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HEAT SEALABILITY OF PAPERBOARD AND FACTORS AFFECTING SEALABILITY

Master of Science Thesis
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ABSTRACT

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Heat sealing of polymer coated paperboards requires a heat source, pressure and dwell time. The seal is formed when temperature and pressure are applied to the seal area, after which the seal is allowed to cool down for the seal to be formed. Some of the popular heat sealing methods include hot air sealing and hot bar sealing, which differ from one another as temperature and pressure are applied simultaneously to the sealed materials in hot bar sealing, but in hot air sealing, temperature is applied first and pressure is applied afterwards. Hot air and hot bar sealing methods were used in the study.

Adhesion describes the state where two dissimilar bodies are in close contact, which is crucial variable in sealability. Adhesion is affected by wetting of the surfaces, which can be inspected by droplets and their contact angles to measure surface free energy of the surface. The surface energy describes the excess intermolecular forces that are present on a substrate that can be divided into polar and dispersive components.

Various types of peel tests are used to measure the adhesion of a seal. Hand peel test is the quickest one to execute and was used to evaluate the seals of the study. Hand peel test estimates the fibre tear of the sealed area after the seal has cooled from the heating.

This study focuses on finding differences in sealing parameters between different polymer coated paperboards and identifying the reasons for the differences. There were three PE-coated paperboards in the study, two of which had an additional mineral coating and one was uncoated from the other side. Heat sealing results indicate that polymer-polymer seals and polymer-coating seals have different sealing temperatures between the samples. Sample 1 and sample 2 were the mineral coated samples, and sample 1 had higher sealing temperatures in all cases.

Surface energy measurements found out that one reason for sealability differences was that the mineral coating of sample 2 has much higher surface energy and especially higher polar component than the sample 1's coating. Coatings were compared and it was found out that the coatings use different latexes in mineral coatings, which can explain the surface energy differences. There were also different distributions of carbon bonds in the coatings, which can also have an effect on the surface energies.

Polymers of the samples were studied to be LDPE. From nuclear magnetic resonance spectroscopy test, NMR, it was determined that both polymers have polyethylene branches of butyl groups in them, but sample 2 had higher amounts of branched pentyl and ethyl groups than sample 1. These differences between the LDPE's is significant and can be estimated to have a difference in the sealability of the samples.

Keywords: Heat sealing, adhesion, sealing temperature, surface free energy, coating, polymer

The originality of this thesis has been checked using the Turnitin OriginalityCheck service.

TIIVISTELMÄ

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Polymeeripäällystettyjen kartonkien kuumasaumautuvuus tapahtuu, kun prosessissa on mukana lämpölähde, paine ja pitoaika. Sauma muodostuu, kun saumattavalle alueelle johdetaan lämpöä sekä painetta, minkä jälkeen sauman annetaan jäähtyä sauman muodostumista varten. Kuumailmasauma ja kuumapalasauma ovat yleisiä kuumasausmenetelmiä, joita käytettiin tämän tutkimuksen tekemisessä. Nämä menetelmät pystytään erottamaan toisistaan tutkimalla miten menetelmät johtavat lämpöä ja painetta saumausalueelle. Lämpö johdetaan yhtä aikaa paineen kanssa kuumapalasaumauksessa, jossa kuumennettu pala asetetaan saumattavalle alueelle. Kuumailmasaumauksessa lämpö johdetaan ensin erikseen saumattavalle alueelle, ja lämmityksen jälkeen paine johdetaan alueelle.

Adheesiolla kuvataan tilaa, jossa kaksi toisistaan erilaista pintaa on lähikontaktissa toistensa kanssa. Adheesio on erittäin tärkeä osa saumautuvuutta. Vettyminen on adheesioon vaikuttava tekijä, jota tutkitaan nestemäisillä pisaroilla laskemalla pintaenergia pisaroiden ja pintojen välisistä kontaktikulmista. Pintaenergia, millä kuvataan saumattavien pintojen atomien välisiä energioita, jaetaan polaariseen ja dispersiiviseen osaan.

Monia repäisykokeita on kehitetty adheesioita mittaamiseksi varten. Käsirepäisykoe on nopein repäisykoe ja tutkimuksessa käytetty adheesioita mittaamiseksi. Käsirepäisykokeessa näytteen annetaan jäähtyä kuumasaumauksesta, ja kuiturepeämisen määrä saumausalueella arvioidaan kun näyte on revitty.

Tutkimuksessa selvitettiin erilaisten polymeeripäällysteisten kartonkien kuumasaumautuvuuden eroja. Tutkimuksessa oli kolme polymeeripäällysteistä kartonkia, joista kahdella oli myös mineraalipäällyste toisella pinnalla ja kolmas oli toiselta puolelta päällystämätön. Kuumasaumautuvuustuloksien tuloksista tiedetään, että polymeeripolymeerisaumojen ja polymeeri-päällystesaumojen saumauslämpötiloissa on eroavaisuuksia. Mineraalipäällysteiset kartongit nimettiin näyte 1:ksi ja näyte 2:ksi. Näistä näyte 1:llä oli aina korkeammat saumauslämpötilat.

Pintaenergiamittauksissa selvisi, että näyte 2:lla oli korkeampi pintaenergia mineraalipäällysteessä kuin näyte 1:llä, mikä on mahdollisesti yksi syy näyte 1:n korkeammille saumauslämpötiloille. Erityisesti polaarisen komponentin osuus oli suurempi näyte 2:lla. Lisäksi näytteiden päällysteissä oli käytetty eri latekseja, joilla voidaan mahdollisesti selittää eriarvoiset pintaenergiat. Erilaisten hiilisidosten suhteellisissa määrissä oli myös eroavaisuuksia, joista voidaan myös saada syy eri suuruisille pintaenergioille.

Kartonkien polymeerit määritettiin LDPE-polymeereiksi. Tarkempi tutkimus näytteiden polymeereistä selvitti, että polymeerit koostuvat polyetyleneistä, joissa on haarottuneena butyyli-ryhmiä. Lisäksi näyte 2:ssa on enemmän haarautuneita pentyyli- ja etyyli-ryhmiä kuin näyte 1:ssä. Nämä eroavaisuudet ovat huomattavia ja näillä voidaan arvioida olevan vaikutusta kuumasaumautuvuuden tuloksiin.

Avainsanat: Kuumasaumautuvuus, adheesio, sauma lämpötila, pintaenergia, päällyste, polymeeri

Tämän julkaisun alkuperäisyys on tarkastettu Turnitin OriginalityCheck –ohjelmalla.

PREFACE

The work was done in Tampere University's Paper Converting and Packaging Technology Research group and in Metsä Board Äänekoski's R&D group in Excellence Centre.

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LIST OF SYMBOLS AND ABBREVIATIONS

BCTMP	Bleached chemi-thermomechanical pulp
CTMP	Chemi-thermomechanical pulp
DSC	Differential scanning calorimetry
EC	Excellence Centre, Metsä Board's facility center in Äänekoski
ESCA	Electron spectroscopy for chemical analysis
FTIR	Fourier transform infrared spectroscopy
HAS	Hot air sealing
HBS	Hot bar sealing
LDPE	Low density polyethylene
LLDPE	Linear low-density polyethylene
mPE	Metallocene polyethylene
NMR	Nuclear magnetic resonance spectroscopy
Optitopo	Optical topography
OSD	Optitopo surface deviation
PE	Polyethylene
SFE	Surface free energy
TAU	Tampere university
TGA	Thermogravimetric Analysis

F	force
p	pressure
t	time
T	temperature
T_g	glass transition temperature
T_m	melting temperature
θ	contact angle
γ	surface free energy
γ_P	polar component of surface free energy
γ_D	dispersive component of surface free energy
σ/γ	surface tension

1. INTRODUCTION

Paperboards coated with polymeric films are commonly used in a large variety of packaging applications. Medical industry requires that the seals of the packaging are hermetic to keep out any environmental hazards, such as moisture and toxins, including bacteria. In food industry, packages have similar requirements than in medical industry, as in both industrial fields the protection of products is crucial. [1, 2]

Heat sealing is a sealing method that can fulfil needs of both of the industries. Heat sealing is a method of adhering materials together, where heat and pressure are applied to the area of the seal. After the applications of heat and pressure in a certain time, the seal needs to be allowed to be cooled down, for the seal to be fully formed. The materials used in hot air sealing are generally thermoplastic polymers but paperboards and other paper products can also be used in heat sealing. Heat sealing can be used to seal multitude of different products, such as packages for medicines and pre-heated and sterilized foods and paperboard cups used to hold hot and cold beverages. [1, 2]

In this study, the main focus of heat sealing methods are on hot air sealing and hot bar sealing, both of which are common methods of heat sealing used worldwide. Sealability of materials is affected by heat, pressure and dwell time as well as other material variables. Target of the study is to understand the material differences and factors explaining different sealing results. [1]

The three tested paperboards in the study all have polymer coating on the back side of the paperboard. One of the sample is uncoated on the other side, and the other two samples have a mineral coating. The focus of the study will be on the two materials with mineral coating on the top and polymer coating on the back side. Reason for this is that if these two materials have differences in sealability, the paperboards can be compared directly against one another, making it easier to identify the factors that enable the possible differences. Uncoated paperboard is still studied to see the effects that fibre has on sealability and to compare the fibre-polymer seal to polymer-polymer and polymer-coating seals.

The literature part of the study looks into different heat sealing methods that are available worldwide and the comparison of these methods. As use of polymers with paperboards is common, different types of polymers used in coatings are also presented. Adhesion and wetting are crucial variables in sealability, which are the base elements of sealability. The theories of how adhesion takes form between two substrates are presented and the effects of wetting has on adhesion. Wetting can be inspected by contact angle measurements, which can then be used to calculate surface free energies of the surfaces, which can be used to predict the sealability of materials. There are different equations to calculate surface energy from contact angles and some of these calculations are presented in the study.

In the experimental part of this work, after the sealing tests are done, studies of the compositions of the polymers and coatings are in closer inspection. Chemical and physical characterizations of these surfaces are done to identify differences in the coatings and polymers of the paperboards. Differences in the compositions of elements, used components and different polymers in coatings and polymeric films are a few different factors that can influence the sealability. These factors are studied and their effects on sealability is inspected with the heat sealing results.

The results gained from this work will provide better understanding on the different factors affecting sealability and the effects these factors have on sealing. The results can then be used in development of paperboards used in packaging and paperboard cups to increase the effectiveness of the sealability in these applications.

2. HEAT SEALING OF POLYMER COATED PAPERBOARDS

Paperboards are commonly coated with polymers with extrusion coating process to increase the end-use properties that are required from packaging materials. Some of the needs include barrier properties for moisture, air and flavour, printability and sealability, especially heat sealability. Polymer coatings also provide better applications in sterilization of products and improved durability of the packages. [2]

Heat sealability of these products is affected by multiple different variables, one of the most influencing factors being the baseboard and the type of polymer coating. Paperboards are made of multiple plies of different pulps, which can then be further processed to have a polymer coating or mineral coating or both. Polymers in the coatings can be composed of different types of polymers, either fossil-based or biopolymers, of which fossil-based LDPE is one of the most common coating polymers. Dispersion coatings are also a possible coating for paperboards, which are made of polymers and other fillers. [2, 3]

Heat sealing can be achieved by a variety of different sealing methods, including hot air sealing, hot bar sealing and ultrasonic sealing. Cold sealing is also a sealing method, which does not require any heat source for the seal to be formed, rather an adhesive web is used to form the seal. All these methods have a heat source and a form of providing pressure to the seal area, making them heat sealing methods. Differences between the methods are in the heat forming, application of temperature and pressure simultaneously and the final use of these methods.

2.1 Paperboard grades

Folding boxboard is commonly used as packaging materials for cosmetics, healthcare, food service and food packaging materials in direct contact with foods. Folding boxboards, or FBBs for short, are comprised of three to four plies. The middle ply being made of bleached chemi-thermomechanical pulp (BCTMP) or other mechanical pulp and top and bottom plies are made out of bleached chemical pulp. The possible fourth ply of FBBs can be also made with BCTMP or either mechanical pulp or chemi-thermomechanical pulp, CTMP. On the top most layer of FBB, a coating can be applied as a single or double mineral pigment coating. A coating can also be applied to the bottom layer, but the top side coating is more common. [18]

Food service boards, or FSBs for short, is a paperboard grade that has three defined plies of pulps. The top and bottom plies are composed of bleached chemical pulp and the middle ply is a mixture of BCTMP and chemical pulp. FSB can be coated similarly to FBB with mineral pigment coating, but this is not required for all of the different types of FSB. FSBs with extrusion coated polymers are most commonly found in paper cups holding hot and cold liquids and other beverages, like ice creams. FSB paperboards can also be coated with mineral pigments to provide a smooth, more printable and optically improved surface for the paperboard. The applications are similar to the uncoated FSBs but printing on the coated FSB paperboards has more variety in the printing methods. Figure 1 gives a schematic presentation of the plies and their relative amounts in the structure of FSB paperboards. [26]

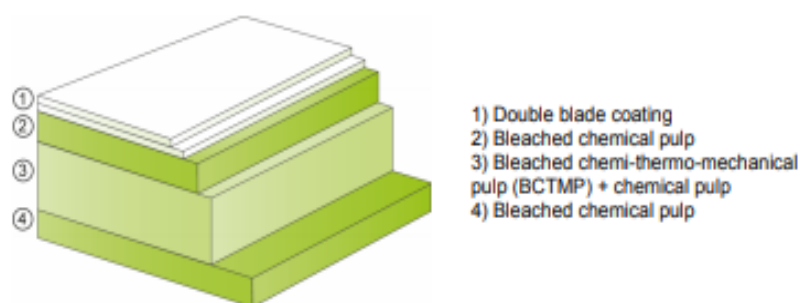


Figure 1. Structural illustration of the different plies in paperboard [26]

2.2 Polymers in heat sealing

Low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) are common polymers used as sealable coatings on paperboard. Other common polymers include polypropylene (PP) and copolymers of previously mentioned polymers with combination of each other's and other polymers.

Both LDPE and HDPE materials are commonly used as heat sealing polymers in packaging, though LDPEs are more common of the two. One of the reasons for this is because of the lower minimum heat sealing temperature of LDPE, as explained by Tuominen et al. (2013). Lower heat sealing temperature result in broad range of heat sealing temperatures, which enables multiple applications of use for LDPEs. Melting temperatures of some of the most common polymers used in heat sealing researched by Hishinuma (2009) are presented in Table 1, as well as other temperature related properties. Morris (2017) provides information on the melting temperature of HDPE, which is 135°C. Compared to LDPE's melting temperature of about 110°C, it is clear that LDPE is superior choice for sealing applications. [1, 3, 18]

Table 1. Thermoplastic packaging films and their temperature properties
[1, 3, 13, 28, 31, 42]

Materials	Melting temperature (°C)	T _g or softening temperature (°C)	Heat sealing window (°C)
LDPE	98 – 115	75 – 86 (Softening temperature)	100 – 115
LLDPE	105 – 123	– 110	100 – 130
PP (Retort pouch)	155 – 170	150–155 (Softening temperature)	140 – 165
PP co-polymer “Nippon polyace”	–	–	116 –
Polylactic acid	165 – 170	40 – 70 (T _g)	62 – 100

Also in rise of popularity are bio-based polymer films. These include but are not limited to: Polylactic acid (PLA), which is polymerized from lactic acid, bio-PE produced from sugarcane and bacterial derived polyhydroxyalkanoates, PHAs. [43]

2.2.1 Metallocene in polyolefin production

Most common method of polymerization of polymer is done by what is known as the Ziegler-Natta method. Metallocene is a catalyst used to polymerize polyolefins to produce metallocene polymers, such as metallocene polyethylene, mPE. [13]

Metallocenes are metallic catalysts that consist of two cyclopentadienyl anions with atomic rings of 5 atoms. The metallic component of metallocene is located in the middle of the structure, sandwiched between the two cyclopentadienyl anions by bonding to the aromatic rings with π -bonds. One of the more common metals to add to the structure is iron to form ferrocene, which is presented in Figure 3. [13, 25, 36]

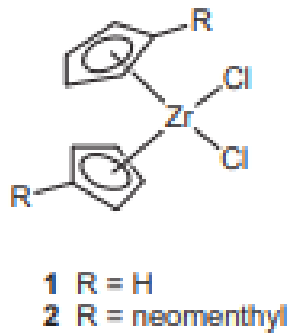


Figure 2. A structure of metallocene used to polymerize olefins [13]

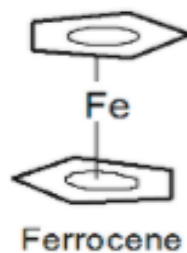


Figure 3. Structure of ferrocene [25]

In a study conducted by Sierra (2000) in of which the effects of mPE in LDPE blends affects the seal properties in a lamination seal. The lamination consisted of biaxially-orientated polypropylene (BOPP), aluminum foil and PE sealing layer, of which the PE layer was studied. The study found that metallocene lowered the required temperatures to form a seal with a hot bar sealing machine by tenfold of degrees. These results were gained with content percentages 10, 15, 20 and 33 % of mPE in the LDPE blend. The lowered seal forming temperatures were acquired as the mPE lowered the glass transition temperature and the melting temperatures of the blends. Studying the effects of mPE in smaller quantities in blends were not studied in detail by Sierra (2000), which could be studied as well as the effects of mPE in hot air sealing. [37]

2.2.2 Biopolymers

As mentioned in a previously in this chapter, biopolymers have increased in popularity of use in heat sealing applications. The production of biopolymers has been in the rise for a few years, as has the number of producers of biopolymers, trying to meet the need for sustainable polymers. These needs are also possible to achieve via copolymerization, which was by Liewchirakorn et al. (2018), as they studied transparency and peel-sealability of PLA and poly(butylene adipate-co-terephthalate), PBAT, co-polymer. One of the main advantages of biopolymers is that unlike petrol-derived polymers, biopolymers are fairly easy to recycle. [6, 23]

Biopolymer try to reproduce mechanical properties of most common polymers, such as LDPE and PP. PLA or polylactic-acid is one of the more common biopolymers in use because of its very similar properties to LDPE, which makes PLA very desirable biopolymer to use. PLA is polymerized from lactic acid, which can be gained from various grains such as corn. Figure 4 presents polymerization of PLA from corn to lactic acid and through cyclization to lactide and finally to PLA after lactide has been processed with ring open polymerization. [13]

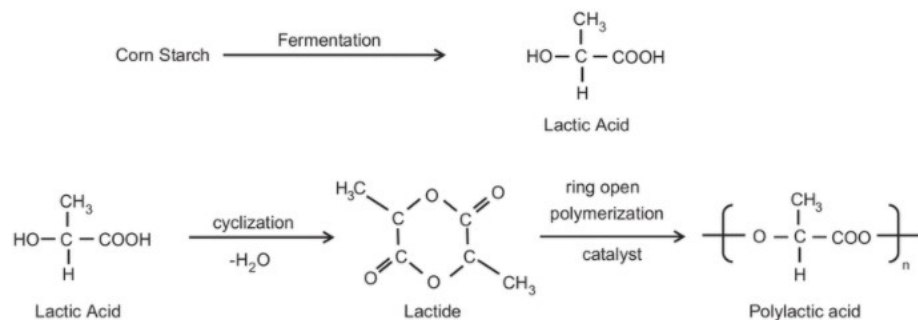


Figure 4. Structure and polymerization of PLA from corn to lactic acid to PLA [13]

2.2.3 Dispersion barriers

Dispersion is a method of forming a polymeric barrier film for paperboard to enhance certain barrier properties. Dispersion itself is liquid latex mixture consisting of water-insoluble comonomer e.g. butyl acrylate and styrene, water-soluble comonomer e.g. acrylic acid and methacrylic acid and a wide arrange of fillers, antioxidants, emulsifiers, plasticizers and buffers. The latex mixture can include any amount of fillers and polymers in it, providing almost infinite amount of different formulations of mixtures to make, which is why the specific recipes for dispersions are withheld by the companies and providers. Extrusion coating is a similar process to dispersion, in both the aim is to provide extra barrier coating to paperboard. The main difference between the two is that extrusion coating uses typical barrier polymers, like LDPE, whereas in dispersion coating latexes are used, which enables the use of other polymers. For this reason, barrier polymer dispersion is also called as barrier dispersion or polymer dispersion, to differentiate the two methods from each other. [21]

Dispersion is applied to the surface of paperboard similarly to pigment coating, where the coating is first applied to the substrate, then dried and finally cooled followed by winding back to a roll. The application of dispersion to the paperboard is achieved with an application roll, a rubber-covered roll that transfers the latex from a pool to the substrate. When the latex is applied, the polymer film forms in three distinct states. The first step is water evaporation, which occurs after drying and the water is evaporated from the latex until there are nothing else but polymer particles in the dispersion. Dense packing occurs after the water evaporation, when the polymer particles start packing themselves on to the surface of the substrate and on each other. Coalescence is the final step, during which the particles finalize the stacking by forming a uniform layer. These processes are presented in Figure 5. [21]

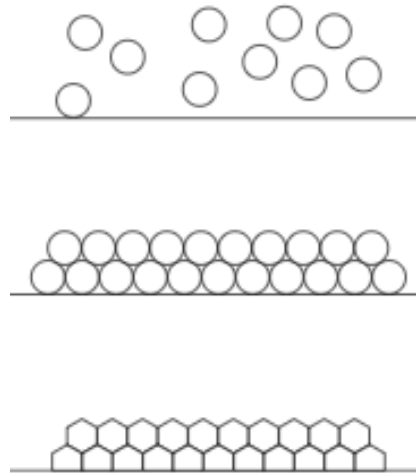


Figure 5. Dispersion polymer film formation [21]

Dispersion coating requires an uniform polymer film, which is gained right after the application, before the drying stage, with a rod, an air doctor or a blade. There are other methods to meter the dispersion film, but these methods are taken into consideration because these methods form different dispersion surfaces. There are two main possibilities for the dispersion film surface to form, even surface and even coating. With the blade, an even surface is achieved, as the blade evens the surface and removes the excess dispersion from the surface, and this provides a great surface for printing. Even coating is gained with the air doctor by following the grooves of the substrate as the dispersion is evenly dispersed throughout the surface. The surface of the dispersion follows the dents of the substrate, so this surface is not as suitable for printing as even surface is but there is less dispersion and polymer particles in the even coating. The rod is used to form a coating somewhere between even surface and even coating. Differences between the two is dispersion coats are illustrated in Figure 6. [21]

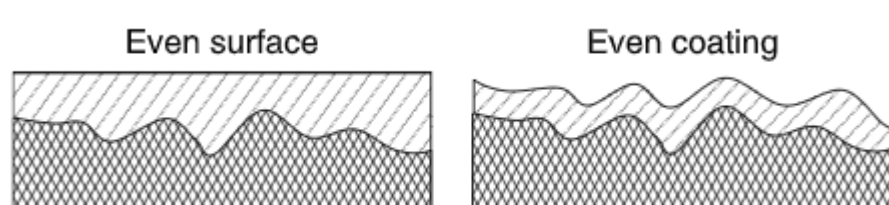


Figure 6. Illustrated difference between even surface and even coating of polymer dispersion coating [21]

2.3 Sealing techniques

Paperboards require perfect, hermetic seal in order to function properly. The following chapters will go into detail on various sealing methods used to produce seal explained beforehand. Most of the methods mentioned in the preceding chapters will include heat and pressure being applied to the areas of the seal to be formed, but some do not include heat as a part of the mechanisms of sealing. This is used to give perspective in different sealing methods that use heat as a part of the sealing process and those that do not use heating in major functions of the methods.

