TAMPEREEN TEKNILLINEN YLIOPISTO
TAMPERE UNIVERSITY OF TECHNOLOGY

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SILICONE TRANSFER IN PAPER LINER

Master of Science Thesis

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Examiners and topic approved by the Faculty Council of the Faculty of Engineering Sciences in Tampere, Finland, on 05.10.2016

ABSTRACT

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The silicone transfer has been an ever-present phenomenon in the pressure sensitive adhesive (PSA) field. Understanding and reducing the silicone transfer would improve label quality in multiple ways. Foremost, label’s adhesion and printing finish would improve and become even more predictable. Furthermore, as the printing process is very delicate in its nature, removing or at least reducing the silicone transfer would reduce issues encountered in printing.

The original goal of this thesis was to evaluate and compare the silicone suitability, before their use in production, by assessing silicones in laboratory for their extractable-content. Namely, the extractable-content is one indicator for silicone transfer and its severity. The idea was, to eventually, find out the best silicones to be used with specific release liners. Also, there were interest in determining, whether there were batch to batch differences in the received silicones.

However, it was quickly learned that the original goal was unrealistic within the given framework. Therefore, the new goal of the thesis, was to concentrate on finding a correlation between coat weight and extractable-%, but even this goal proved to be challenging. In the end, the goals truncated into method development as no correlation was found. Nonetheless, an insight was gained into quality control methods, where basic yet fundamental issues were uncovered, and corrected for more accurate quality control. With the gained insight, further suggestions for improving the quality control methods will be presented.

In the future, if there is a desire to accomplish the original goals, it is advised to co-operate with an independent laboratory possessing the suitable equipment and seasoned laboratory technicians. Additionally, it would be reasonable to replicate the current experiment with better equipment, knowledge, and reduced variables to settle whether correlation between coat weight and extractable-% exists or not.

TIIVISTELMÄ

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Silikonisirtymä on aina läsnä ollut ilmiö tarralaminaattien valmistuksessa. Silikonisiirtymän ymmärtäminen ja sen vähentäminen parantaisi etikettien laatua monella tapaa. Ensinnäkin, tarran adheesio ja painatusjälki paranisi. Tämä mahdollistaisi tarran ominaisuuksien paremman ennustettavuuden. Etikettien painoprosessin ollessa hyvin herkkäluonteinen, poistamalla tai edes vähentämällä silikonisiirtymää voitaisiin poissulkea monia painoteknisiä ongelmia.

Diplomityön alkuperäinen tavoite oli vertailla ja arvioida silikonien soveltuvuutta, ennen niiden käyttöä tuotannon prosesseissa. Tämä oli määrä tapahtua vertailemalla silikoneja laboratorio-olosuhteissa niiden uutto-% perusteella. Uutto-% on yksi indikaattori silikonisiirtymän vakavuudesta. Lopullisena päämääränä oli löytää paras yhteensopivuus silikonin ja nimenomaisen taustapaperin kanssa. Osana tätä selvitystä oli myös tarkoitus tutkia vastaanotettujen silikonierien välisiä eroavaisuuksia.

Hyvin pian alkuperäinen tavoite osoittautui epärealistiseksi ottaen huomioon annetun viitekehyksen ja työhön käytettävän ajan. Täten, diplomityön uudeksi tavoitteeksi tuli keskittyä löytämään korrelaatiota sivelyn ja uutto-%:n kesken. Tämänkin tavoitteen saavuttaminen osoittautui jotakuinkin haasteelliseksi. Lopulta tavoitteeksi muodostui menetelmän kehitys, sillä tilastollista korrelaatiota ei pystytty osoittamaan. Epäonnistumisista huolimatta diplomityön aikana laadunvalvonnan parista löydettiin perustavaa laatua oleva virhelähde, joka korjattiin. Täten laadunvalvonnan tarkkuutta uutto-%:n osalta saatiin huomattavasti parannettua. Diplomityön aikana kasvaneen tietämyksen ansiosta lisäsuosituksia voidaan tehdä laadunvalvonnan parantamiseksi.

