of materials that possess wide range of modifiable physical properties. Polymers are formed by different polymerization reactions, such as chain polymerization, addition polymerization or condensation polymerization. (IUPAC, 2025) These reactions link together monomer units to form the polymer macromolecules. Common synthetic polymers are for example poly(vinyl chloride), polystyrene and poly(vinyl acetate). Because of the variety of their properties, polymers are used in wide variety of applications such as adhesives, paints, fibres and flexible films. (Reusch, 2013)

2.1 Synthesis of Polymers

Polymerization is a process where polymers are manufactured from monomers. There are multiple pathways how monomers can be joined together where there are multiple reaction mechanisms. These vary depending on the functional groups of the reacting monomers. (Speight, 2011) In organic coatings the two common classes of polymerization reactions are chain growth or step growth reactions. All chain growth polymerizations have addition reactions, but addition polymerizations can have both chain growth and step growth reactions. (Jones, et. al., 2017)

If the monomer structure remains unchanged when the chains are linked together, the polymerization can be classified as addition polymerization. Addition polymerization is a

chain-growth polymerization and the common denominator in addition polymerization is that the reactions are chain reactions. (Speight, 2011; Jones. et. al., 2017) The most used polymerization reaction to produce vinyl polymers that are often acrylics is free-radical initiated chain growth polymerization. Radical polymerization is a polymerization method that involves the formation of free radicals that are caused by an initiator when it decomposes. It can convert wide range of different vinyl monomers into high molecular weight polymers. The decomposition of this radical can be caused by light, temperature, or redox reaction and this causes a reaction that forms a polymer network. The radicals' ability to tolerate many functionalities make radical polymerization versatile and easy to implement because the tolerance makes it compatible with wide range different monomers as well as solvents. Two types of radical polymerizations are free or controlled/living radical polymerization. (Poli, 2019) Out of these chain growth polymerizations solution and emulsion polymerization are most interest. Chain polymerization has four chemical reactions that are initiation, propagation, termination and chain transfer. (Jones. et. al., 2017) The general steps of free-radical chain polymerization is shown in figure 1.

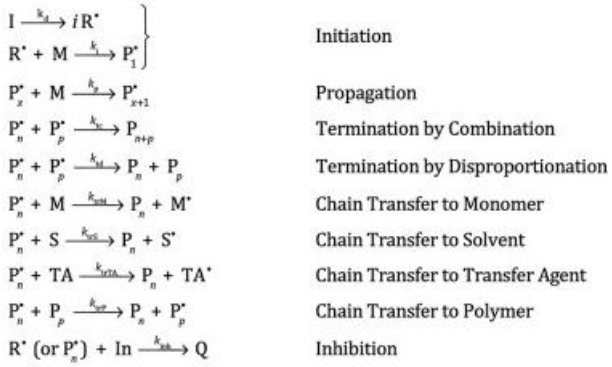

Figure 1. Steps of Free-Radical Chain Polymerization. (Lovell, Schork, 2020)

Initiator is usually an unstable compound that has symmetric structure and decomposes at the reaction temperature thermally to form two radicals. In initiation an initiator creates the free radicals that interact with the monomers', that are generally structured like CH2=CXY, carbon double bond. This interaction generates a product radical that is free to react forward with other monomer molecules like before and increase the polymer chain length. This chain growth continues until the polymer chain loses its active radical site, which can happen by chain transfer reaction with another species present in the polymerization or by termination reaction with another free radical. (Lovell, Schork, 2020)

In propagation monomer molecule adds successfully to the end of the polymer chain. Propagation reaction rate coefficient is dependent on the chain size and reduces with the addition of repeat monomer units. This reaction is essentially irreversible if the system temperature is kept below the ceiling temperature of the monomers. Termination occurs when two live chain radicals either undergo combination or disproportionation. Combination forms a dead chain if length that equals to the sum of the length of the polymer live chains. Disproportionation results in formation of two dead chains which have the length that is equal to the length of the live chains at the instant when they react together. (Lovell, Schork, 2020)

Other polymerization pathway is the step growth polymerization, where the linking monomers end up smaller than the initial monomers. This is because the complete monomer is not incorporated into the polymer molecule and it results in some common small molecule, usually water, to be chemically eliminated from the polymer structure. (Speight, 2011; Jones. et. al., 2017) The step growth polymerization is used to prepare coating resins for use as vehicles, or for cross linking after application to a substrate. (Jones. et. al., 2017)

2.1.1 Emulsion Polymerization

Emulsion polymerization is a radical polymerization method that is used to produce wide range of polymers for variety of uses such as adhesives, coatings and paints. (Paulen, et. al., 2013) Emulsion polymerization starts from emulsifying a monomer that are relatively soluble on water, into surfactant's aqueous solution. Monomer is dispersed into droplets by adding shear into the mixture and these droplets are stabilized by absorption of a surfactant. This absorption happens at the monomer – water interface. The actual polymerization is initiated by adding a free radical initiator to the solution that is water soluble. The polymerization proceeds and surfactant molecules stabilize the polymer particles. Most emulsion polymerizations are free radical polymerizations, but some controlled radical polymerizations are beginning to be used mostly for more specialist applications. This means they share the three stages of radical polymerization. (Lovell, Schork, 2020)

2.1.2 Solution Polymerization

Solution polymerization is a radical polymerization method where organic solvent is used as a medium for the polymerization reaction of organic monomers whit an initiator present. For example, toluene, cyclohexane, heptane, or other hydrocarbons are used as solvents for polymerization of other hydrocarbons and their derivatives. It is important that the solvent does not react chemically with the initiator in the process. The formed polymer can be soluble to the solvent. Insoluble polymers precipitate out of the solvent. Soluble polymers form polymer solutions which, for example, can be used directly in polymeric coatings for different substrates where the solvent is removed after application. Solution polymerization is used to produce polyvinyl acetate and polyacrylamide for example. Solution polymerization system has low viscosity, caused by the solvent, which makes stirring easier. It also has good heat control and removal, because of the possibility of solvent reflux. However, solution polymerization is not suitable for dry polymers. Complete solvent removal from the final product is also difficult. This can have negative effects on the polymer bulk properties. The solvent for the polymerization also has to be selected carefully so chain transfer reactions are avoided. (Umoren, Solomon, Saji, 2022)

3 Acrylics

Poly(butyl acrylate) used in the wound care products is an acrylate that is commonly used in adhesives. Acrylic is a more general term for polymers formed from acrylic acid where the simplest of these acrylics is acrylic acid. (Dunn, 2015; Kema, 2020) Acrylates are conjugate bases, esters or salts of acrylic acid and acrylic or methacrylic acid derivatives, where its monomers are vinyl group containing esters. (Kema, 2020) This chapter discusses about acrylics, their properties and utilizations.

3.1 Structure and Properties of Acrylics

Acrylates' vinyl group consists of two carbon atoms double bonded to each other that is directly attached to ester group's carbonyl carbon. Common acrylate monomers include butyl acrylate, ethyl acrylate or methyl methacrylate for example. (Kema, 2020) Figure 2 shows examples of the common acrylic monomers.

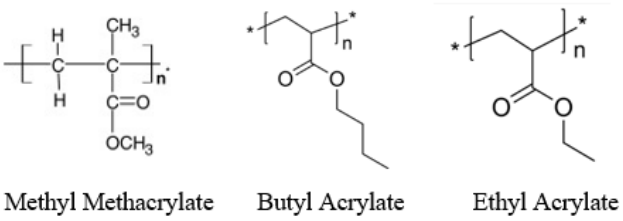

Figure 2. Monomers of Methyl Methacrylate, Butyl Acrylate and Ethyl Acrylate. (Polymer Science Inc. 2025A; Öztürk, Aydınoğlu, Hazar, 2023; Polymer Science Inc. 2025B)

This vinyl group is able to trigger polymerization and has multiple functionalities with amines or alcohols. (Kema, 2020) Vinyl group polymerization path is classified as free radical polymerization. (Polymer Science Learning Center, 2025) Polyacrylates are classified as vinyl polymers that are made from acrylate monomers. The acrylate monomer can contain an extra methyl group in its chain making them methacrylates. (Kema, 2020) The methyl group gives the polyacrylates different properties compared to a plain acrylate group. (Polymer Science Learning Center, 2016) For example, polymethyl acrylate is a soft, white and rubbery at room temperature. Compared to that, polymethyl methacrylate appears

clear and hard plastic with a glassy aspect at room temperature. (Corsaro, Neri, Santoro, Fazio, 2021) Differently as well, acrylic acid is a liquid with a tart aroma at room temperatures. (Brown, 2014) Polyacrylates have medium to high molecular weights and form emulsions with water. These emulsions offer low viscosity liquids that still have a high percentage of solids. (Dunn, 2015; Kema, 2020) The emulsions are produced when the acrylic monomer undergoes polymerization in the presence of an initiator and emulsifier with water as a solvent. They are water-based polymers that are produced from butyl acrylate, methyl methacrylate, acrylic acid and methyl acrylate for example. (Ruico Global, 2021)

The physiochemical properties of acrylate depend on the side chain substituents of the acrylic polymer and is a key to obtain the desired physiochemical properties for the polymer. The polymerization occurs by the vinyl group. (Corsaro, et. al., 2021; Corsaro, Neri, Santoro, Fazio, 2021) Acrylates have properties that make them rubbery, tough and soft. Physically they are transparent and elastic. (Kema, 2020) Poly(acrylic acid) and poly(methacrylic acid) and their anionic polyelectrolytes, and corresponding salts have good hydrophilicity and better ability to swell when compared to polyacrylates and methacrylates. (Corsaro, Neri, Santoro, Fazio, 2021) The polymeric products that are used in waterborne, solvent or solids reactive acrylic adhesives all have common characteristics in that they are durable, have good optical properties, water resistance and wide adhesion spectrum. They are also easily formulated and have low toxicity. (Skeist, 1989) Acrylic emulsions share the properties of acrylics for their application. They form soft and elastic as well as scratch and mar resistant coatings. They have great UV, water and weather resistance, good adhesion and flatness. (Lonroy, 2015)

3.2 Acrylic Acid

Acrylic acid, or 2-propanoic acid is simplest unsaturated carboxylic acid and it third carbon atom has both carboxyl group and double bond linked to it. The carboxyl group and double bond are the enablers for its ability to polymerize. Acrylic acid esters and salts are called acrylates that can combine with other monomers or themselves to produce polymers and copolymers. Acrylic acid is produced from propylene by two-step gas oxidation. (Goldberg I., Rokem J.S., 2009) At first step of the oxidation propylene is oxidized to acrolein by use

of a metal catalyst. The second step converts the reaction mixture in another reactor into acrylic acid with another type of catalyst. Both reactions have high reaction temperatures and are energy intensive. (Kharandiuk, et. al., 2022) Because of the high demand for propylene and acrylic acid, alternative methods to replace the conventional propylene oxidization has been researched. Other raw materials such as more available propane, or bio-based materials such as biomass or glycerol are considered. (Kharandiuk, et. al., 2022; Goldberg I., Rokem J.S., 2009) Polymers, or copolymers that contain carboxylic acid groups, like acrylic acid, tend to be pH sensitive because of the availability of their anionic carboxyl groups. (Bashir, et. al., 2020) At low pH polyacrylic acid (PAA) adopts a compact globular conformation which undergoes a reversible conformational transition in around pH level of 5. Increasing pH level initiates an ionization of the molecule where it expands into an open coil conformation that is fully solvated. (Swift, et. al., 2016) Forming of the carboxylate ions due deprotonation, causes electrostatic repulsion that causes swelling of the particle. (Bashir, et. al., 2020)

3.3 Utilization of Acrylates

Acrylic polymers and their emulsions have many utilizations. Acrylate polymers are utilized in dentistry and other biomedical applications as well as different cosmetic products, hair fixatives and packaging products. Acrylic acid forms its corresponding esters, acrylates, in the presence of alcohols. The acrylates have film forming characteristics and they are important materials in manufacturing plastics, diapers, coatings and adhesives, for example. (Kema, 2020)

The acrylic polymer emulsion films are alkali and water resistant due to the carbon-carbon bonds located in the main chain. (Okamoto, et. al., 1996) They are used in different adhesives, solvent-born coatings, emulsion paints, labels and printing inks for applications that need quick drying rates, as well as textile finishes and pressure sensitive adhesives, for example. The pressure sensitive adhesives of different tack strengths are used in automotive products, tape adhesives and high temperature, oil resistant elastomers. The applications also utilize the great aging characteristics and versatile adhesion properties of acrylic polymers. Acrylics also have applications as a plasticizer that improve the plasticity of other more rigid, brittle plastics. (Okamoto, et. al., 1996; Skeist, 1989; Kema, 2020) Acrylic materials can also

be used as thickening agents in laminating and packaging adhesives. (Skeist, 1989) For example, acrylic acid polymer is often used as a thickening agent in acidic conditions since it disperses into water and the formed dispersions thicken when the pH starts to increase. Methacrylates have reactive double bonds and form polymers easily. They have pH dependent water solubility which makes them useful in drug delivery systems as a coating agent. Methyl methacrylate has good ability to efficiently distribute stresses and interface strain energy. It can provide a buffering effect where it absorbs shocks from forces. This makes methyl methacrylate a great material to produce dental materials and bone cement for orthopaedic repairs. Ethyl acrylate is an ethyl ester of acrylic acid. It is a pungently smelling colourless liquid. It is reactive monomer that makes it useful in enhancing cleaning product effectiveness in liquid detergents. It is also used as paint and textile production and as reactant for alkyl acrylates in polymer manufacturing via transesterification. Butyl acrylate, or n-butyl acrylate is a butyl ester of acrylic acid. It is a soft monomer that is considered to be the largest volume acrylate ester that is utilized in preparation of acrylic, vinyl acrylic and styrene acrylic copolymers. The major application of butyl acrylate is in production of paints, sealants and adhesives. (Kema, 2020)

4 Adhesives

Adhesive is determined as a substance that can hold two materials together resisting separation by surface attachment. Adhesives can be natural, like animal glues, or synthetic. All synthetic adhesives are composed of polymers. The polymers that are used in adhesives are thrown into two categories: thermosets and thermoplastics. Thermoplastics, like polyesters and acrylics form a durable adhesion in normal temperatures and are softened by heating without degrading. Thermoset adhesives such as silicone and different rubbers, form permanent insoluble bond that is heat resistant and cannot be modified without degradation. (Pike, 2021) Adhesives can be classified with different methods for example by the adhesive carrier types whether they are wate-based, solvent-based, solids or hot melts. Other classifications can be by bonding mechanism, or bond formation type by either curing or drying. (Chemique Adhesives, 2025) This chapter discusses about different types of adhesives, application of adhesives and production of poly(butyl acrylate).

4.1 Water Based Adhesives

Water-based adhesives are classified as adhesives that are made from materials that are only able to disperse in water. Some of common water-based adhesives are polyvinyl acetate, polyacrylates and polyurethanes. There are two types of water-based adhesives: solutions and latexes. Solutions consist of polymers that are soluble in water or alkaline water. Natural polymers and soluble synthetic polymers are two sources of water-soluble polymers. Examples of a water-soluble polymers are different skin adhesives, methyl cellulose or polyvinyl acetate. Latexes are dispersions of polymeric material in aqueous medium that are stable. If the dispersion is stable and it consists of two or more immiscible liquids, that are held in suspension by an emulsifier, the dispersion is an emulsion. Synthetic latexes are aqueous dispersions that are manufactured by emulsion polymerization. (Ebnesajjad, 2011) Polyacrylates are suitable for making dispersion adhesives. (Skeist, 1989) Waterborne acrylic dispersions are important part of coating and painting industries. These dispersions are esters that are prepared from acrylic and methacrylic acids by emulsion polymerization. Acrylic water dispersion latexes have environmental advantages over solutions, because in most applications they don’t require any purification before use. (Nunes, et al., 2016)

4.2 Pressure Sensitive Adhesives

Pressure sensitive adhesives (PSA) are a class of adhesives that are characterized by instantaneous adhesion upon light pressure application. PSAs retain their fluid state after the bond is built between the adhesive and substrate and remain in permanently tacky state. This tack will let the adhesive to adhere to vast variety of different solid surfaces. The tack is defined as an ability for the adhesive to form a bond with the surface of another material upon brief contact and light pressure. The tack, peel strength and shear strength are the main adhesive properties that are considered to determine the PSA performance. These properties are influenced by the polymer that makes the adhesive which makes the careful selection of right chemical, physical and rheological properties to produce tailored PSAs a must. Most influential polymer factors to determine the inherent properties of the PSA are for example copolymer composition, its microstructure, molecular weight and molecular distribution. These factors affect the PSA's physical properties, such as glass transition temperature, and rheological properties like viscoelastic regions. Pressure sensitive adhesives are used in three major categories of pressure sensitive products. These are labels, tapes and protective films. PSA products can range from self-adhesive envelopes to sophisticated bioelectrodes. There are three major classes for PSA's depending on the technology they are produced with. They are produced with either solvent-based, emulsion based, hot melt and radiation cured polymerization. (Jovanović, Dubé, 2004)

Acrylics that are used in PSAs can be applied as solvent-free, solution, or water-borne systems and they are made from higher alkyl esters of acrylic acid where the dominant ones are butyl acrylate and 2-ethylhexyl acrylate. (Zbigniew, 2024; Zbigniew, Agnieszka, 2011) Commonly hydrophobic acrylic monomers like n-butyl acrylate or 2-ethylhexyl acrylate are used in PSAs to supply the adhesion tackiness for the adhesive. Ethyl or methylacrylate are used because of their hardiness to adjust the glass transition temperature of the PSA. Hydroxyl acrylates as well as vinyl carbonic acids are used to enhance the adhesion to different substrates and act as active groups for subsequent crosslinking reactions which provides better cohesion to the adhesive. Better cohesion provides more shear strength and reduces cold flow. (Czech, Milker, 2003)

4.2.1 PSAs In Medical Applications

Acrylic polymers that are inherently pressure sensitive are used in acrylic pressure sensitive adhesives. As mentioned, they contain combination of soft, hard and functional monomers. The acrylic PSAs for medical applications are produced mainly by polymerization from variety of different acrylic and methacrylic monomers. They can be either solvent or water borne as well as solvent free adhesives. (Zbigniew, Agnieszka, 2011) An example of a PSA chain of an acrylic copolymer is shown in figure 3.

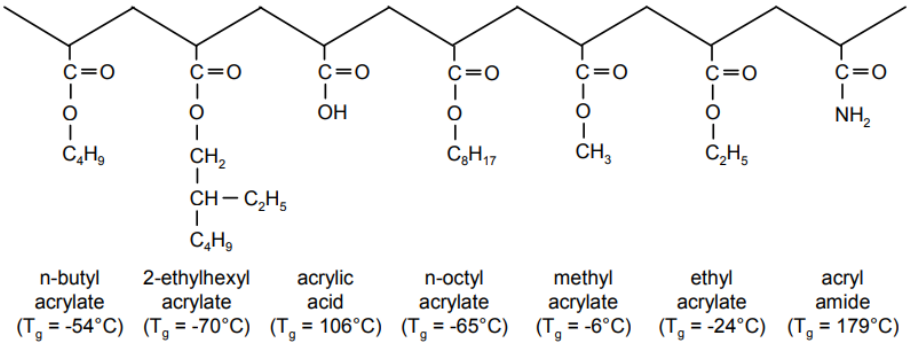

Figure 3. Acrylic PSA Copolymer Chain (Zbigniew, Agnieszka, 2011)

The acrylic PSAs can be tailored for defined product purposes. The main target application of the PSAs is skin adhesion, and self-adhesive medical products, but their application in medical field reaches also to different plasters, pads, transdermal drug delivery systems, OP-tapes, self-adhesive hydrogels, OP-tapes as well as surgical drapes. (Zbigniew, Agnieszka, 2011)

4.3 Synthesis of Butyl and Poly-butyl Acrylate for Typical PSA's

Butyl acrylate can be synthesized via multiple methods. One way is to utilize direct esterification from acrylic and methacrylic acids such as esterification reaction between acrylic acid and n-butanol, where water forms as a byproduct. (Engin, 1998; Ostaniewicz-Cydzik, et al. 2014) The esterification reaction between acrylic acid and n-butanol is shown in equation 1 below.

$$C_3H_4O_2 + C_4H_9OH \leftrightarrow C_7H_{12}O_2 + H_2O \qquad (1)$$

This reaction is slow and requires either homogenous or heterogeneous catalysts, such as sulfuric acid or ion-exchange resins. When produced from acrylic acid and n-butanol, butyl acrylate production is commonly a multistage process that is catalysed by a homogenous catalyst. In the production process there are two reactors and three distillation columns for the product purification. (Ostaniewicz-Cydzik, et al. 2014) Other option is transesterification of alcohols. For example, butyl acrylate can be produced from methyl acrylate transesterification reaction with butanol. (Engin, 1998)

Butyl acrylate polymerize readily with exposure to heat, light or catalysts. Free radical polymerization is the most common method for producing poly(butyl) acrylate and it can be synthesized from butyl acrylate monomers via free radical emulsion polymerization. (Hunt, 1993; Ballard, Hamzehlou, Asua, 2016)

4.3.1 Safety of Acrylate Adhesives

It is extremely important that acrylate polymers that are utilized for medical purposes do not contain toxic or aggravating components. (Zbigniew, Agnieszka, 2011) Especially in products that are meant for more intimate human applications, like medical products, the quality control for observing the amount of acrylate monomers in the polymer product is important. This is because acrylate monomers that are utilized to produce the polyacrylates have allergenic and irritating effects on exposure to the human skin or cause systematic effects if they penetrate through the skin. (Hunt, 1993) Studies show that acrylate esters show higher acute toxicity compared to methacrylates and shorter alkyl chains in the ester group show higher toxicity. (Waegemaekers, 1985) Adhesive materials that are made of acrylate monomers are especially important to take into consideration because they are likely to result or be used in intimate skin contact. The acrylate esters that enter the body through tissue exposure are prone to hydrolysis that result in the release of acrylic acid and the alcohol group that corresponds with the acrylate. With large doses, the unreacted acrylate ester monomers can be absorbed into the body and found remote from the application site, in organs. (Hunt, 1993)

4.3.2 Transesterification of Acrylates

Esters can be produced by various routes, but commercially direct esterification (Ficher esterification) and transesterification are the most common routes. (Devale, Mahajan, 2024) Transesterification is a reaction in organic chemistry where alkoxy group of an ester is exchanged by alcohol. (Clark, 2023) The reaction can be catalysed by multiple different catalysts, acids and bases. Industrially both heterogenous and homogeneous, as well as homogenized catalysts are used. (Devale, Mahajan, 2024) The homogeneous catalysts utilized are based on transition metal acylates or alkoxides. Most used are titanium or tin derivatives. (Gaudino, et al., 2005) In transesterification, another alcohol is used to displace the alcohol from the initial ester. Though the general mechanism of the reaction is the same, it varies depending on the reaction conditions. (Clark, 2023) Transesterification can be performed in acidic or basic conditions. Transesterification under basic conditions is done by treating the ester with an alkoxide base. Under acidic conditions, the ester is treated with an excess amount of alcohol with the presence of a strong acid catalyst, such as hydrochloric acid. (Ashenhurst, 2022) An example of transesterification under basic conditions is shown in figure 4. An example of transesterification under acidic conditions is shown in figure 5.