All heat sealing techniques needs to establish specific ranges of temperatures, where the sealing temperatures enable the materials to be sealed perfectly. This is crucial for the heat sealing process, as too low temperatures might leave the seal too weak as the polymers in the substrate have not melted enough. The other problem comes if the substrates are heated using too high temperatures or for too long, as the prolonged heating can cause the substrates to burn, which will make the seal not as good. [29]

The previously mentioned specific temperatures are called seal initiation and plateau initiation temperatures. Figure 7 presents these temperatures in a temperature-seal strength curve, where the seal strength axis can be changed according to the used parameters of evaluation of seal strength. The seal initiation temperature is the temperature where the sealability starts to increase, as both seal strengths and adhesion values become higher as the temperature rises. This will reach a high point at the plateau initiation temperature, at which point the seal will reach the highest seal strengths and the best sealability is achieved. If the temperature rises after the plateau initiation temperature, the seal will lose its strength and the adhesion will be weaker. [29]

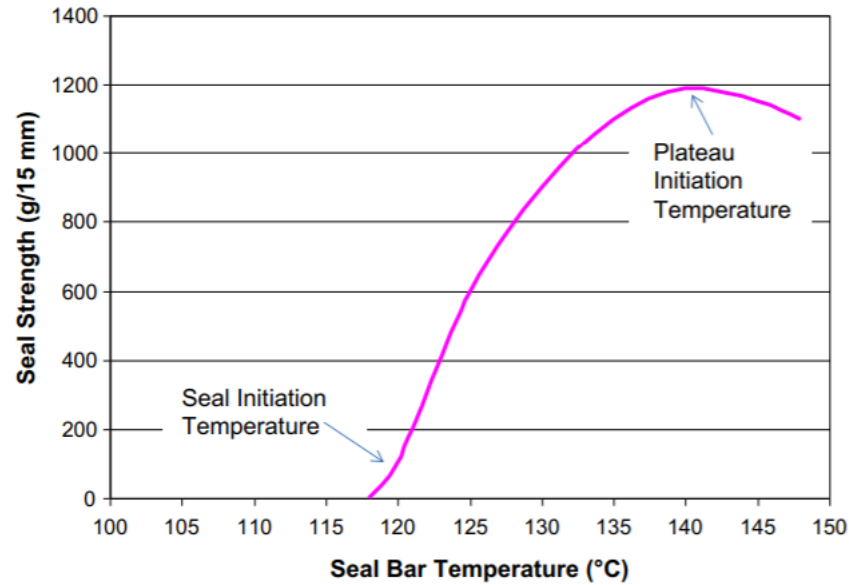


Figure 7. Seal initiation temperature and plateau initiation temperature of a polymer film in hot bar sealing [29]

It is necessary to make sure that the surfaces to be sealed are clean and uncontaminated. This is universal for all sealing methods, heat or cold sealing. Bamps et al. (2019) studied how solid contamination particles affected the sealability of different polymer films commonly used in packaging applications. Contaminations on the surfaces were imitated with ground coffee and blood powder and for both contaminants, seal strength decreased with contaminants on the sealed areas and seal temperature and seal time both had narrower processing windows than uncontaminated seals. [4]

2.3.1 Hot air sealing

Hot air sealing is a widely used method to seal multiple paperboard grades and a great variety of plastic films. As the name suggests, hot air sealing produces a seal by using hot air that is blasted to the sealing area with hot air nozzles.

Unique to the hot air sealing method is that the heating is done for both of the surfaces simultaneously to ensure good sealability. Hot air is applied to sealed surfaces from heating nozzles. Common sealing times range between 0.3 to 1.5 seconds. Polymeric films are the ones that are mostly affected by the heating, as the polymer films will start melting at these temperatures, as shown in the Table 1. For base and coating materials, heating provides better adhesion by increasing surface energy of the sealing area. The effects of surface energy in adhesion are discussed in more detail in chapter 3.3.

After the heating is done, materials are transferred to pressing plates to be pressed together and for the seal to be formed. Pressing tools should be unheated and large enough to completely cover the sealed samples. The time it takes for the substrates to be transferred to pressing from heating is called open time, which would be zero seconds in optimal cases but in reality open time is usually about one second. Open time can be reduced by improvements to the machinery, like closing the distance between the heating nozzles and the pressing tools or making the moving unit move the samples faster.

There are two temperatures that are measured in hot air sealing, the blown air temperature and the surface temperature of the sample. The blown air temperature is also called set temperature because it is the temperature of the air that is blown to the substrates, and this temperature is set into the sealing machine. Surface temperature is measured, as the name implies, from the surface of the substrate. This temperature is usually only taken from one of the samples, not from both of them. The surface temperature is the average of three temperature measurements of the surface that is measured, to ensure proper result. Either of the temperatures can be presented as the final results, as either temperature can be used as a comparison to other heat sealing methods.

Hot air sealing is a great method to form side seals for paperboard cups, which cannot be gained with hot bar sealing. The hot air sealing apparatus provides possibility to heat cups side seams from inside and outside and press them together to form the seal. The bulky structure of hot bar sealer does not have room for the tight structure that the cup sealing requires. [19]

2.3.2 Hot bar sealing

Hot bar sealing is the other widely used heat sealing method used in a large range of different products in multiple fields of application. Hot bar sealing is sometimes called hot jaw heating, but for this thesis the term hot bar sealing will be used, when referring to the process unless term is used in a direct reference from a source.

Hot bar sealing produces a seal as two heated bars are pressed together with the sealable materials between the bars. There are also systems with only one heated bar, where the samples are pressed against a base that does not affect the sealing results, for example in systems where the base is made of thermoset polymers. The process is fairly similar to the process of hot air sealing, but the pressure that is applied to the paperboards is applied at the same time as the heating is occurring, so there is no open time parameter to evaluate. Because pressure is applied to substrates with heat in hot bar sealing, temperatures are typically lower than in hot air sealing, as pressing the samples during heating makes the polymers to adhere to surfaces while heating. Figure 8 presents differences in sealing temperatures of hot air and hot bar sealing, where blue pillars represent the temperature of the blasted hot air in hot air sealing (HAS) and green pillars are the temperatures of the bars in hot bar sealing (HBS). [1, 19]

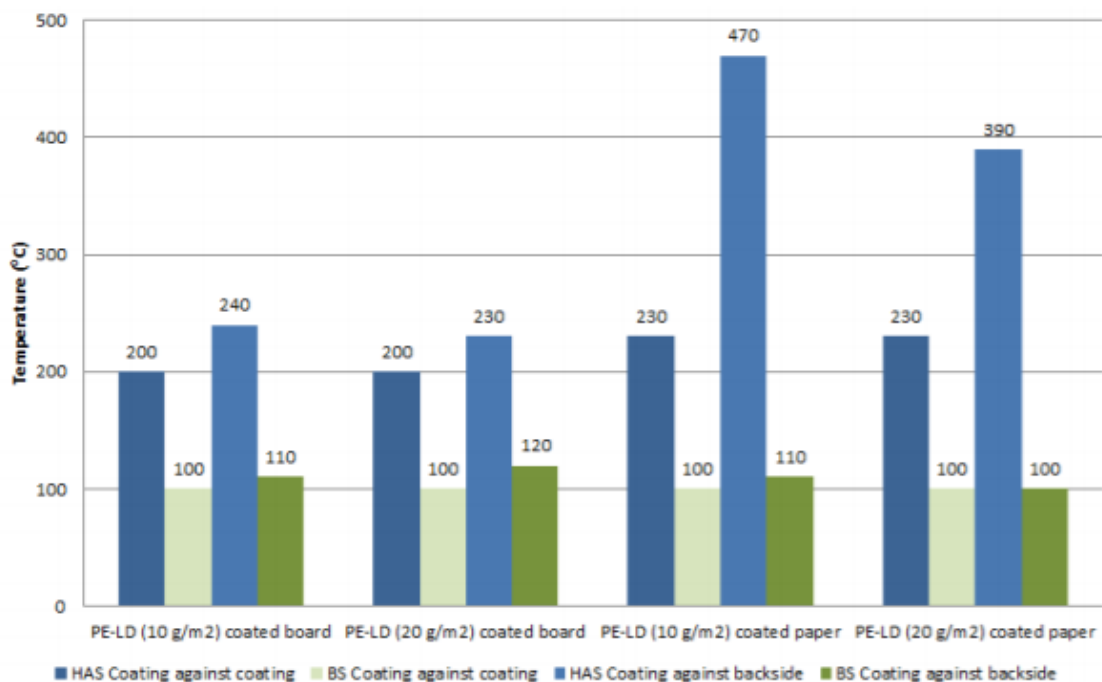


Figure 8. Typical sealing temperatures of paperboards for hot air and hot bar sealing [19]

The Figure 8 presents differences in sealing temperatures between hot air and hot bar sealing. The Figure 8 also present differences between sealing two polymer substrates and sealing polymer substrate with a backside of a substrate. The backside of the substrates were not disclosed in the poster, but in general, the backside can be coated with a coating or it can be uncoated and having the fibres be the other substrate to be sealed. The Figure 8 shows that in hot air sealing, polymer-backside seal increases the sealing temperatures compared to polymer-polymer seal. As both polymers are melted during the heating, the diffusion of the two polymer films becomes easier and adhesive bond forms between the substrates. For polymer-backside seal, as there is only one polymer film that provides the adhesion for the seal, it makes the polymer-backside a less effective way of sealing when focusing on the sealing temperatures, as higher sealing temperatures require higher amounts of energy to be applied to the surfaces. [19]

The Figure 8 also compares the effects of materials with different thicknesses and base materials. The two left-most groups of bars show differences of hot air and hot bar sealing of coated boards and the two groups of bars in the right are sealing temperatures for coated paper. Blue bars indicate the hot air sealing temperatures and green bars are temperatures for hot bar sealing, and it is clear that hot bar sealing provides perfect seals at lower temperatures. [19]

Pressure is similar in both methods, but in hot bar sealing, the heating is occurring at the same time as the pressure is applied, whereas in hot air sealing the seal has time to cool before the application of the pressure for the open time duration. The temperature of the bars can be determined with temperature sensors inside the bars, where the heating unit of the bars are also located. This is a method for one kind of hot bar sealer unit, there are other methods to heat and measure the temperature of the bars. The illustration of the bars and the units inside the bars is presented in Figure 9. [1]

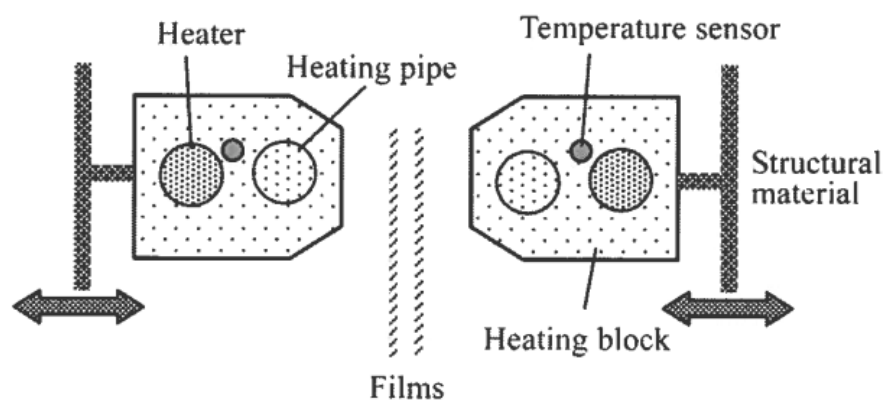


Figure 9. Hot bar system with two heating bars [1, p. 31]

To measure the temperature of the bars, one of the more common methods is for the device to calculate the temperature with either sensors inside the bars or based on the amount of energy put into the heating systems. The sensors calculate the temperature based on the input of energy and the heat capacity of the material the bars are made out of. The energy input is measured by joules generated from the heaters, but not all of the energy is lost during the heating, which is taken into consideration on the calculations. [1]

Farris et al. (2009) had an experiment focused on similar issues as this study, which is how different sealing conditions effect PP film with bio-based thin films seal strength during hot bar heating process. The results indicated that increasing temperature increases the seal strength, as the polymer film melts more and spreads across the films providing better adhesion. Pressure was another of the parameters studied, but unlike temperature, increasing pressure close to 4.5 bars decreased the seal strength, as the researches hypothesized that the polymer film would be pushed out between the two bars pressing the film. [9]

2.3.3 Ultrasonic sealing

Ultrasonic sealing is an unique method of sealing, because unlike other sealing methods, ultrasonic sealing uses vibrations in conjunction with pressure to produce a seal. Ultrasonic sealing machine produces seals by converting low frequency electric energy from the generator into high frequency mechanical energy using piezo-magnetic and piezo-electric elements. The mechanical energy is amplified in converter and booster until the energy is transmitted to sonotrode or the ultrasonic horn. The vibrations are focused to the materials to be sealed via the horn. To produce the seal, two materials, at least one of which needs to have been laminated with polymer film, vibrations need to be converted between an anvil and the horn, as the combination of vibration and pressure melts the polymers between the materials and press them against the surfaces for adhesion. All of the components and equipment for ultrasonic sealing machine are presented in Figure 10. [1, 41]

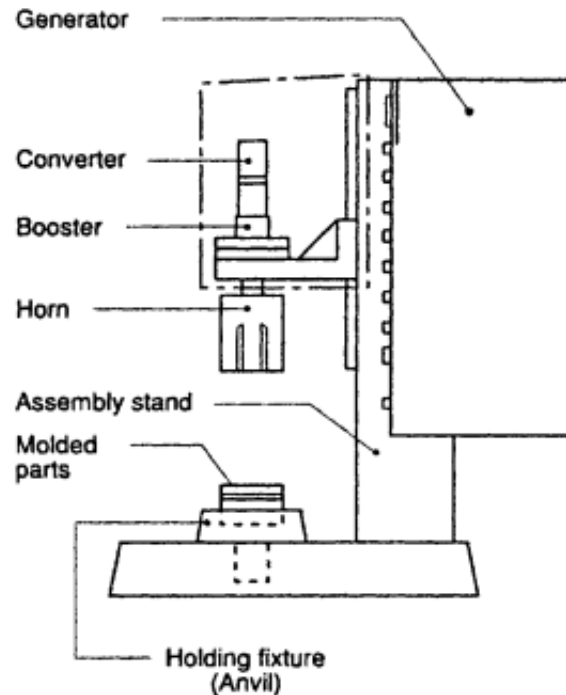


Figure 10. Components of an ultrasonic welder [39]

Ultrasonic seal is formed in four distinct stages. In the first stage, the horn makes contact with the substrate perpendicularly and pressure is applied starting from this point. The vibrations generated from the sonotrode are also starting to hit the material at the welding joint, as the heat generation gains the highest values at this point. Decrease in the distance between the sealed materials, displacement, increases during the first phase as the melt flow increases and melted polymer flows towards the edges of the surfaces. The two surfaces to be sealed make full contact at the second stage. As the surfaces meet, pressure increases between the surfaces increasing melting rate. Third stage, also known as stationary melt-off phase, the melted polymer starts forming a constant melt layer with constant thickness forms in the seal. The even thickness of polymer melt also provides constant temperature distribution throughout the melt. The maximum displacement is reached in the fourth stage of ultrasonic sealing process, also known as the holding stage, and any excess polymer melt flows out of the seal. During this stage, new polymer chains are being made in the polymer melt by the intermolecular diffusion if two polymeric surfaces were sealed together. After a certain threshold of time, energy or distance between surfaces is reached during the holding phase, the converter is turned off and the vibrations end but the pressure is still applied by the horn to ensure the best seal quality as the seal cools. [39, 41]

Choosing the sealing materials is crucial for ultrasonic sealing, because the vibrations do not affect the paperboards but rather the coatings. Molecular structures of the materials make it so that the vibrations melt different materials differently. Metallic coatings are not as suitable for ultrasonic sealing, as the vibration friction bounces off of the metallic surfaces and the energy is transmitted closer to the opposite substrate. [1]

Main advantage of ultrasonic sealing is that the method is the fastest way to produce a hermetic heating seal. The combination of ultrasonic vibrations focused in a small area and pressure applied in the said area, produces high temperatures very quickly and the pressure from the horn pressed against the anvil seals the surfaces together as the heating occurs. [8]

2.3.4 Cold sealing with pressure

This method is used commonly for packaging of products that are sensitive to heat, like chocolates and food products, as for these products, heat might cause harm or defect the packaged goods in various ways.

Coatings are an essential part in cold sealing, as the coatings act as the adhesives in cold sealing, as it provides the cohesive features needed for sealing. Some of the ingredients of the emulsions include water, ammonia, surfactants, biocides, natural rubber latex and an acrylic component, two last of which are responsible for the cohesive and adhesive applications respectively. [2, 7]

Cold seals are not that common seals used in packaging technology because of the required adhesive layers on top of the boards. Machinery is kept more simple when additives are not needed. This is not to say that cold sealing cannot be applied, some other methods are just used more. [2]

2.3.5 Flame sealing

Flame sealing can be seen as the predecessor to hot air sealing. Both methods are using hot air streams to form seals for polymer coated paperboards. Flame sealing has one great advantage that as the substrates are heated, they are also in the effects of surface flame treatment. The effects of flame treatment is discussed in more detail in the chapter 3.4.2.

As predecessor of hot air sealing, flame sealing was used to seal milk cartons and paperboard cups. The method is not as common nowadays, as open flames in paper and paperboard sealing applications can possess dangers to users and to the materials, as the possibility of burning is present in open flame sealing.

2.4 Comparison of the sealing techniques

Table 2 present differences between the different sealing mechanisms presented in the previous chapters. Their differences are presented by looking into their advantages and disadvantages. Some advantages include sealing a package with a product placed in the package whilst the product remains unharmed and unaffected. Disadvantage would be the opposite of this, as the mechanism cannot seal a products package without effecting the product. For these examples, cold sealing can produce seals without affecting the products in the packaging, while all the other methods can affects the products if they were used.

Cold seals have one great advantage over the other sealing methods, and that is the fundamental difference between the methods that cold seals do not require any additional heating. This lower the total costs of producing a seal, as heating requires high amount of energy to keep the high temperatures in a steady temperature. Other advantage of cold seals is that the sealing itself can be done in a short amount of time. The seal, as mentioned, does not require heating so the only step necessary is to place the materials together and apply pressure to form the seal.

Pressure being mentioned, the pressure can be seen as the more universal variable for the sealing methods, because it is required in all of the methods. Differences here are with hot air and flame sealing, where the pressure is applied after the heating is done, whilst in hot bar and ultrasonic sealing the pressure and heat are applied simultaneously.

Some of the sealing applications are also presented in the Table 2. Different packages sealed using heat sealing are presented in the Table 2, some of which might be unique to some sealing methods and some packages can have multiple choices of methods to pick from. For some applications, the geographic location might also influence the choice of sealing method, as ultrasonic sealing is a popular method of paper cup side seam sealing and in the western world, the same is commonly achieved with hot air sealers.

Table 2. Comparison between different sealing mechanisms [2, 7, 42]

	<i>Hot air sealing</i>	<i>Hot bar sealing</i>	<i>Ultrasonic sealing</i>	<i>Flame sealing</i>	<i>Cold sealing with pressure</i>
<i>Advantages</i>	Formed seal is very similar to the seal of final application Fast temperature changes	Heat and pressure applied simultaneously Low sealing temperatures Small scale testing	Heat and pressure applied simultaneously Low seal time especially with thicker samples Decontamination of sealing area	Simultaneous flame surface treatment	No heating required Saves on energy Sealing with the product in package Resealability
<i>Disadvantages</i>	Equipment costs Small scale testing can be difficult High sealing temperatures	Temperatures adjust slowly Bulky sealing equipment	Expensive and specific equipment Large seal impossible with one seal	Dangers of open flame and flammable gases Extra gas expenses	Adhesive or web required on either sealed surface Weak bond strengths
<i>Sealing applications</i>	Paperboard cups	Polymer films, single or multi-layered	Medical filters and other medical applications Sensors	Milk cartons and similar carton liquid packages	Chocolate wrappers Ice cream bars

3. PAPERBOARD AND POLYMER INTERACTIONS

Interactions between paperboard and polymer are crucial for the adhesion and other functions of sealing applications. The interactions can take multiple forms depending on the materials that are interacting with each other and environment the substrates are interacting.

Adhesion describes the interaction between substrates that can be either sealed together or adhered with adhesives together. Adhesion is often measured by seal strength of the materials, the force that is required to break the bond between two adhered materials. Seal strength measurement can be done by different peel tests. Some of the peel tests require large equipment where the sealed materials are pulled in a certain angle with a certain amount of force to calculate the seal strength. One of the more simple methods to measure adhesion is hand peel test, where the formed seal is broken by hand by tearing the materials and inspecting the fibre tear of the seal.