Tulevaisuudessa, jos on tarvetta saavuttaa alkuperäinen tavoite, niin on suotavaa tehdä yhteistyötä itsenäisen laboratorion tai instituution kanssa, joka omaa tarvittavan laitteiston että laitteiston käytössä kokeneen laboratoriohenkilökunnan. Lisäksi, olisi järkevää toistaa nykyinen mittaus koskien sivelyn ja uutto-%:n korrelaatiota paremmalla laitteistolla, tietämyksellä ja vähemmällä määrällä muuttujia ennen kuin voitaisiin varmuudella sanoa esiintyykö näiden muuttujien välistä riippuvuutta vaiko ei.

ACKNOWLEDGEMENTS

First of all, I would like to thank UPM Raflatac as a company for making this thesis possible and Sipi Asu for granting this opportunity. Secondly, Mika Pirisjoki has been the go-to-guru throughout this experiment, and therefore especially big thanks to him for literally everything.

Mervi Lehtimäki's advices and help with the XRF and other methodology in the lab was valuable to get me started with the lab experiments. I would also like to thank the UPM Raflatac's lab and factory personnel for their cooperation and helpfulness whenever I have been in distress.

Elisa Domínguez has been the overseas technical assistant when discussing the matters relating the thesis layout, structure, and formatting. Docent Terttu Hukka from Tampere University of Technology has provided invaluable criticism and maintained high standards throughout the writing process.

Last but not least, I wish to express my special gratitude to my mother, brother and late father for all their support and understanding.

In Tampere, Finland, on 29.11.2016

Raul Kanter

PROLOGUE

“*What do you want to do when you grow up?*” asked by teachers in the school, and parents at home, is perhaps one of the most complex questions of them all. Maybe they are still looking the answer themselves? To my mind, a person cannot answer such question before growing as a person and learning about the surrounding world. Throughout my childhood I never really knew what to answer, but I have thought about the age-old question every now and then. Perhaps not everyone has one true calling?

Nonetheless, the best description what I have found so far is following: “What you want to be when you grow up is something that only you know, and it’s something that only you can take the time to figure out. It’s something that may evolve throughout your life, but it’s likely that the passion and motivation that leads you in one direction, will come along for all of your journeys and pursuits throughout your life.” – Jodi Weiss, Author | CEO & Founder of EverythingSmart

When starting with the thesis, I still had not figured out what I am interested in or what I would like to do. In the process of writing the thesis I *might* have found an answer to what I have been wondering along the years; *where I am good at, and what I would enjoy doing in the future?* The realization was; learning new, and solving problems.

Fortunately, there are endless supply of problems and things to learn in the evolving world. Every day, as science evolves problems are solved, circumvented or have become obsolete due to newly available solutions. The scientific evolution also creates new questions to which there are no ready answers, hence – solutions are required to drive the evolution.

Over the years at the university, I have discovered and learned; obtaining a solution to a problem is to realize there is a problem. Secondly, the problem must be examined, and learned about by questioning (what, when, why, how, etc…). The solutions to a problem emerge on the way – not in the end. It is about a journey of exploring around the problem, not the problem itself.

– In the end there is no problem, only solutions.

“A little known secret is that a physicist is one of the most employable people in the marketplace — a physicist is a trained problem solver. How many times have you heard a person in a workplace say, 'I wasn't trained for this!' That's an impossible reaction from a physicist, who would say, instead, 'Cool.'” – Neil deGrasse Tyson

After writing the above, it occurred to me how similar conclusions have been made by different people, in different fields, in different words time after time:

“With every advance in our scientific knowledge new elements come up, often forcing us to recast our entire picture of physical reality. No doubt, theorists would much prefer to perfect and amend their theories rather than be obliged to scrap them continually. **But this obligation is the condition and price of all scientific progress.” –** Louis-Victor de Broglie