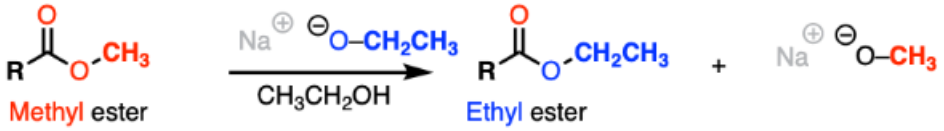

Figure 4. Transesterification Under Basic Conditions. (Ashenhurst, 2022)

Figure 5. Transesterification Under Acidic Conditions. (Ashenhurst, 2022)

The products of transesterification are another ester and the displaced alcohol. This causes the reaction to be reversible with an equilibrium constant close to 1. Le Chatelier's principle can be used to tip the reaction towards the products which is achieved easiest by using the reactant alcohol as a solvent for the reaction. (Clark, 2023)

4.4 Application of Adhesives

Adhesion can be considered as an interaction between two surfaces at atomic level. (Padsalgikar, 2017) Tying adhesive bonding into a single mechanism can be difficult, and it is usually caused by combination of different mechanisms. There are different theories on adhesion, where the most recent are mechanical interlocking, electrostatic, diffusion, wettability, chemical bonding, weak boundary layer and acid-base adhesion. These theories describe actions on different scales from macroscopic to atomic scale. (Ebnesajjad S., Ebnesajjad C., 2013) Polymers' ability to adhere to other polymers or non-polymer substrates are important abilities for many applications. The factors affecting their molecular level interactions include multiple factors such as surface chemistry and physics, rheology, stress and fracture analysis, polymer physics. (Padsalgikar, 2017)

Once applied to the surface; to achieve a bond between the adhesive and the substrate, the adhesive must be able to solidify. There are three methods to do this: drying because of solvent evaporation, chemical reaction by curing agents, pressure or heat, and cooling from molten liquid. (Ebnesajjad, 2011) Adhesives are either dried or cured to form a solid film. Drying adhesives means that they lose liquid components of the adhesive with evaporation as the carrier of the leaving solvent or water. Curing adhesives refers to an actual chemical reaction that happens between two components cross-linking or reacting where it results in a change from liquid to solid. Depending on the solidification method, the adhesive film has different properties, cured adhesives are more water and temperature resistant than dried adhesives. (Apollo Roofing, 2023) The drying of acrylics is discussed later in the research. Acrylic adhesives cure by free-radical addition polymerization reaction. Differently polyurethane and epoxy adhesives cure by condensation polymerization reaction. (Special Chem, 2025) As said before, free radical polymerization reactions are chain growth reactions, where solution and emulsion polymerization are most interest. (Jones. et. al., 2017) Molten liquid adhesives form a bond with the substrates by cooling. These adhesives are classified as hot melt adhesives. (Ebnesajjad, 2011)

4.4.1 Bond Formation of Different Adhesives

Pressure sensitive adhesives form pressure sensitive bonds. The adhesive bond forms at room temperature when light pressure is applied, without any chemical reactions. (Dexterials, 2024) The adhesion between the adhesive and substrate forms in three stages. In the first stage a compressive force is applied to the adhesive film which provides the adhesive bond formation. Second stage starts when the bonding force is withdrawn, and the adhesive is allowed to relax. This relaxation releases a part of the energy expended at the first stage. The final third stage is the adhesive bond failure under debonding stress. (Novikov, et. al., 2005)

Contact adhesives are well known solution-based rubber adhesives where different rubbers such as natural, butyl and polychloroprene rubbers are widely used. (Handbook of Plastics Joining, 2009) Contact adhesives form bonds by diffusion process in which the adhesive is applied to both surfaces that are to be joined. To achieve good polymer chain diffusion the adhesive has to have good wettability by smooth or rough substrate surfaces and to have fitting viscosity. After the adhesive is applied to the substrate, a solvent evaporation happens either spontaneously or is forced. This forms a dry adhesive film on both surfaces. The two dry adhesive films are then placed in contact to develop the adhesive bond. (Martín-Martínez, 2002)

Hot melt adhesives are thermoplastic adhesives that are applied as melts and form their bond and strength through cooling. They generally melt at temperatures ranging from 65 to 180 C, where usually they melt at 79.4 ˚C. Hot melt adhesives are applied commonly at higher temperatures from the melting temperature. It ranges from 149 ˚C to 288 ˚C. (Ebnesajjad, 2011)

In thermosetting, the adhesive goes through a curing process that is irreversible where it becomes substantially infusible and insoluble. Thermosetting adhesives are both condensation and addition polymers. (Ebnesajjad, 2011) Thermoset materials cannot be heated and melted after their cure. For application depending on the adhesive, thermosetting adhesives can require only contact pressure or they can on the other hand need considerably high pressure. Thermoset adhesives can be divided into one – or two-part systems. One part system commonly requires elevated temperature in their cure process. Two-part systems can cure in room temperatures and cure fast in elevated

temperatures. The two systems also have differences in shelf life, where one-part systems have shorter shelf life. (Ebnesajjad, Landrock, 2015)

4.4.2 Curing

Curing is a process occurring during the use or application of the adhesive where the properties of the adhesives are obtained or improved by chemical reactions or component cross-linking reactions. These reactions result in a physical change of the adhesive from liquid to solid. (Apollo Roofing, 2023; Wanying, et al. 2021) Types of curing can be categorized into light-initiated curing, moisture curing, or thermoset curing. In light-initiated curing, ultraviolet light is typically used to activate the curing process. Thermosetting curing is initiated by heat. (Wanying, et al. 2021) Moisture curing diffuses moisture (water) from atmosphere or the substrate into the adhesive where it reacts with the polymer group. (Sun, et. al., 2020)

Successful application and curing of adhesives are important since they tend to be sensitive to contaminants on the substrate surface. These contaminants can be absorbed by the substrate or the adhesive during curing or prior. They can also remain in the adhesive or substrate interface. If the contaminant remains in the interface of either component, it can act as a physical separation between the adhesive and substrate which interferes with the inter-molecular bonding between them. This can result in weak bonding or even debonding of the adhesive and substrate. The contaminant effect on the adhesives is a complex topic because it depends on the adhesive and contaminant as well as their interactions with each other. (Borges, et al., 2023)

4.4.3 Thickening

Thickening of acrylic latex materials is useful to control their flow properties because they can be kept in lower viscosity and thickened later in the process to achieve the desired processing as well as application properties. (Otakar, et al., 2001; Kheirandish, et. al., 2008) This is important in the stage of their production and industrial practice and when acrylic dispersions are used waterborne coatings, they require thickening. (Nunes, et al., 2016) Rheology of the organic acrylic adhesives can be controlled with rheology control agents or

modified by adding thickeners to the adhesive that increases their apparent viscosity. (de Souza, et. al., 2017; Kheirandish, et. al., 2008) There are two ways to thicken waterborne acrylic coatings: by adding an associative thickener, or by alkali neutralization. (Nunes, et al., 2016)

In associative thickening, a thickener that is soluble in the continuous water phase is absorbed on the surface of the coating formulation particles. This causes particle bridging that forms a network of particles where particles that have absorbed chains work as a node. This raises the apparent viscosity of the emulsion. (Nunes, et al., 2016) These thickeners are a subclass of associative polymers that form super molecular structures in the solution. The polymers used in coatings are usually long-chain and nonpolar hydrocarbon groups spaced along either the backbone or end of the polymer chain. Examples of associative thickeners are ethoxylated polyurethanes, or hydrophobically modified alkali-swellable emulsions. (Jones, et. al., 2017)

For acrylic copolymers that contain some amounts of acrylic acid, the polymer dispersions show a good thickening efficiency. An addition of a thickening agent to the organic polymer emulsion triggers the increase of the viscosity in the material flow. (Otakar, et al., 2001) In thickening triggered by alkali neutralization, the thickeners that are used can consist of acrylic acid, or methacrylic acid that is present in some amounts in the main organic emulsion. (Nunes, et al., 2016) The mechanism of alkali neutralization of acrylic acid monomer with sodium hydroxide is shown in figure 6.

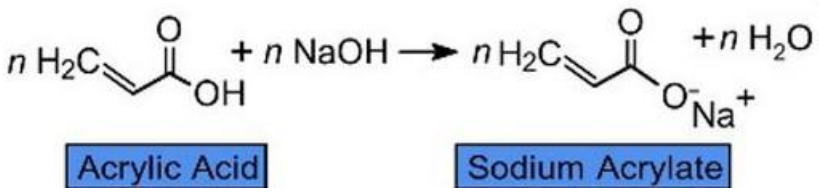

Figure 6. The Alkali Neutralization of Acrylic Acid with Sodium Hydroxide. (Takematsu, et. al., 2023.)

The amount of thickeners that are used in alkali neutralization vary from about 2 to 50 w%. (Nunes, et al., 2016) The carboxyl group can participate in alkali neutralization using different bases like NaOH. As the carboxyl groups are neutralized by increasing the pH of the adhesive, the formed carboxylate groups favour a solubilization of part of the macromolecular chains, which increases the viscosity. (de Souza, et. al., 2017)

4.4.4 Mechanism of Thickening

The mechanism of the thickening is thought to be caused by the swelling of the polymer particle. The swelling is assumed to be caused by the alkalization of the acidic material where the electrostatic repulsion between the present ionized carboxylic groups in the polymer chains with the thickener causes the particle swelling. This swelling increases the steric and electrostatic interactions between the particles. The structural changes bring a deformation in the flow field because of the high resistance brought upon by the changes. This causes increase in non-Newtonian viscosity. (Otakar, et al., 2001) Figure 7 shows an example of alkali thickening of latex with diethylethanolamine (DMEA).

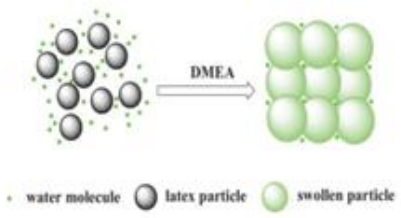

Figure 7. Thickening of Latex with DMEA. (He, et al., 2015)

In the figure 7, DMEA is added to the alkali-swellable latex dispersion. The latex particles swell with a large amount of dissociative water. This increases the electrostatic repulsion between the carboxyl groups and stretches the polymer chains causing larger hydrodynamic volumes of the latex particles. The packed up swollen particles confine the residual water molecules within their gaps. (He, et al., 2015)

4.4.5 Ammonolysis

The monomers that have not polymerized are more chemically reactive than the high molecular weight polymers that are more resistant to chemicals. (Kemal, 2024) This is because monomer structure is simpler than the usually more complex and diverse structure of polymers that have varying configurations between linear, cross linked and branched. (PSIBERG, 2023) Esters in general have low reactivity, but they are reactive enough to undergo transesterification, hydrolysis, alcoholysis or aminolysis. (Ophardt, et. al., 2022)

Aminolysis is a type of reaction where in double decomposition the ammonia is split into amino function and hydrogen atom. The amino function becomes the part of the amine and hydrogen part of substituted radical, for example an alcohol. Other ammonolysis reactions are dehydration, where ammonia reacts to produce water and amines, addition where both fragments of the decomposition become part of the formed amine and multiple activity reaction that produces secondary and tertiary amine derivatives. (Speight James G., 2017) The reaction mechanism of aminolysis is shown in figure 8.

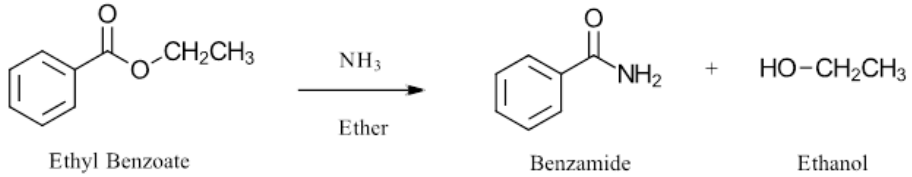

Figure 8. Aminolysis of Ethyl Benzoate with Ammonia. (Ophardt, et. al., 2022)

Hydrolysis, alcoholysis and ammonolysis can chemically depolymerize polymeric materials. Ammonolysis reaction can occur in catalytic or noncatalytic systems to break down for example polyesters such as polyethylene terephthalate (PET). The ammonolysis of the polyester produces a monomer amide and alcohol. In PET case the amide monomer formed is terephthalamide and alcohol ethylene glycol. (Clark, Shaver, 2024) This reaction is shown in figure 9.

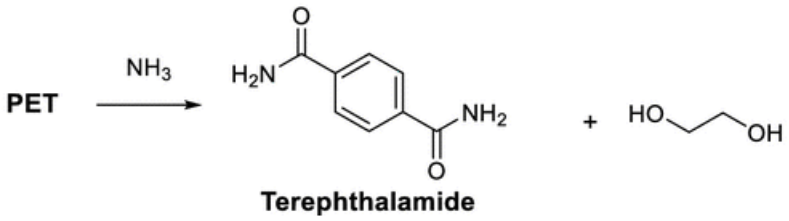

Figure 9. The Ammonolysis of PET. (Clark, Shaver, 2024)

This opens up a possibility of acryl amides being present in the acrylates exposed to ammonia.

5 Lamination Methods

Lamination is a process where two or multiple layers of materials are bonded together, creating a single composite structure. The process consists of applying an adhesive between layers and bonding them together using pressure, heat or both. The applied adhesive can be in form of film, powder or liquid. Lamination is an important technology for product manufacturing since it has variety of applications. Lamination offers several benefits to products, for example increased stiffness, moisture resistance, protection and barrier properties. Many different industries utilize lamination. These include electronic, automotive, packaging and construction industries. (KDWPACK, 2023) This chapter discusses some of the most common lamination methods.

There are multiple ways to add adhesives to films and produce multi-layered laminates depending on the involved materials and product requirements. Wet adhesive lamination process coats a film with adhesive that is then attached by this adhesive to a second film. The layers create a bond under pressure when they are pressed together. Solventless lamination is similar to wet lamination, but it does not require a use of a solvent. Dry lamination process uses solvent or water-based adhesives onto a film after when the solvent is removed by drying. Extrusion lamination uses an extruder and extruder die to produce a molten resin layer between two films where they form a multilayer lamination. (KDWPACK, 2023)

5.1 Extrusion Lamination

Extrusion lamination uses an extruder to provide a layer of molten resin forced through a die of a certain shape to bring two film layers together. Extrusion lamination produces better thickness, puncture resistance and stiffness in the product laminates than adhesive lamination processes. (CP Flexible Packaging, 2024) An example of the basic extruder process is shown in figure 10.

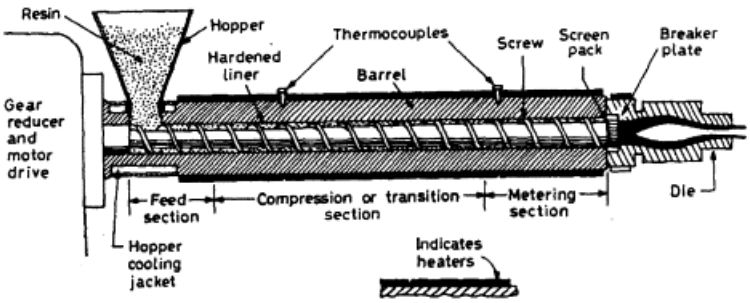

Figure 10. Extrusion Process. (Cheremisinoff, 2001)

As a concept extrusion is designed to convert a softened material continuously to a certain form. The base of this process is a screw conveyor set inside a barrel. A resin feedstock is fed into the barrel and screw from a hopper. The screw conveyor transfers and squeezes the feedstock material forward and along with the friction formed by the flow as well as added external heaters, the resin melts into a liquid stream. In some cases, the friction formed by the flow alone is enough to melt the feedstock material and keep it in molten form. As the material moves along the screw it builds up pressure that is highest at the die entrance. Before the die there is a screen pack to keep any bigger solid particles from entering the die. The extruder die is the part that determines the shape of the final product. After the product exits the die, it is cooled down generally either by water or air that is added by sprays, baths or cooled rolls. (Cheremisinoff, 2001)

Extrusion can be used to also produce multi-layered laminates. It can be considered as sheet extrusion where the adhesive material exits the extruder via slit die as a thin film. This process can be a coating process, where a film is coated with the material from the extruder, or a process where two sheets are laminated together by the adhesive added between them from the extruder. (Qenos, 2015; Dong Soo, et al., 2017) Figure 11 shows a typical paper/polyethylene laminate extrusion process. Figure 12 depicts an extrusion process where two films are adhered together.

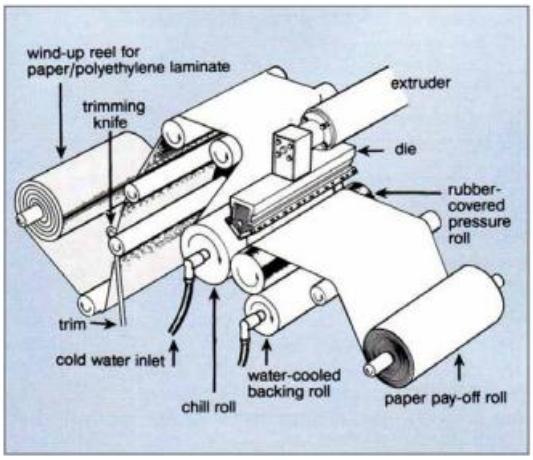

Figure 11. Paper/PE Laminate Extrusion Process. (Qenos, 2015)

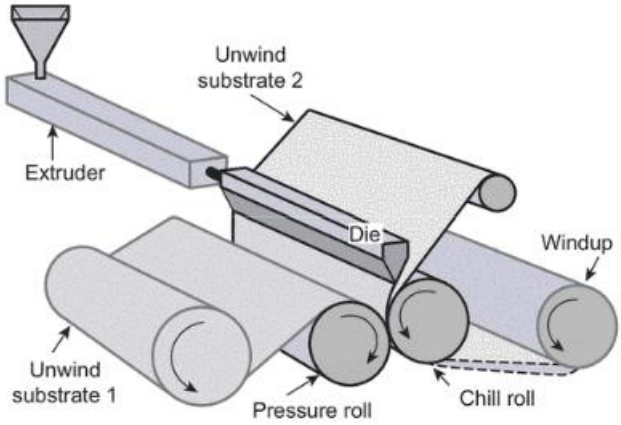

Figure 12. Multi-Film Extrusion Process. (Mount, Wagner, Giles, 2014)

Extrusion coating and lamination has variety of applications and with coextrusion it can produce very complex structures for food, industrial and medical packaging applications. Extrusion coating and lamination is used to produce for example fil laminates, dairy packages, foils, carpet coatings and photographic papers. (Mount, Wagner, Giles, 2014)

5.2 Roll Coating

Roll coating is a widely used method to apply coatings and adhesives to uniform cylindrical or flat surfaces, for example extrusion coated polyethylene (PE) paper and film. Roll coating uses a series of rollers to apply liquid coatings of certain thicknesses onto substrates. (National Polymer, 2024) There are different roll coating methods that can be determined by the number of rolls used in the process, the roll rotation direction or the surface texture of

the roll. (Shim, 2019) A film of coating liquid is first formed to the roller surface that is then applied to the substrate material by the roll. The amount of coating material applied can be controlled by the fluid rheology and the rotation speed of both the substrate and roll. (Shim, 2013) The film thickness on the roll can also be further controlled by an additional metering roller, that meters the coating film thickness onto the applicator roller. (Shim, 2019) The coating material can also be fed into the process by a pan or a nip.

5.2.1 Roll Coating Methods

Kiss roll coating is the most widely used and well-known of the roll coating methods. It is performed with a single roller that is immersed halfway into the coating material pan. This roll acts as both metering and applicator roll. (Texochem Industries, 2024) An example of kiss roll coating process is shown in figure 13.

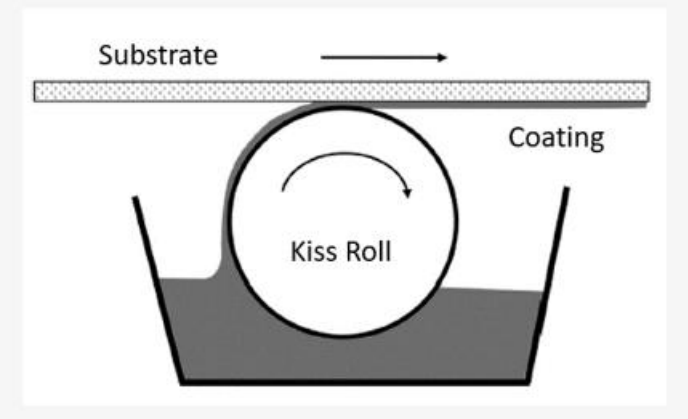

Figure 13. Kiss Roll Coating (Texochem Industries, 2024)

When the roll rotates, a film of the coating material forms to its surface. This thickness is determined by the hydrodynamics of the applied coating material. Part of this film transfers to the substrate material surface from the upper part of the roller not submerged into the coating material. The amount of coating transferred into the substrate material is determined by the rotating speeds of the roll and substrate and the fluid properties of the coating such as viscosity and surface tension. (Shim, 2019)

Other roll coating methods can have two to four separate rollers in the process. For example, a 3-roll nip feed coating that has three rollers is shown in figure 14.