Adhesion can be improved by successful wetting of the adhered surfaces. Wetting inspects the close contact between the adhered materials, and is crucial in adhesion and further in the formation of a seal. Wetting is commonly inspected by contact angle measurements, in which a droplet of liquid is placed on the surface of a material and the angle between the surface of the material and the droplet is measured. The contact angles can then be used to measure surface free energy of the surface, which can be used to estimate the sealability of the surface.

3.1 Adhesion and wetting

Adhering two different objects is accomplished in one of two different methods, one is done by gluing adhered surfaces together. The other adhesion describes the state in of which two dissimilar bodies or surfaces are held together by adhesive forces. The contact provides mechanical force to be dispersed along the interface of the bodies. Adhesion is commonly associated with the force that is required to break the bond between coating and substrate material. Adhesion can be achieved by heating the substrates, one of which needs to be a polymeric material, and pressing them together. The melting provides the adhesive of the seal, and pressing makes the melted particles to intermingle between the pressed surfaces. After the pressing, the seal is allowed to cool down and the seal forms as the melted polymers solidify. Other method of forming adhesion is by using external adhesives, like glues, to form the adhesive bond between the substrates. Use of adhesives can be identified by the five distinct zones that will form with the use of adhesive. These layers are from the substrates, the adhesive and the interfaces between the adhesive and the substrates. [2, 36]

Wetting is an integral part of adhesion that is defined as the close contact between adhered materials. Wetting is crucial part in forming good adhesion and in conjunction with adhesion, they are necessary, when two or more materials are combined together. Wettings effects can be inspected by the spreading in liquids placed on to the surfaces of substrates. The easier the spreading of the liquids on the surfaces, the better the achieved wetting is. [36]

There are many theories on the subject of what causes the adhesion of two surfaces. Theories include but are not limited to: Mechanical interlocking, adsorption theory and diffusion theory. Following chapters will look into many theories of how adhesion occurs between adhered surfaces, how the theories differ from one another and what the functions for adhesion to occur are.

3.1.1 Mechanical interlocking

Mechanical interlocking is a theory describing adhesion between two surfaces occurring because one surface is penetrating into surface irregularities of the other material. Porous substrate, such as wood and paper, is a prerequisite for this theory to take place, as the pores in the surfaces of paperboard allow the adhesive to flow into the paperboard and provide high strength. When the adhesive is penetrating into the substrate, there are a few mechanisms on how the interlocking is happening. These mechanisms are presented in Figure 11. [10]

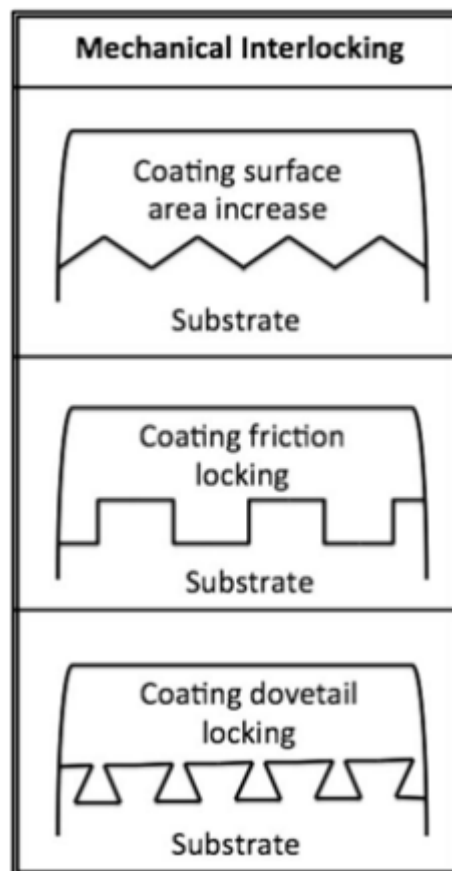


Figure 11. Schematic presentation of different mechanical interlocking mechanisms [11, p. 130]

The Figure 11 presents different mechanisms for mechanical interlocking to take place. Two of the illustrated mechanisms, coating friction and dovetail interlocking, are possible if the substrates surface has structure that enables the polymer melt to be locked between the porous surface. The irregularities provide structures that hold the melt in place and make the peeling harder. The top image presents the most usual surface structure for mechanical interlocking, as this is the most natural form of the three that surfaces can have and it is the easiest to achieve mechanically. As mentioned, increase in surface area does make the adhesion strength stronger. [10]

The adhesion is highly effected by the surface roughness, as studies made by Steffner et al. (1995) and Gardner et al. (2015) show that roughness increases porosity of the surfaces. And as mentioned previously, the rougher the surface, the more space there is for the adhesives to flow and provide higher adhesion strength. The increase of surface area is also shown by Gardner et al. (2015), as they demonstrate that the surface area increases from flat surface to rough surface with peak angels reaching 60°. This conclusion has some effects in peel strength, as the increased surface area gained from the rough surfaces produces higher peel strengths. [11, 41]

3.1.2 Adsorption theory

Adsorption theory's most integral part is in between the close contact and molecular and physical interactions. These same variables are also present in the wetting of a surface, which is why the adsorption theory is also referred to as wetting theory. In adhesion theory, wetting is a precondition required for adhesion to take effect. [3]

When two materials are adhered together, there are numerous forces determining the wetting process and the adhering of the materials. The forces, such as Van der Waals forces, covalent bond and hydrogen bond forces, distribute unequal charges that have different potential energy. The dispersive forces should, in theory, have more impact in the bond strength, but according to Wu (1982) this not always reached in practise. The total amount of these energies is what informs us if the wetting has been successful. [3, 44]

3.1.3 Diffusion theory

Diffusion theory is similar to adsorption theory, as both of the theories focus on the different forces affecting the surfaces of the materials to be adhered. Diffusion theory is according to Gardner et al. (2015) based on the solubility of two materials and as these materials are brought together, they form an interphase when in contact. After the formation of the interphase, the two surfaces are bonded together as the materials dissolve into one another. The materials are then mixed together and a seal between materials is formed. [11]

Comparing to other previously mentioned adhesion theories, mechanical interlocking is usually associated with substrates with porous surfaces, including paper and wood products. Diffusion theory is more related to polymeric surfaces, as in diffusion theory, only compatible materials with solubility values and parameters equal to one another are able to form a transition zone. The zone then allows for the molecules of the materials to diffuse together and form a seal. The higher the compatibility or the similarity of molecules of the materials is, the better the diffusion is and further the higher the peel strength of the seal is, which is why polymers are ideal for diffusion theory. The peel test and the function of it will be explained more in chapter 3.2.1. The interdiffusion between polymers requires almost identical polymers, but this might not be an issue because especially in packaging applications most common polymers are PE-based polymers, like LDPE and HDPE. [21, 34]

3.2 Peeling tests

After the sealing process has completed, the next step in testing the adhesion of the formed seal is peel testing. There are a few common methods to measure the strength of adhesion, each focusing on different area of adhesion. Peel seal tests determine the interfacial adhesion, which can be observed as increase of seal strength with the increase of heat temperature. Melt adhesion is measured with tear seal tests. These methods and their affects in adhesion is shown in Figure 12. The differences in the different polymers can be explained by the molecular weights of the polymers and their melting window. Medical grade PE has a very narrow melting window, meaning that there is only a few degrees Celsius between the highest and lowest melting temperature for PE, which makes the peel sealing zone so narrow. For PP copolymer, the reason for the wider peel sealing zone is the increased molecular weight of two different polymers in the copolymer. The higher the molecular weight, the higher the specific heat capacity of the material. Different polymers also widen the peel sealing zone as all of the polymers in the mixture might not have the same melting temperatures. [1]

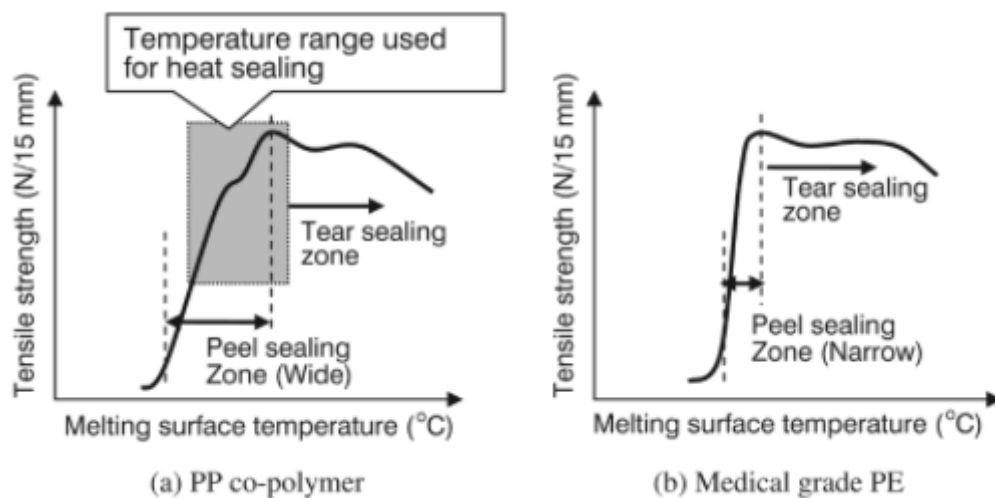


Figure 12. Changes in tensile strength as a function of melting surface temperature in different polymers [1, p. 8]

3.2.1 Peel and tear seal

As mentioned before, peel seal tests are used to measure the impact of interfacial forces being applied to the substrate through the adhesion, and tear seal measures cohesive adhesion. [1, 31]

T-peel systems are common testing system to study a formed seal and the strength of the seal. A schematic illustration of the T-peel testing system is presented in Figure 13. As the Figure 13 shows, as the seal is formed much closer to the other end of the samples to provide the claps of the T-peel system a handle to pull the samples. As the sample is pulled by the clamps, the seal experiences stress. The seal breaks as a peel seal, if the seal has been formed only by the interfacial forces, meaning that the seal does not penetrate deep into the structures of the substrates. If the seal has penetrated the substrate surfaces deeper and made a cohesive bond between the materials, the seal is considered as tear seal. Tear seals that are broken with T-peel systems will break the substrates from other areas other than the seal area. The cohesive bond is a strong bond and hard to break, which is why the tearing occurs outside the seal area. The T-peel test system is highly affected by the angle of the pulling direction, which is why it is essential to make sure that the angle of the two clamps pulling the sealed materials is 180° . If only one clamp is available, the angle would be 90° . [1, 29, 35]

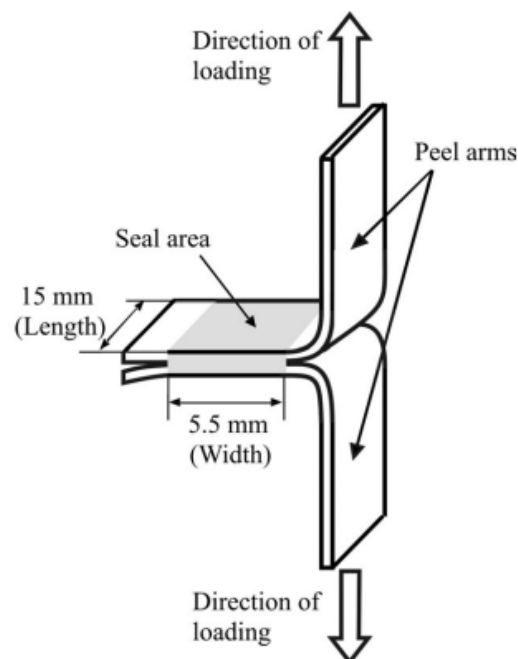


Figure 13. Illustration of 180° T-peel test system [31]

Nase et al. (2013) conducted a study to compare the effects of heat conductive sealing and ultrasonic sealing using T-peel sealing. The study did not specify the method of heat conductive sealing, but based on the given values of parameters, the method is most likely hot bar sealing. The T-peel system did not differentiate between the two systems, but the study focused on which parameters can be inspected as having equal impact on the seal strengths. [32]

3.2.2 Hand test

Hand test is the simplest one of the peel tests. The method does not require any additional mechanisms other than the sealing machine. The method is usually the fastest way to test the seal strength of a seal.

Hand test is done as the name suggests by hand. After the seal is formed with any method that are available to the tester, the seal is allowed to cool down. When the seal is cool enough that it feels cool to the hand, the seal is ripped by hand and the amount of fibre tear is inspected. The amount of fibre tear correlates to the value of adhesion the seal is given, which is presented in Table 3. [19]

Table 3. *Hand test sealability evaluation scale [19]*

Adhesion value	Evaluation of the value
0	No seal
1	Weak adhesion
2	Adhered but no tear
3	Under 50 % fibre tear
4	Over 50% fibre tear
4,5	Over 90% fibre tear
5	100% fibre tear

As can be seen from the Table 3, the hand test does not measure any specific values of units as the seal strength. This makes this method ideal for quickly measuring and comparing seals of different materials and surface combinations. More specific values can be gained from the peel and tear seal tests, as explained in the respective chapters. The two methods are also usually done after the formed seals have cooled down to room temperature overnight, whereas hand test can be done fairly quickly after the seal has been formed, making the hand test a good method for quick referencing for researchers. The hand test was the test method used in this thesis.

3.3 Surface energy

Surface energy, or surface free energy in some instances, described by Packham (2003) is associated with the excess energy that is present in the surface of the material. The excess energy of the surface is present because of intermolecular forces. In the interior of any material, the atoms are in an equilibrium, and in crystalline structured material, the interatomic forces, such as Van der Waals forces, are in balance. The stability of the forces between the interior atoms makes the bulk of the material stable, but the same is not occurring in the surface. According to Marshall et al., the exterior surface “is likely to be at least 5 atomic layers thick” (2009) and does not experience intermolecular interactions because the atoms there are not totally covered with other atoms than in other parts of the material. The difference of an atom in the exterior of the surface and an atom in the bulk of material is what surface free energy, γ , describes. [18, 34]

The effects of the surface energy can be divided to two force types: polar and dispersive. According to Sinayobye (2012), the sum of these forces is the surface energy or the free energy any surface has. The dispersive forces are formed from the interactions of Van der Waals forces being applied, whereas the polar forces are formed from multiple sources, such as dipole-dipole, hydrogen bonding and π bonding forces. [22, 36]

3.3.1 Contact angle measurement

Contact angle measurement is used to calculate the wettability of a surface, which can further be used to determine the surface energy of any given surface.

Contact angles are marked with a θ -symbol and the angle is measured from the base of the droplet in relation to the surface of the substrate. There are a few ways to place the droplet onto the surface of a substrate. The most common method, and the method used in this thesis, is called a sessile drop method. A sessile drop describes a liquid droplet sitting on a solid surface, which is then imaged with a camera as the droplet is placed in front of a light source. An image that the camera takes is presented in Figure 14.

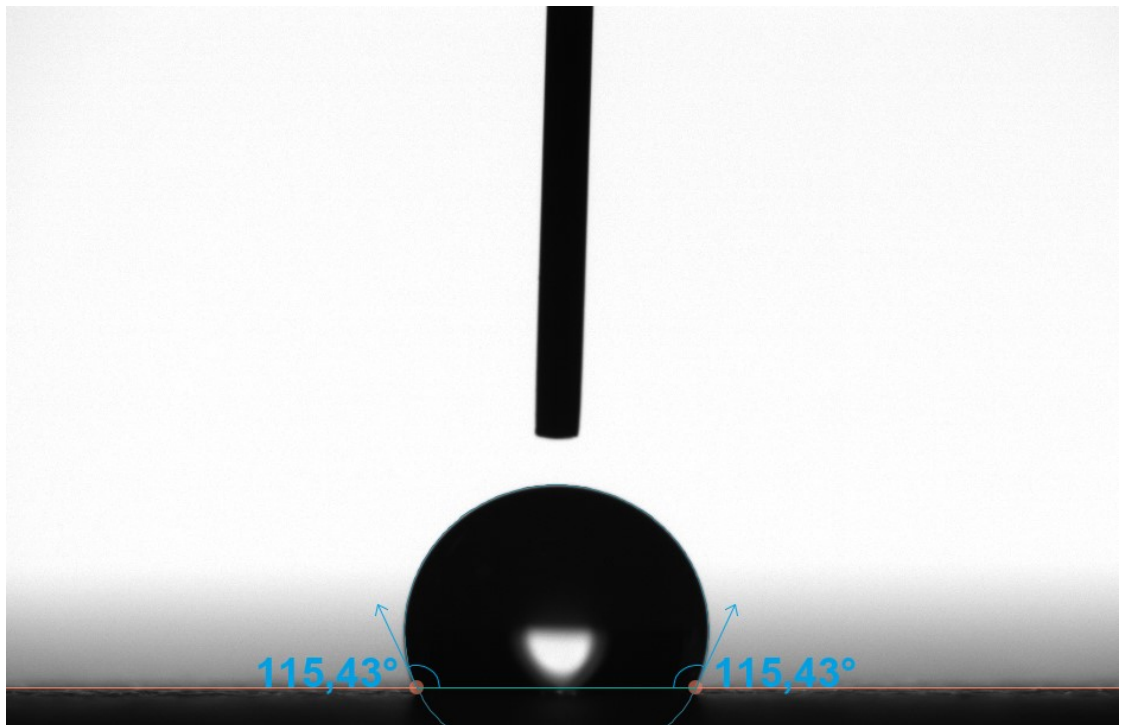


Figure 14. Sessile drop picture used to measure contact angles

The baseline of the droplet is where the contact angle is measured, and it is placed on the base of the droplet at the surface of the substrate. The baseline is automatically placed by the program, but it can be moved manually as the program can misplace the baseline. The contact angle is calculated on both sides of the droplet and the average contact angle is the final value used in calculations to come. The contact angle is used most commonly is Young-Laplace method to calculate the surface energy of a substrate. The Young's equation is as presented in equation 1: [34, 38]

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta_C \quad (1)$$

where the different angles of the contact angle are marked with γ_x , where the x can be either replaced with either L , S or SL . γ_L is the interfacial force of liquid deposited, γ_S is the solid deposited and γ_{SL} is the interfacial tension between the liquid and solid tensions. The θ measured the contact angle between the droplet and the substrate's surface. The Figure 14 shows that the contact angles are marked as the blue numbers. The angles are measured from the orange and green baseline, which is the surface of the substrate, and the base of the droplet placed on the substrate. In some cases, the tensions can be marked with σ instead of γ . This does not change the equations in any way, but it is common to see these being used interchangeably. [38]

There are a few options for contact angle calculations. Wu has a formula that is derived from Young's equation and has similar properties but is used more for polymers with relatively low surface energies, maximum of those being around 40 mN/m. Wu's equation is presented in equation 2: [44]

$$\sigma_{ls} = \sigma_l + \sigma_s - 4 \left(\frac{\sigma_l^D \cdot \sigma_s^D}{\sigma_l^D + \sigma_s^D} + \frac{\sigma_l^P \cdot \sigma_s^P}{\sigma_l^P + \sigma_s^P} \right) \quad (2)$$

In the equation 2, the subscripts mark the same tensions as mentioned previously in the chapter. The superscripts of D and P are used to mark the known dispersive and polar parts of the surface tensions of liquids. These are required in the measurement when using Wu's equation, and these parts need to be known from at least two liquids. Other prerequisites include that at least one of the liquids must have polar tensions greater than zero, as polar parts of liquids are not as commonly found as dispersive parts. [43]

When using multiple liquids, Fowkes expanded on the Young's equation to include more critical analysis on the different liquids. The equation Fowkes presented is presented in equation 3: [14]

$$\gamma_{ls} = \gamma_l + \gamma_s - 2 \left(\sqrt{\gamma_s^a \gamma_l^a} + \sqrt{\gamma_s^b \gamma_l^b} + \sqrt{\gamma_s^c \gamma_l^c} \right) \quad (3)$$

Equation 3 shows tensions marked with γ instead of σ , which shows the interchangeability of the two variables. The superscripts of the variables in the equation 3 present different liquids that are used in testing, the amount of which can be changed according to the place of testing. Some might use more liquids in the testing, which would increase the amount of variables in the equation, and others might use less liquids and the equation would in contrast have fewer variables. [14]

The contact angle can provide information on the succession of the wettability of the surface. When the surface wetting is poor, the contact angles will result in angles higher than 90° , forming a liquid droplet with an almost circle presence. A successful wetting decreases the surface energy of the substrate. Lower surface energy of the substrate effects the surface tension of the liquid placed on the substrate, as the droplet will try to minimize the surface area by adopting different shapes. When the surface energy of a substrate is lowered, the liquid's surface tension is also lowered as these values will equal when the droplet takes its shape. On the other hand, when the contact angle is lower than 60° , the wetting can be considered to be good, as the liquid spreads well across the surface. The presentation of different contact angles is shown in Figure 15. [40]

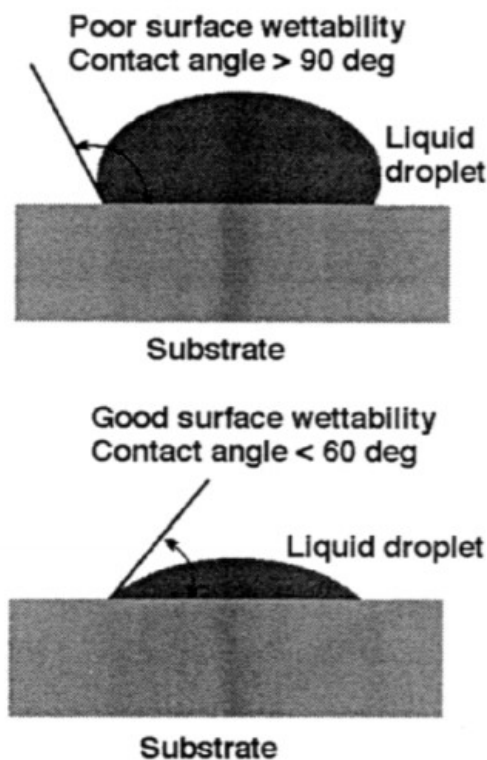


Figure 15. Effect of wettability of a surface to the contact angle between liquid droplet and substrate [40]

3.3.2 Effects of paperboard structure

Paperboards, as presented in the chapter 2.1, can have different amounts of plies in them. Generally, the thicker the material, the harder it is to seal the material. Thicker paperboards make it harder for the heat to penetrate material, making it generally more difficult to seal materials that are thicker or have greater grammages.