“Water does not resist. Water flows. When you plunge your hand into it, all you feel is a caress. Water is not a solid wall, it will not stop you. But water always goes where it wants to go, and nothing in the end can stand against it. Water is patient. Dripping water wears away a stone. Remember that, my child. **Remember you are half water. If you can’t go through an obstacle, go around it. Water does.” –** Margaret Atwood

“Don't get set into one form, adapt it and build your own, and let it grow, be like water. Empty your mind, be formless, shapeless — like water. Now you put water in a cup, it becomes the cup; You put water into a bottle it becomes the bottle; You put it in a teapot it becomes the teapot. Now water can flow or it can crash. **Be water, my friend.”** – Bruce Lee

My own observations and the quotes sound all too similar?

Well, probably because everything *is* a remix.

Find out more googling: “everything is a remix”

An algorithm to create anything in this world we live in:
Copy | Transform | Combine | Simulate

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TERMS AND DEFINITIONS

m/min	Unit of speed, meters per minute
g/m^2	See Grammage
Al	Aluminium
Alu	Aluminium sample sheet
Calendering	Finishing process for cloth, paper, or plastic film to smooth, coat, or thin the material
Doctor Blade	Thin blade used to apply and remove excess silicone from the aluminium surface. In gravure printing the doctor blade (originally from *ductor* blade) removes the excess ink from the smooth non-engraved portions of the image carrier and the land areas of the cell walls
Edge ooze	Term is used to describe the flow of adhesive out of the edge of the laminate. Edge ooze causes a sticky edge and can cause feeding problems and contamination in some printing processes
Emulsion	Fine dispersion of minute droplets of one liquid in another in which it is not soluble or miscible
Extractable test	A test where sample is measured before and after dissolvation into MIBK and calculating the percent difference
Extractable	See extractable-%
Extractable-%	Percent value calculated using formula (Pre-Post)/Pre*100%
Facestock	Print side of the laminate
FINAT	Abbreviation of the French title: **F**éderation **IN**ternationale des fabricants et transformateurs d'**A**dhésifs et **T**hermocollants sur papiers et autres supports
GC-MS	Gas Chromatography–Mass Spectrometry
Glassine	Smooth and glossy paper that is air, water and grease resistant
GPC	Gel Permeation Chromatography (see SEC)
Grammage	Term used in the pulp, paper and fabric industry to denote mass of a product per unit of area g/m^2 i.e. gsm; grams per square meter
Kaolin	See Kaolinite
Kaolinite	Naturally occurring mineral, with the chemical composition of $Al_2Si_2O_5(OH)_4$, used to surface size paper and give it a glossy look
Kraft	Porous and coarse paper with high elasticity and high tear resistance
Laminate	An assembled multi-layer object by heat, pressure, welding or adhesives
Lamination	The technique of manufacturing a material in multiple layers
MIBK	Methyl isobutyl ketone
MWD	Molecular Weight Distribution
Pd	Palladium
Đ$_M$	Dispersity Index
PDSM	Polydimethylsiloxane
ppm	Parts Per Million
PSA	Pressure Sensitive Adhesive
Pt	Platinum
Release Liner	Paper or plastic film coated with release agent
Release	The release depicts the force required to remove the pressure sensitive adhesive’s face from the release liner. This “release” force is required to break the secondary bonds between the adhesive and silicone surface

Rh	Rhodium
SEC	Size Exclusion Chromatography (see GPC)
Si	Silicon
Tack	Property of a pressure sensitive adhesive that allows it to adhere to a surface under very slight pressure
Tackifiers	Chemical compounds used to increase the tack in adhesives
TTY	Tampereen Teknillinen Yliopisto
TUT	Tampere University of Technology
UPM	United Paper Mills
v-Alu	Varnished aluminium sample sheet
XRF	X-Ray Fluorescence, emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by using high-energy X-rays

1. INTRODUCTION

1.1 UPM & UPM Raflatac

UPM-Kymmene Corporation (UPM) leads the integration of bio and forest industries into a new, sustainable and innovation-driven future. UPM emphasizes renewable raw materials and recyclability in their products. Therefore, UPM's Biofore strategy challenges the long-lived ”take-make-dispose” economy. UPM's Biofore promotes a circular economy where resources are kept in use for as long as possible and finally are recovered, recycled and regenerated into new products, materials and energy. [1][2]