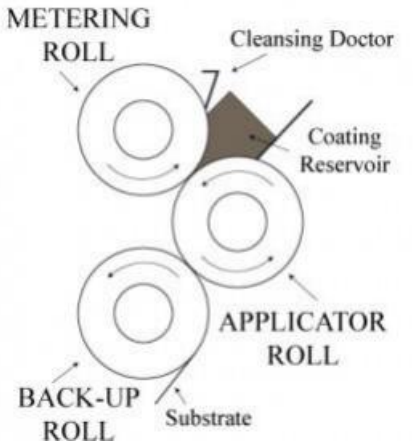

Figure 14. 3-Nip Feed Coating Method. (Performance Coatings International, 2014)

The system consists of a nip that feeds the coating material to the applicator roll and a metering roll. A metering roll controls and forms a film of wanted thickness onto the applicator roll. It has an attached doctor blade to clean up the roll surface to prevent any coating defects. A backup roll brings the substrate material into contact with the applicator roll. This 3-roller method can also be 3-roll pan coating, where instead of the nip, the coating is transferred onto the applicator and metering roll by submerging them halfway into it, like in kiss roll coating. In a four-roller method, a pickup roll is added to the process that transfers the coating material onto the applicator roll from the pan of coating. (Shim, 2019)

These multi-roller systems can be reverse metering or forward metering processes depending on the direction of the applicator and metering rollers. In forward roll coating the applicator roller and metering roller rotate in the same direction. Reverse roll coating methods have the application roller and metering roller rotate in the opposite direction. Reverse roller coating is a more common method since it produces smoother and more stable film. (Shim, 2019; National Polymer, 2024)

In gravure or engraved roll coating the applicator roll surface has an engraved surface that carries the coating material instead of a smooth surface. The engraving acts as a metering device in place of a metering roll where the amount of material applied to the substrate is determined by the engravings. The engraving cell depth, volume, angle, opening and space as well as the land area determine the coating liquid amount applied. A doctor blade is also used on the applicator roll before the substrate to remove excess coating. (Shim, 2013) An example of engraved roll coating is shown in figure 15.

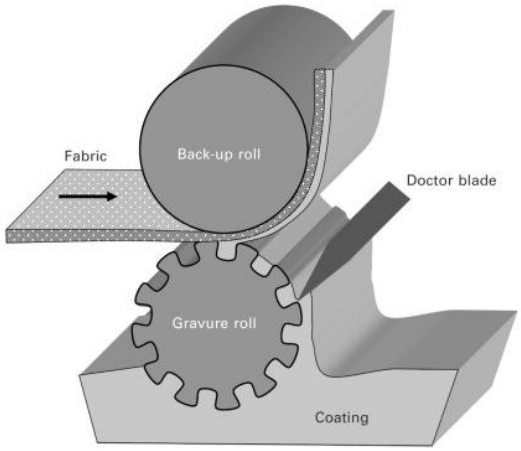

Figure 15. Engraved Roll Coating. (Shim E, 2013)

Knife coating is a method that can be used to produce continuous sheet material films. In knife coating the coating, or adhesive can be applied by other coating techniques, such as roller coating, but the coating thickness is then controlled and reduced by a doctor knife as it passes under it. This coating method works well when the wanted coating thickness is very thin. It also works efficiently with high-viscosity coatings since the knife pressure determines the film thickness. (Turner, 1999) An example of a knife coating method using rollers is shown in figure 16.

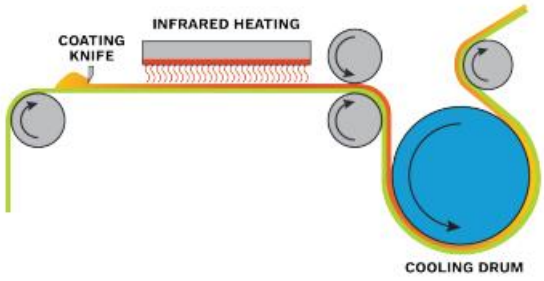

Figure 16. Knife Coating Process. (Bostik, 2023)

5.3 Spray Coating

Spray coating is a coating method where its basic principle is to produce overlay coatings in three steps. A first step is to create an appropriate coating material composition. These can be in rod, wire or powder forms. In second step sufficient kinetic and thermal energy is applied to the material to create a confined high energy particle stream that is propelled

forward in the third step towards a substrate using high pressure carrier gas. The impact with the substrate deforms the particles and the energy of the impact causes them form cohesive adhesive bonds with the substrate. If the spray coating involves only kinetic energy without heat, the process is called cold spray technology, in the presence of heat the process is a thermal spray technology. In cold spray coating process, the coatings are kept in relatively low temperatures compared to other different spray coating processes. Kinetic energy is solely applied to the coating material to apply it to the substrate. The cold spray technology requires specific nozzle design to achieve the gas to first compress and then rapidly expand causing the exiting gas velocity to reach supersonic levels. Coating materials for cold spray are powders that are injected into the nozzle by a carrier gas that is usually air, helium, nitrogen or mixture of them. The temperature of the process is kept below the melting point of the coating material. In thermal spray coating process, thermal energy is used in the coating deposition. The suitable coating material is first melted and then propelled to the substrate where it forms the coating. There are different sources for thermal energy used in thermal spray coating: from detonation of combustion gases in detonation gun process, from flame created by combustion gases in flame spray, from plasma that is created by electrical discharge in plasma spray and from electric arc in arc spray process. These processes have very high temperatures. For example, a flame spray process uses a flame temperature ranging from 3000 to 3300 ˚C. (Sudhangshu, 2018) Figure 17 shows an example of a flame spray process.

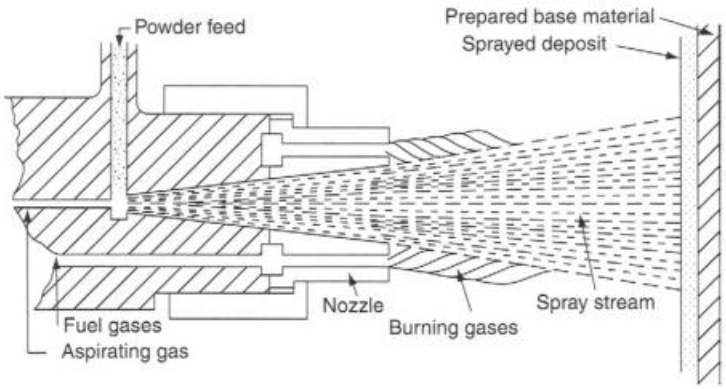

Figure 17. Flame Spray Process. (Sudhangshu, 2018)

5.4 Transfer Coating

Transfer coating is a process which is utilized to create layered coatings by applying multiple layers of coating to a substrate in a single process. (Trelleborg, 2024) In the process, a continuous carrier, usually release coated paper, is coated with a resinous coating. The carrier then transports the coating resin through a heated oven. (Hearl, 1980) After the oven another layer of coating can then be applied to the carrier and similarly transported through an oven. Ovens are applied in between each coating layer to properly ensure the adhesion and curing of the coating. After the application of the last coating layer, the actual substrate is then unwound where it is then laminated onto the coated paper. The laminate then is led into a final oven that bonds the substrate to the coatings. (Trelleborg, 2024) An example of a fabric transfer coating process is shown in figure 18.

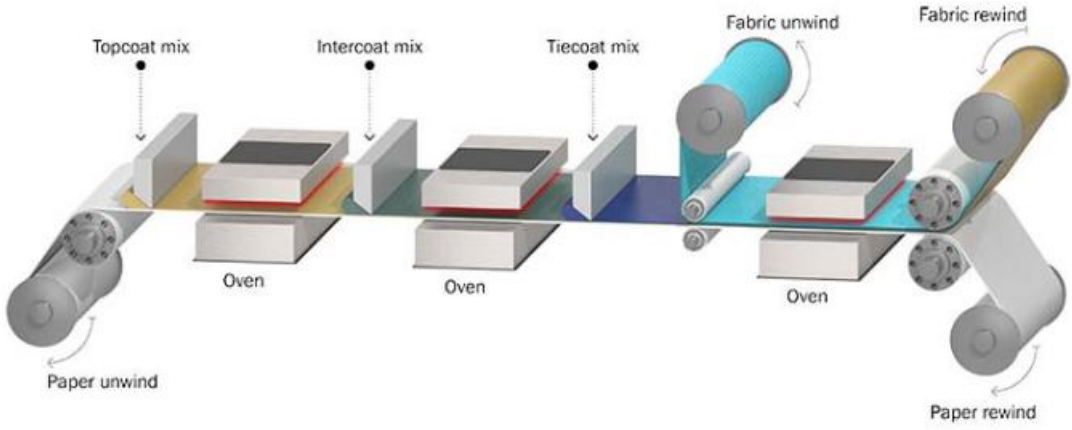

Figure 18. Transfer Coating of a Multi-Layered Fabric. (Trelleborg, 2024)

Transfer coating is commonly used to produce transfer coated polyurethane fabrics as well as upholsters, footwear and gloves. (Lamberti, 2020)

5.5 Viscosity and Solvent Effects on Adhesion

Adhesion of the applied coatings is important since it significantly influences the coating physical properties. Good coating adhesion is achieved by efficient interfacial contact between the substrate and coating. (Schuman, Thames, 2005) Viscosity is the most important

characteristic of liquid coatings and has effect on the adhesion strength. (Butt, et. al., 2008) Fluids can be considered to fall into two different categories depending on their response to applied forces. Newtonian fluids obey Newton's law of viscosity and can be considered to have absolute viscosity that cannot be affected by shear or application, but all coatings show significant changes in viscosity with different applied forces. This makes them non-Newtonian fluids that do not obey Newton's law of viscosity, and their viscosity enhances or declines under applied shear. (BioTrib, 2023; Butt, et. al., 2008) In addition to physical boundary surface requirements, viscosity must be considered when considering an effective bond between the adhesive and substrate. Viscosity of the adhesive must be low enough to allow the bonding functional groups an opportunity to orientate towards the substrate. Also, in addition to the viscosity, the surface tension of the adhesive needs to be lower than the surface tension of the substrate at those low viscosities. Otherwise, higher tension in the adhesive can result in coating defects such as dewetting effects resulting in uncoated areas. (Butt, et. al., 2008) Surface tension depicts the work or energy required to affect the intermolecular forces to increase the surface area of a liquid. The nature of the liquid and solutes in the liquid affect the intermolecular forces resulting in different surface tension properties between liquids. (Aldridge, Brar, 2023) Solid substrates have a constant surface tension, but the solvent evaporation and polymerization of the liquid phase can change its surface tension. This promotes the importance of understanding the rheology, flow and deformation of the coating used to achieve proper quality control. (Butt, et. al., 2008)

6 Adhesive Drying Methods

From the different types of pressure sensitive adhesives, solvent or aqueous emulsions require drying before lamination where the solvent or water is removed by evaporation. (Lightfoot, 2023) The drying process of water or solvent based pressure sensitive adhesives film formation goes through three stages. First concentrating the particles by the evaporation of water. Second, deformation of particles into space filling polyhedra and third, polymer chain interdiffusion among the particles as well as improved cohesive strength. So, the evaporation of the water causes the polymer particles to deform, and this develops the mechanical properties of the adhesive surface. In the drying process of the adhesive, the drying rate and softness of the polymer particle are most important parameters for the polymer. (Shiri, Ahmadi-Dehnoei, Ghasemirad, 2023)

Drying process optimization to achieve the required adhesive coatings is important. The dryer is often a limiting factor in production line, so understanding the dryer optimization and the drying process for the adhesive coating is important. The evaporation of the liquid is a complex step in processing of the coating material and time consuming. (Robeling et. al., 2021) The type of substrate where the coating is added must be considered when selecting the dryer and configuring the drying process. Thickness range, temperature resistance and tensile strength of the substrate are important parameters to consider when selecting the dryer technology. Coating thickness affects the drying process. (Pyradia, 2024) There are three main dryer types used in drying of adhesive coatings: Infrared, convection and flotation dryers. Infrared dryers use heat generated by electromagnetic waves to evaporate water quickly. (Metal Manufacturing Alliance, 2022) For surface drying or dehydration of thin films, sheets of paint, or textiles for example, infrared technology drying can be sufficient as a main drying process, but for thicker films infrared technology can be used as a preheating option before the substrate enters the main dryer. (Ratti, Mujumdar, 2006; Pyradia, 2024) Because of the IR penetration limits using it to dry thicker films results in uneven heat distribution. (Metal Manufacturing Alliance, 2022) Convection dryer can be used for thinner and thicker films as a main drying option. (Pyradia, 2024) They have good even heat distribution because of the high-speed airflow and dry products evenly. Convection dryers are also suitable for wide range of substrates. (Metal Manufacturing Alliance, 2022) Dual sided impingement dryers or flotation dryers can be used to

simultaneously heat both the substrate and coating sides. These dual side drying methods are suitable option for thick coat applications. (Pyradia, 2024) Flotation dryers are suitable for heat sensitive coatings and sensitive substrates. (Metal Manufacturing Alliance, 2022)

Viscosity of the adhesive plays a part of the visual coated surface of the adhesive coat layer since the convection dryer air flow impinges the coated surface. This can affect the surface especially if the viscosity is low. (Pyradia, 2024)

6.1 Convection Dryer

Convective drying uses hot circulating air to remove moisture from materials. Convective drying creates good even temperature profile and controlled environment to achieve gentle and uniform drying by circulating hot air to accelerate evaporation. The method is gentle and has low risk of damage even to more delicate materials. There are multiple different industrial dryers that use convection dryer technology. These can be belt, fluidized bed, rotary and tray dryers for example. (Sinothermo, 2023) Fluidized bed dryers are used for drying materials that are different kinds of powders, fertilizers, tablets, granulates or plastics. (General Kinematics, 2018) Rotary dryers are used widely in drying of various bulk materials in agriculture, mining and mineral industry, or drying of biomass for example. (Seim, 2024) Tray dryers are good for drying different types of materials that can require long drying times in non-continuous process such as crystalline materials, pastes, granular masses, chemical powders or equipment parts. Tray dryers are also suitable for sticky materials. (Killi, 2022) Belt dryers are good for continuous air drying and cooling process applications. They can handle large quantities of material with high moisture loads. (Tema Process, 2022)

Belt dryer is a continuous dryer system. It usually consists of a feeding device, conveyor belt, air circulation system and heating system. In the dryer, the material is transported through the dryer evenly distributed on a belt by a feeder device. (Haomai Drying, 2016) The belt can be multiple or single belt system. The dryer is divided into drying zone segments. (Tema Process, 2022) The conveyor speed is regulated to a fitting speed for the material drying by a regulator device. The drying process is performed by a fan transporting hot air through the material layer from either top to bottom or vice versa. The air humidifies as a result and part of it is discharged from the dryer by a drying box. The other part of the

air is mixed with new dry air. The dried material is discharged from the dryer outlet. (Haomai Drying, 2016) Belt dryers can also have integrated cooling zone at the end of the process, if the product needs to be cooled down before discharge. (Tema Process, 2022)

There are two different types of convective belt dryers depending on the direction of the air flow. In cross flow circulating belt dryer, the belt is made of steel mesh or porous plates where the hot air passes through the belt and comes in contact with the material. In horizontal type belt dryer, the air moves parallel to the material without any holes in the belt material. (Haomai Drying, 2016)

Conduction belt dryer has steam boxes distributed along the length of the dryer. These steam boxes are underneath the belt and the heat for the drying process is transported through a heat transfer wall. Usually, conduction belt dryers do not have fixed specifications, but are designed according to the process conditions. Conduction dryer is more suitable for heat sensitive materials or materials that oxidize easily. (Haomai Drying, 2016)

6.2 Flotation Dryer

High air speed in convection drying can lead to quality problems when drying coated materials due to surface non-uniformities. One recognized issue with the aggressive drying is a skin formation on top of the coated film that hinders the evaporation of the solvent. To achieve a high enough heat transfer for the solvent evaporation from the coatings, flotation dryers do not need as high air velocities. (Thompson, 2011) Flotation dryers are suitable for drying single sided coatings as well as films that are coated on both sides, or more delicate films that cannot be mechanically supported. (Glenro Inc., 2024; Thompson, 2011) Flotation dryer consists of two impingement dryers, where it has one for each side of the sheet. (Valmet, 2012) This double-sided air flow produces effective heat transfer per dryer length. (Glenro Inc., 2024) Air is led into the dryer through the drive side of the dryer. (Valmet, 2012) Flotation dryer has specialized nozzles throughout the dryer length both on the top and bottom, that create a bed of air that supports the product, technically floating it. (Glenro Inc., 2024) This flotation and heated air dry the substrate efficiently while supporting the substrate and eliminating the substrate contact with the roller. (Metal Manufacturing Alliance, 2022) The nozzle setup of the dryer is shown in figure 19.

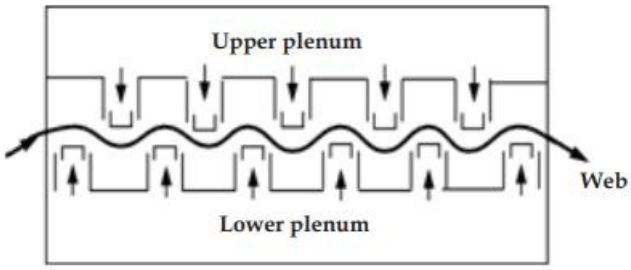

Figure 19. The Nozzle Setup Principle for a Flotation Dryer. (Thompson, 2011)

Typically, flotation dryer is heated with steam coils or gas burners. The heat source depends on the needed temperature. Gas burners can generate higher temperatures. (Valmet, 2012) The challenges in using flotation dryers are the proper nozzle arrangement. (Thompson, 2011)

6.3 Infrared Dryer

Infrared drying generates heat directly within the material using infrared (IR) radiation. The IR thermal radiation wavelength ranges between 0,78 to 1000 µm in the electromagnetic spectrum. The IR radiation can be classified into three categories depending on the wavelength. Short wave IR ranges from 0,78 µm to 2 µm. Medium wave IR ranges from 2 µm to 4 µm. Long wave IR ranges from 4 µm to 1000 µm. (Baldwin Technology Co., 2024) The wavelength and heat intensity, or penetration depend on the IR generator temperature where higher temperatures have shorter wavelength. The wavelength selection depends on the material. Some materials like paints, or varnishes benefit from the shorter wavelength radiation. Shorter wavelength is suitable for drying transparent materials, for example, since some of the short wavelength passes through the material without generating heat. IR radiation dries the inner layers efficiently before the hard surface forms on the coating. (Dryden, 1982) The radiation is applied to the material directly, so there is no other heat transfer medium needed in between. (Kent, 2018) The electromagnetic waves transfer heat efficiently within the coating because of the lack of the transfer medium and evaporates water and solvents efficiently. (Pyradia, 2024; Baldwin Technology Co., 2024) This is caused by the radiation energy that causes molecular oscillation and internal heating in the material. The temperature difference between the ambient air stream and vaporized water,

or solvent is the driving force in IR drying. The temperature difference causes a partial pressure gradient from inside of the heated material to outside that enforces the moisture removal. (Kent, 2018)

The IR dryers can be both continuous and batch types, but the continuous dyers are more common. IR drying usually involves a hot element within an IR lamp or bar generator as a heat source, to transfer radiation energy to a substrate that is lower in temperature. (Baldwin Technology Co., 2024; Dryden, 1982) Figure 20 shows an example of an IR lamp drying setup.