Paperboards that are used in food segment packaging applications are commonly coated with polymers to give paperboards additional properties of barrier against water or grease or both. The polymer coating also provides good surface for heat sealing, as polymer films make it easier for the board to seal to other polymer substrates, as the similar compositions of the polymer films will provide better sealability than if there were a polymer substrate against a paperboard fibre.

Gardner et al. (2008) studied the effects of cellulose crystallinity on the surface energies and found that crystallinity does not affect the surface energies of paperboard grades that much. Crystallinity of cellulose is commonly something that is not taken into account in studies, and this was studied by Gardner and determined that in general, it is fine to ignore these effects. [12]

3.4 Pretreatments of surfaces

Pretreatments are mainly used to increase the surface energy of a given surface. Depending on the method of pretreatment, the method can also provide sterilization of the surface or improved printability. The following chapters will inspect corona and flame treatments in more detail. The functions of these methods will be explained, as well as the applications for their uses.

In addition to corona and flame treatments, there are other methods to treat surfaces. Plasma treatment is used to achieve similar results as corona and flame treatments do, but will not be described in this thesis, as plasma treatment was not used during the testing.

3.4.1 Corona treatment

Corona treatment is a pretreatment done to plastics and plastics coated materials. The aim of corona treatment is to increase the surface energy of the substrate to increase the adhesive properties. Increased surface energy provides better wetting of the material, which makes any liquids placed on the surface spread over a larger area. Corona treatment units can be found in e.g. extrusion-coating lines.

The components of a corona treatment unit consist of treater station and power supply. The treatment units main application is to provide discharge from the energy of the power supply in the form of ionizing spray of electrons. Some of the electrons are accelerated by the voltage and blasted towards the substrate, which is placed over a nip roll that is electrically grounded. When the electrons are blasted towards the film, they impact with gas molecules and are accelerated even more. When the electrons acquire enough energy to penetrate the gas molecules orbiting electrons, they hit the positive ions inside the molecules. These ions are attracted to the treater and release even more electrons to the gap between the treater and the film. This increase of free electrons is seen as a purplish hue in the gap between treatment unit and the film, as presented in Figure 16. The electrons hit the film with high speeds and release positive ions from the film, in a similar way that the ions are removed from the gas. If corona treatment is kept going for too long, it might make the surface layer too thin and weak, making the adhesion harder rather than easier. So close inspection on the time of the treatment and the number of electrons blasted on the surface is crucial. The number of electrons is controlled by the power output. [3, 5,19]

When calculating the total effects that the corona treatment will have on the substrates, a unit energy of corona treatment is used to present the effects. The energy of corona treatment is marked with E ($W \cdot \text{min}/\text{m}^2$), and the equation to calculate the energy total is presented in equation 4: [15]

$$E = \frac{P}{uL} \quad (4)$$

The L in the equation 4 presents the length of the corona treater's discharger, or the width of the treated line, whichever is the smaller in meters. The u is line speed of the film in meters per second. The P is the discharge power of the corona treater, the units of which can be either kJ/s or W depending on the machine and the preferred unit of power. [15]

Cellulose has a great effect on the polarity of the substrate, which means that corona treatment can decrease the effects that cellulose has on the surface energy, according to Ovaska et al. (2017). The study conducted that the corona treatment of pigment-coated paperboard, such as the samples 1 and 2, increased the roughness of the coated surfaces. This increase in the surface roughness makes the contact angles of liquids higher, which in the case of a pigment-coat barrier provides better barrier properties, so corona treatment provided increased barrier properties. [29, 33]

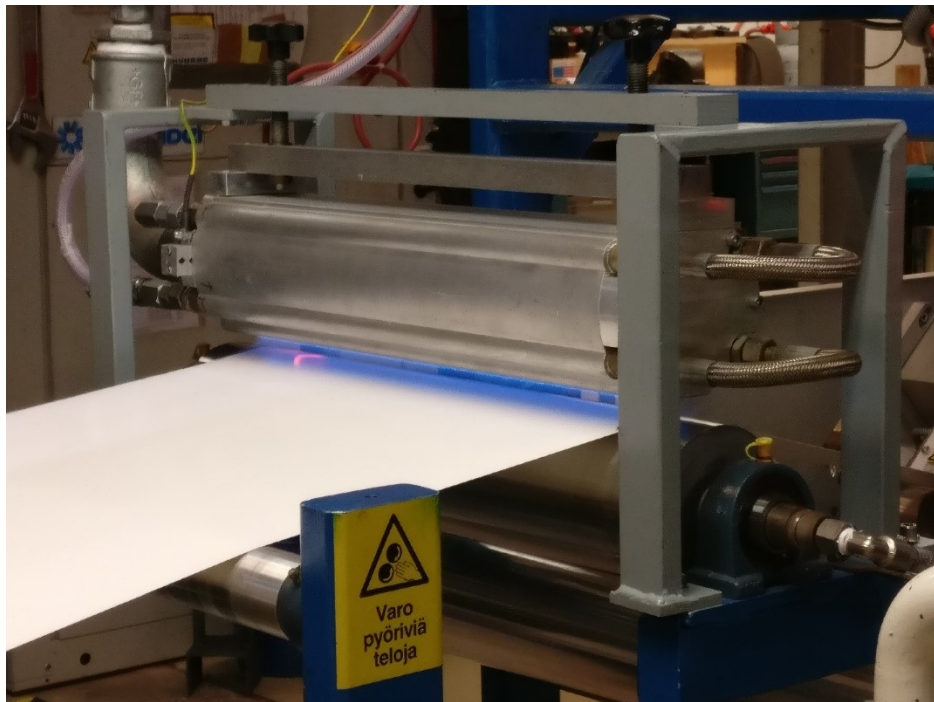


Figure 16. Active corona treatment unit of paper converting and packaging technologies research unit in TAU

3.4.2 Flame treatment

Flame treatment is a type of plasma treatment methods, in which the surface of a substrate is blasted molecules that are formed from combustion reaction occurring in the combustion chamber of the machine. The type of gas that generates the combustion in the combustion chamber can change depending on the manufacturer of the machinery, natural gas is a common choice.

The combustion reaction forms atoms, such as oxygen and nitric oxide, from free electrons of the gas. The molecules are then directed towards the substrates surface, where they impact and react with the surface atoms and the resulting functional groups improve the adhesion of the surface. One addition to the effects the flame treatment has is that the method provides is oxidation of the surface. According to Lahti and Tuominen (2007) the oxidation occurs for only a thin layer on the surface. Depending on the treated polymer, the affected layer can have a thickness ranging from 4 to 9 nm for PE-films and 5 to 20 nm for PP-films. [20]

4. RESEARCH METHODS AND MATERIALS

The target of the thesis was to study heat sealability of paperboards and factors affecting the sealability. Some of the factors can be a part of the heating process and other can be some properties of the substrates.

Three different paperboards were measured in the study. Samples were sealed by hot air and hot bar sealing to find differences in the methods and the materials. The heat sealings were done at TAU's Paper Converting and Packaging Technology Research unit and at Metsä Board Äänekoski's Excellence Centre's laboratory.

4.1 Studied paperboards

Paperboards that were studied for the thesis had properties and structures to suit drinking cup applications. The cups can be either used for hot or cold beverages.

When the results are assessed in upcoming chapters, the materials used in the testing are named based on their structure and baseboard grammage. There were three different paperboards used in the studies, where all of the paperboards had a PE-coating having a grammage of 15 g/m². Sample 1 is a coated paperboard with a grammage of 295 g/m², calcium carbonate and clay used as coating pigments. Sample 2 is also a coated paperboard with a grammage of 255 g/m², with same coating pigments as in sample 1. Sample 3 is an uncoated paperboard that has a grammage of 245 g/m². This means that the sample 1 is the heaviest by grammage and sample 3 the lightest of the samples, which will be taken into account when analysing the results. Thicknesses of the samples were measured and are presented in Figure 17.

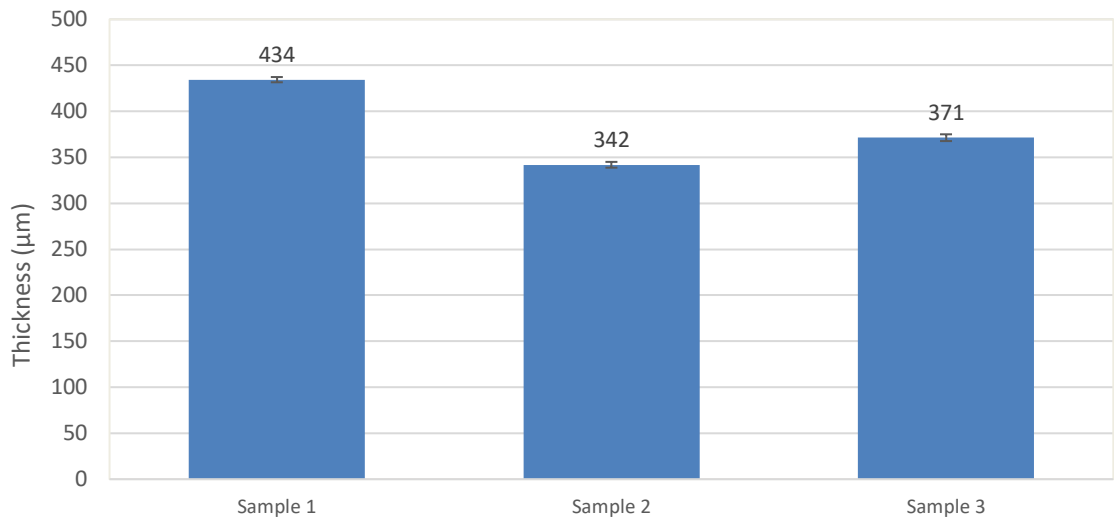


Figure 17. Thicknesses of samples

Sample 1 is the thickest sample, which was expected as the sample had the highest grammage. Sample 2 is slightly thinner material than sample 3, although sample 3 is lighter than sample 2, but this difference between the samples is insignificant in sealing applications. We can calculate the densities of the samples as we have grammages and thicknesses of the samples determined. These are presented in Table 4.

Table 4. Densities of the samples 1, 2 and 3

	Sample 1	Sample 2	Sample 3
Density (g/cm ³)	0.68	0.75	0.66

Thicknesses of the samples can have impact on the heat sealing results, but the effects of thicknesses are expected to be low. Densities were measured to give information on the possible effects, and as the densities of the samples are close to one another, the impacts of the structures of the paperboards can be expected to be low.

Other samples were tested during the time of this thesis, but only the samples 1, 2 and 3 will be under closer inspection. The materials used in certain tests will be mentioned as the part of the presentation of the results.

4.2 Heat seal forming machines

Tampere University's Paper converting and packaging research unit provided a hot air sealing machine for the experiments for this thesis. The machine operates by using two heating nozzles and two pressing plates. One of the pressing plates 150 mm in length and 3 mm in width and the other has width of 10 mm and the same length. The heat sealing nozzles heat standard sized samples with a length of 155 mm in cross direction and width 110 mm in machine direction. The samples are heated in machine direction through the full length of the nozzles. Each nozzle heats one side of a sample, the other nozzle heats the top of the bottom sample and the other the bottom of the top sample. After the heating, the samples are transported to clamps where the seals are pressed together to form the seal. [19]

Figure 18 below shows the hot air sealing machine at the paper converting and packaging research unit at TAU. Next to the sealing machine is the thermal imaging camera also used in the research.

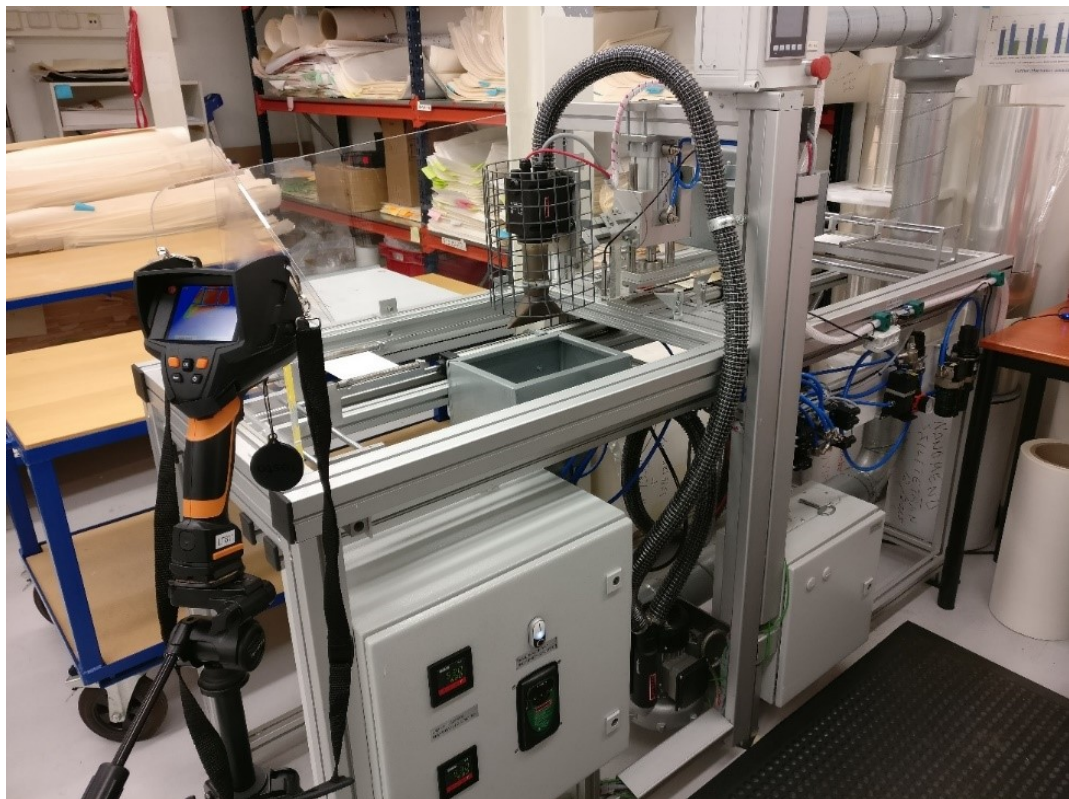


Figure 18. Thermal imager and hot air sealer in TAU

Hot bar sealing was the other method that was used to form seals. Figure 19 presents this machine located in Metsä Board's Excellence Centre in Äänekoski. The hot bar machine has two bars with different widths, which are used to form two different seals with a single press. The narrower bar has a width of 3 mm and the wider one has a width of 6 mm. The heat is applied from the bars only to the samples to be sealed, the base is made of a thermosetting polymer, which does not affect the measurements.



Figure 19. Hot bar sealing device

4.3 Contact angle

Contact angles were measured using Attension Theta contact angle measurement system with a sessile drop test.

Contact angles were measured using distilled water and di-iodomethane (DIM) as the polar and dispersive liquids, as these are the parts that comprise total surface energy. Some measurements were done by using ethylene glycol. DIM has advantage for measuring dispersive part of the surface energy, as DIM has only dispersive properties as a liquid. Ethylene glycol has some dispersive properties in it but also some polar properties, which can alter the results a bit because it does not provide a pure dispersive properties of a contact angle.

5. ANALYSIS OF RESULTS

The results of heat sealing and surface energy tests were gathered by the writer of the thesis. These results were gained with the assistance of the personnel of the TAU's Paper Converting and Packaging Technology Research unit and the Metsä Board Äänekoski's Excellence Centre. Some of the tests were conducted to other companies with the equipment to produce the results.

5.1 Hand peel tests

For the hand tests, the adhesion values were estimated visually with hand test, which was presented in the chapter 3.2.2 in more detail. The hand peel tests were done for both hot air and hot bar sealing.

5.1.1 Hot air sealing

Table 5 present the hot air sealing process that goes to reach an adhesion value of 5. Adhesion value 5 was always the target for the tests, because this was considered as the only option in commercial use during the testing. The process starts by setting blow time to 1.2 seconds, the longest time used in tests. For the tables that present these variables, the samples and their sides that were sealed will be marked to the top left corner of the tables. Then temperature was set to a temperature based on references from previous measurements and studies and then the first seal was inspected. Depending on the hand test result, the temperature was set to a higher or lower temperature until seal reached adhesion value 5. After the adhesion value 5 had been achieved, the test was done a second time with the was made sure by testing with the same parameters. If the seal is still perfect, the blow time was set to 1.0 seconds.

Table 5. Hot air seal, process of finding the lowest sealing temperature for a specific blow time

Sample 1 PE-side vs. Sample 1 PE-side	Blown air temperature (°C)	Surface temperature (°C)	Blow time [s]	Adhesion value
	200	96.7	1.26	1
	220	100.7	1.26	2
	230	105	1.26	3
	240	111.1	1.26	3
	250	113.4	1.26	3
	260	119.9	1.26	3
	270	123.7	1.26	4.5
	280	127.4	1.26	5
	280	128.5	1.26	5

Looking at the results presented in the Table 5, there are a few notes. Firstly, the surface temperature was measured from the sample that is mentioned first in the Table 5. This sample is the bottom sample of the seal and the surface temperature is measured right after the hot air has been fully applied to the substrates. Secondly, as the adhesion value of 5 has been reached at blown air temperature of 280°C, the next measurements will be done with blow time of 1.0 seconds and with blown air temperature of at least 280°C, as it is reasonable to expect that the seal will not reach perfect adhesion value with lower blow time, but sometimes the seal can form at the same temperature with lower sealing times.

Table 6 shows the variables for a PE-PE seal from sample 1's PE-films, the same material against itself. Only the combination of temperatures and blow times that resulted in perfect adhesion are presented in the Table 6. Table 7, Table 8 and Table 9 present other hot air sealing results.

Table 6. *Sample 1 PE - Sample 1 PE seal in hot air sealing*

Sample 1 PE-side vs. Sample 1 PE-side	Blown air temperature (°C)	Surface temperature (°C)	Blow time (s)	Adhesion value
	280	127.4	1.26	5
	300	128.2	1.06	5
	330	121.3	0.86	5
	360	124.5	0.66	5

Table 7. *Sample 1 Coating – Sample 1 PE seal in hot air sealing*

Sample 1 coating side vs. Sample 1 PE-side	Blown air temperature (°C)	Surface temperature (°C)	Blow time (s)	Adhesion value
	250	120.4	1.26	5
	280	126.6	1.06	5
	310	131	0.85	5

Table 8. *Sample 2 PE – Sample 2 PE seal in hot air sealing*

Sample 2 PE-side vs. Sample 2 PE-side	Blown air temperature (°C)	Surface temperature (°C)	Blow time (s)	Adhesion value
	230	104.7	1.25	5
	240	103.1	1.06	5
	270	107.1	0.86	5
	300	109.2	0.66	5

Table 9. *Sample 2 Coating – Sample 2 PE seal in hot air sealing*

Sample 2 coating side vs. Sample 2 PE-side	Blown air temperature (°C)	Surface temperature (°C)	Blow time (s)	Adhesion value
	240	115.7	1.26	5
	270	120.3	1.06	5
	290	119.7	0.86	5

Comparison of the results is presented in Figure 20, where blown air temperatures is shown as a function of blow time. Sealing curve indicates the lowest possible temperature for perfect seals. The heat sealing curves presented in this thesis will all follow this same principle of showing the combination of temperatures and blow times where adhesion reached the value of 5 in the hand peel test.

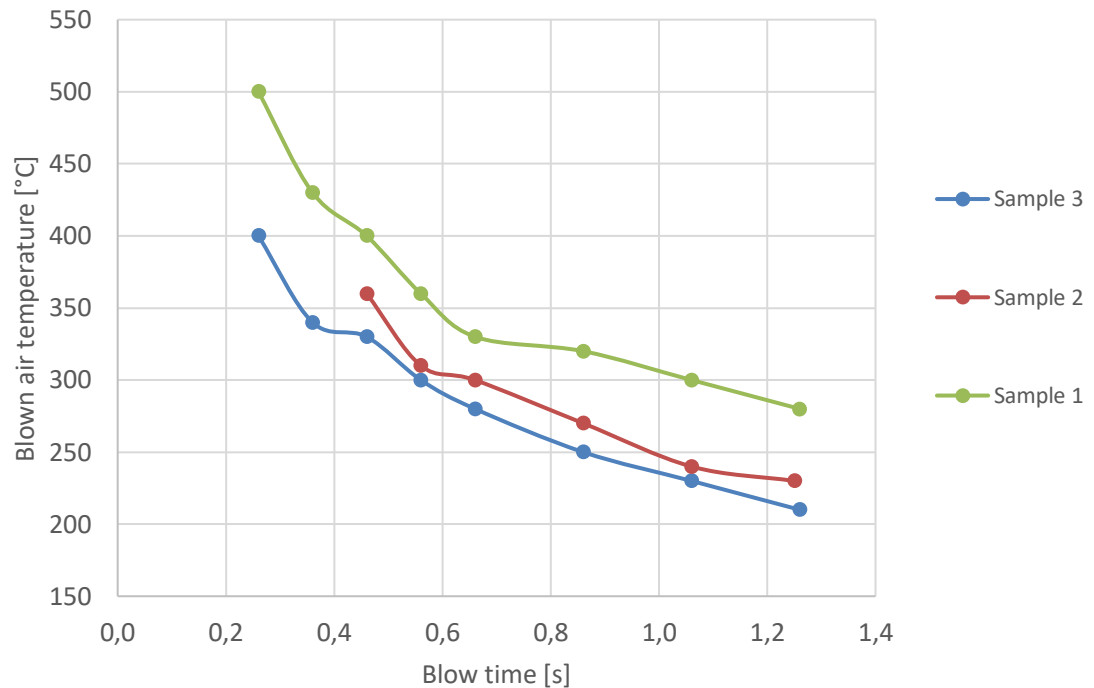


Figure 20. *Lowest sealing temperatures for perfect seal with PE-PE seal*

The Figure 20 indicates that the sample 1 has the highest sealing temperatures of the tested samples for reaching adhesion value 5 in hand peel test. Sample 2 does not have tests done for blow times at 0.36 and 0.26 seconds but based on trends of the curves of the Figure 20, it is fair to assume that the sample 2 would have lower sealing temperatures than sample 1 but higher than sample 3. The differences of the sealing temperatures are not that significant in the final sealing applications, where the temperatures cannot be changed easily, but the results give indications on the sealability of the samples. From the Figure 20, it can be estimated that sample 1 will have highest sealing temperatures, making the sealability of the sample harder.