As of fall 2016 UPM consists of six business areas: UPM Biorefining, UPM Energy, UPM Paper Asia, UPM Paper ENA (Europe and North America), UPM Plywood and UPM Raflatac. UPM products include pulp, paper, plywood, sawn timber, composites, bioenergy, biofuels, biochemicals and nano products. UPM employs globally 19,600 people and its annual sales are approximately 10 billion EUR. [2]

UPM's subsidiary Raflatac is the second largest manufacturer of pressure sensitive laminates worldwide. UPM Raflatac's pressure sensitive adhesive (PSA) laminates are used for product and information labelling across a wide range of end-uses – ranging from pharmaceutical and security applications to food, beverage, retail, logistic and transport labels. [2][3]

UPM Raflatac employs 2,900 people worldwide and its customers include small and large label printers who focus on roll-to-roll printing, and packaging providers. UPM Raflatac manages 11 factories, 24 distribution terminals on five continents and wide network of sales offices selling label stock products in both rolls and sheets. Annual sales in 2015 were 1.4 billion EUR. Production plants are located in Brazil, China, Finland, France, Malaysia, Poland, United Kingdom and USA. [2][3]

1.2 Problem Background

As UPM Raflatac is committed to constantly improve its products' quality and cost effectiveness in a competitive market, the UPM Raflatac's R&D is focused on improving all areas of PSA laminate manufacturing. As printing and label making processes are complex endeavours they are constantly under research and development. The aim of this thesis was to be in understanding and possibly reducing *silicone transfer* (i.e. silicone migration from silicone webbing to the printing surface). This undesired migratory phenomenon, when present in laminate, heavily influences printing quality on labels. However, the goal was quickly found to be unrealistic, and too ambitious. Wiser from the mistake, it was rather focused on finding correlation between coat weight and silicone extractable-%.

As printing is a complex and quite delicate process, the printing issues can be caused by various factors. A wide variety of problems can be encountered: poor ink wetout on printed surface, pinhole formation in compact printed areas, uneven dot gain in half-tone printed areas, blurry picture, and poor ink adhesion on filmic face materials. Reasons for the aforementioned problems within the printing process can be found from used ink, flexo-printing plates, printing pressure, anilox rollers or from surrounding ambient conditions inside the printing hall.

External reasons causing the aforementioned printing problems may, for example, include faulty facestock provided by raw material manufacturer or silicone contaminated printing surface. Due to possible silicone contamination from the UPM Raflatac’s side it is critical for UPM Raflatac to minimize silicone contamination within its processes. Therefore, UPM Raflatac has decided to take the initiative to refine their own processes, focus on quality control and improve product quality by minimizing the err on their side.

Laminate quality can be assessed by various tests FINAT Test Methods 21 & 22 [4] for ink adhesion on printed samples, ink wet out analysis with densitometer, silicone extractable test, and UPM Raflatac’s own silicone transfer tests. However, acquiring exact data on silicone quantities in silicone transfer or contamination is not possible.

Silicone transfer has been an issue in the past, and it has been studied on multiple occasions but the underlying reason for silicone transfer is yet to be discovered. Complete understanding of the silicone transfer has been challenging due to multiple variables present in the lamination process. Co-operation with silicone suppliers has helped to reduce some of the silicone transfer issues, but the main problem still persists.

1.3 Thesis Goals and Structure

The original goal of this thesis was to evaluate and compare the suitability of various silicones, before their use in production, by assessing them in laboratory for their extractable-content. The silicones were tested in a laboratory scale for their theoretical silicone extractable content in percentage of silicone extracted and compared to the values obtained from process conditions.