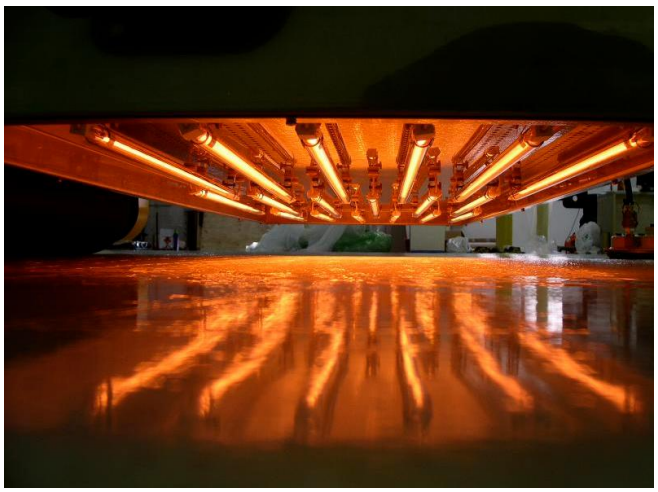

Figure 20. IR Lamp Setup for Drying. (Infralight, 2018)

There are two types of IR dryers depending on mode of heating. If the IR is obtained by an electric current that passes through a resistance. This resistance raises the temperature in the system. Common materials for the resistance are quartz lamps, quartz tubes, or metal sheath radiant rods. The other mode is gas-fired radiators have perforated plate where one of its surfaces is heated by gas flames, and this raises in temperature emits the radiation to the system. The surface temperature determining feature in a gas fired radiator is the porosity of the perforated plate. The usual operating temperatures of these gas-fired radiators range between 1500 to 1700 ˚C. (Ratti, Mujumdar, 2006) In addition to the IR heating element, the dryer can have reflectors that are the surfaces around the IR heaters. They are used to direct the formed radiation towards the dried material to improve the energy efficiency of the heating as well as improve more even heating. The driers also consist of air circulation systems in form of fans that circulate the air and remove moisture from the drying chamber. (EngiTech, 2024)

The IR drying is a more compact drying option compared to air dryers or ovens. (Baldwin Technology Co., 2024) They also are versatile in suitable materials for drying, offer uniform heating, are energy efficient and fast. (EngiTech, 2024) Gas-heated generators can give higher intensities and temperatures compared to the lamp generators. (Dryden, 1982) IR drying lamps can be efficiently controlled by simple on and off controllability to avoid the application of too much or little heat. The IR power setting can be adjusted to different production speeds or substrate materials. (Baldwin Technology Co., 2024)

6.4 Acrylic Adhesive Drying: Evaporation of Water, Solvents and Ammonia

Acrylic adhesives can be solvent or water-based adhesives. Solvent based adhesives are acrylic polymers that are in organic based solvents. Water-based acrylic adhesives, or emulsion, dispersion and solvent-free adhesives have acrylic polymers in water, where the water separates the adhesive molecules. When these solvents, or water are evaporated, the adhesive forms the bond with the substrates. (Self S.L, 2021) Water has advantages over organic solvents in that it is non-toxic, has no emission, or disposal problems directly attributed to its use and water is not flammable, making it safer to utilize. Organic solvents however have different evaporation characteristics. This enables a fine tuning in solvent-based coating evaporation rates. This cannot be done with water since it only has one kind of evaporation rate. Water also has high heat capacity and heat of vaporization, which makes its evaporation energy intensive. In similar available energy and vapor pressures, water also evaporates more slowly than the organic variants, though its vapor pressure does increase quickly when temperatures are higher. Water evaporation is also affected by the relative humidity. Relative humidity variations in water-based coatings can lead to problems. Water also increases equipment corrosion, often need surfactants, because of higher surface tension, and are vulnerable to foaming. (Jones, et. al., 2017)

Film formation process is an important part of adhesive films since it influences the film morphology. Film morphology affects the mechanical properties and permeability of the dry film. The film formation process depicts the polymetric dispersion transformation into an isotropic polymeric film in the drying process. This process can be depicted with three steps: first step is the solvent, or water evaporation. The evaporation brings the polymer particles closer together. In second step deformation of particles forms polyhedral cells. This structure

is weak. This stage is controlled by ratio between the resisting and driving forces of the polymer particle deformation, where main dominant factors are the drying temperature and temperature of the latex. The temperature where the particle deformation forces are dominant is the minimum film forming temperature. Drying above the minimum temperature provides homogenous and mechanically significantly superior films. (Jovanović, Dubé, 2004)

At the first stage of the film formation the solvent, or water evaporation from the film, the rate of evaporation can be considered independent from the polymer's presence. Evaporation rate is dependent on the vapor pressure of the solvent at certain temperature, surface area to volume as well as the air flow that travels over the surface. When the solvent evaporates, viscosity of the coating increases and free volume decreases. This causes the evaporation rate beginning to be limited by how quickly the solvent molecules can diffuse to the surface of the film. the solvent loss increases the glass transition temperature of the polymer, which further slows down the evaporation. The glass transition temperature increases with solvent evaporation from the polymer. The drying temperature should therefore be higher than the solvent-free polymer's glass transition temperature. The temperature therefore needs to be higher than the film formation temperature if the glass transition temperature is higher. (Jones, et. al., 2017) The final stage in the film formation consists of the further coalescence if the polymer particles. Interdiffusion of the polymer molecules across the boundary between adjacent particles form the cohesive strength of the film. The diffusion depends on multiple parameters in the process or polymer. Temperature and pressure as well as the molecular weight of the polymer and presence of plasticizer compounds, like solvents, affect the diffusion. (Jovanović, Dubé, 2004)

During application and cure of the water-borne coating, its evaporation rate depends highly on humidity and temperature variations. Above critical humidity level, water evaporates slower than any organic solvent. If the relative humidity approaches 100 % water might start to be absorbed into the coating rather than evaporating. In middle ranges the relative humidity effects can be controlled by increasing the temperature. (Jones, et. al., 2017)

Ammonia is highly soluble in water because of the hydrogen bonding between water and ammonia molecules. Aqueous solution of ammonia is considered to be weak bases, because of formation of ammonium and hydroxyl-ions (OH^-) that form from H_3O^+ or proton addition to ammonia from the water. (Lyle Kenneth. 2015; Appl, 2011) However, equilibrium for

this is shifted strongly to the free ammonia side. (Appl, 2011) This is why it can be used to control pH of other solutions.

In the process complete ammonia evaporation is required. Ammonia evaporation depends on the system conditions that control ammonia volatilization. The ammonia conversion to ammonium and vice versa is an equilibrium reaction whereas said, the equilibrium is shifted significantly to ammonia side. pH level influences ammonia evaporation. More alkaline conditions promote ammonia evaporation, while acidic or more neutral conditions, where pH ranges from 5 to 7, ammonia evaporation is lower. At pH 7 and above, ammonia evaporation is higher. (Dari, Rogers, Walsh, 2019) This is because with high pH levels ammonium ions are converted to ammonia, making it more available to evaporate. (Dykstra, et. al., 2014) With pH levels 6 or above, ammonia starts to evaporate with water. (Ramm-Schmidt, Laajaniemi, Koistinen, 1999.) Increased temperature and ammonia concentration increases ammonia evaporation. (Dari, Rogers, Walsh, 2019) The ammonia evaporation decreases as the concentration and temperature decrease. (Corruchaga, Casal, 2015) Ammonia itself evaporates at - 33,3 ˚C and free ammonia will evaporate from and with water when heated. This is different for dissolved and ammonium ion forms of ammonia. (Engineering Toolbox, 2003; Delmarva Water Solutions, 2019) With this it can be considered that in the drying process ammonia evaporates fast at the start of the dryer but slows down over time due to the decreasing concentration and pH level. Ammonium cation can form salts with different anions, depending on what is available. These anions can be halogens or other molecules such as carbonate or sulphate ions. (Alfa Chemistry, 2025) These salts have high boiling temperatures, for example ammonium chloride has a boiling temperature of 338 ˚C. (National Center for Biotechnology Information, 2025)

7 Analysing Adhesive Laminates

The functionality and customer satisfaction of the adhesive products depends on good quality control and development of the product. This is achieved by utilizing pure high-quality materials as well as product research and development. Important part of quality control and product development is to find proper analysis and research methods to assure the product functionality. This chapter consists of types of challenges in producing acrylate polymers and laminates as well as different methods for analysing and recognizing failures in acrylates and adhesive films and laminates. Additionally, the end of this chapter discusses analysis methods to recognize the presence of ammonia and nitrogen from materials as well as the introduction to the main analysis methods for the experimental part of this work.

7.1 Acrylic Polymers' Chemical Analysis

In manufacturing acrylic polymers, each different acrylic monomer yields a homopolymer that have significantly different chemical and physical properties. (Sega, 2023) The physical, chemical and therefore adhesive properties depend significantly on the type and amount of the acrylic monomers, so determination of these acrylic monomers and their purity is important from quality control perspective. (Sega, 2023; Mai, et al. 2023) The impurities in the acrylics can have unwanted effects to the properties of the synthesized homopolymers or copolymers. (Sega, 2023)

Sega, 2023 paper on high performance liquid chromatography (HPLC) analysis of acrylate polymers demonstrates a liquid chromatography method, with a photo diode array (PDA) detector for analysing acrylate purities.

Acrylic pressure sensitive adhesives (SPSAs) are synthesized by copolymerization of different acrylic esters such as methacrylates and acrylates that consist of 4 to 17 carbon atom alkyl group, and hydroxyl, or carboxyl group containing monomers. (Mai, et al. 2023) Mai Matsueda, et al. 2023 quantitative analysis of acrylic acid in acrylic pressure sensitive adhesives by reactive pyrolysis, pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) was used as an analytical technique to study and determine the composition of different polymers.

Drzal Peter L, Shull Kenneth R, 2005 paper on a subject of adhesive failure of model acrylic pressure sensitive adhesives describes an axisymmetric probe test method for characterizing and studying PSA's performance. In the tests a probe is added to the PSA layer and retracted until adhesive failure occurs. The performance is depicted by PSA's tack energy or work adhesion.

7.2 Adhesive Failure

There are two types of failures to adhesive layers. If the separation failure occurs between the adhesive and the substrate, the failure is an adhesive failure. Separation failure within the adhesive, where both substrate surfaces remain covered by the adhesive, is a cohesive failure. The adhesive bond can also be so strong that it causes the substrate bond to fail, which is called a cohesive failure of the adherent. Bond failures rarely consist of only one type of failure. This is why the failure is often described as a percentage of adhesive and cohesive failures. The determination of the type of failures is important for quality control of the produced materials. Detection and characterization of bonding surfaces are important in the adhesion failure analysis. The surface analysis of the adhesives and substrate require various analytical techniques. (Ebnesajjad S., Ebnesajjad C., 2013)

Predicting and detecting the causes for adhesive failures can be challenging. There are various factors affecting the adhesive bond, like external and internal stresses and chemical internal and external factors. (Ebnesajjad S., Ebnesajjad C., 2013) The successfulness of the adhesion is also dependent on the substrate surface preparation, adhesive type and curing as well as the presence of different types of defects. (Omairey, Jayasree, Kazilas, 2021) Internal stress can cause the bond to fail since the substrate and adhesive share different physical properties and the adhesives' tendency to shrink during setting. These differences cause internal stress to the bond between the adhesive and substrate. The thermal expansion coefficients for the adhesive and substrate should be similar to each other to limit the internal stress occurring in the bond due to temperature changes. Chemical factors affecting the adhesion internally can be substrate's effect on the adhesive, plasticizers and staining. External chemical factors can be the effect of different chemical agents such as acids or solvents. The bond durability is affected by the rate the adhesive is applied and its orientation

to the substrate. Adhesives are also affected by different environmental factors such as moisture, oxidation, light and biological factors. (Ebnesajjad S., Ebnesajjad C., 2013)

Curing is an essential part in application of adhesives. Poor adhesive curing reduces the final strength of the adhesive that can lead to adhesive and cohesive failures. Poor partial cure can be the result of incorrect mixing of the adhesive system, wrong formulation of the adhesive, insufficient thermal exposure or poor following of the cure profile. (Omairey, Jayasree, Kazilas, 2021)

When drying water based acrylic PSAs, the particle coalesces and surfactant segregates to inparticle domains. This can cause pathways inside the adhesive film where moisture can enter. The moisture contained in the film can cause the film to lose some of its cohesive strength while enhancing its flow properties. This can cause significant changes in the film's tack, peel and shear properties. (Houtman, et. al., 2007)

Particle deformation mechanism in the water-borne coating film formation second stage plays an important role in the film formation microstructure and its other properties such as flexibility and strength. (Yi, et al., 2019) As a multi-material composite, laminate is significantly dependent on the efficiency on its layer performance, knowledge of the layer structure, layer chemical identity, layer thickness and layer compactness. These are determining factors in the adhesive laminate's quality control, failure analysis and lifetime assessment. (Yuliya, Chernev, Eder, 2014)

7.3 Adhesive Films and Laminates Analysis Methods

For surface analysis of films and laminates, various techniques can be used. Infrared spectroscopy (IR) uses electromagnetic radiation in the infrared spectrum to determine the chemical compounds that are present. (Ebnesajjad S., Ebnesajjad C., 2013) Chemical bonds absorb different amounts of infrared energy at various wavelengths that translates into an IR spectrum of a material that can be utilized for its identification. Infrared spectra can also be obtained from sample surface if obtaining the IR spectrum is impossible to obtain by transmission technique. In that case, a high reflective index crystal is used to obtain a multiple internal reflectance of the IR beam when it enters into the crystal at an angle.

(Ebnesajjad S., Ebnesajjad C., 2013) The principle of the IR surface analysis with the crystal is shown in figure 21.

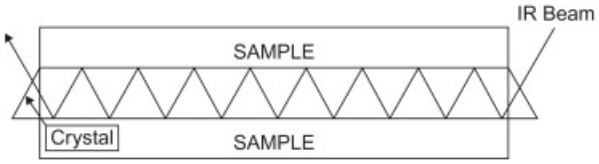

Figure 21. The Principle of the IR Surface Analysis with a High Refractive Index Crystal. (Ebnesajjad S., Ebnesajjad C., 2013)

Raman spectroscopy utilizes light scattering at two different wavelengths: Rayleigh scattering and Raman scattering to acquire the energy difference between them as Raman shift. Raman spectroscopy can be used for qualitative analyses or discrimination of organic and inorganic compounds from mixed materials. (Ebnesajjad S., Ebnesajjad C., 2013)

Multiple surface analysis techniques that probe the material surfaces with ion beams such as Secondary ion mass spectroscopy (SIMS) are used for laminate and film analyses. These techniques strike the material surfaces with beam of ions that knock the atoms off the sample material which ionizes the atoms. The atoms can then be identified and measured with mass spectrometry. Ion scattering spectroscopy (ISS) is also used, that uses the beam reflection to identify the mass of the reflected atoms from the energy of the backscattered particles. (Ebnesajjad S., Ebnesajjad C., 2013)

Other techniques for surface analysis are different methods where the surface is struck with either x-rays in Auger spectrometry and energy dispersive x-ray spectroscopy (EDX), or x-rays in x-ray photoelectron spectroscopy (XPS) and total reflection x-ray fluorescence (TXRF). Optical surface structure analyses in microscopic scale can be performed using optical microscopy (OM), scanning electron microscopy (SEM), or atomic force scanning probe microscopy (AFM/SPM). The different analysis methods have variable analysis depths that have to be taken into consideration. (Ebnesajjad S., Ebnesajjad C., 2013)

XPS can be utilized to characterize polymer surfaces and is able to detect all elements excluding hydrogen. XPS measures photoelectron kinetic energy that translates into the binding energy of an electron which can be used to identify elements. XPS also provides shifts in binding energies between different atoms can be utilized to gain information about the molecule structure itself. SEM can be used to analyse plastic surfaces or any other surface that is able to survive in a vacuum. SEM applies a collimated beam of electrons that focuses

into a small probe to scan across a sample surface. The material and beam interaction result in electron and photon emission. The emitted particles are collected into a detector that yields information about the sample surface and produces a final product image of the surface. Transmission electron microscopy (TEM) has similar working principle to SEM, but the beam passes through the sample. The electrons scatter coherently or diffract from lattice plains in crystalline phase materials. This yields a phase identification of the material. The X-rays generated can be collected into separate detector to achieve qualitative elemental analysis. (Ebnesajjad S., Ebnesajjad C., 2013)

Yi, et al., 2019 research on the properties of solvent-based and water-borne butyl acrylate and styrene copolymer films utilized different techniques to study the water evaporation. These techniques include minimum-film forming temperature (MFFT), cryogenic scanning electron microscopy (CSEM), gravimetry methods (GMM), as well as environmental scanning electron microscopy (ESEM). Latex particle deformation and packaging stage is usually studied with TEM and SEM. Latex film coalescence and interdiffusion stage can be studied with fluorescence resonance energy transfer (FRET), transmission spectrophotometry and small-angle neutron scattering (SANS). (Yi, et al., 2019)

There are different analysis options for identifying contaminants and other reasons for defects in laminates.

Garrido-López, Tena, 2010 research on multilayer packaging delamination x-ray photoelectron microscopy, Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR) analyses were utilized to obtain and study the adhesion mechanisms between the surfaces and atomic composition of the different delaminated surfaces to recognize any contaminants on the material surfaces or that could cause delamination.

Yuliya, Chernev, Eder, 2014 research on spectroscopic investigations on thin adhesive layers in multi-material laminates studies the changes in adhesive layers of photovoltaic blacksheets to identify environmental effects such as temperature and humidity's effect on the adhesive layers. The study uses different spectroscopy imaging techniques, such as FTIR-ATR and Raman imaging. These techniques are thought to yield complete description on the compactness, thickness and chemical structure variations since they combine

chemical information, that's obtained from vibrational spectroscopy, with spatial information, that's obtained from microscopy.

Houtman, et. al., 2007 research on the properties of water-based acrylic PSAs in aqueous environments, atomic force microscopy was used to characterize structures and chemical composition of PSA films.

7.4 Mechanical Analysis

For all adhesives tackiness is a factor, and for pressure sensitive adhesives, tackiness is a very important factor for their performance. For research purposes it is possible to screen and quantify tack using different techniques. Adhesive industry uses different methods to measure tack, such as probe tack test, loop tack, quick stick and rolling ball test, depending on the product type. (Netzch, 2022) In probe tack test the adhesive tape is added over a cylindrical weight that has an annular opening. A probe that has a flat or slightly curved face is pushed through the annular opening and it makes contact with the tape. This contact has a sufficient extension to lift the weight which bonds the probe to the adhesive for a brief contact time. The probe is then removed at specific speed and the removal force is measured. (Everaerts, Clemens, 2002) An example of a probe test is shown in figure 22.

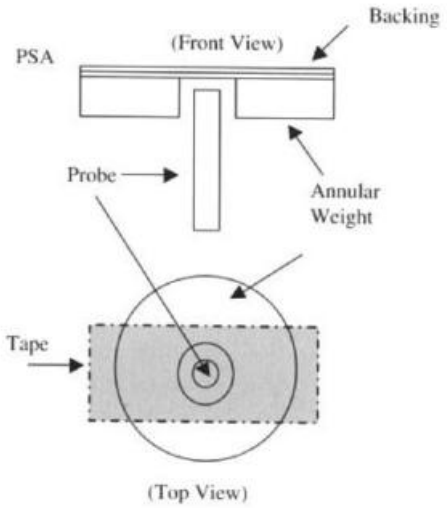

Figure 22. Probe Tack Test Setup. (Everaerts, Clemens, 2002)

Loop tack test uses a tear shaped loop of conditioned tape that comes into contact with a test surface that has a specific surface area. The force used for the tape is limited to the weight

of the tape. The ends of the loop are held in a tensile tester and the tester is engaged after a moment of contact time which removes the tape at specified speed. In rolling ball tack test, a steel ball of certain diameter is rolled down a grooved incline onto an area of pressure sensitive adhesive. Rolling ball tack is specified as the length of the ball travels before it stops. (Everaerts, Clemens, 2002)

Important abilities for adhesives are their bond formation and strength. Peeling force is one option to characterize the adhesion of materials and a peel test is basic to PSA characterization. Peeling force is determined as force required to separate the substrate from the adhesive. The force is calculated by using constant peel speed rate that is divided by the average peel force required. The peel test can be performed with different angles where 90 and 180 degrees are the most common angles. (Awalekar, Takalkar, Shinde, 2018)

Shear strength tests an adhesive's ability to resist creep under applied load. In the shear strength test a conditioned tape is rolled down with specific pressure and substrate. The substrate panel is fixed vertically or is slightly tilted. A weight is added at the other end of the tape and the test reports the time required for the tape to creep a certain distance. It is reported as shear strength. (Everaerts, Clemens, 2002)

Tensile testing puts the adhesive bond under stress. There are multiple test methods to test the tensile strength of an adhesive. A typical method is to place the adhesive between two metal rods that are polished to the point that they don't cause any butts that would cross the adhesive gap. The rods also need to be machined to a position where the surfaces are parallel to each other. (Pocius, 2021) An example of the rod method is shown in figure 23.

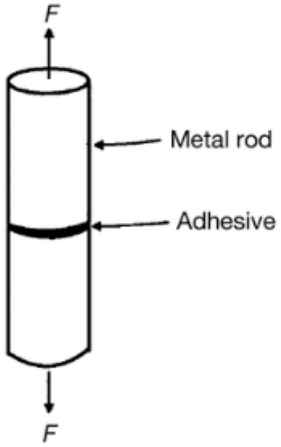

Figure 23. Tensile Test of an Adhesive Using Two Metal Rods. (Pocius, 2021)

The rods are loaded to tension till failure once the adhesive sets or cures. The results give tensile stress at break as well as mode of failure. (Pocius, Alphonsus V. 2021)

7.5 Recognizing Ammonia and Nitrogen in Analyses

There are multiple ways for ammonia detection for different levels of concentrations. Metal oxide detectors, catalytic ammonia detectors and polymer ammonia detectors are some of the most common commercial methods for ammonia detection. Metal oxide ammonia gas sensors are the most common ones and are typically based on SnO_2 sensors. The usual model is based on the metal oxide film that contains high number of grains that is contacting at their boundaries. The governed electrical behaviour by the double Schottky potential barriers at the interface of adjacent grains is caused by the charge trapping that happens in the interface if the grains. The height of the Schottky barrier determines conductance. Chemically reducing gas, like ammonia oxidizes at the grain surface that decreases the barrier height leading to detection. The metal oxide detectors are not selective to one particular gas but can be enhanced by using metals or additives to absorb only specific gasses. The lowest ammonia detection for metal oxide meter in literature is 1 ppm. (Timmer, Olthuis, van den Berg, 2005)

Catalytic ammonia sensors the charge carrier concentration in the catalytic metal of the sensor is altered by the concentration change of the gas that is detected. This causes a charge change that can be quantified utilizing a field effect device such as transistor or capacitor. The selectivity of catalytic sensor can be altered by different parameters like the catalytic metal, operating temperature and morphology of the metal layer. Ammonia field effect transistors use palladium gate material that results in 1 ppm detection limit. (Timmer, Olthuis, van den Berg, 2005)

Conducting polymer gas detector uses polymers for ammonia detection. The different polymer films react irreversibly with ammonia or ammonia can reversibly reduce the oxidized form of the polymer. This causes reduction of the polymer film material that is detected by a conduction change that can be measured. The ammonia is detected by a change in frequency of a resonator. Conducting polymer gas detection is suitable for resistometric and amperometric ammonia detection. (Timmer, Olthuis, van den Berg, 2005)

Ammonia can be optically detected by using a reagent that changes colour when exposed to ammonia, or optical absorption detection. Spectrophotometry techniques utilize the colour changing reagent as form of detection. pH paper is a common example since for example ammonia water is sightly alkaline. (Timmer, Olthuis, van den Berg, 2005; Li, et al., 2020) For ammonia, Nessler reaction is the best known and available example, tough the reagent is toxic and consists of dipotassium tetraiodomercurate(II) that is in a dilute alkaline solution. This method is commonly used to detect ammonia from water systems. Optical adsorption spectroscopy is utilized in the most selective and sensitive ammonia detectors. (Timmer, Olthuis, van den Berg, 2005) Spectroscopy methods can be used for ammonia detection where the change in spectrum versus a reference spectrum due to absorption of radiation at specific wavelengths is observed. UV and IR wavelengths are used to measure the ammonia concentration from the air. (Shah, Westerman, Arogo, 2006) The lowest detection limits of 1 ppb use a laser with a spectrograph. (Timmer, Olthuis, van den Berg, 2005) Ammonia can also be detected via chemiluminescence where it is converted into nitric oxide and the nitric oxide concentration is then read by chemiluminescence based NO monitor. Fluorescence is another optical method option for ammonia detection. (Shah, Westerman, Arogo, 2006) Optical detection methods for ammonia from water are similar to the gaseous ones. From water, ammonia optical detection applies spectrometric IPB method, fluorescence, fibre-optic detection and others. Spectrometric IPB method involves the solution colour change due ammonia oxidation into chloramine under alkaline conditions and chloramine reaction further with phenol. This reaction leads to colour change of the solution where the intensity depends on the ammonia concentration. In fluorescence detection, ammonia is reacted with o-phtaladehyde (OPA) and sodium sulphite in alkaline medium. The reaction forms a fluorescent compound that emits light in certain wavelength where the intensity depends on the concentration. (Li, et al., 2020)

Different chromatography methods can also be utilized for ammonia or ammonium-ion detection. Gas chromatography can be utilized to detect ammonia gases and ion chromatography can be utilized to detect ammonium-ions. (Michalski, Pecyna-Utylska, Kernert, 2021; Zaffaroni Riccardo et al. 2020)

7.6 Analysis Methods for The Adhesive Laminate

Five analysis methods were chosen for the analysis of the adhesive laminate, there are four chemical analyses, and one mechanical analysis method utilized.