Figure 21 and Figure 22 present different seal curves for different combination of substrates to study how factors presented previously affect the seal curves. The Figure 21 and Figure 22 do not have all of the measured curves in them, all sealing results are presented in the appendix A.

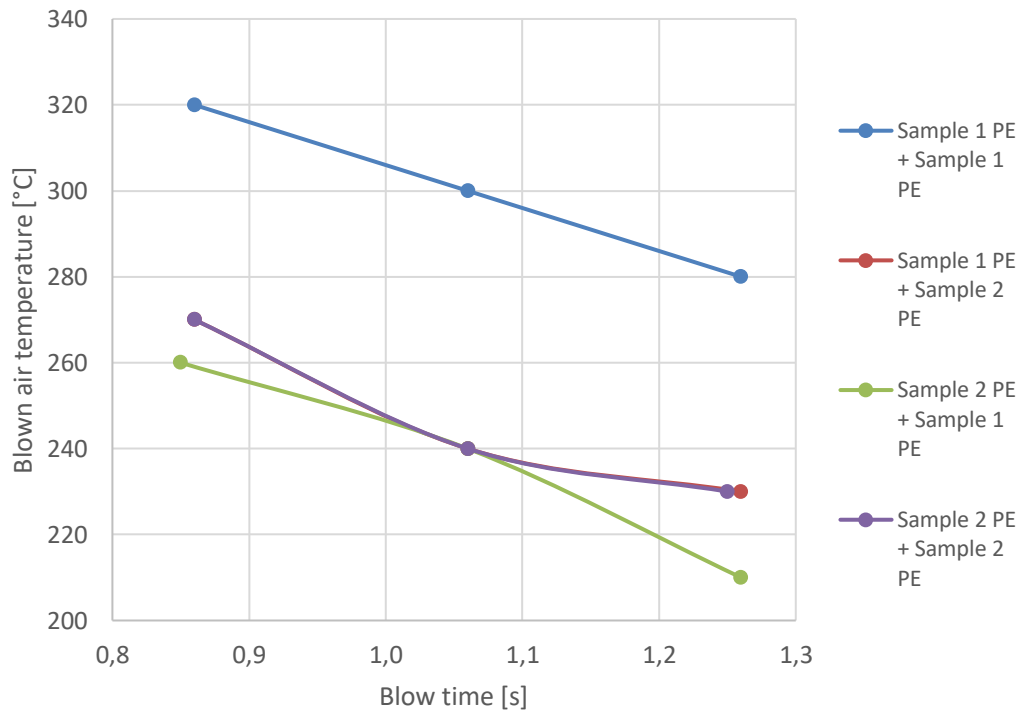


Figure 21. PE-PE seals in hot air sealing

The Figure 21 presents the blown air temperature-blow time sealing curves to study the effects of the PE surfaces of sample 1 and 2 in hot air sealing. Each of the PE-coatings were tested against itself and against the other PE-coating of the other sample. This way the effects of the different PE's can be inspected. The sealing curves of the PE-seals indicate that the sample 1 is sealed in temperatures ranging from 280°C to 320°C, the highest temperatures that were tested. Sample 2's PE-seals sealing temperatures range from 230°C to 270°C, and the combination of the two different PE's provide sealing temperatures at similar temperatures. The sealing curve of two sample 2's PE-coatings have identical sealing temperatures as the seal of sample 1's and sample 2's PE-coatings, so the curves of the two are on top of each other.

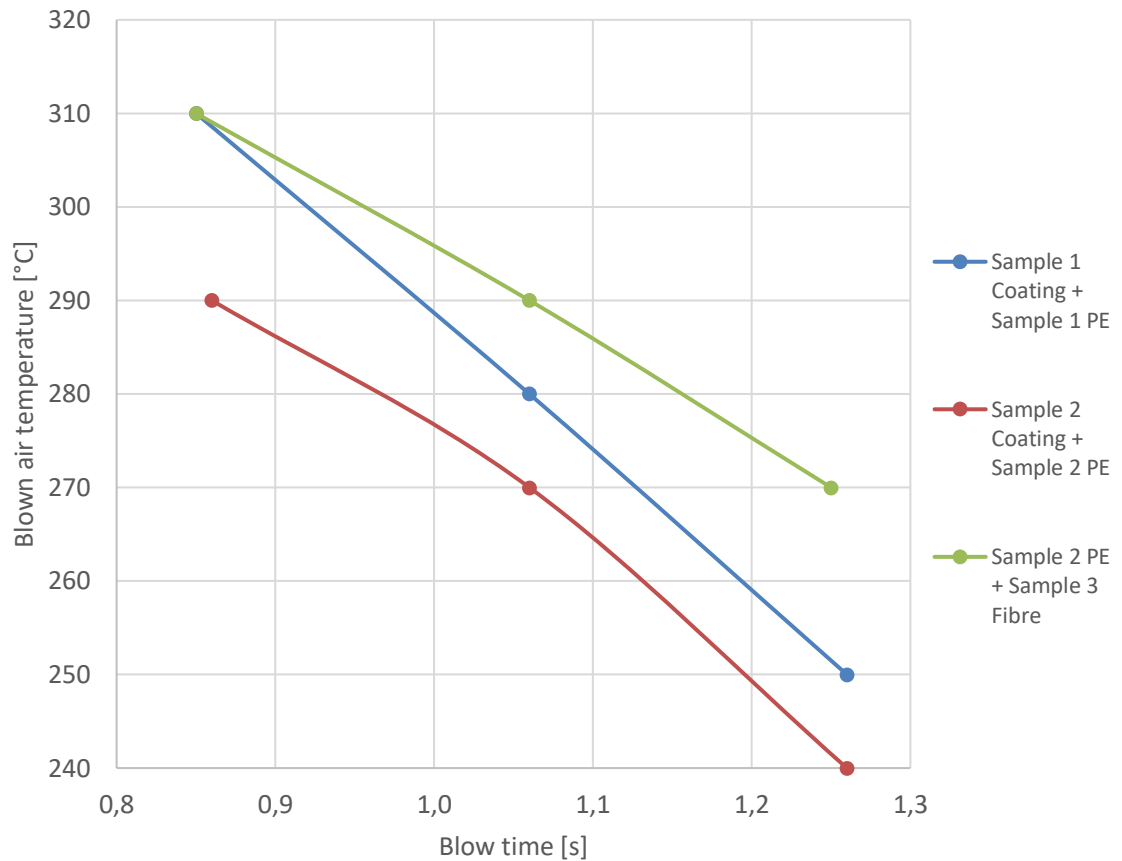


Figure 22. Effects of different surfaces on the sealability of samples

The Figure 22 present the effects that different surfaces have on sealing temperatures. Coating-PE seals have similar overall results as the PE-PE seals, where the sample 1 has the higher overall sealing temperatures than sample 2. The use of coatings in seals increase the sealing temperatures slightly compared to PE-PE seals' sealing temperatures. The same impact is seen when the uncoated fibre side of sample 3 is used with the PE of sample 2. The sealing temperatures of the different coatings with PE-coatings are relatively close to each other, differing from one another by an average of about 20°C.

Hot air sealing also measures the surface temperature of the seal. The surface temperatures are always measured from the surface of the first substrate mentioned in the seal, e.g. in sample 1 PE-sample 2 PE seal the surface temperature will be measured from the surface of the sample 1's PE. The results are not presented, because the results indicate similar results as the heat sealing curves with blown air temperatures. The heat sealing curves with surface temperatures for PE-PE seals are presented in the appendix A.

5.1.2 Hot bar sealing

The following results present the test results of hot bar sealing tests. As mentioned in the chapter 4.2, the hot bar sealing machine has one heating unit with two differently sized sealing bars. To ensure no polymers would melt onto the hot bars and affect the sealing results, the top samples always had the PE-side facing down.

The hot bar sealer has two pressing bars, 3mm and 6mm widths. These are similar to the two nozzles of the hot air sealing unit, so the results are comparable. The sealing curves in this chapter use the adhesion values gained from the wider bar used in the hot bar sealing device.

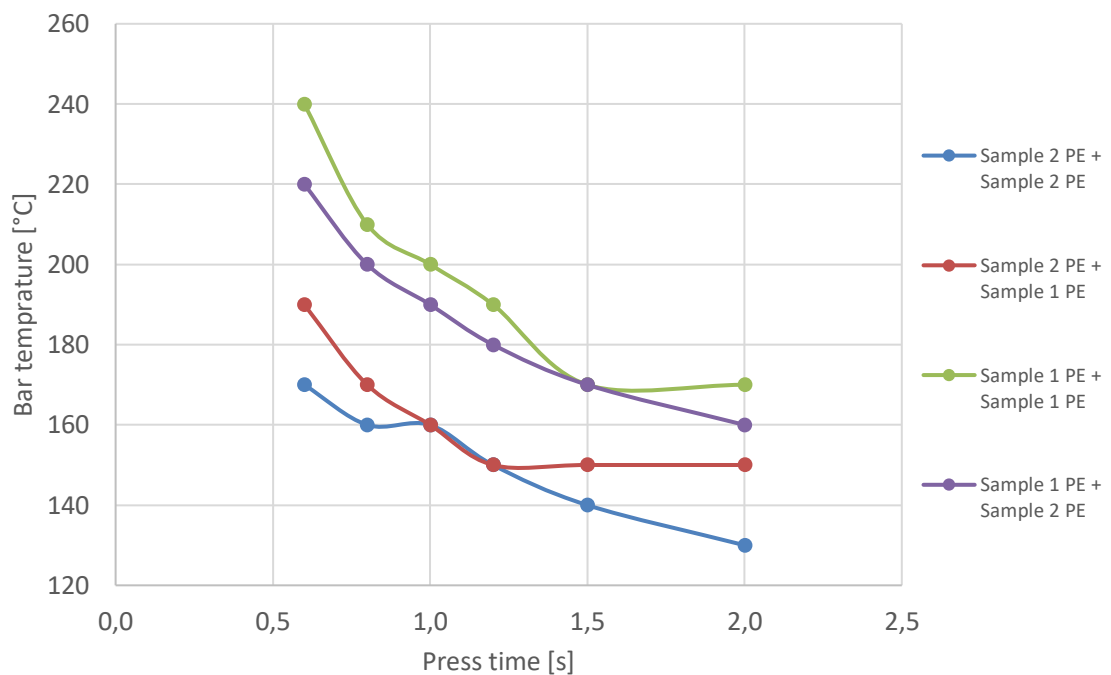


Figure 23. Sealing curves for PE-PE seals in hot bar sealing

First noticeable difference between the hot bar and hot air sealing curves is the significantly lower sealing temperatures in hot bar sealing, as presented in the Figure 23. For example, the PE-PE seal of PE-films of sample 2 produces perfect seal at around 250°C in hot air sealing, but in hot bar sealing the same temperature is only 160°C. This is because in hot bar sealing, pressure and temperature are applied to the seal area simultaneously. The pressure increases the effectiveness of the sealing by allowing the polymers to diffuse to the substrates while melting, making the sealing temperatures lower.

Regarding the differences in sealing temperatures between the samples, the hot bar sealing indicates similar results as the hot air sealing did. Sample 1's PE-PE seal still has the highest sealing temperatures of the tested samples, and the sample 2's PE-film appears to lower the sealing temperatures when used.

The Figure 23 also shows that the placement of the sample in the sealing process has impact on the result, as the comparison of the second and fourth curves of the Figure 23 show. When the sample 1 was placed as the top substrate for the sealing, the sealing temperatures increased in all pressing times, the minimum change in temperature being at around 10°C. The reason for this cannot be said with certainty, but the differences in composition of PE films can be presumed to have some effect on the matter, as the heat is transferred from one side only. The heating will melt the polymer film of the substrate in direct contact with the hot bar more than the other substrate.

5.2 Pre-treatment of the surfaces

The effects of corona and flame pretreatments on hot air sealing parameters and the longevity of the treatment effects were studied. The materials in the testing were not the samples that were presented in the chapter 4.1. The tests were done as a part of another study, so the materials in the testing, marked as sample 4, were not the samples that were presented in the chapter 4.1. The treated samples were paperboards with a water-based dispersion on one side and no coating on the other side.

Both corona and flame treatments were done at the Pilot line of the paper converting and packaging technology research group in Tampere University Hervanta Campus.

The materials were treated with either corona, flame or with both treatment methods to differentiate the effects of each method. Corona treatments were done for the dispersion-coated sides and fibre sides were treated with flame treatment. Other part of the research was to see if storing of the material inside a winded roll effects the treatments, so the treated films were stored in NTP conditions for 3 days and films were also hot air sealed right after treatments were done as a reference point.

For the corona treatment, the corona density was calculated with the equation 4 to be $15W \cdot \text{min}/\text{m}^2$. The flame treatment cannot be calculated as accurately but the effects of the flame treatment were set to be as close the corona density as possible. The differences in effects of the treatments are presented in Figure 24. If a surface was treated with either corona or flame, it will be marked at the end of the name of the sample, e.g. a corona treated surface would be marked as: Sample 4 Coating Corona.

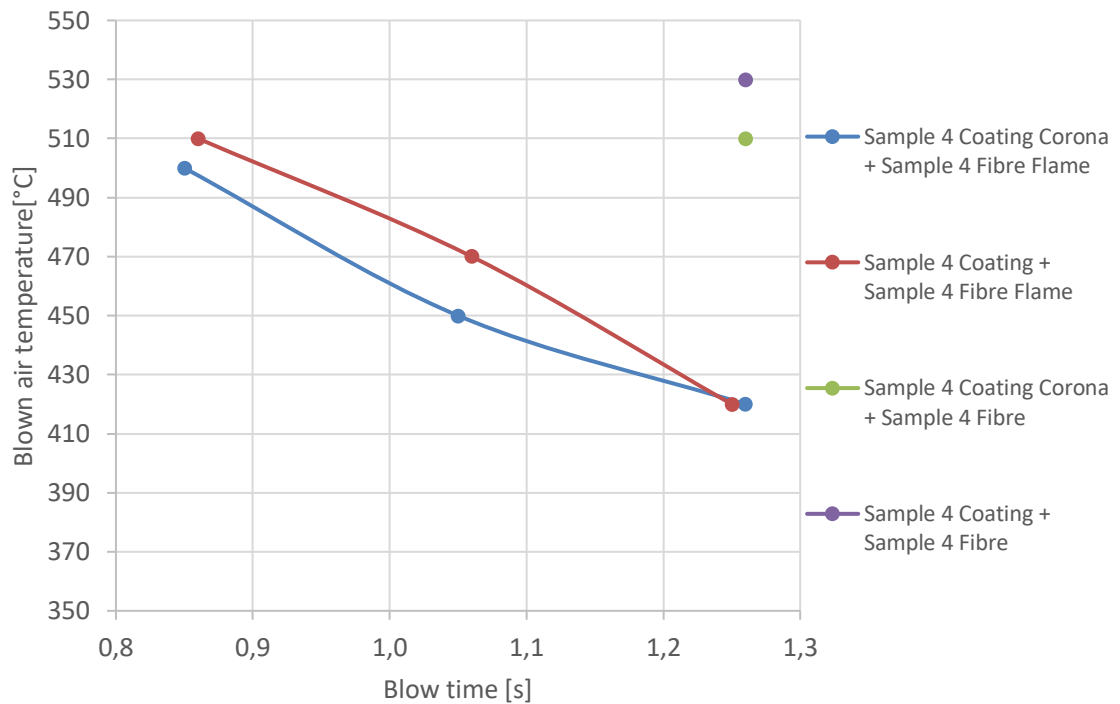


Figure 24. Pre-treatment effectiveness comparison in hot air sealing

The Figure 24 illustrates clear difference of effects, as flame treatment provides significantly lower sealing temperatures compared to non-treated surface or only corona treated seals. There are only one measurement points for corona-flame treated seal and corona-untreated seals because the sealing temperatures reached the maximum sealing temperatures of the hot air sealing unit. Lowest sealing temperatures were achieved when both treatment methods were used, which is expected. The corona treatment does not have as great of an impact on the sealing as flame treatment has, but corona treatment still has some effect. All of the sealing temperatures presented in the Figure 24 are very high for hot air sealing applications, so the samples as they are not very suitable for hot air sealing applications. But if the materials were to be used in these applications, both surface treatment methods should be used to lower the sealing temperatures.

The reason for the difference of the effectiveness's can be reasoned to be in the differences in the amounts that the treatment units put out. The corona treatment unit's energy output can be calculated and controlled easily, but the same cannot be said as easily for the flame treatment units, where the gas output cannot be as easily controlled. Other reason can be in the surfaces that were treated. The dispersion film might not be as effected by the corona treatment as the fibre side is for flame treatment.

To study this hypothesis, surface energies of the surfaces were measured. During these measurements, the longevities of the surface treatments were also studied. After the treatments of the surfaces were complete, the roll that held the samples after the winding was stored in NTP conditions, where the temperature is 20°C and pressure is about 1 bar. First surface energy measurements were done right after the treatments and then after 3 days of storing. These results are presented in Figure 25.

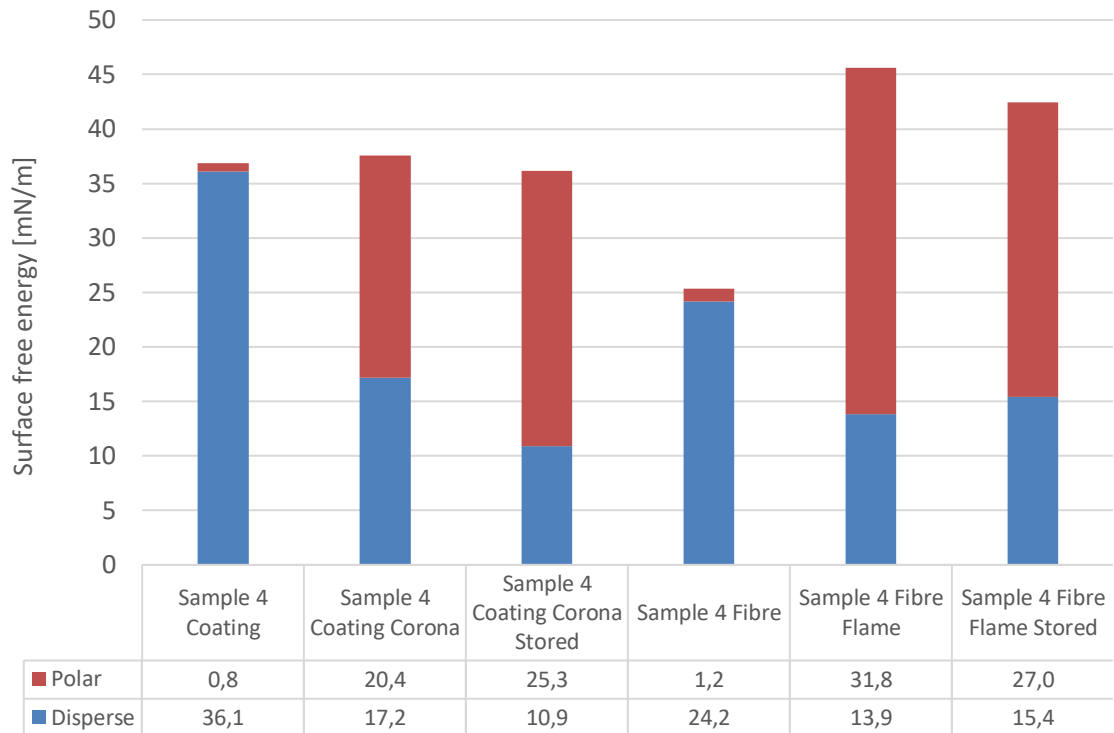


Figure 25. Surface free energies of sides of sample 4

The total surface free energies in the Figure 25 are divided into the polar and dispersive components of SFE. Contact angle measurements were done with water and ethylene glycol according to Wu's equation presented in the equation 2.

Corona treatment on the coated side did not change total surface energy. However, the effects of the corona treatment can be seen in the difference in its polar component, which was increased remarkably, but the dispersive component decreased to keep the total SFE the same. Flame treatment increased the total surface energy significantly on fibre side of the sample, increasing the SFE value from 25 to 45 mN/m. The same effects in polar and dispersive components can be seen in flame treatment as in corona treatment, as polar component increased and the dispersive component decreased. Comparing the two pre-treatment methods, it is clear that flame treatment had a greater impact on the treated surface, as corona treatment had almost no effect on the total SFE but flame treatment provided almost two times higher SFE compared to the untreated surface.

For both of the surfaces, the effects of the treatments are seen to be minimized as the samples were stored in NTP conditions. For fibre side, the majority of the lost surface energy is lost from the polar component. And for dispersion coating side, the dispersive component loses more of the effects as time passes.

It is clear that for sample 4, flame treatment of the fibre side increases the total surface energy and the polar component at such high quantities that the proper sealing can be achieved at much lower temperatures with the flame treatment. The corona treatment on the dispersion coating slightly increased the SFE but the effect is only minor. The effects of corona treatment seem to decrease the dispersive component on the coating, increasing the relative effect of the polar component. The same is present in the flame treated uncoated surface, but in higher relative amounts. The best adhesion and sealing results are gained when both corona and flame treatments are present in the dispersion coating-fibre seal.

5.3 Thermal images

Thermal imaging was used to see how the heat spreads over the surface of the substrate during hot air sealing process. The thermal images were taken with Testo Thermal imager 875.