Furthermore, it was required that the test methodology was reliable, relatively fast, simple, and possible to be carried out with the existing equipment found in the R&D lab. Given such research criteria the test protocol was to be derived from the existing methods used for measuring silicone coat weights and calculating silicone extractable. These criteria required coming up with a novel way to create siliconized samples manually as this had not been done previously. However, quickly it became evident that the original goal was unrealistic. Hence, it was concentrated on method development and finding a correlation between coat weight and extractable-% instead.

In the literature review, the pressure sensitive adhesive laminate's value chain, structure, used materials and manufacturing process are briefly explained. A closer look is taken on chemical structure of the cured silicon (Si) i.e. *silicone* and its components, curing chemistry and additives. Also, silicone release properties and factors in silicone transfer are discussed in more detail. Finally, gel permeation chromatography (GPC) and gas chromatography-mass spectrometry (GC-MS) are introduced as other tools for determining the silicone coat weight.

In the beginning of the experimental section, the principle of the X-ray fluorescence (XRF) characterization technique in quantifying the silicone extractable is described, followed by research methods and materials used. At the end, the results and discussion will be followed by the future development recommendations and conclusions.

2. LABEL STOCK VALUE CHAIN

The complete label stock value chain consists of multiple companies and operators worldwide. To manufacture a label for an end-use product there are multiple processes to go through, the label stock value chain from raw materials to the finished labels is described briefly in this chapter and illustrated in Figure 1.

The manufacturing process starts by selecting the desired raw materials for facestock, release liner, release coating (silicone) and adhesive. Paper based facestocks and release liners are manufactured in bulk by big enterprises like UPM Label Papers. The release coatings and adhesives are usually mixed, on site, from components supplied by their respective manufacturers. [5][6][7]

Next in the value chain is the self-adhesive label material manufacturing. Here the raw materials are combined into the label stock by companies such as UPM Raflatac. This is done by coating the release liner with a thin layer of silicone, curing the silicone, applying adhesive layer on the silicone layer, drying the adhesive and finally laminating the facestock to the release liner. Finished products are shipped to label converting businesses. [5][6][7]

Figure 1. *The label stock value chain illustrated, value increases to the right. UPM Raflatac's position circled in the chain. [5]*

The label converting businesses turn the self-adhesive laminate into application ready labels. This is done by printing visual information, (including anything from: text, barcodes, graphical images or everything combined) onto the self-adhesive laminate, die cutting the label into shape and removing the waste matrix i.e. leftovers. [5][6][7]

Next, the packaged goods or beverage companies apply the application ready labels to the end use product by automated label dispenser lines. For example, the beverage companies use automatic dispenser lines which may label 60,000 bottles per hour and labels may be applied simultaneously to the bottle’s neck, front and back. High application demands require high application speed and optimal release performance from the siliconized release liner. [5][6][7]

After the product has been labelled accordingly to the manufacturer’s likings it can be visually identified by computers or people depending on application. Barcodes are for computers whereas visual looks and product descriptions are directed for consumers. [5][6][7]

3. THE COMPOSITION OF THE PSA LAMINATE

The PSA laminate consists of four major components which are facestock, adhesive layer, release coating and release liner as shown in Figure 2. Following sections explain aforementioned components in more detail. [5][6][7]

Figure 2. *Components of the "Engineered with Raflatouch by UPM Raflatac" PSA. [5]*

3.1 Facestock

Facestock functions as a base for the printed graphics and its purpose is to convey information to the end user or to make the product appealing for the consumer. The word refers to the printing side of the label. Facestock materials can roughly be classified into: uncoated and coated papers, plastic films and special materials. Each type of the material has different properties regarding recycling, durability, appearance and converting. Furthermore, facestock's density and surface topography varies from material to material. Facestock's processing capabilities are determined by its characteristics: stiffness, smoothness, porosity, printability and surface energy. [5][6][7][8]

PSA laminates' facestock selection is determined by the end use of the label and converting process. For example, thermal papers are coated with heat-sensitive coating, thus information can be conveyed onto the label surface by using heat or by conventional printing methods. Plastic labels, when compared to paper ones, are more durable and can withstand moisture, oils, greases and chemicals better while retaining its intended shape and looks. Additionally, for example, PE films are conformable, that is they can be applied onto uneven surfaces such as bi-axially curved perfume or shampoo bottles. [6][7]