7.6.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is an analysis technique where a substance is subjected to a controlled temperature change in a controlled atmosphere. The mass of the substance is monitored as a function of time or temperature with a sensitive balance and any changes in the mass are recorded. (PerkinElmer, 2015; XRF Scientific, 2025) Changes in the mass can be caused by a chemical or physical process. These are for example sample decomposition, oxidation or dehydration. TGA consists of a supported sample pan that resides in a furnace. The furnace can be heated up or cooled down depending on the experiment. Sample purge gas is utilized to control the environment. The gas used can be either reactive, such as oxygen, or inert such as helium. TGA can be utilized, for example, to characterize materials used in various applications such as foods, petrochemicals and pharmaceuticals. (PerkinElmer, 2015) It has good versatility for analysing variety of materials while providing quantitative information although the data interpretation can be complex. (XRF Scientific, 2025)

7.6.2 FTIR

FTIR spectroscopy is an analysis technique that is used to analyse materials by measuring their ability to absorb infrared light. Certain wavelength of radiation can induce the molecular bonds of a material to vibrate, and the different wavelengths are absorbed by the material. In FTIR this is achieved by passing infrared light through a sample. Different chemical bonds vibrate in specific ways which determines how much light they absorb in certain wavelengths. This absorption in different infrared wavelengths form a spectrum that can be used to identify molecules. There are various FTIR sampling techniques, but most used technique is attenuated total reflectance FTIR (ATR-FTIR). This method can be used to measure liquids, solids, semisolids, pastes and powders. The FTIR machine has a crystal

that the sample is placed on. The infrared light travels through the crystal and is reflected at the crystal-sample interface. Some of the light is absorbed by the sample and rest of the reflected light travels to the FTIR detector. Other common techniques for FTIR are transmission FTIR and reflectance FTIR. (Agilent Technologies, 2025)

7.6.3 Elemental Analysis

Elemental analysis (EA) is an analytical technique that can be used to determine elemental composition of chemical compounds by determining which elements are present in the studied material. The analysis determines how many percent by mass of each chemical element is in the studied material. In EA, the sample is fed into a reactor where it undergoes a controlled, dynamic combustion where it combusts into different oxides. The combustion happens in a temperature-controlled column filled with oxidizing-reducing catalytic bed. The gases created by the combustion are then directed to an analyser that is in most cases a simplified gas chromatograph. The chromatographic columns separate the gases that are then detected by thermally conductive detector. An example of EA setup is shown in figure 24.

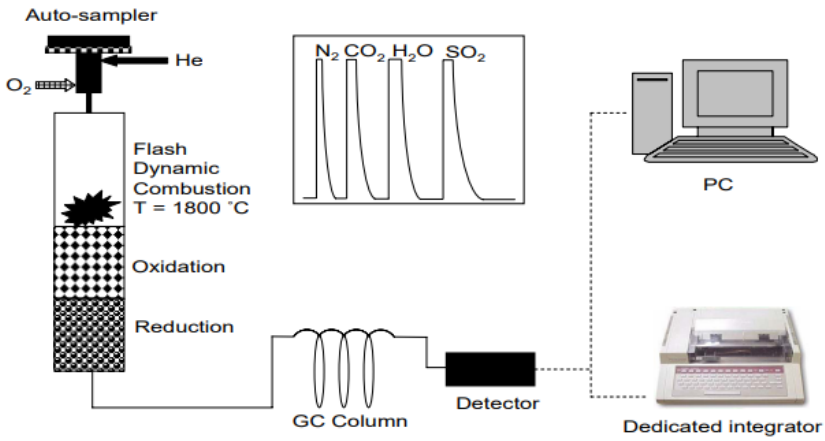

Figure 24. CHNS Setup. (The Royal Society of Chemistry, 2008)

Since EA determines the amount of carbon, hydrogen, nitrogen and sulphur, it is commonly called CHN or CHNS, depending on the application. For the analysis, the samples are coiled to either tin or silver crucibles. EA can use different atmospheres. Argon and helium are used to create an inert atmosphere. (Frąckowiak, et. al., 2022)

7.6.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is an analysis technique that is a type of electron microscopy. It is utilized to receive detailed surface information of samples and high-resolution images. SEM projects and scans a focused stream of electrons to a sample material surface. The projected electrons interact with atoms of the sample. This interaction produces various signals that are then used to obtain information about the surface composition and topography by the help of detectors. (NanoScience Instruments, 2025) SEM working principle is shown in figure 25.

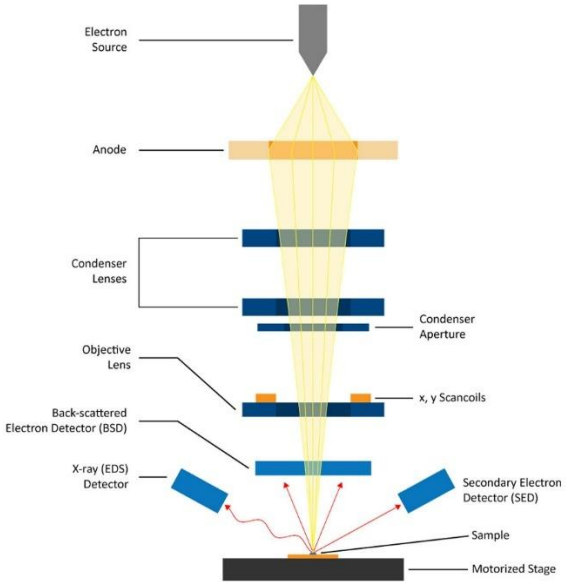

Figure 25. Working Principle of a SEM. (NanoScience Instruments, 2025)

SEM can be used to directly analyse wide variety of solid materials, but some samples require low-vacuum or low kV imaging to prevent surface charging and beam damage to the material. Gold and platinum coating is used on samples to minimize their charging. (NanoScience Instruments, 2025)

Experimental Part: Pre-Drying Effect on The Quality of Adhesive Laminate

Researching the subject of adhesives and laminate quality analysis reveals that there are multiple books on science, application of adhesives and general analyses for quality control methods of the adhesive bonds, surface and laminates. There is information about different kinds of adhesive quality analyses, if searched by just the adhesive, like silicone or acrylics. There are also different kinds of studies on quality control for multiple different industries that utilize the adhesives. However, it seems that the industries that information is easier to find are more industrial-related, like automotive, or paints and coatings. In the medical field the more common studies on adhesive curing or bond quality are in dentistry. There is a clear knowledge gap for self-adhesive or skin adhesive laminate product quality analyses.

This research studies quality control of a medical grade adhesive laminate for wound care products. The primary laminate is composed of a process paper, that is coated with an acrylate adhesive that contains mainly (poly)butyl acrylate. The acrylate adhesive is then dried when the water-medium and ammonia evaporate from the adhesive. After drying the secondary adhesive layer is added to the laminate. Huge success variation has been observed with the curing of this secondary adhesive. The worst defects recorded have been incomplete cure that leads to complete adhesive failure and separation of the adhesive from the substrate and leaving gooey traces onto the process equipment as well as skin when used. Adhesive curing reactions are sensitive to contaminants. The research focuses on the methods for recognizing these contaminants and their removal with an addition of IR-pre-drying.

8 Research Plan

This chapter explains the research plan for the experimental part. It goes over the sampling, trial run and the analyses for each sample.

8.1 Sampling and Trial Run

The study focuses on two different sample types depending on where in the process they are collected. The first sample material is an adhesive laminate that consists of silicone and LDPE coated process paper, primary layer of acrylate adhesive and polyurethane (PUR) film. These samples are collected after the first lamination process and amount to two different samples. Second samples are collected after the application of a secondary adhesive layer. These samples are acquired from the production line, where three samples are collected on different process conditions along the production line. The machinery is utilized to apply a secondary adhesive layer after the IR pre-drying. The conditions are without pre-drying and with the IR dryer on different power settings to control its heating capacity. The three samples from each trial run are collected from the start (standard acrylate laminate), in the middle (after IR-drying) and at the end of the production line (secondary adhesive applied and cured/finished product). These samples are materials before IR drying, after IR drying and after secondary adhesive coating and curing. A minimum of three samples is taken from each process step.

Note: For the analysis of ammonia, the PUR-film is substituted with PET film, since the nitrogen content in the PUR-film interferes with the results. If complete water removal is required, for example elemental analysis, samples are dried further using silica gel to avoid ammonia loss from samples.

The samples that are standard laminate contain either PUR-film or PET-film. The amount of material produced is 1000 m of PUR-film standard laminate and 500-1000 m of PET-film standard laminate. After the coating and lamination, the first samples are produced. The samples collected are cut into 10 A4 sized pieces. The acrylic laminate samples are marked as AnHi-001-PUR and AnHi-001-PET. After sample collection, the produced rolls are split into two 610 mm wide rolls and left to sit to stabilize for 1-2 weeks.

Note: The first 500 m of the test rolls include the acceleration ramp and process stabilization material, which are cut out and used in IR-heater tests before the actual trial runs. This is to make sure the lamps are working as intended.

10 A4 sized samples are collected right before the IR-drying and marked as AnHi-001-PRE.

The production line is run for 5 minutes where after the trial samples are collected immediately after the IR-heater. The sample cut is 1,5 m long. The samples collected after the IR-heater are produced in two different conditions:

1. At high heat, where web temperature reaches 100 ˚C.
2. At medium heat, where web temperature reaches 70 ˚C.

The collected samples are cut into 10 A4 sized pieces and marked as AnHi-001-100 and AnHi-001-70.

The last samples are collected after the addition and curing of the secondary adhesive coating. From the produced roll at the end of the production line 1,5 m piece is collected from the end of the roll that is then cut into 10 A4 sized pieces and marked as AnHi-001-END100 and AnHi-001-END70 for different temperatures.

Additionally, 10 meters of each trial sample for physical analyses.

The remaining trial base laminate is run into a reference roll without the IR-heaters. 10 A4 samples are collected from the end of the roll and marked as AnHi-001-REF. All the collected samples are packed into zip-lock bags.

The sample names are shown in table I.

Table I. Trial Samples.

Sample Name	Description
AnHi-001-PUR	Standard laminate with PUR-film.
AnHi-001-PET	Standard laminate with PET-film.
AnHi-001-PRE	Sample before IR-drying.
AnHi-001-100	Sample after IR-drying at 100 ˚C temperature.

Table I. Trial Samples. (Continued from last page)

Sample Name	Description
AnHi-001-70	Sample after IR-drying at 70 ˚C temperature.
AnHi-001-END100	Sample with cured secondary adhesive/finished at 100 ˚C.
AnHi-001-END70	Sample with cured secondary adhesive/finished at 70 ˚C.
AnHi-001-REF	Reference sample without IR-drying.

8.2 Analyses

The analysis methods are divided into chemical and physical analyses. Chemical analyses are focused on inspecting the laminate surface for water, ammonia and ammonium. FTIR is utilized to analyze the sample for any water residue. FTIR is able to provide a qualitative answer to whether water is present or not, but not a quantitative analysis of how much water there is. Thermogravimetric analysis (TGA) with mass spectrometry is chosen as the main analysis method in the detection of ammonia, ammonium and other possible contaminants in the laminate surface. The TGA analyses are performed in helium atmosphere, since nitrogen or air mediums contain nitrogen that distort the results. The TGA is set to operate up to 300 ˚C temperature to also be able to vaporize the possible ammonium salts in addition to water and ammonia. Elemental analysis is also applied to determine nitrogen presence that is used to detect differences between normal and pre-dried samples. For this, PET laminate sample is provided to be compared to the PUR sample. However, the success of this analysis is limited by the accuracy range of the analysis. Scanning electron microscope (SEM) is used to image the laminate surface if there are any observable differences between the samples.

Physical analysis methods are used to test bond strength and adhesion between samples. Primary acrylate adhesive adhesion is tested against glass surface according to Mölnlycke

test method T-1082. Secondary adhesive layer is tested for adhesion against steel according to Mölnlycke test method T-261.

Table II. shows the planned analyses for each sample.

Table II. Analysis Methods for Each Sample.

Sample	TGA	Elemental Analysis	SEM	FTIR	Physical Analyses
AnHi-001-PUR	X	X			
AnHi-001-PET	X	X			
AnHi-001-PRE	X		X	X	
AnHi-001-100	X		X	X	
AnHi-001-70	X		X	X	
AnHi-001-END100	X		X	X	X
AnHi-001-END70	X		X	X	X
AnHi-001-REF	X		X	X	X

9 Trial Run

This chapter contains the details of the trial run that was performed for the process to acquire the samples needed for the study. It consists of the steps, the sampling, and some observations from the trial run.

The trial run for this study was performed in two stages. First stage is the producing of the base laminate sample rolls, that contain paper, acrylic adhesive and a protective film. Two different rolls are produced: one where the protective film is PET, and the other contains PUR protective films. The first samples are collected from these rolls, AnHi-001-PUR from the PUR roll and AnHi-001-PET from the PET roll. Rest of the produced PUR-laminate roll is split into two different rolls for further processing at the secondary adhesive coating line.

9.1 Base Laminate

The base laminate samples that contain the acrylic adhesive and protective PUR-film, were produced at a bigger laminate production line. The production line consists of a lamination machine with multiple roll coater sections, and a dryer. The lamination process consists of unwinding the silicone and low-density polyethylene (LDPE) coated paper to the first roll lamination process where the acrylic adhesive is added with an applicator roll onto the paper surface. After the primary acrylic adhesive layer is added the laminate is then led into a dryer. The dryer consists of a chain of eight individual dryers, that form a drying zone. The dryers are set to peak of 120 ˚C around middle of the dryer chain and 80 C at the inlet and exit. However observing the local HMI feed, the web temperatures do not quite reach the set target temperatures. The web temperature measurements are between 80 to 90 ˚C across the drying zone. The ambient moisture in the process is recorded and was measured to be 60% in PUR-laminate production and 60 % in PET-laminate production. Ater the dryer, the main film substrate is (PET or PUR) laminated onto the acrylic adhesive surface. The produced rolls are wound into 1000 m product rolls. The PUR roll is split into two smaller rolls. The PUR and PET-rolls are wrapped into plastic for protection and set to stabilize for two weeks.

Comparing the collected AnHi-001-PUR and AnHi-001-PET samples, there is a significant difference between the lamination result and look of the PET and PUR films. The PUR-film

has smooth surface and is attached uniformly to the adhesive surface compared to the PET. The PET-film has more wrinkly appearance and worse attachment to the acrylate adhesive. The difference between the samples is shown in figure 26.

Figure 26. PUR-Laminate (left) and PET-Laminate (right).

9.2 Secondary Coating Line

All the other samples for the study are taken from the secondary coating line. The coating line consists of the roll feed, IR-pre drying, cooler, heated curing line and product roll up, where a protective film is added onto the secondary adhesive surface to keep the adhesive surface contaminant free. At the start of the lamination process, the PUR-film is peeled off from the laminate before it is led into the coating process. Next the laminate can be pre-dried, before it enters the application of the secondary adhesive. Then the secondary coating is added, where the laminate enters a heated conveyor where it is cured. After the curing, another protective layer is added into its surface and the product laminate is then rolled up for further processing. First, AnHi-001-PRE sample is collected from the end of the process. This sample is a normal stabilized PUR-film laminate without the secondary adhesive or pre-drying.

Next, the IR-lamps are engaged, but not the adhesive applicator, and samples that are produced next are AnHi-001-70 and AnHi-001-100. There are two IR-lamps in the dryer that can be heated to different temperatures apart from each other. The lamps are set to target 50 ˚C and 70 ˚C operating temperature. The temperature settings for the lamps to achieve

70 ˚C pre-drying conditions are 50 ˚C for the lamp 1 and 70 ˚C for the lamp 2. AnHi-001-70 sample is collected at the end of this stage.

When set to 70 ˚C, the laminate achieved the set temperature quickly in couple of minutes. The air cooler cycle after the IR-lamps can operate on reasonable settings at this temperature range. The 100 ˚C temperature posed challenges for the system. With the current setup, the 100 C drying temperature was not achievable as the cooling system was not sufficient and resulted in the lamps overheating. Because of this, the secondary dryer temperature and target temperature for the study was lowered to 90 ˚C. For this target temperature he set temperature for lamp 1 was 70 ˚C and lamp 2 90˚C. At this temperature, the production line was able to operate once the lamp internal safety limit was raised from 120 ˚C to 140 ˚C. AnHi-001-100 sample obtained from the end of this stage.

After the dried acrylic samples were acquired, the IR-dryer was disengaged and heated curing zone and secondary adhesive applicator were added to the process. The heated curing zone was used to thermos cure the secondary adhesive. AnHi-001-REF sample was produced with this setup. This sample corresponds to a normal product produced from the coater with normal settings.

Lastly the IR-dryers were engaged and the samples AnHi-001-70END and AnHi-001-100END were collected. These samples are pre-dried with the secondary adhesive.

There was a huge difference in the straightness of the paper between the pre-dried and normal samples. The pre-dried samples were more set and straight, where the normal samples tend to curl up when cut away from the roll.

10 Materials and Methods

There were five analysis methods used for the sample analyses: peeling force, TGA, FTIR, SEM and EA. This chapter goes over the preparations and execution of the analyses.

10.1 FTIR

FTIR analyses were performed immediately on site after the sample acquisition. This method was utilized to recognize the possible remaining moisture from samples and compare if there is any difference between the pre-dried samples AnHi-001-70, AnHi-001-100 and not pre-dried AnHi-001-PRE sample.

The FTIR instrument details are shown in table III.

Table III. The FTIR Instrument Details.

Model	Detector	Source	Scan Speed	Number of Scans
Frontier FT-IR/NIR	MIR TGS	MIR	0,2	4

Mid infrared light (4000 – 400 cm^{-1}) was used for the analyses. An identical rectangular piece was cut from each bigger sample sheet. This sample was set paper side facing onto the FTIR crystal and pinned down with the sample holder. Three repetitions for the analysis were done on each sample. Each repetition was done from different part of the sample.

10.2 EA

The EA analyses were performed at LUT university in Lappeenranta. This analysis is used to determine the amount of nitrogen in the samples to observe if there is any remaining ammonia present in the laminate. The samples AnHi-001-PUR and AnHi-001-PET were

used for this analysis. This is to firstly compare the amount of nitrogen between these samples and then see if any nitrogen is present in the PET sample.

The samples are cut into thin slices that weigh around 150 mg and folded into a small enough ball to fit through the reactor opening. The samples are then placed into tin cups for the analysis. The tin cups were used because with the tin foil wrap the sample couldn't fit through the opening. Inert helium gas is used as an atmosphere for the analysis to remove any additional nitrogen. Three repetitions were done on each sample. Table IV shows the masses of each sample.

Table IV. Masses of The EA Samples.

Sample Name	Mass [g]
AnHi-001-PUR1	0,1723
AnHi-001-PUR2	0,1691
AnHi-001-PUR3	0,1809
AnHi-001-PET1	0,1223
AnHi-001-PET2	0,1295
AnHi-001-PET3	0,1323

10.3 TGA

The TGA analyses were performed at LUT university in Lappeenranta. This analysis is used to determine the existence of possible residual amounts of water or ammonia and possible ammonium salt contaminants remaining in the laminate by the possible mass loss on different temperatures. All the samples were used for this analysis. Temperature ranges for the analyses were from 22 to 300 ˚C. The heating rate for the instrument was 10 ˚C per minute. Helium gas is chosen as both purge and protective gas to not interfere with nitrogen and ammonia recognition. The gas flow for the purge gas is 40 mL/min and protective gas 40 mL/min. The TGA instrument setup is shown in table V. TGA used in the analysis is shown in figure 27.

Table V. TGA Instrument Settings.

Maximum Temperature [C]	300
Heating Rate [K/min]	10
Purge Gas	Helium
Protective Gas	Helium
Purge Gas Flow Rate [mL/min]	40
Protective Gas Flow Rate [mL/min]	40

Figure 27. TGA Setup.

A single sample cup is used in the analysis at once. The empty cup is weighed, and the weight is logged into excel. The laminate samples were cut into small circle pieces with a mallet and a circle die. An example of a sample piece is shown in figure 28. About 5,5 mg of sample is used for each analysis. Table VI shows individual sample names and masses. The sample masses were logged into excel. After the individual sample mass is recorded, the sample cup is weighed again with all the mass. This is done to allow the calculation of the incinerated mass to be recorded manually to compare them to the TGA instrument's scale.