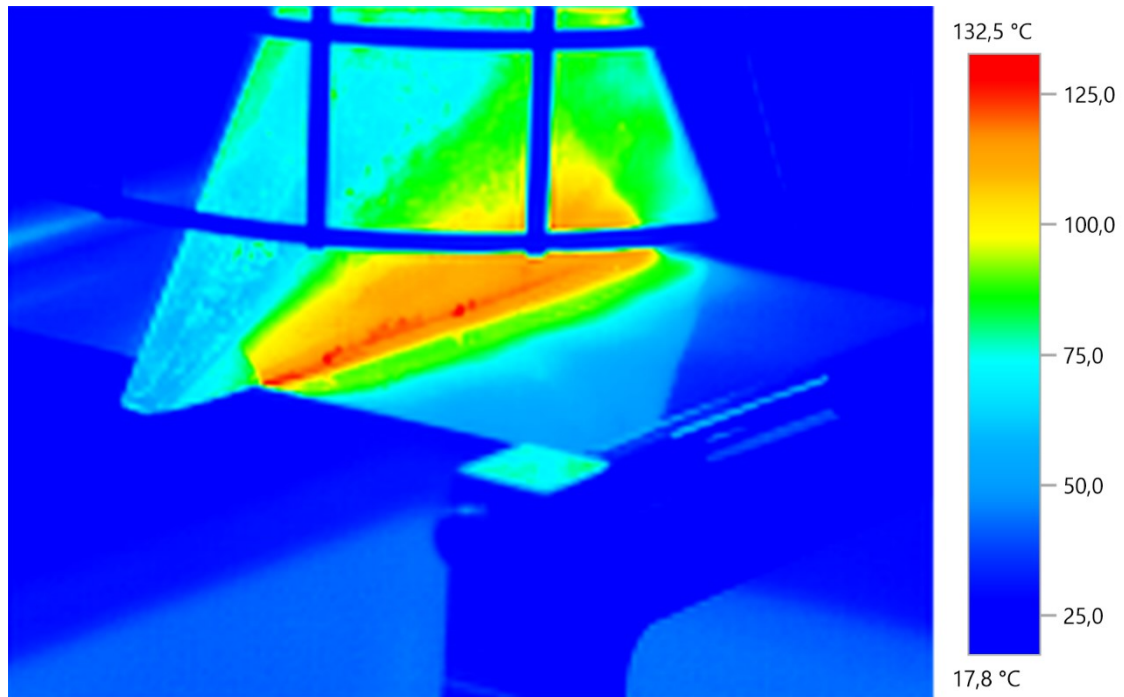


Figure 26. Thermal image of hot air sealing during the heating process

The Figure 26 presents an image taken with the thermal camera, which was accessed and modified with the Testo application. Temperature scale is presented on the right side of the Figure 26, which provides information on the coloration of temperatures that are present in the Figure 26.

The image shows that the heat spreads well close to heating nozzle. The temperature drops rapidly the farther away from the nozzle, which is expected for heat transference on substances. During the heating, the temperature of the nozzle itself dropped a little when the heating process began, as in that point the hot air has a way to escape the nozzle and it cools the nozzle down. It was noticed that during the heating process, the temperature of the bottom of the nozzle was close to the final inspected surface temperatures of the seals.

There is slightly warmer square in front of the sample. This is a part of the hot air sealing machine, which heated up during the testing for some reason. This part does not have an impact on the sealing, as it is a part of the clamps that hold the testing samples in place, so this heated part can be disregarded by the reader.

5.4 Optical topography

Optical topography was used to test the roughness's of the samples. Surface roughness can increase the sealing strength in sealing applications, if the adhesion takes place as mechanical interlocking. It can be estimated that the rougher the surface, the better adhesion can be achieved, but only in cases where mechanical interlocking is the form adhesion takes.

The results of optitopo will be presented in two forms: optitopo surface deviation (OSD) and crater/hill-analysis in different depths from the plain surface. Surface unevenness can be classified to different wavelengths by bandpass filtering. In this study the fine-scale variation lower than 0.5 mm was used to get OSD values. Hills is a term for higher areas of the plain surface and crater is a term for areas under the plain surface. The fine-scale will calculate hills and craters differing 1.5 μm from the plain surface.

Figure 27 and Figure 28 show the fine-scale height map images of the coatings of samples 1 and 2 respectively. Light green areas show plain surface. The more red the colours go, the higher the surface is from plain surface. And the more blue the colour map is, the deeper is the surface from the plain surface respectively.

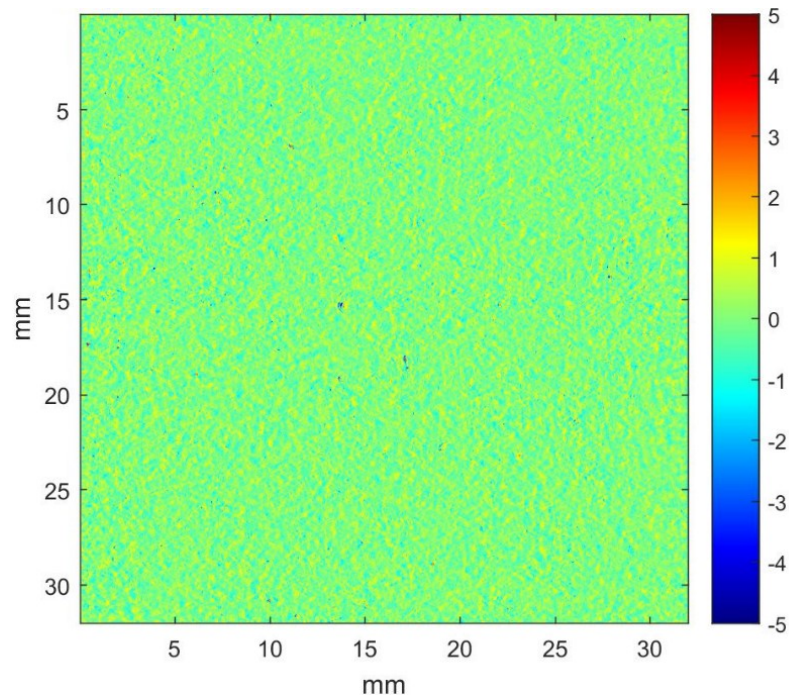


Figure 27. Optitopos height map of sample 1's mineral coating

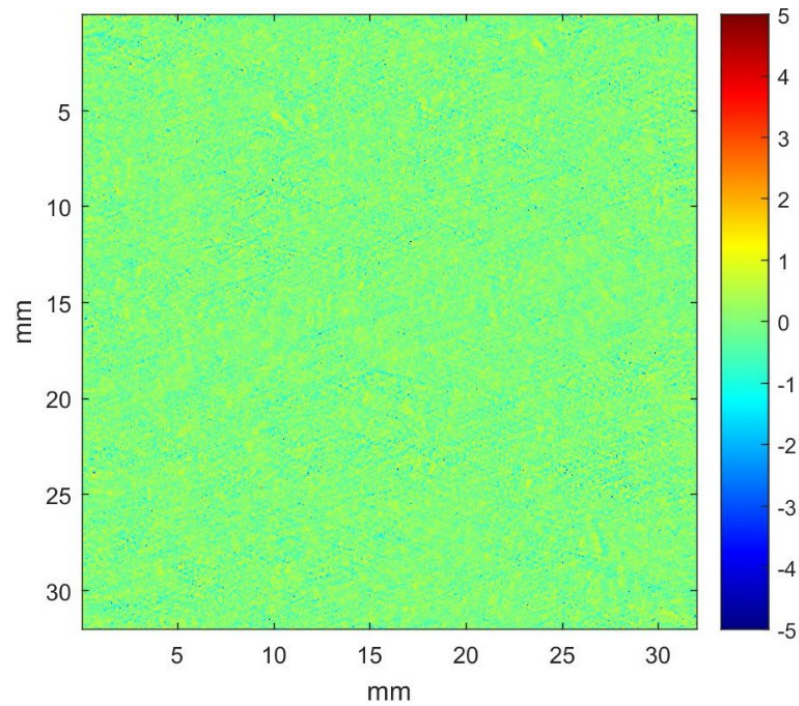


Figure 28. *Optitopo's height map of sample 2's mineral coating*

The marks of BS and TS are used to indicate the top and bottom sides of samples, where BS was used to mark the polymer side of all of the samples and TS was then the coating side for samples 1 and 2, or the fibre side for sample 3. MD and CD indicate the direction of which the samples were lighted from.

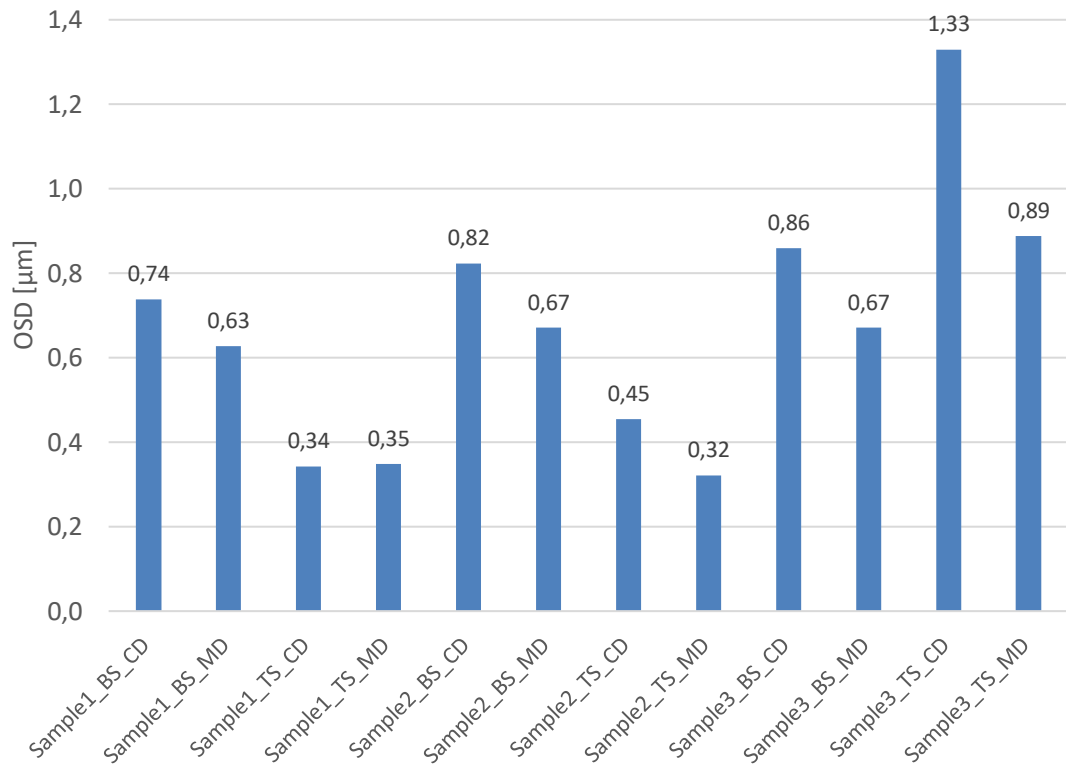


Figure 29. Fine-scale OSD results of fine scale measurement

It can be predicted that the fibre side of sample 3 would have the highest results of OSD because it is the only uncoated surface of the three samples surfaces, and this is confirmed in the Figure 29. All the polymer surfaces have very similar OSD results, which is expected as the surfaces have the same type of polymer in the polymer side, so the results should be close to each other. There is slight differences between the coatings of samples 1 and 2, with coating of sample 1 has slightly lower values than sample 2's coating. The difference between the OSD values is very small, and most likely the differences will not have an effect on sealability of the samples.

5.5 Surface energies and contact angles

Surface energies are calculated from contact angles to predict the sealability of the surfaces. Increased surface energies are indications of low contact angles, and according to the information in the chapter 3.3.1, wetting has been successful and good adhesion should be reached.

Contact angles were measured from both the coating and PE sides of the samples 1 and 2, and will be presented in the appendix B. The sides were marked the same as in optical topography measurements. TS is the coating side and BS is the PE side of the samples. Surface energies were measured from contact angles using the Fowkes method presented in the equation 3. The calculations were done by the Attention Theta device from the contact angles automatically. The results are calculated from the contact angles by the machine after 1.00 second from the placement of the DIM and de-ionized water droplets. The results are averages of 10 measurements.

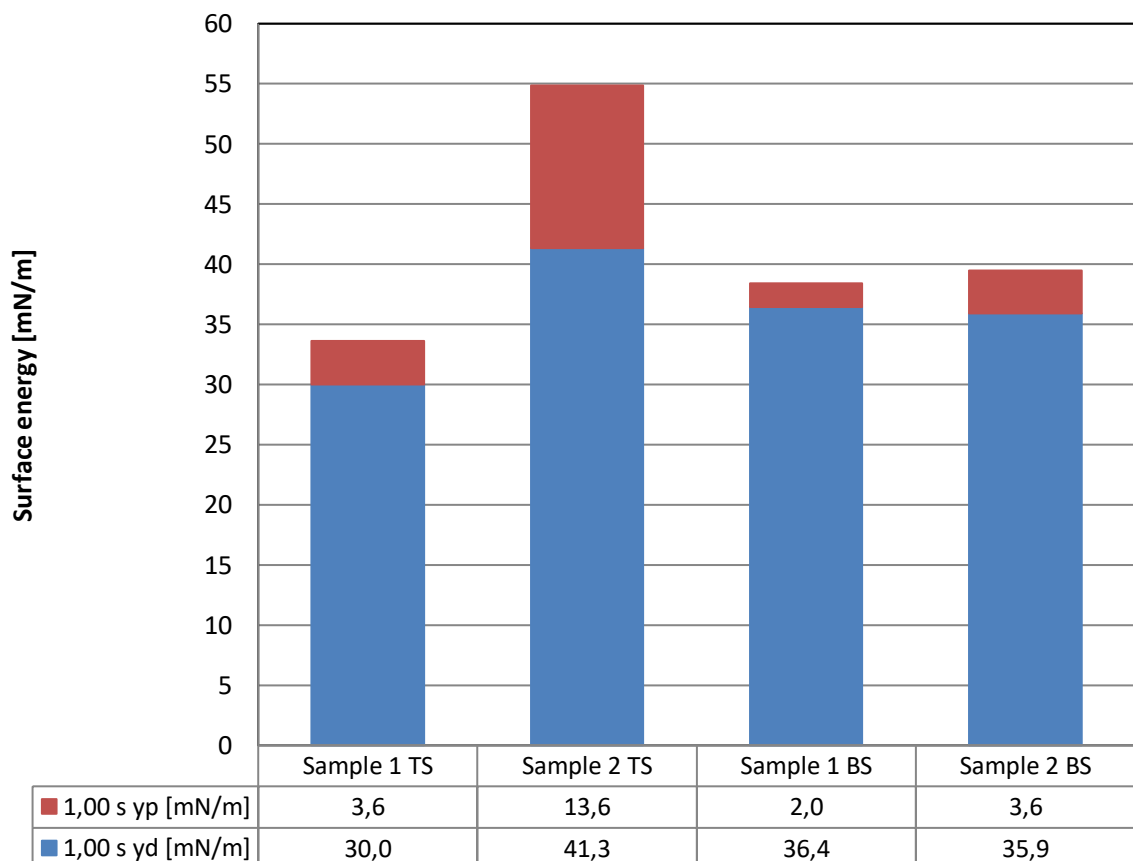


Figure 30. SFEs of polymer and coating sides of samples 1 and 2

There are two findings that can be seen from the Figure 30. Firstly, PE surfaces have little to no difference between samples. Secondly significantly higher surface energy on the sample 2's coating side. It has higher polar component as well as dispersive component comparing to the sample 1. The difference of the coating side surface energies has an impact on the sealability of the samples, and is probably one of the reasons of why sample 2 has lower sealing temperature than sample 1.

Such high surface free energy is likely to be caused by different elements or distribution of elements in the coatings. The coatings will be studied in a future chapter, which will provide more information of the differences of structure and elements the coatings withhold.

5.6 DSC

The DSC testing was done at TAU's Material Science and Engineering department, and the polymer coatings of samples 1 and 2 were tested. Results from both of the samples are marked with different colors representing different phases during the DSC process.

The DSC testing was done with two heating phases and a cooling phase between the two heating phases. The starting temperature was 50°C and the highest temperature was set at 150°C. This ensured that the highest temperature was hot enough to melt the polymer coatings, and the cooling was done to study the crystallization of the polymers. The test was conducted to study the differences in the polymer compositions of the samples, which could be seen as different melting or glass transition temperatures of the curves that are gained from the DSC.

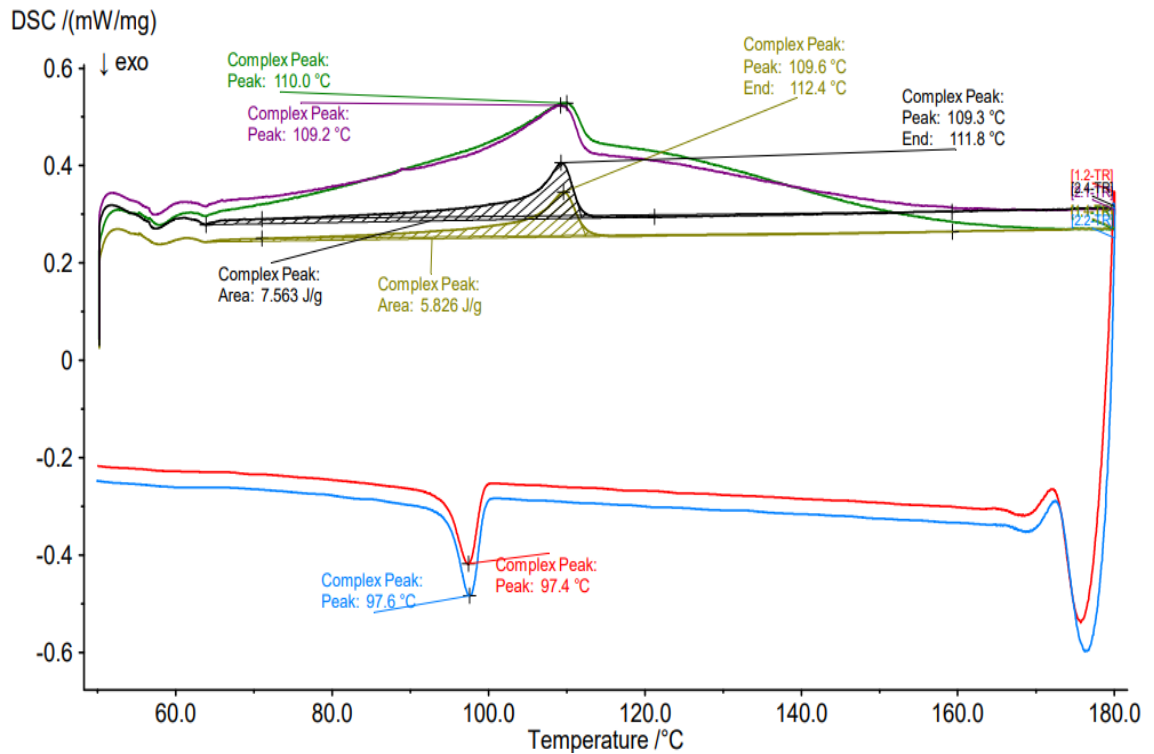


Figure 31. DSC curves of PE's of samples 1 and 2

The blue and red curves of the Figure 31 indicate the cooling phase of the process, red for sample 1 and blue for sample 2. Brown and black curves and complex peak areas present the values gained in the first heating, whereas the purple and green curves present the second heating. Brown and green curves indicate the values for sample 1, and the sample 2's values are marked with black and purple curves.

The curves of samples only have small differences between them in all of the stages of the DSC process. As the temperatures of the samples differ by a degree or two at most, it can be determined that the polymer coating are composed of the same type of polymer for both sample. This information was known prior to the testing, but from the melting temperatures of the DSC it is confirmed that the polymers used in the samples are both LDPE, and neither one is LLDPE or any other form of PE.

Besides the melting temperature, the cooling phase provided information on the crystallization of the samples, which was found out to be at around 97°C. The polymers start to solidify at the crystallization temperature, and for sealability this indicates that the seals starts forming after the temperature of the seal cools to at least 97°C. The melting temperatures indicate that the seal area should be heated to at least 110°C.

5.7 ESCA

ESCA or electron spectroscopy for chemical analysis was conducted to be done at Top Analytica in Turku. The ESCA tests were done for samples 1 and 2 from coating side.

ESCA is used to study the relative weight distribution of carbon bonds and elements in the surfaces of the samples 1 and 2. The following graphs were provided by Top Analytica, where the red curves present the results of the sample 1 and the blue curves will be for sample 2's results.

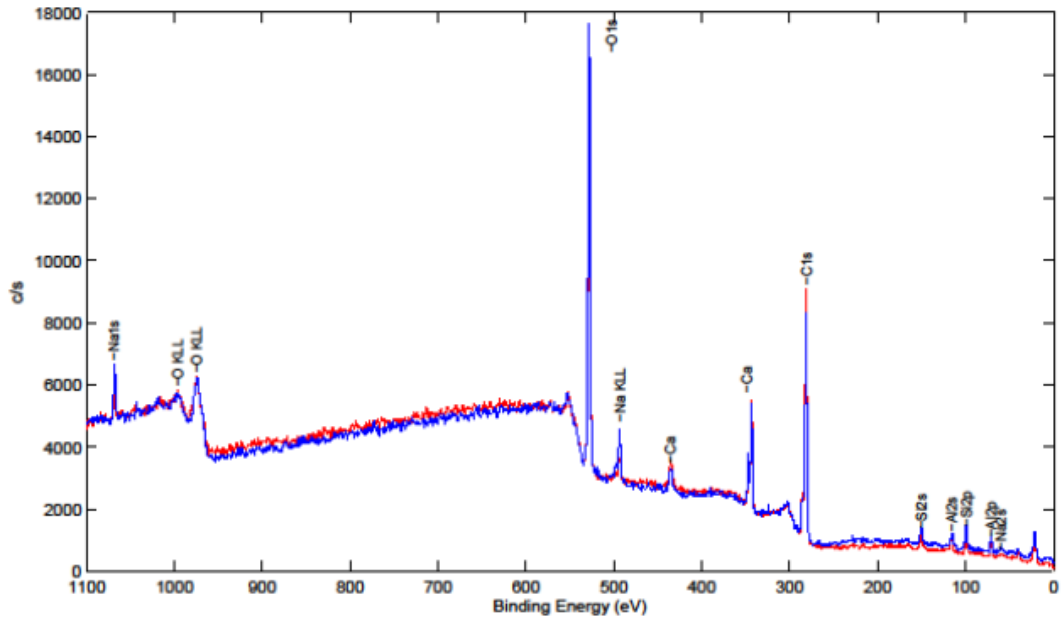


Figure 32. ESCA for elemental analysis in coatings of samples 1 and 2

The Figure 32 shows the elemental analysis of the coatings as a graph for both samples. The binding energy indicates that both of the samples have similar composition of elements in their coatings. Relative weight distribution of carbon, oxygen, sodium, aluminium, silicon and calcium are presented in Table 10. The Table 10 also present the carbon oxygen ratios of the coatings.

Table 10. Relative weight distribution of elements in coatings

	C	O	C/O	Na	Al	Si	Ca
Coating 1	53.5	36.6	1.5	1.6	2.3	1.7	4.4
Coating 2	49.6	39.1	1.3	3.1	1.5	2.0	4.7

The Table 10 informs that the coatings have fairly similar elemental build and distribution, most notable differences being the higher values of carbon in the coating 1 and sodium in the coating 2. These differences are not that significant in sealability, but the higher amount of carbon in the sample 1 might indicate more binder used in the coating.

The other part of the ESCA was to identify types of carbon bonds in the polymer layers of the samples. The carbon bonds gained from the test are aliphatic, hydroxyl, ketone and carbonate bonds. These bonds will be presented as C1, C2, C3 and C4, each corresponding to one type of carbon bond, which will be presented with the relative amount of the carbon bonds in Table 11.

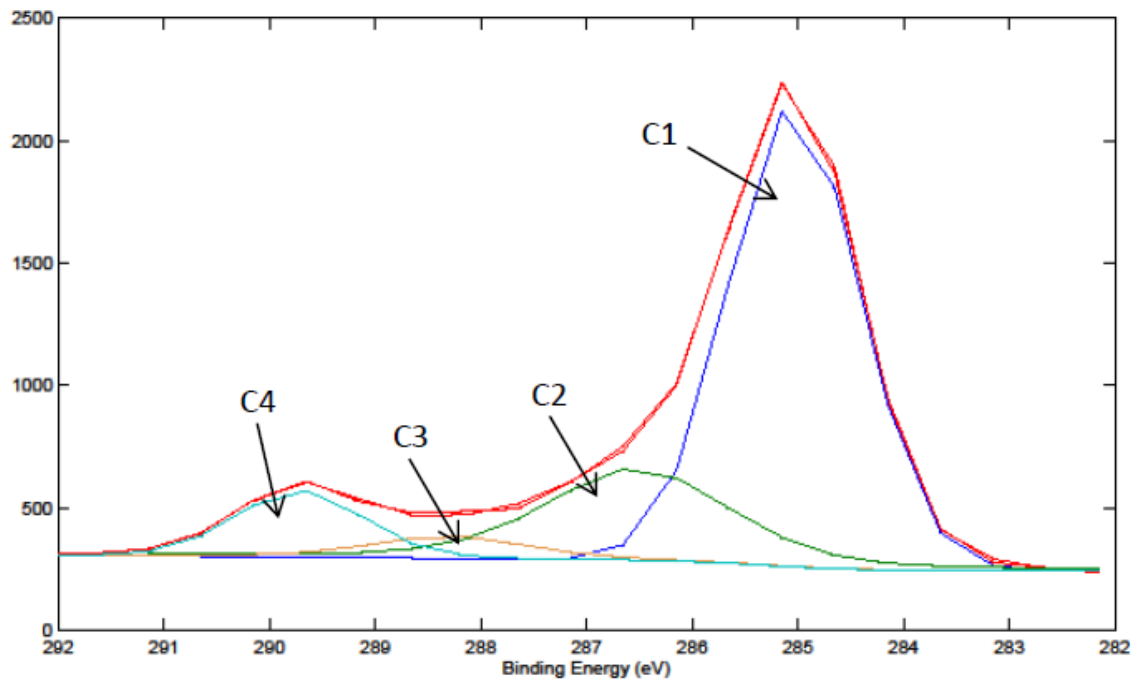


Figure 33. Carbon-spectra of sample 2's coating surface

Table 11. Distribution of carbon bonds in coatings

	C1 (-C-C-)	C2 (-C-OH)	C3 (-C=O)	C4 (CaCO ₃)
Coating 1	75.5	10.6	1.6	12.3
Coating 2	69.6	14.1	5.4	10.8

The Table 11 has the relative amounts and distribution of different carbon bonds presented. Calcium carbonate bonds have the closest values of the bonds, and the aliphatic bonds have the highest relative ratio between the two coatings.

The high amounts of aliphatic and carbonate bonds in the sample 1's coating can provide some information on the added components of the coating, as these results indicate in larger use of binders in the coating of sample 1. The relatively higher amount of C2 and C3 bonds in the coating of sample 2 can explain the high polar portions in the total surface energies of the coating.

5.8 FTIR

FTIR or Fourier transmission infrared spectroscopy is another method to characterize composition of materials. FTIR was used to study all the samples and both of their surfaces. Figure 34 presents the FTIR results of the coating of sample 1, results for sample 2's coating will be presented in the appendix C. Also FTIR spectra's of the PE-coated sides of the are presented in the appendix C.

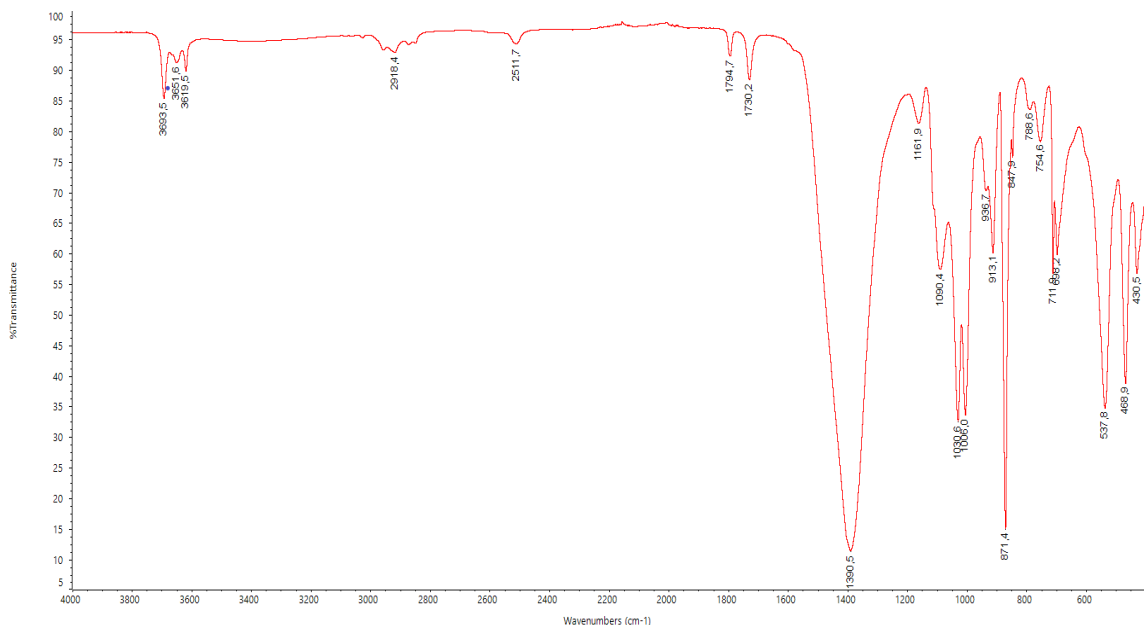


Figure 34. FTIR results of sample 1's of the coating

It was determined that both of the coatings have calcium carbonate and clay as a pigment material. Other finding of the FTIR was in the latexes used in the coatings, where in sample 1 the used in the latex in the mineral coating was styrene acrylate latex (SA-latex), and sample 2 has styrene butadiene latex (SB-latex).

5.9 TGA

TGA or thermogravimetric analysis is a method used to study how materials are affected by very high temperatures and how the materials lose their weight in these temperatures. The weight of the tested material will decrease as the temperature increases, as more of the materials will be burned off. The tested PE's were taken off the paperboards by washing the samples with water. Figure 35 presents the TGA graph for PE of sample 1, TGAs of PE's of samples 2 and 3 are presented in the appendix C.

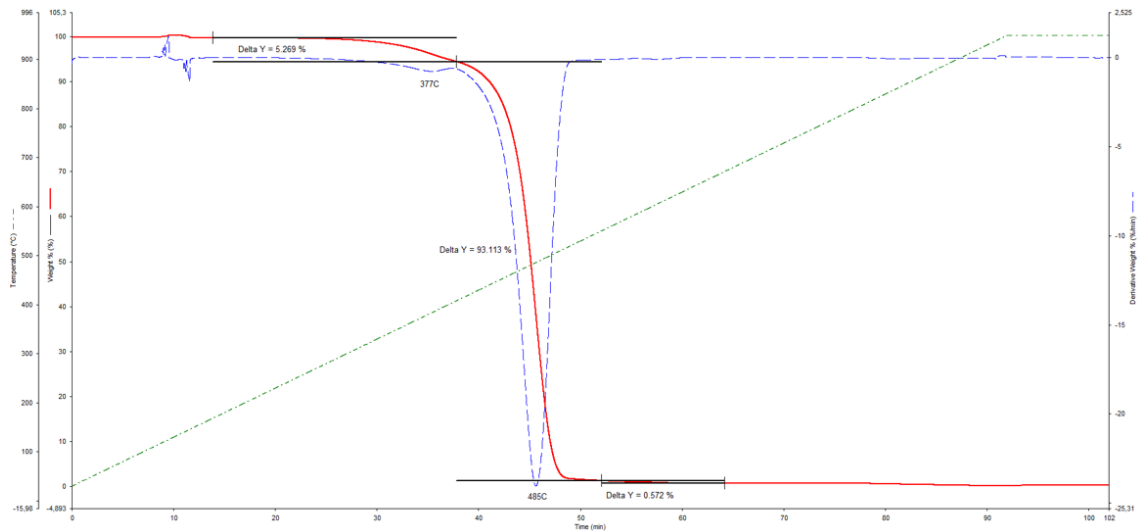


Figure 35. TGA of sample 1's PE film

The TGA curve in the Figure 35 shows the temperature where most of the polymers total weight is lost at around 485°C.

5.10 NMR

The nuclear magnetic resonance spectroscopy, NMR, tests were conducted in the Instrument Centre of University of Turku & Åbo Akademi. The method is specifically used to study polymeric films by analysing the different forms of polymeric bonds in the polymer films.

NMR was done for the PE-films of the samples 1 and 2. The PE films had to be removed from the paperboard by scraping it from the paperboard after it had been soaked in water. After this, the samples were cleaned with 600 μ L of 1,2,4-trichlorobenzene, and after cleaning the NMR spectra was formed with 13 C pulses and 66 μ L of benzene-d₆.

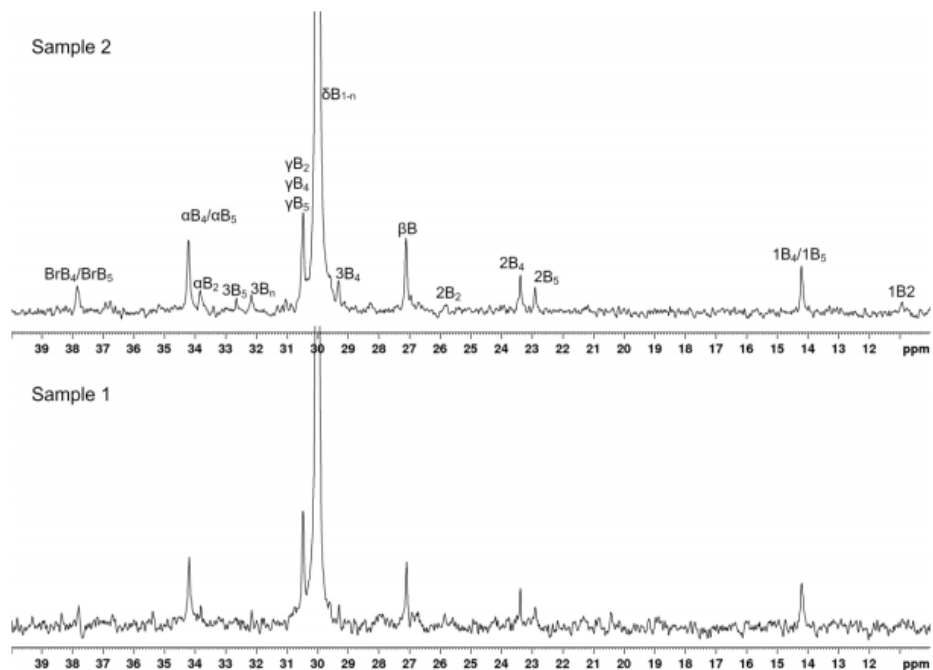


Figure 36. Nuclear magnetic resonance spectroscopy results

According to the results presented by the Instrument Centre, the PE-films of the samples 1 and 2 contain polyethylene with branches consisting mainly of butyl groups. The polyethylene group can be seen as a spike in the 30ppm area in the Figure 36, and the branched butyl groups are present in the 14ppm area.

An interesting finding of the NMR was that the PE of sample 2 also contained significant amounts of branched pentyl groups and branched ethyl groups. This is a significant difference between the PE's of the samples, and might have an impact on the sealability of the samples. The reason for the additional branched pentyl and ethyl groups is unsure, but some reasons might be found from the extrusion processes of the PE's. Other reason might be in the polymer itself, as polymers produced by different companies could have some properties which can lead to these differences.

5.11 Overall results

The following chapter collects all the measurements and the results of the conducted tests for easier inspection. Because of the large number of different testing methods that were used for this thesis, Table 12 is used to summarize all of the measurements into a single table. The Table 12 can then be used as a quick reference of finding out reasons for sealability differences.

To evaluate the results of the measurements and to compare them to each other, the Table 12 will include “+”-marks and zeros. A zero will be placed on the Table 12 if the sample was not tested with the corresponding testing method. Plus marks are used to indicate the effect of the results that the specific testing method had on the sealability, where “+”-marks indicate better sealability. For example, if the results of a specific method would indicate that the sample 1 would result in better sealability than samples 2 or 3 do, then the section for sample 1 in that specific method would have more +-marks than samples 2 and 3. The samples can have the same amount of plus marks, which would indicate that the results of the measurements did not give any significant difference between the samples, where the significancy is dependent on the testing method, which are explained in more detail in the corresponding chapter of the testing method.

Table 12. Comparison of the measurement results of the studied materials

	Sample #1	Sample #2	Sample #3
<i>Optitopo</i>	+	+	+
<i>SFE, Coated side</i>	+	++	0
<i>SFE, PE side</i>	+	+	0
<i>DSC</i>	+	+	0
<i>ESCA</i>	+	++	0
<i>FTIR</i>	+	+	+
<i>TGA</i>	+	+	+
<i>NMR</i>	+	++	0

6. CONCLUSION

Target of the study was to find out differences in heat sealing between PE-coated paperboards and to determine the causes for the differences. The tested materials all had a PE-coating, but two of the materials also had a mineral coating and one of the materials was uncoated.

Heat sealing results showed a definite difference in heat sealing parameters for samples 1 and 2, the mineral coated samples, in both hot air and hot bar sealing. Sample 2 had lower sealing temperature in most cases, when the seal was formed with two PE-surfaces. The lowest sealing temperatures were when two sample 2's PE-coatings were sealed together, and the highest ones were acquired with two PE-coatings of the sample 1. Mixture of the two PE-coatings provided results similar to sample 2's PE-PE sealing results, with slightly higher or same temperatures.

Heat sealing of different surfaces with mineral coatings and uncoated surfaces resulted in generally higher sealing temperatures than PE-PE seals did, which might be due to the lower possibility of diffusion between the surfaces. The coating-PE seals showed that sample 1 sealed in higher temperatures than sample 2, similarly to the results of PE-PE seals. The difference between the mineral coating-PE seals was smaller than between PE-PE seals. The seal of uncoated sample 3 and PE of sample 2 provided similar temperature results as the coating-PE seals.

The tests for the surface energies of the samples showed that the coating of the sample 2 had significantly higher surface energy than the sample 1's coating. The difference between the two was very high, especially in the polar component of the SFE. The PE-films of the samples had little to no difference in their surface energies. The differences in SFEs of the coatings indicate a possible explanation for the different sealing temperatures of the sample 1 and 2.

The reason for difference in SFEs of the coatings was studied more with FTIR and ESCA methods. FTIR resulted in findings that both coatings had CaCO_3 and clay in the coating and that the sample 1 uses SA-latex in the mineral coating and sample 2's coating has SB-latex. This different latexes used in the coatings was concluded to have some impact on the SFE's but it did not explain the differences fully. ESCA was done to study the different elements in the coatings, and as both samples included C, O, Na, Al, Si and Ca, the relative amounts of which were different. These results did not indicate any

significant impact on the sealability. One possible finding from the element distributions is that the coating of sample 1 might have more binders in the coating than sample 2, based on the different amounts of Ca, C and calcium carbonate bonds in the two coatings. ESCA results also showed that sample 2 had higher relative amounts of hydroxyl and ketone carbon bonds, which can provide the reason for higher polar component of sample 2's coating.

Prior to the testing, it was known that the polymers used in the polymer coatings of all the samples was LDPE. DSC and TGA both confirmed that LDPE is the used polymer, with a melting temperature of 110°C and crystallization temperature of 97°C. Melting temperature informs that the surfaces need to be heated to at least 110°C for the seal to be perfect, which is confirmed by the heat sealing results. The crystallization temperature indicates that when the seal is formed, the seal needs to be cooled to at least this temperature, where the polymer starts to crystallize and solidify.

Polymers of samples 1 and 2 both contain polyethylene with branched butyl groups, but the sample 2's polymer coating also had significantly higher amounts of branched pentyl and ethyl groups. These additional branched polymer groups can be one of the reasons of why the sample 2 had lower sealing temperatures than sample 1, as the amounts of these groups was significantly lower in sample 1. The reason of why the additional polymer groups were in the sample 2 was unclear. Possible reasons for this can be in the extrusion processes used, if the two polymers are extruded by using different temperatures and other variables present in the extrusion process. Other possible reason might be that the polymers are not from the same supplier.

Differences in polymer and mineral coatings were studied and found out, and their effects on sealability were determined based on the sealing results of hot air and hot bar sealings. This study provided some insight on the different factors that affect the sealability and their impact on the sealability, which can be used to improve sealability of future products. If the sealability of the studied materials is further researched, the sealing windows of the materials should be in closer inspect, so the effects of high temperatures could be studied. Especially the effects of high temperatures have on the polymers of the samples would be an interesting area of study, as well as finding out more about the origin of additional branched polymer groups in sample 2's PE-coating. Size exclusion chromatography could provide more information on these polymer groups, as well as studies on the polymer granules and the extrusion processes and variables that are present in the coating process.