Figure 28. Pieces of Laminate Sample for TGA Analysis.

Table VI. Name and Mass of TGA Samples.

Sample	Mass [mg]
AnHi-001-PUR	5,74
AnHi-001-PET	5,56
AnHi-001-PRE	5,51
AnHi-001-REF	5,72
AnHi-001-70	5,49
AnHi-001-100	5,54
AnHi-001-70END	5,77
AnHi-001-100END	5,96
AnHi-001-REF_UUSI	5,23
AnHi-001-PRE_UUSI	5,3
AnHi-001-70_UUSI	5,5
AnHi-001-100_UUSI	5,6

The sample is then placed inside the TGA furnace. First, all the sample analyses are started after the TGA scale stabilized. This took about 5 minutes for each analysis. The quick start of the analysis was suggested since there could be gases such as ammonia that can evaporate before incineration. New analysis was performed from the AnHi-001-REF sample. The sample was left to stabilize overnight into an exicator and analysed the following day. Second TGA analyses are performed to the samples without the secondary adhesive. Samples used for this are AnHi-001-70, AnHi-001-100 and AnHi-001-PRE sample. In these

analyses before adding the laminate pieces to the cup, the paper is separated from the acrylic adhesive to able possible trapped compounds to escape the sample during the analysis at right temperatures. The sample analyses are stabilized 20 minutes inside the TGA oven before the analysis is started.

10.4 SEM

The SEM analyses were done at LUT university in Lappeenranta. These analyses were performed by the laboratory engineers at campus and were done to determine if there are any differences in the laminate surface structure of the adhesive laminate with and without pre drying. The samples used for this analysis are AnHi-001-PRE, AnHi-001-100, AnHi-001-70, AnHi-001-100, AnHi-001-70END, AnHi-001-100END, and AnHi-001-REF.

The samples are cut into 5 x 5 cm square pieces and placed into an exicator to wait for the analyses. Since SEM creates a vacuum, the sample adhesion to the sample holder is crucial to prevent it becoming dislodged and contaminating the SEM column. (ATA Scientific Instruments, 2025) Because of this, the samples are adhered to the sample holder by double sided carbon tape. Gold coating is added onto the sample surfaces before the analysis to create a conductive surface for the electron spray.

10.5 Peeling Force

The Peel tests for the acrylate adhesive and secondary adhesive were done on site at Mölnlycke in Mikkeli. These analyses are used to determine the adhesion and cohesion strength of the acrylate and secondary adhesive. The acrylate adhesive is tested against glass surface. The secondary adhesive is tested against steel surface. These analyses are done according to the company’s own method instructions.

11 Results and Discussion

This chapter presents the results and discussion of the results of each analysis.

11.1 FTIR

The results for the FTIR analyses are presented as % transmittance spectrum (the wavenumber ($cm^{-}1$) as factor of % transmittance (T%)). Water forms a OH - group's stretching vibration band to the spectrum around 3400 cm^{-1}. (Xu, Pai, Yunhong, 2022) The presence of water is determined from the % transmittance. In % transmittance spectrum, the peak is the minimum point of the region. Figure 29 shows the FTIR- spectrum of all the samples.

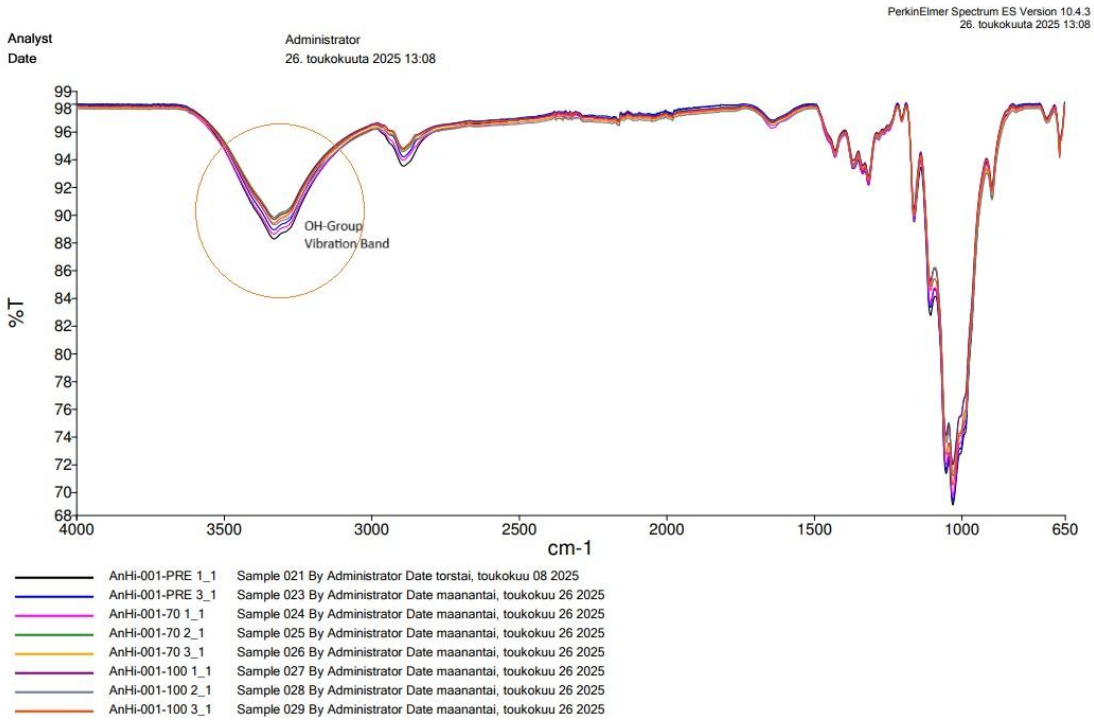

Figure 29. The FTIR-Spectrum of All the Samples.

Comparing the OH-group vibration band of each sample, there is not a huge difference between the intensity between samples. The first AnHi-001-PRE sample has the highest %T

value and second AnHi-001-70 sample has the lowest %T value, but all the other sample spectrums fall between each other. This makes it so there is no clear indication that either of these samples contain more or less moisture than the other. It can just be dependent on the measurement spot of the sample. I conclusion, the FTIR results show no significant difference in moisture between the samples whether they are pre-dried or not.

11.2 EA

The EA results are presented as mass percentage of C, H or N from the total sample mass. The analysis compares the amount of nitrogen between the AnHi-001-PUR and AnHi-001-PET samples. The process paper and acrylate adhesive do not naturally contain nitrogen. PUR is synthesized through an addition reaction between an alcohol and isocyanate and are characterized by the urethane linkage. (de Souza, Kahol, Gupta, 2021) The isocyanate group contains nitrogen which indicates that the sample should hold some nitrogen. The isocyanate and alcohol group PUR reaction is shown in figure 30.

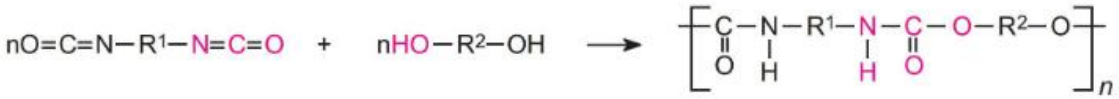

Figure 30. Isocyanate and Alcohol Reaction to PUR. (The Essential Chemical Industry, 2017)

PET is a condensation copolymer of ethylene glycol and terephthalic acid. (American Chemical Society, 2022) The PET molecule structure can be seen from figure 31.

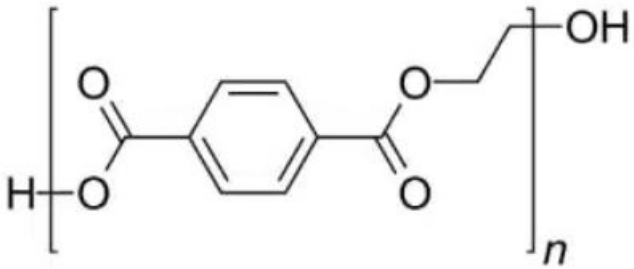

Figure 31. PET Molecule Structure. (USEON, 2024)

Based on its molecule structure, PET should not contain nitrogen. The poly(butyl) acrylate or the process paper does not contain nitrogen either. This means the nitrogen should show

up in the AnHi-001-PUR samples and be absent in the AnHi-001-PET samples. The EA results are shown in table VII.

Table VII. EA Results.

Sample	C [%]	H [%]	N [%]
AnHi-001-PUR1	63,39	8,02	0,94
AnHi-001-PUR2	62,42	8,45	0,66
AnHi-001-PUR3	62,20	9,25	0,70
AnHi-001-PET1	54,18	7,41	0,057
AnHi-001-PET2	54,02	7,76	0,050
AnHi-001-PET3	54,29	7,77	0,069

The nitrogen from the PUR-film can be seen clearly from the results. The PET laminate should be void of nitrogen but has an average of 0,06 % nitrogen content. This means nitrogen exists in some form in the laminate after the drying of the acrylate adhesive. There is a possibility that some ammonia or ammonium remain in the product. However, the laminate trapping some nitrogen from the air while handling the samples is also a possibility.

11.3 TGA

The TGA results are presented as the change of mass percentage (TG/%) in function of the heating temperature. There are multiple phenomena that can cause mass changes in TGA analysis, and these can be separated into physical and chemical phenomena. Physical ones are gas absorption/desorption and matter phase transition, vaporisation and sublimation. Chemical phenomena are break down reactions, gas reactions, decomposition and chemisorption. The mass change phenomena appearing in this analysis are expected to be polymer decomposition and water or ammonia evaporation.

TGA gives three different curves as an analysis result. First is the mass percent change in function of temperature. Second is the TG derivate curve that records the speed of the temperature changes during the analysis. Third is the differential thermal analysis (DTA) curve.

The study analysis searches mass change at the ammonia and water evaporation temperatures. Ammonia evaporates around - 33,3 ˚C. (Engineering Toolbox, 2003) At such low evaporation temperature, ammonia should evaporate immediately in the analysis. It can be considered however that the ammonia could be trapped beneath the laminate layers and released after the polymers break down at higher temperatures. If any moisture remains in the laminate, its evaporation should be seen till around 100 ˚C temperature. At higher temperatures the contents of laminate itself start to decompose. The paper starts to burn at around 230 ˚C. (Lewis Chung, 2003) Polyurethane's non-flaming thermal degradation starts around 250 ˚C, but it can start to initially degrade at around 150 ˚C temperatures. (American Chemistry Council. 2014) Organic silicone coatings can start to break down around 315 ˚C but depending on the coating can stand temperatures up to 370 ˚C and above. (Silico Products, 2025) Acrylate polymers can first start to thermally degrade near 250 ˚C and 300 ˚C. (Czech Zbigniew et al., 2015) The simplest ammonium salt is ammonium chloride, which starts to decompose at 338 ˚C temperature. (Haynes, 2014)

11.3.1 First TGA Analysis

These analyses were performed by initiating the analysis immediately when the TGA scale stabilized. This took 2 minutes. The combined result plots can be seen from figure 32.

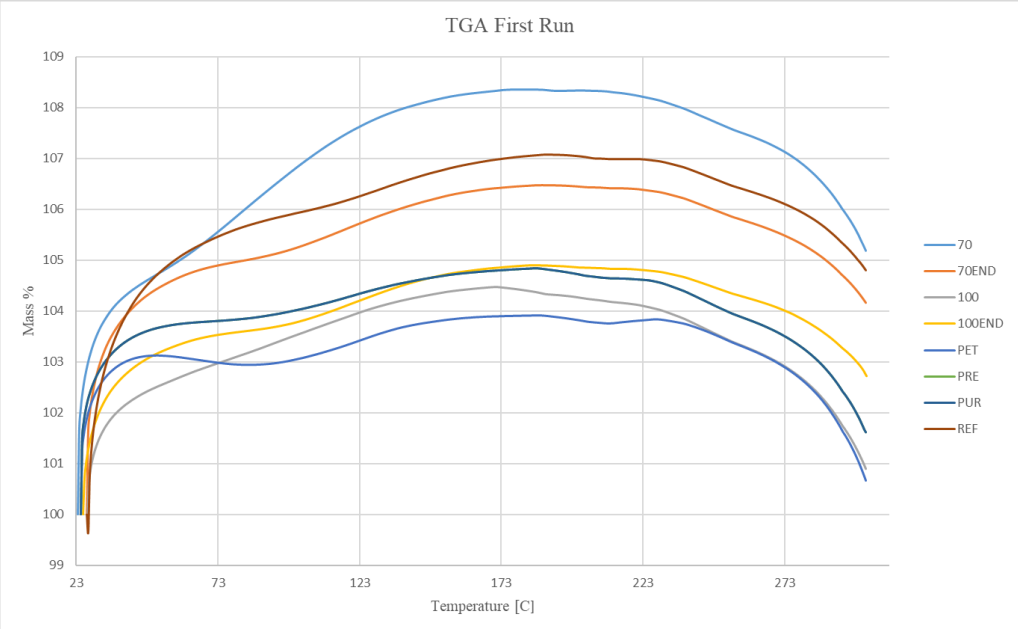

Figure 32. TGA First Run Results.

It can be seen from the results that all the sample masses start to increase at the beginning of the analysis, and they increase almost until the end of the analysis, only starting to decrease after their peak at about 200 ˚C. The mass loss at the end is most likely caused by the thermal degradation of the polymers. The cause for the significant mass increase at the beginning is unknown but it could be due to the short sample stabilization time inside the TGA furnace before the analysis. This is addressed in the third round of the analyses. Because the analysis is performed inside helium atmosphere, there should be no reactions happening between the materials and the gas. It is unlikely that the laminate also would absorb the gas within itself. The residual mass in all the analyses finishes higher than the starting mass. The mass change peaks for each sample are compared in figure 33.

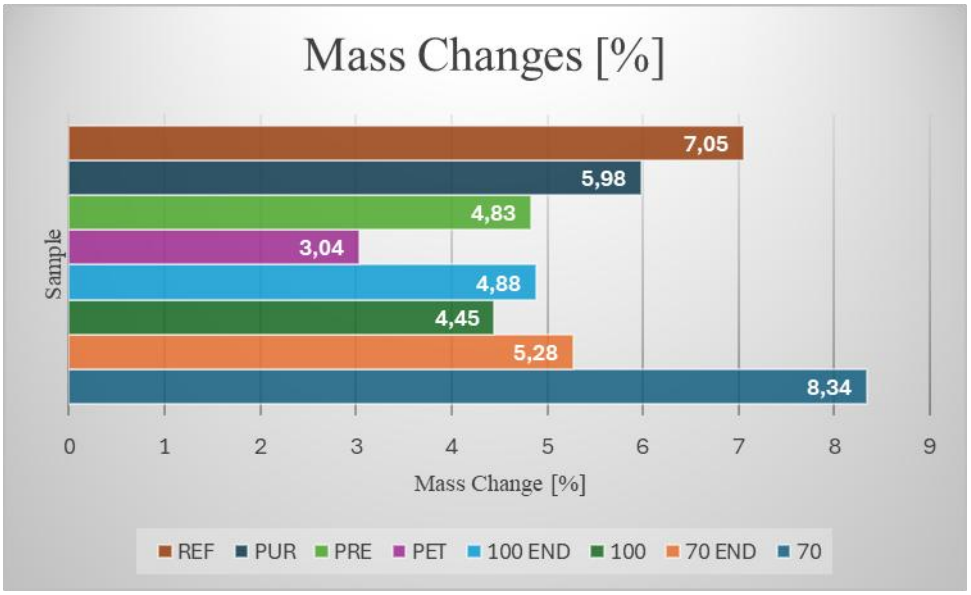

Figure 33. The Peak Mass Change Percentages Between Samples.

The comparison shows that there is also no link between whether the laminate has the secondary adhesive layer or not. On contrary to the results, from the manual sample weighing, it can be seen that all the samples have lost mass during the analysis. The actual mass changes are shown in table VIII below.

Table VIII. First TGA Sample Residue Masses and Mass Lost.

Sample	Residue Mass [mg]	Mass Lost [mg]
AnHi-001-PUR	5,62	0,98
AnHi-001-PET	4,78	0,86
AnHi-001-PRE	4,95	0,90

Table VIII. First TGA Sample Residue Masses and Mass Lost. (Continued from last page)

Sample	Residue Mass [mg]	Mass Lost [mg]
AnHi-001-REF	5,28	0,92
AnHi-001-70	5,07	0,92
AnHi-001-100	5,07	0,92
AnHi-001-70END	5,21	0,90
AnHi-001-100END	5,8	0,97

The occurring mass increase makes the first TGA analyses inconclusive.

11.3.2 Second TGA Analysis

Single repeat analysis was performed where the sample was left to stabilize in an exicator to see if it would prevent the mass increase issue during the analysis. Figure 34 shows the results of the repeat analysis of AnHi-001-REF.

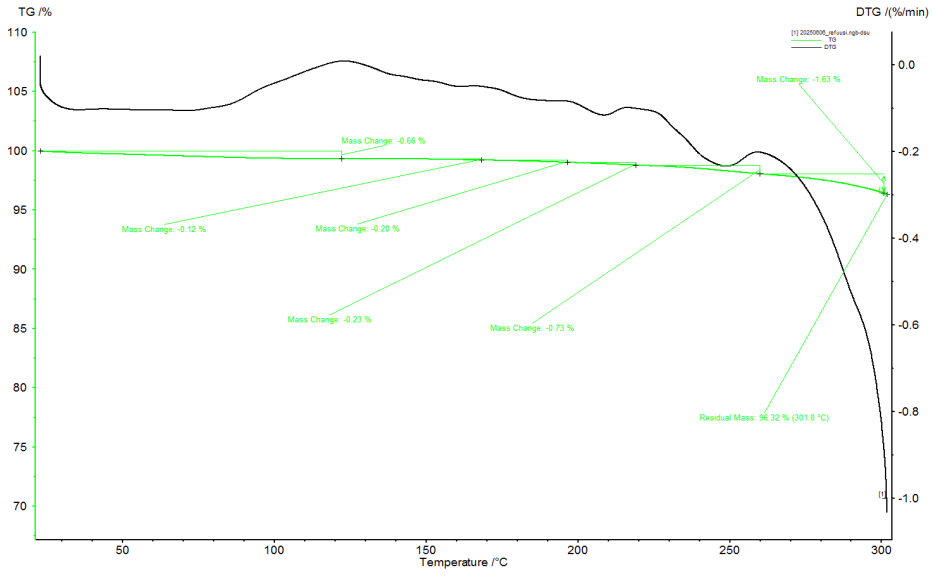

Figure 34. REF Sample Repeat Analysis.

From the figure 34 it can be seen that the weight of the AnHi-001-REF sample still increases throughout the analysis and starts to drop only in the end. This time the total weight of the sample sits lower than the starting weight. The drop at the end can be seen as the polymers

disintegrating. The derivative curve only tied to the mass increase speed. Because of the weight increase, this analysis is also inconclusive.

11.3.3 Third TGA Analysis

Three repeat analyses were performed where the samples were left to stabilize inside the TGA for 20 minutes each to see if it would prevent the mass increase issue during the analysis. Figures 35, 36, and 37 show the results for each of the samples.

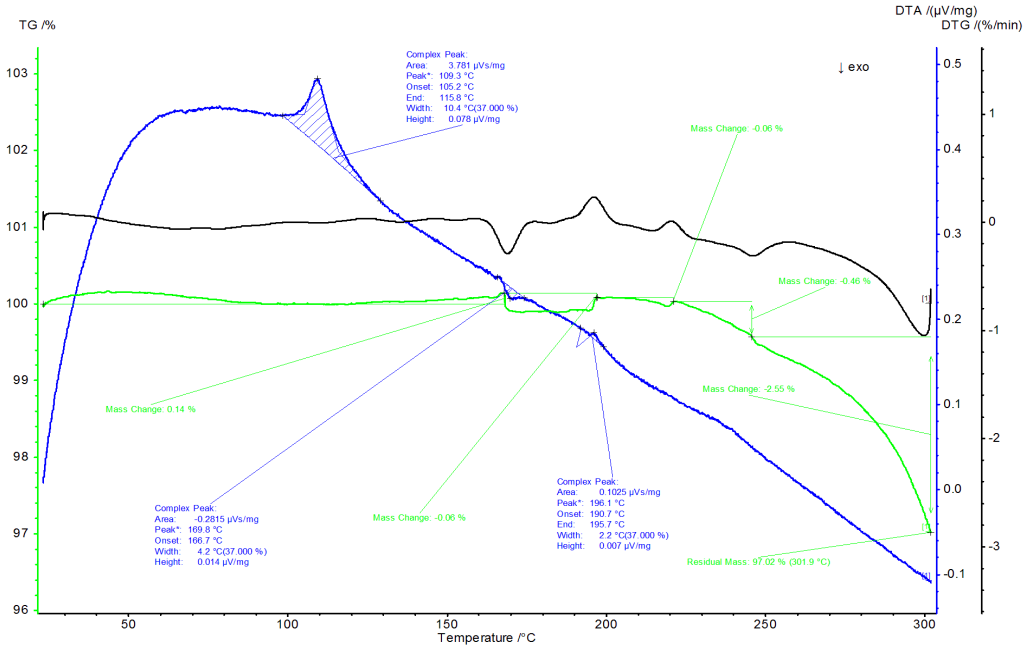

Figure 35. The TGA Results of PRE Sample.