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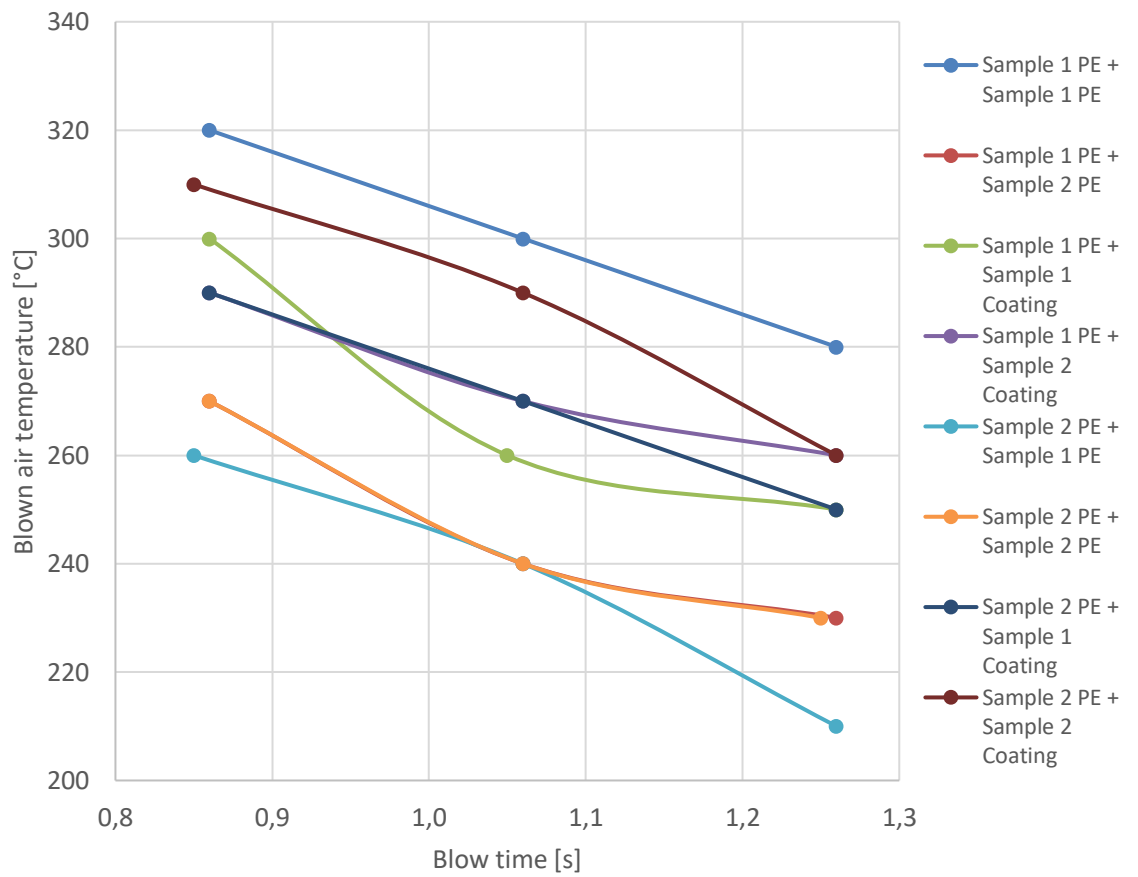
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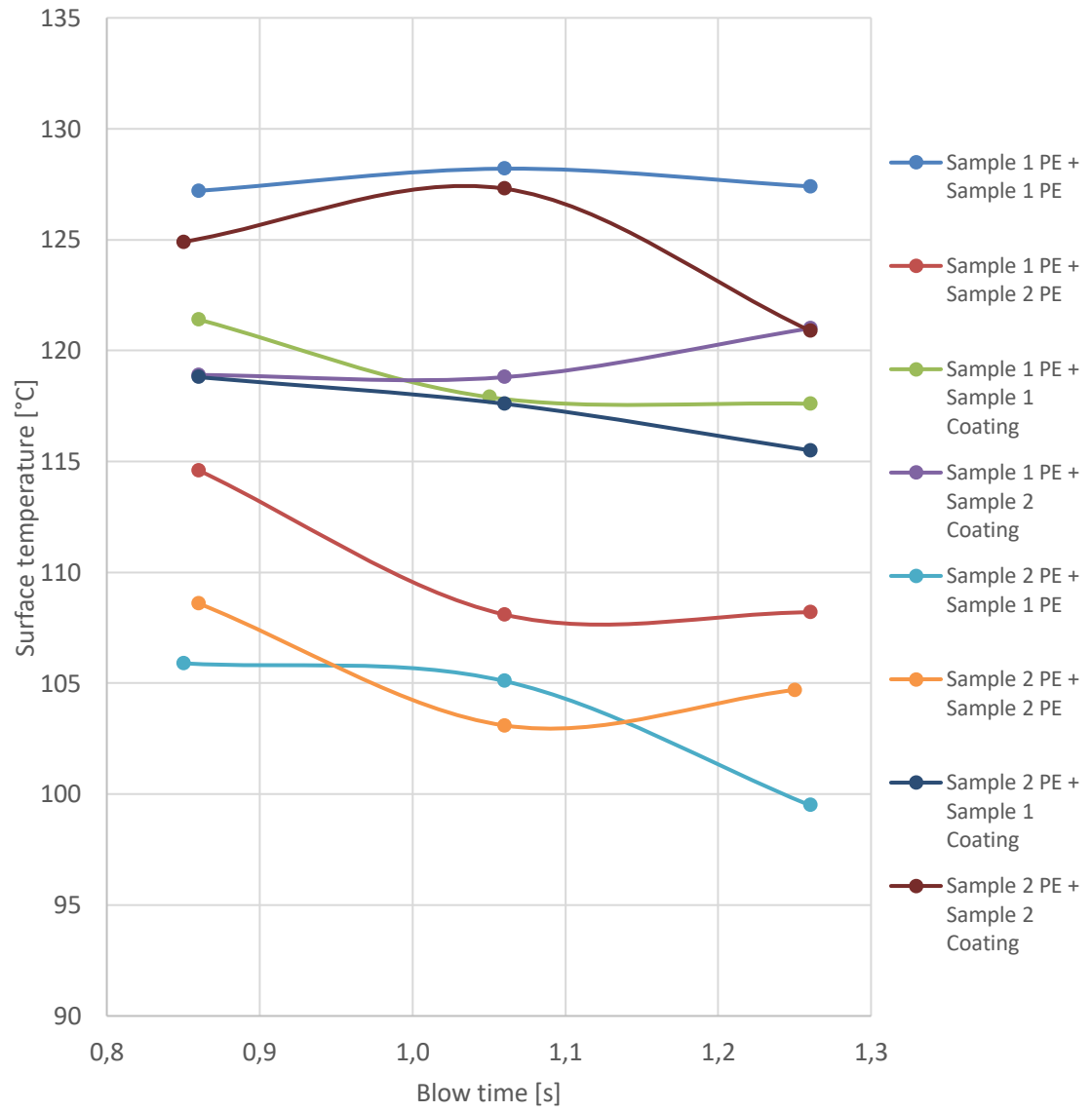
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APPENDIX A: HEAT SEALING CURVES

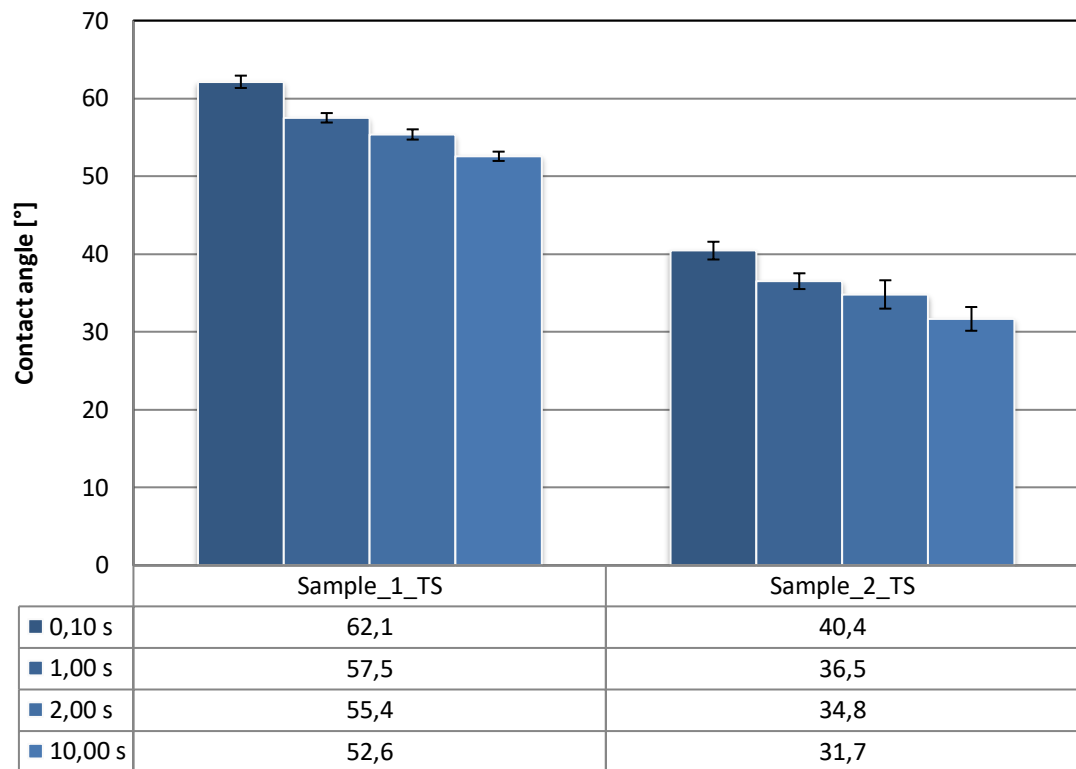


Blown air temperatures in hot air sealing for various seals

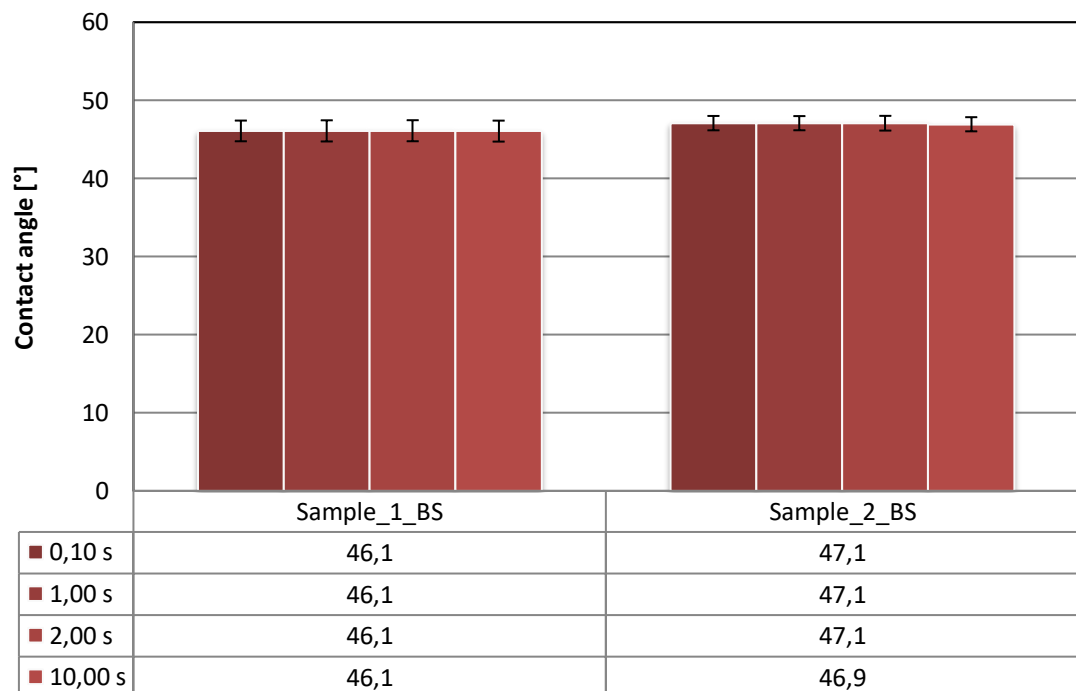


Surface temperatures in hot air sealing for various seals

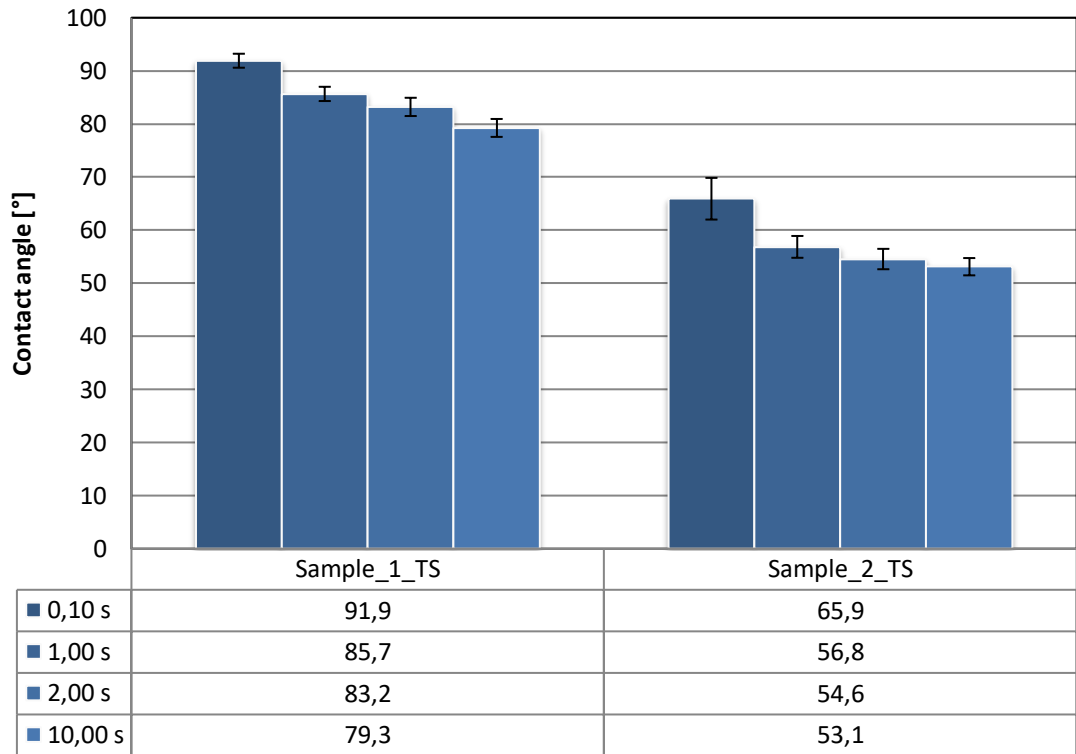
APPENDIX B: CONTACT ANGLES FOR SFE



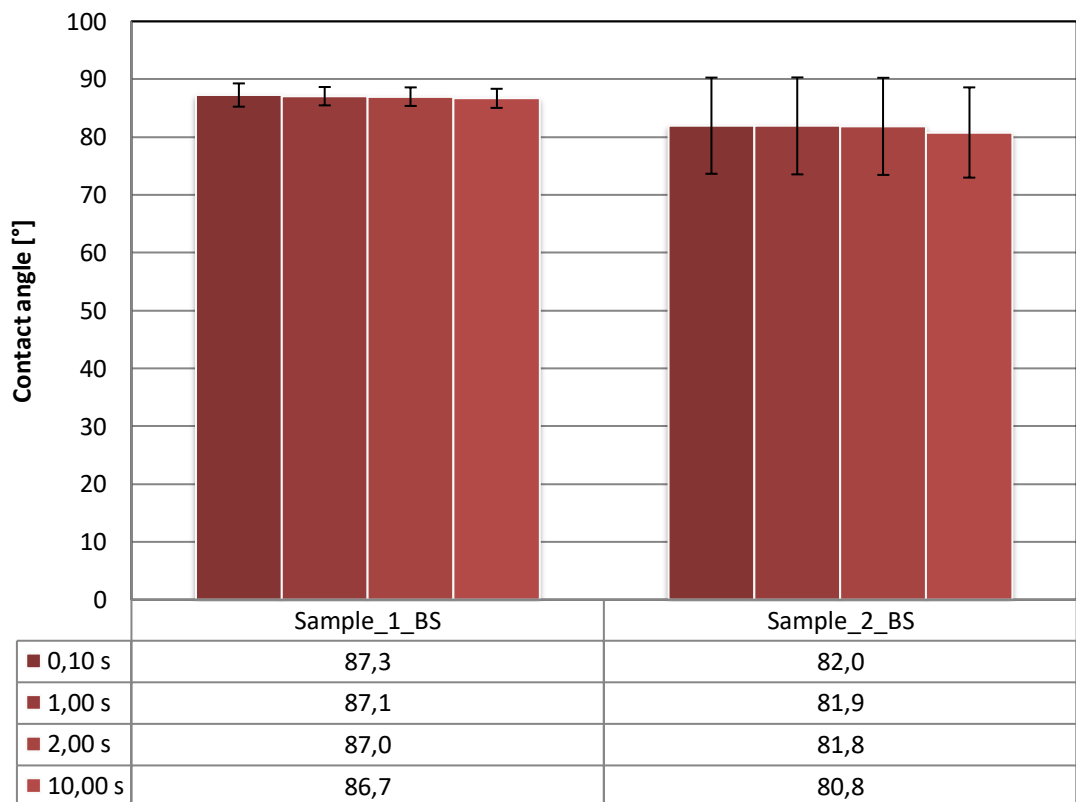
DIM's contact angle development over time on top of coatings



DIM's contact angle development over time on top of polymers

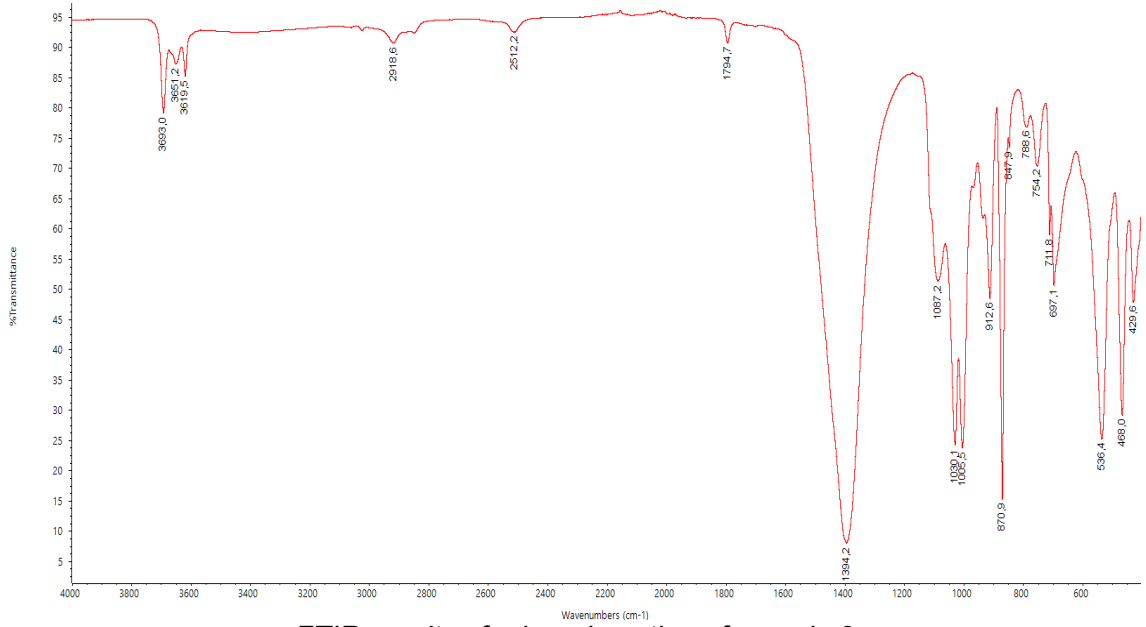


Deionized water's contact angle development over time on top of coatings

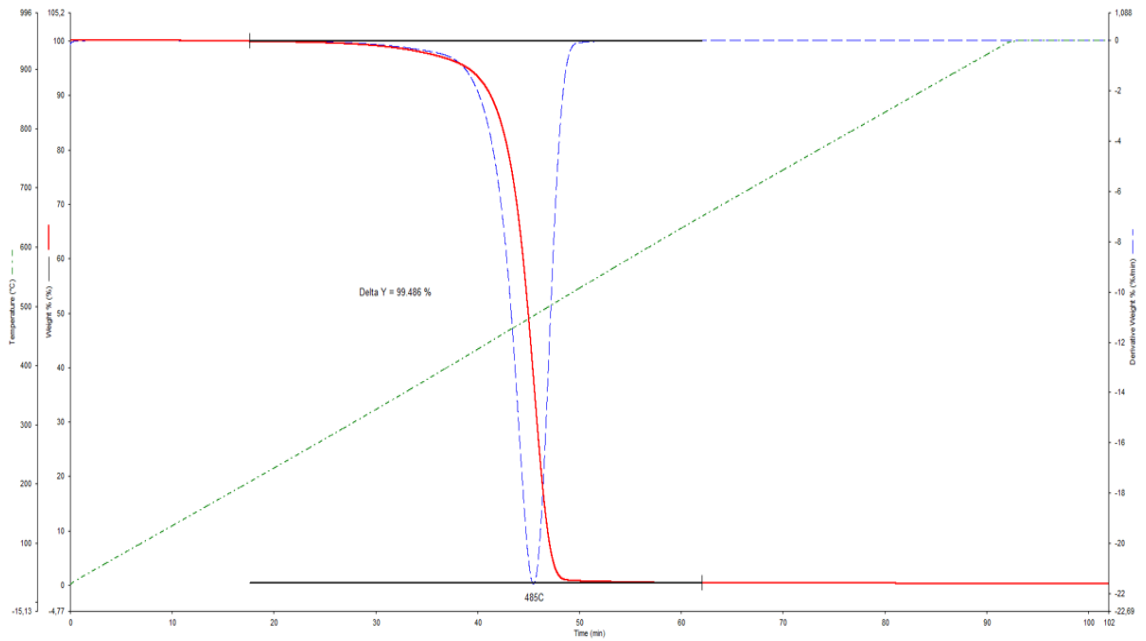


Deionized water's contact angle development over time on top of polymers

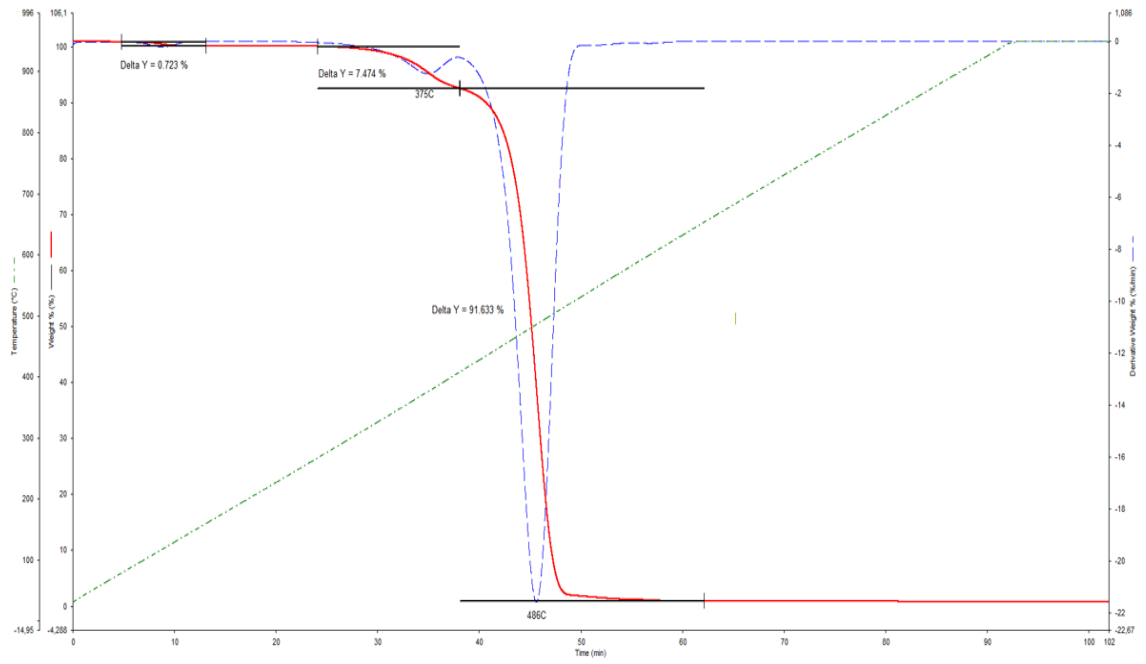
APPENDIX C: FTIR AND TGA CURVES FOR PE FILMS



FTIR results of mineral coating of sample 2



TGA curve for PE surface of sample 2



TGA curve for PE surface of sample 3