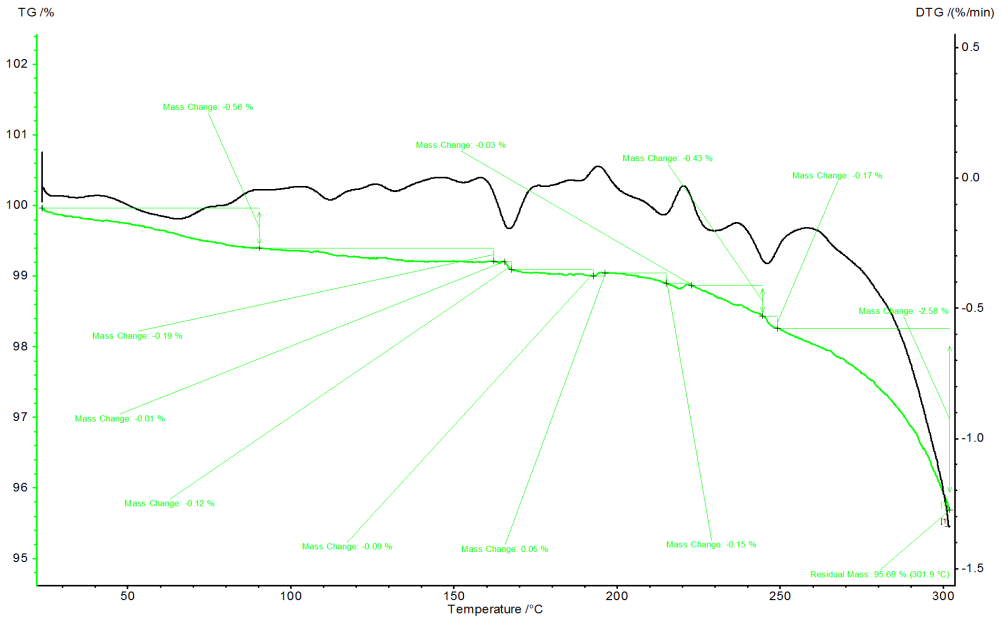

Figure 36. The TGA Results of 70 Sample.

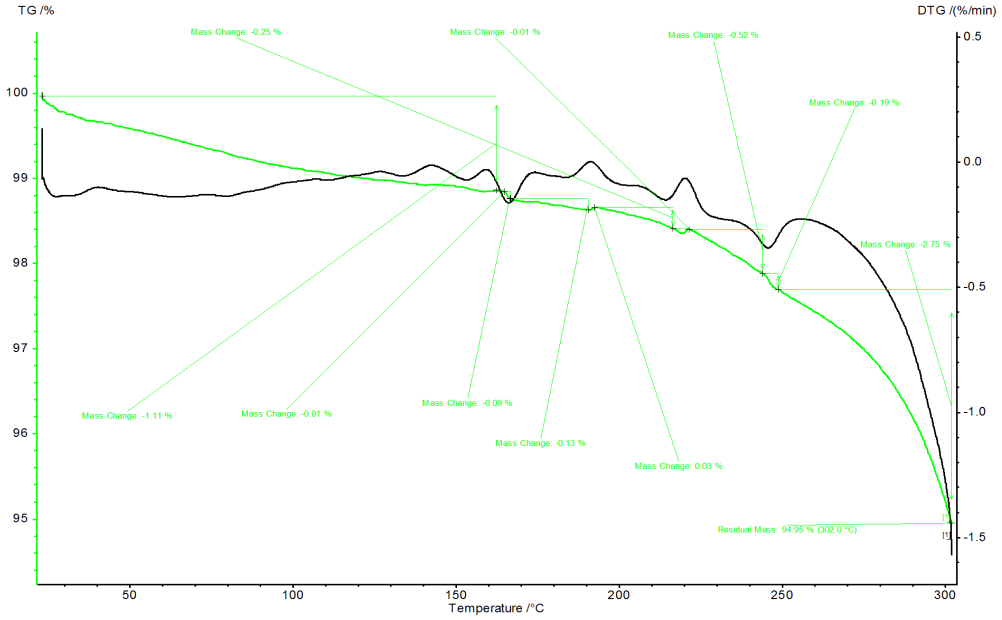

Figure 37. The TGA Results of 100 Sample.

The pre-dried samples AnHi-001-70 and AnHi-001-100 both have more significant mass loss at the beginning of the analysis. Both share a steady loss from the beginning till 150 ˚C where the polymer decompositions start. The AnHi-001-PRE sample has almost no mass changes till the 150 ˚C temperature. This mass loss at the beginning could indicate moisture evaporation from the samples. The mass changes between the starting temperature and 150 ˚C are compared in table IX.

Table IX. TGA Sample Mass Loss Till 150 ˚C.

Sample	Mass Change [%]	Mass Change [mg]
AnHi-001-PRE	0,14	0,0074
AnHi-001-70	0,75	0,041
AnHi-001-100	1,11	0,062

The TGA shows a differential thermal analysis (DTA) curve that shows the reaction enthalpies and whether they are endo or exothermic in function of temperature. Downward peaks in this case on the DTA curve are exothermic reactions. The DTA curve shows a significant peak at 110 ˚C temperature for all samples. This can be interpreted as water evaporation that is an endothermic reaction. The DTA curve for all samples is shown in figure 38.

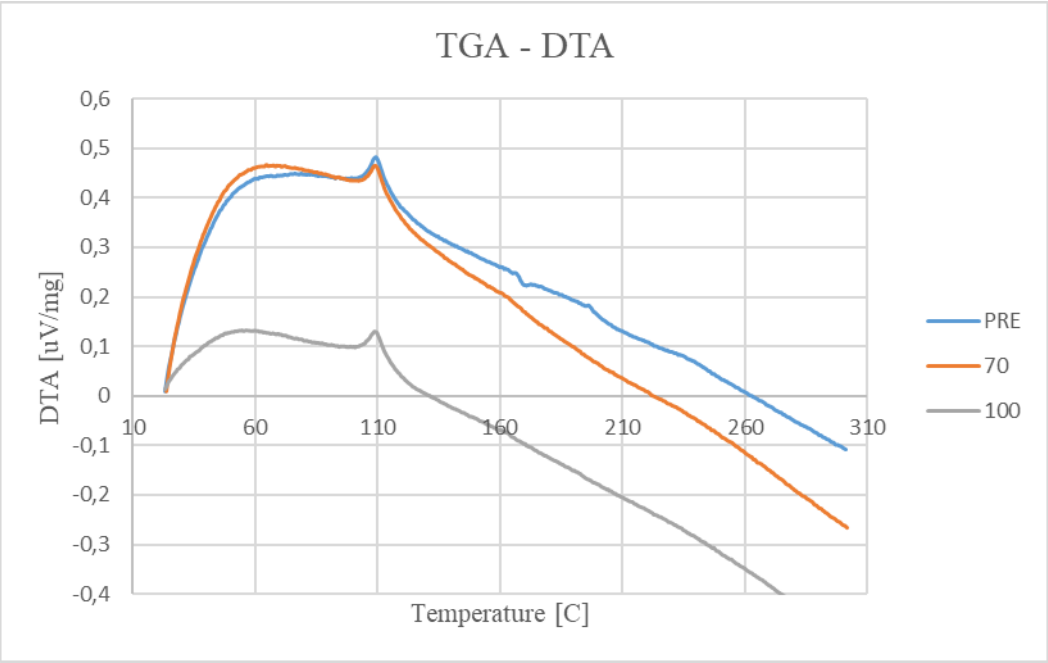

Figure 38. DTA Curves.

The TGA also provides a derivative curve (DTG) that depicts the mass change speed. All the DTG curve shows multiple small peaks. The upward peaks depict decomposition reactions of the polymers. Downward peaks depict melting. These can be seen from figure 39. First significant peak appears at 150 ˚C and starting from around 185 ˚C there are three different peaks. These are most likely linked to the polyurethane degradation since

polyurethane starts to initially degrade at 150 ˚C temperatures and go through non-flaming thermal degradation starting at around 250 ˚C. (American Chemistry Council. 2014)

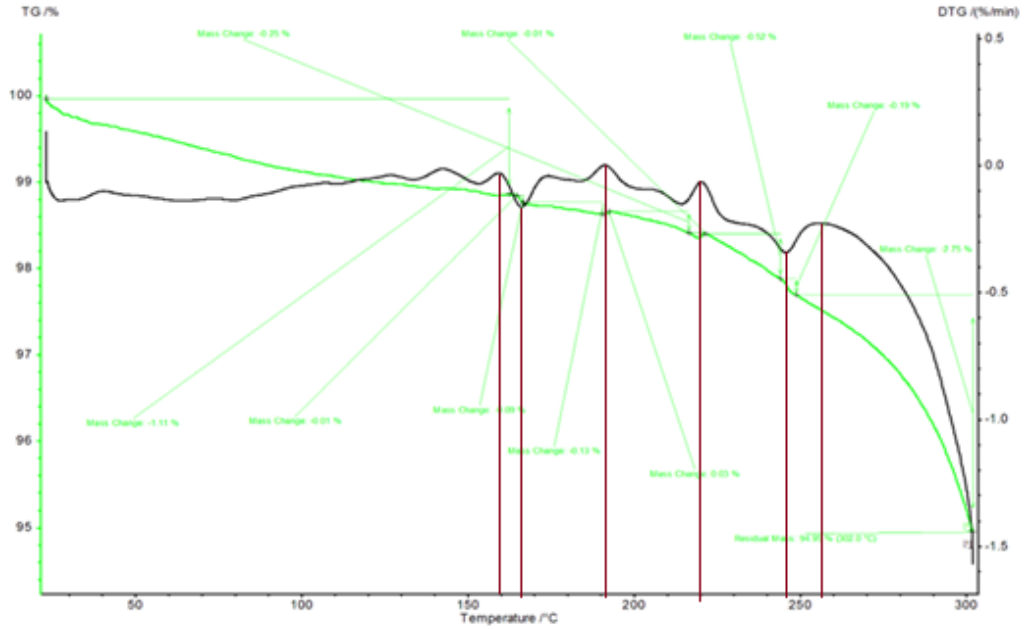

Figure 39. TG Derivative Peaks.

All the samples share the same temperature points for the peaks where the sample mass decreases. These are shown in figure 40.

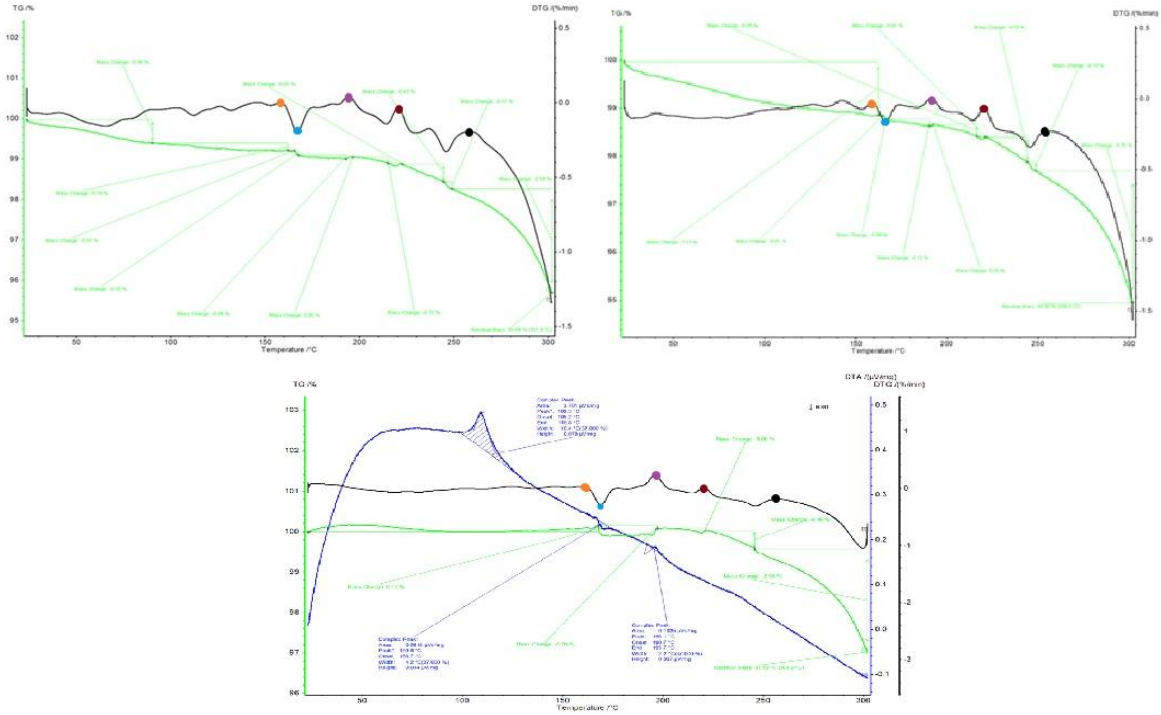

Figure 40. TG Derivative Peak comparison for Each Sample.

All the samples show the following phenomena in their DTG and TG % curve: First decomposition reaction at 165 ˚C temperature. This decomposition peak is immediately followed by a melting peak at 170 ˚C. At around 200 ˚C there is another decomposition peak and mass increase, so it could indicate oxidation of a polymer that can occur the heating rate is slow in oxidizing atmosphere and prior decomposition. (Menczel, Prime, 2009) At 225 ˚C another decomposition happens followed by another melting point. After 270 ˚C, there is massive decomposition peak that lasts till the end of the analysis. As mentioned, the peaks are most likely caused by the PUR-film degradation. The other organic polymers and possible ammonium salt contaminants in the laminate can withstand higher temperatures.

All the samples had lost mass at the end of the analysis. The temperature of the analysis is not hot enough to say that all the remaining weight is inorganic material. All the residue masses according to the TGA scale is shown in table X.

Table X. Third TGA Analysis Residual Masses.

Sample	Residual Mass [%]	Remaining Mass (TGA) [mg]	Mass Lost (TGA) [mg]
PRE	97,02	5,14	0,16
70	95,69	5,26	0,24
100	94,95	5,32	0,28

Interestingly the sample AnHi-001-100, that has been pre-dried in the warmest conditions had most significant mass change.

The TGA analyses showed no clear signs of ammonia evaporation at the beginning of the analyses. They also showed no clear answers to the water content of the samples, since the pre-dried samples lost more mass at the start of the analyses where water would evaporate. It was also discovered that the laminate needs a significant amount of time to stabilize inside the furnace to achieve a successful analysis.

11.4 SEM

SEM analysis results show images from the laminate surface with different resolutions. The resolutions chosen are 100, 500, 1 000 and 5 000. These pictures are utilized to observe

surface morphology differences between samples. Figure 41 shows the sample surface images 100 times resolution. Figure 42 shows the sample surface images 500 times resolution. The samples without the secondary adhesive are placed into the upper row. Samples that contain the secondary adhesive are on the lower row.

It can be seen from the figures that there are no differences between the AnHi-001-PRE- and pre-dried samples AnHi-001-70 and AnHi-001-100. This means no changes occur to in the acrylate adhesive surface during the IR-drying. This is true for the samples containing the secondary adhesive as well. There is interestingly also almost no difference in the surface appearance between the acrylate adhesive and secondary adhesive. Both share the same smooth lumpy surface. There are some spots observed however where the adhesive seems to be splattered beneath the film surface. This is seen in for example AnHi-001-70END sample. This is shown in figure 43.

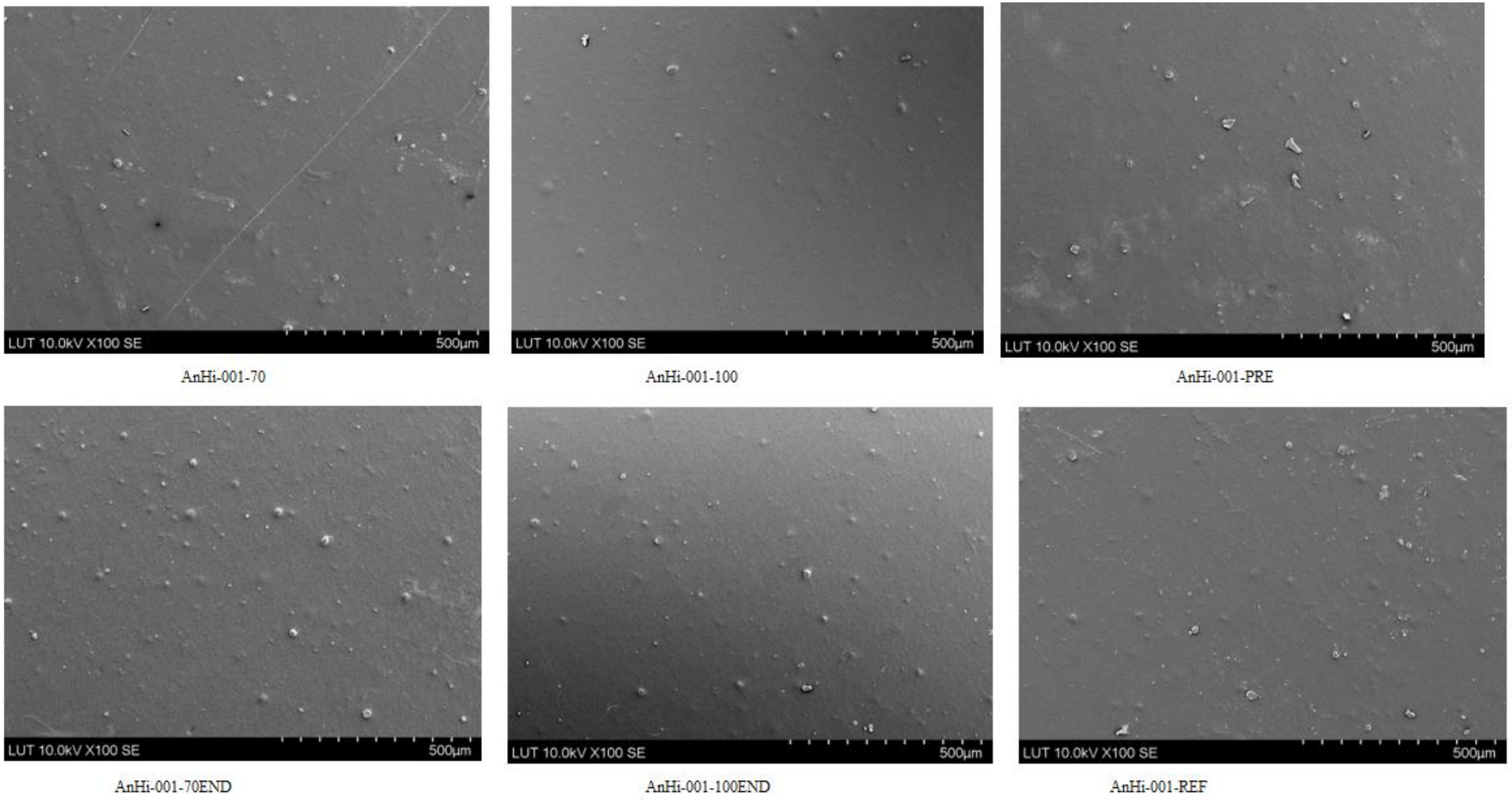

Figure 41. SEM Sample Surfaces with 100 Resolution.

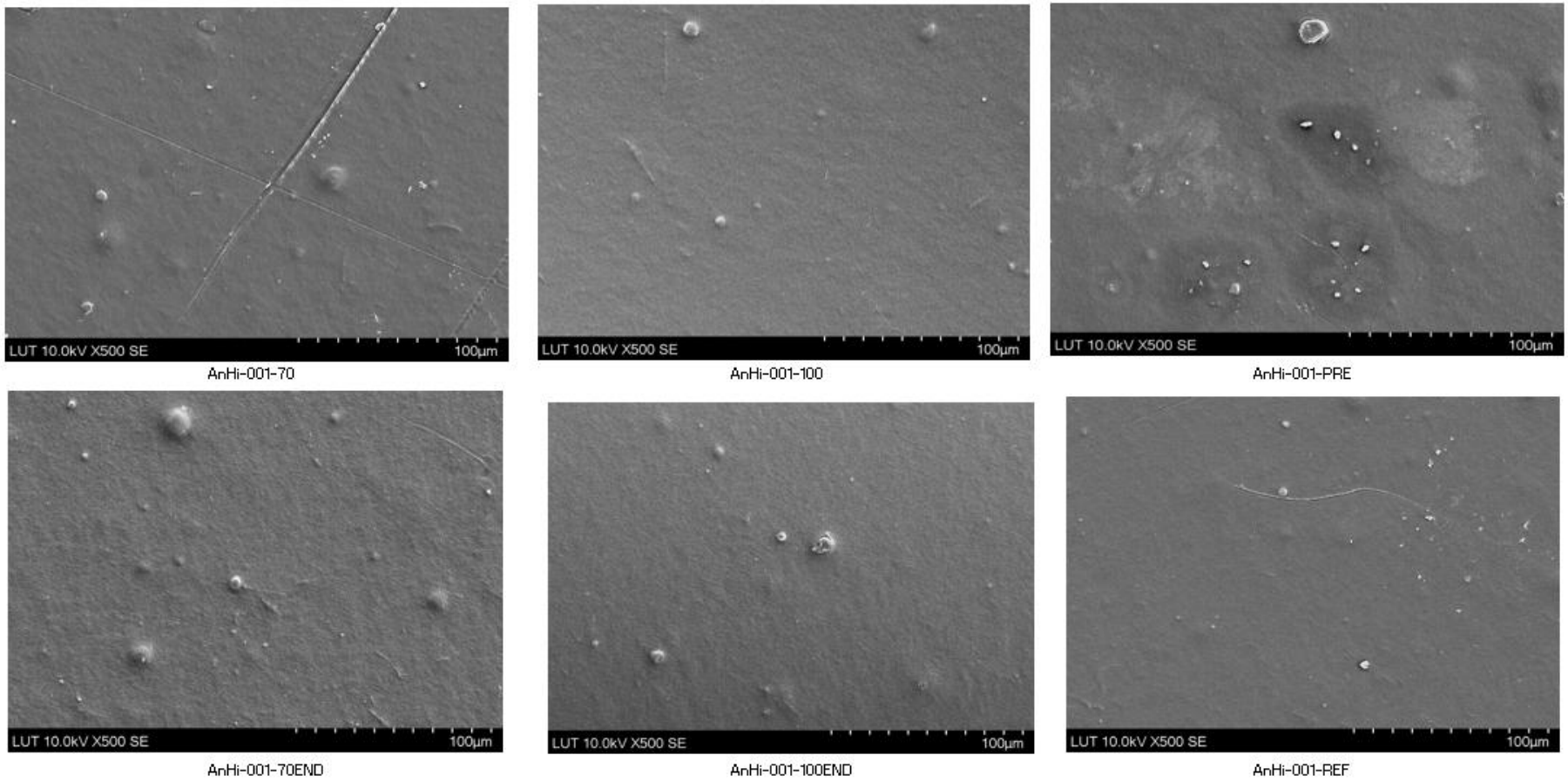

Figure 42. SEM Sample Surfaces with 500 Resolution.

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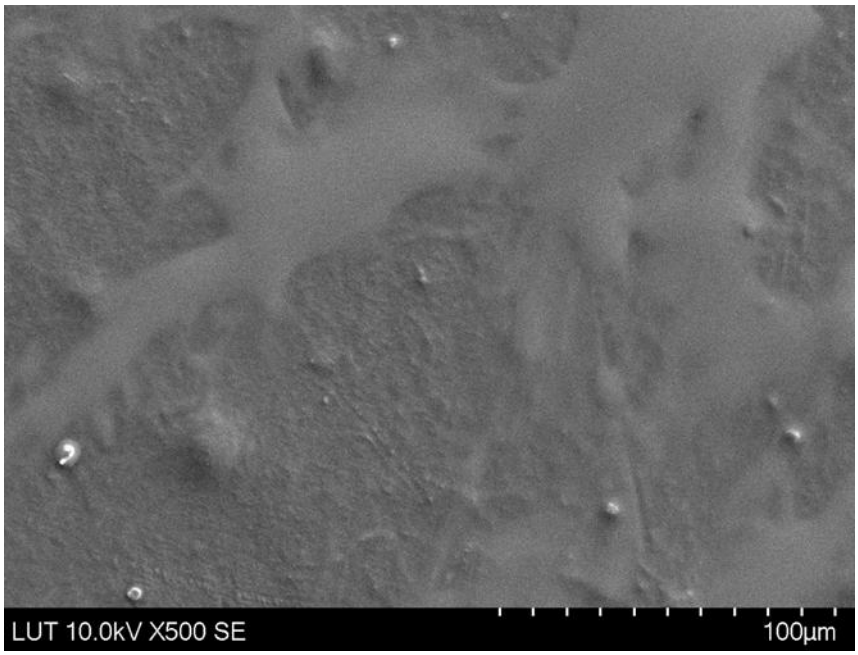

Figure 43. The Splattered Surface of AnHi-001-70END.

11.5 Peel Tests

The peel test results to test the adhesion and cohesion of the adhesives are reported as a boxplot and Newtons per 25 mm of laminate. The poly(butyl) acrylate was only tested for adhesion to a glass surface. The result for this analysis is shown in figure 44.

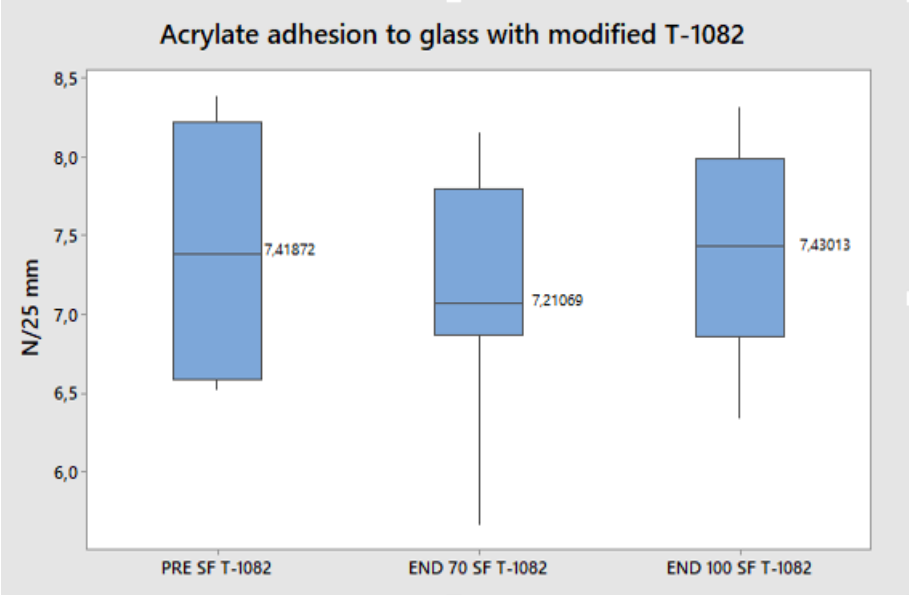

Figure 44. Acrylate Adhesion to Glass.

It can be seen from the boxplots that the distribution of values is quite symmetric with AnHi-001-PRE and AnHi-001-100END samples but is quite negatively skewed with larger variability. The average for AnHi-001-PRE sample is 7,42 N/25 mm, AnHi-001-70END is 7,21 N/25 mm and AnHi-001-100END is 7,43 N/25 mm. This means that the average values between samples are close together, so there is no significant difference in acrylate adhesion whether the laminate is pre-dried or not.

The secondary adhesive was tested for adhesion to steel as well as its delamination from the PUR-film. The analyses were also performed with holed version of the laminate. Results from the adhesion to steel test can be seen from figure 45 and delamination from the PUR-film from figure 46.

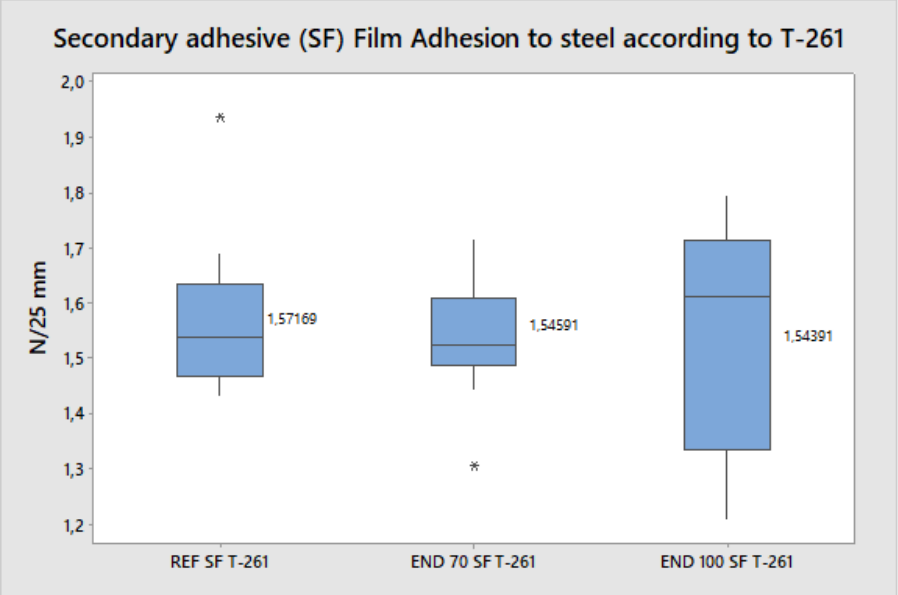

Figure 45. Secondary Adhesive Adhesion to Steel Results.

It can be seen from the boxplots that the distribution of the values is slightly negatively skewed with the AnHi-001-REF and AnHi-001-70END samples, and significantly positively skewed with the AnHi-001-100END sample. The average value for AnHi-001-REF is 1,55 N/25 mm, AnHi-001-70END is 1,55 N/25 mm and AnHi-001-100END is 1,54 N/25 mm. This means that the average values between samples are close together, so there is no significant difference in secondary adhesive adhesion to the steel whether the laminate is pre-dried or not. The PUR-film delamination plots are negatively skewed for all the samples. The average value for REF is 3,55’7 N/25 mm, AnHi-001-70END is 3,59 N/25 mm and AnHi-001-100END is 3,55 N/25 mm. This means that the average values between samples are close together, so there is no significant difference in secondary adhesive adhesion to the PUR-film whether the laminate is pre-dried or not.

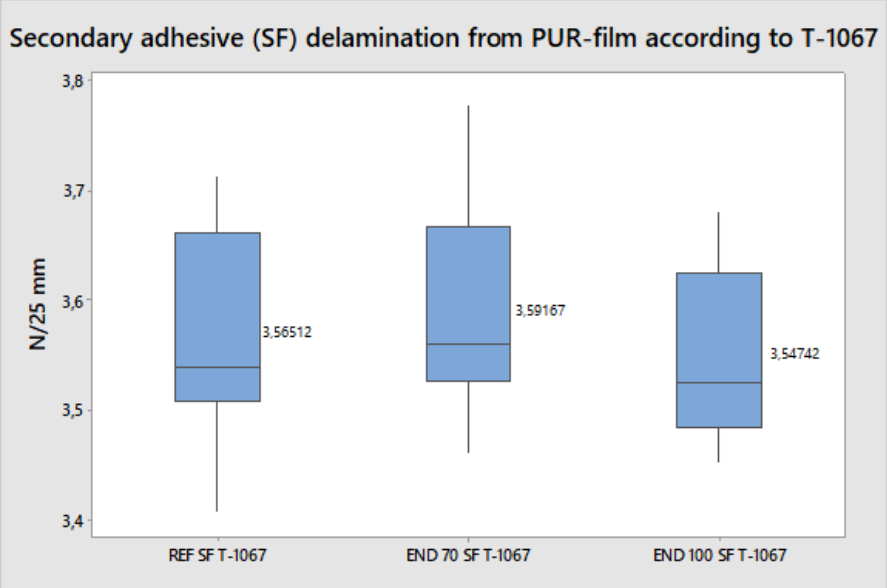

Figure 46. Secondary Adhesive Delamination from PUR-Film Results.

The produced laminate was further processed to be perforated, and the secondary adhesive adhesion and delamination tests were performed for this laminate as well. The adhesion to steel can be seen from figure 47 and delamination from figure 48.

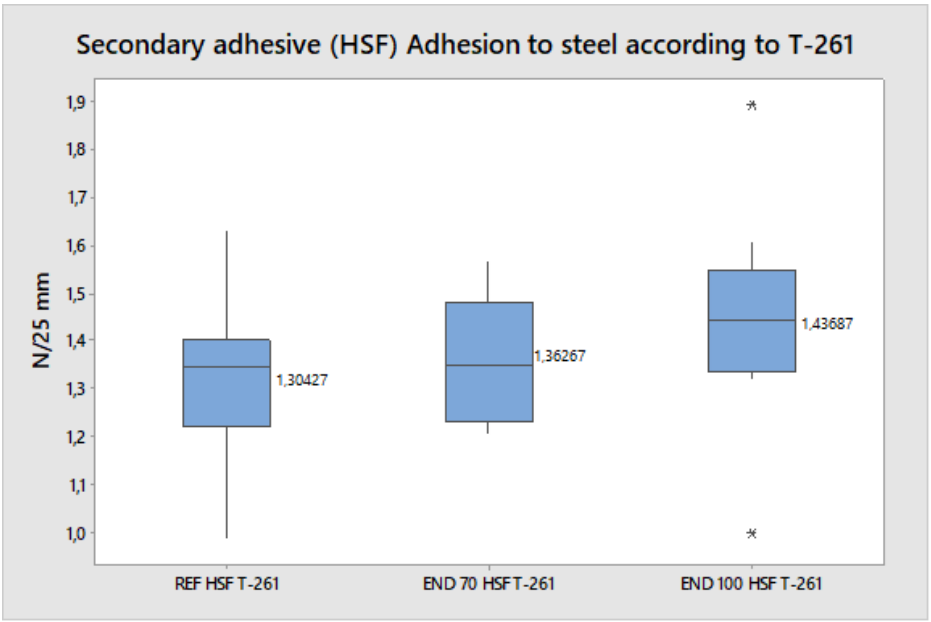

Figure 47. Holed Secondary Adhesive Film Adhesion to Steel Results.

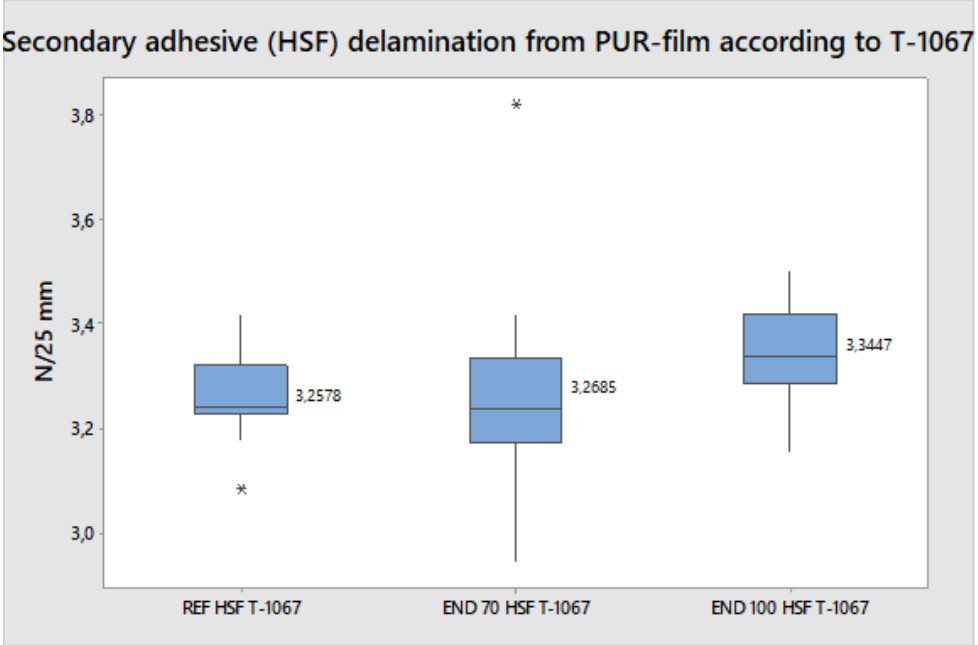

Figure 48. Holed Secondary Adhesive Film Delamination from PUR-Film Results.

The variability and data distribution are quite small and even for both of the tests. The average value in the holed film steel adhesion for REF is 1,30 N/25 mm, AnHi-001-70END is 1,36 N/25 mm and AnHi-001-100END is 1,44 N/25 mm. The averages of REF and 70END samples are close together. AnHi-001-100END steel adhesion is noticeably higher. Since the adhesion strength increases between the REF and pre-dried samples, pre-drying seems to slightly strengthen the holed secondary adhesive film adhesion according to this test.

The average value in the PUR-film delamination for AnHi-001-REF is 3,26 N/25 mm, AnHi-001-70END is 3,27 N/25 mm and AnHi-001-100END is 3,35 N/25 mm. This means that the average values between samples are close together, so there is no significant difference in holed secondary adhesive film adhesion to the PUR-film whether the laminate is pre-dried or not.

Figure 49 shows the summary of all the peel tests. In conclusion, all the peel tests show no significant difference between the sample delamination and adhesion strengths. This means that here is no change in the laminate adhesion or cohesion qualities whether the samples are pre-dried or not.

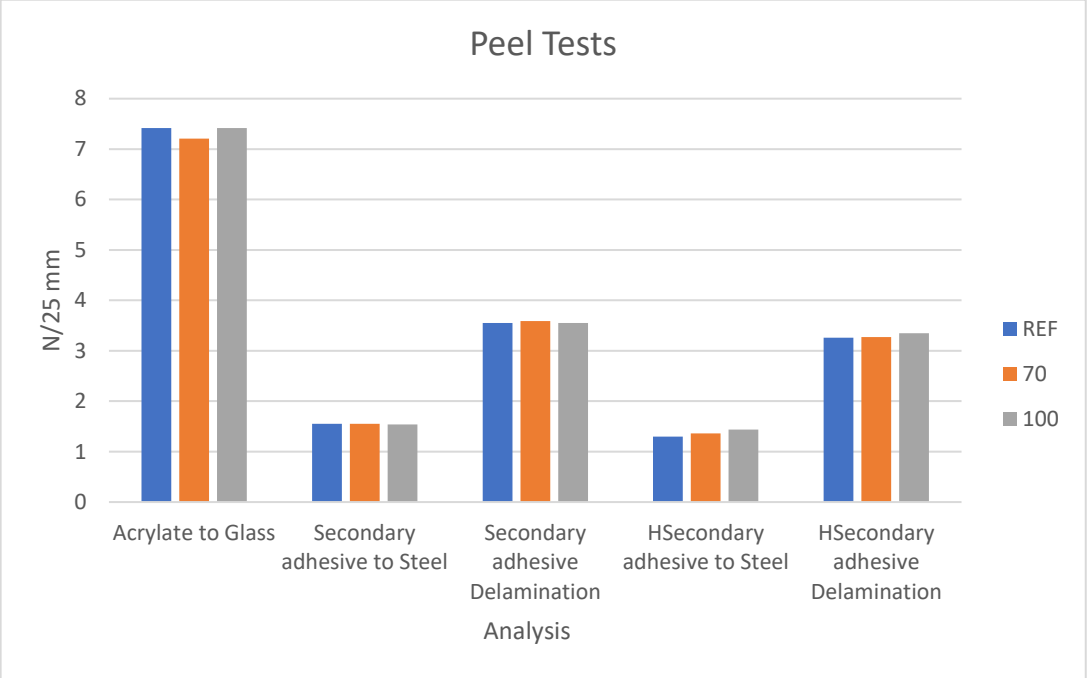

Figure 49. Peel Test Result Summary.

11.6 Result Summary

Table XI shows summary of all the analyses.

Table XI. Result Summary.

Analysis	FTIR	EA	TGA	SEM	Peel Tests
Results	Comparing the vibration bands of each sample there is no significant difference between the samples. The samples contain similar amount of moisture according to the analysis.	The PET-film samples contain 0,06 % of nitrogen. This indicates that the sample contains some kind of nitrogen compound, possibly ammonia.	Two first analysis attempts failed due to the sample gaining mass during the analysis. In the successful results, the pre-dried samples lost more mass at the beginning of the analysis, indicating that they could contain more moisture or impurities.	There were no differences in surface quality between samples, whether they were pre-dried or not.	No significant difference was observed between the samples in terms of adhesion strength.

Conclusions

In this thesis there were two main parts. First part was to produce a literature review to understand organic adhesives, adhesion, laminates and the production of laminates. This part was constructed to support the planning and understanding of the second experimental part of the thesis. The experimental researched the effect of pre-drying in production process of adhesive laminate. The part consisted of research plan, trial run explanation and the analyses. Five analysis methods were chosen in FTIR, TGA, EA, SEM and peel tests.

Different organic adhesives are used in pressure sensitive adhesives. These adhesives have many applications and are used widely for example in medical applications. The effectiveness of organic adhesives relies on their bond formation between the adhesive and substrate. This bond cam be formed by either drying or curing the adhesive. Curing of the adhesive is a chemical or cross-linking reaction that changes the adhesive from liquid to solid. This reaction is sensitive to contaminants.

An issue in curing of a secondary adhesive was observed at the production of adhesive laminates that are used for medical applications. The reason for this issue was hypothesized to be caused by contaminants on the primary acrylic adhesive surface that could interfere with the curing process of the secondary adhesive and cause adhesive and cohesive failures within the laminate. The main contaminants remaining in the primary adhesive were suspected to be water and ammonia that can remain in the primary adhesive after drying. A solution for this issue is proposed to add an IR pre-drying to the production process. Different analysis methods were chosen to recognize the contaminants and observe the pre-drying effect on the laminate quality.

FTIR was chosen to observe differences in moisture content between the normal and pre-dried samples. This was done by comparing the OH-group vibration bands between samples. There were no significant differences in the spectrums between samples indicating that they do not have significant difference in moisture content whether they are pre-dried or not.

EA analysis was chosen to recognize possible ammonia residue in the acrylate adhesive. This was done by preparing two different samples, where the other is a sample from normal production with a PUR-film and the second is made with a PET-film and should not contain

any nitrogen. These results are then observed to see how much nitrogen the normal sample contains and does the PET sample contain any nitrogen. The results show that the PET-sample has a 0,06% nitrogen content, meaning there can be some ammonia left from the drying process.

TGA analysis was chosen to qualify and quantify water and ammonia residue from all the laminate samples. This was done by comparing the mass change percent, derivate curve and differential thermal analysis plots between the samples. Three TGA analysis rounds were performed. First and second round analyses were inconclusive due to the sample collecting mass during the analysis. Third analysis round was successful. The results showed similar mass change, derivative and differential analysis curves to all samples. The different polymer decompositions could be identified in all samples. However, the analysis showed bigger mass change at the beginning of the analysis for the pre-dried samples. It is not clear what substance is evaporating from the laminate samples but is most likely moisture evaporating. It could be ammonia as well in the lower temperatures. This is unexpected because in theory they should contain less moisture or ammonia that would evaporate in the beginning of the analysis.

SEM analysis was chosen to observe any optical differences in the sample surfaces whether they were pre-dried or had the secondary adhesive layer. This was done by comparing the sample images to each other with different resolutions. All the samples had similar smooth appearance with small occasional bumps. From these results it can be said that the pre-drying had no optical effects on the quality of the adhesive laminate.

Pull tests were performed on the primary acrylate adhesive and secondary adhesive layers. These were done to see if there was any change in the strength of the adhesives after pre-drying. These tests were done according to the company's own test methods. The strength of the acrylate adhesive was done against a glass substrate. The strength of the secondary adhesive and was tested against a steel substrate both intact and perforated. The secondary adhesive's delamination from the PUR-film was also tested. The results from these tests show that there is no change in the adhesive properties of either adhesive whether pre-dried or not. All the pull test average values varied very little from each other.

The EA and TGA results on the identity of the possible contaminants is unclear. From the EA results however, it can be suggested that at least some ammonia resides in the acrylate

adhesive after drying. TGA shows some mass loss, but it is difficult determine if some of the leaving mass is ammonia or not. The analysis shows other mass leaving that has high likelihood of being water. To get more detailed answers, TGA would need some additional analysis instrument added to the analysis, for example mass spectrometry. FTIR was not able to show any answers to the water existence in the laminate. All the analysis results show no clear benefit from the addition of the IR-pre-dryer to the process. However, the research also proves that there is no harm in adding the pre-drying into the process either. If utilized in this specific process, it can be run on just 70 ˚C, since running it on higher temperatures show no real benefit to the laminate quality. This was also proven to be more sustainable for the process to avoid overheating.

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