Papers and synthetic polymer films (PE, PP, PET) are mostly used in common label solutions related to food industry, home and personal care, beverage, retail, logistic and transport and pharmaceutical labels. Facestock papers usually come in different shades of white, whereas films are either white, clear (PP, PET) or hazy (PE). [5][6][7]

UPM Raflatac's Film & Special Business (FSB) unit in Tampere occasionally uses facestock materials such as aluminium, copper, hologram films, wood, fabric. High visibility coloured papers are used to produce eye catching discount labels or void films for product security applications. [6][7]

3.2 Adhesive Layer

The function of the adhesive layer is to attach the label to the product permanently or temporarily depending on the purpose. All of the adhesives in PSA industry can be classified into organic rubbers or acrylic polymers. Both of the adhesive types have general purpose and speciality applications. The general structure of such adhesives is shown in Figure 3. [9][10]

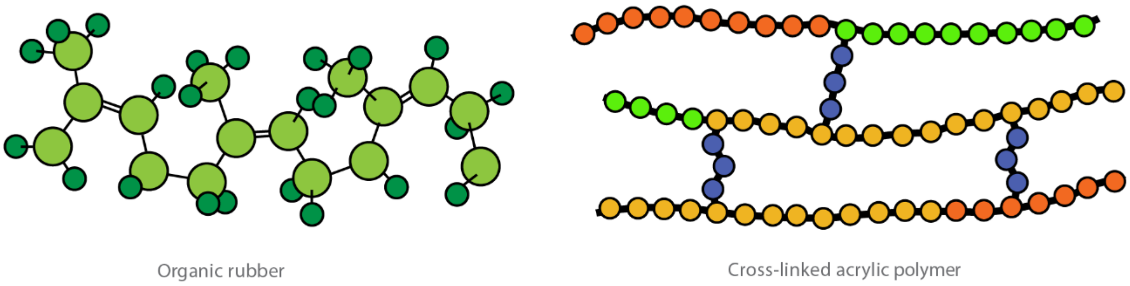


Figure 3. *Simplified structure of rubber and acrylic based adhesives. (Modified from [9])*

Organic, rubber-based adhesives are derived from natural or organic rubbers and resins. Due to double bonds in polymeric structure they are affected by oxidation and radiation. Generally, rubber-based adhesives have softer polymeric networks, and therefore, their initial tack properties are higher, however, softer network also makes the adhesive prone to an adhesive flow (i.e. edge ooze) producing sticky laminate edges. Removable rubber-based adhesives are prone to increase adhesion strength throughout the label life and risk to become permanent. [9][10]

Acrylic-based adhesives are made by cross linking acrylic polymers. They are slightly more expensive, but also have better resistance against high temperature and oxidation. Acrylic-based adhesives have smoother polymeric networks and therefore their initial tack properties are lower, requiring longer set-up period to obtain their maximum adhesion. Acrylic-based adhesives are less likely to present edge ooze and also maintain more consistent level of removability of labels. Although, both of those properties are highly dependent on the acrylate's glass transition temperature, T_g, i.e. the temperature where the polymer transforms from a hard glassy material to a soft rubbery material. There are acrylic-based adhesives containing tackifying resins to increase initial tack and improving adhesion onto surfaces with low surface-energy. This comes at the cost of losing some ultra violet (UV) and solvent resistance. [9][10]

The pressure sensitive adhesives can be divided into water-emulsions, 100 % solids (hot-melts and UV-curables) and organic solvents, based on the used technology (Figure 4). Adhesives can be further classified by chemical composition into: rubber-based or acrylic and permanent or removable. Labels using permanent type adhesives are tacker or are designed to break on removal, whereas removable labels are utilizing less tacky adhesives so they can be transferred or removed easily from the applied surface. [9][10][11]

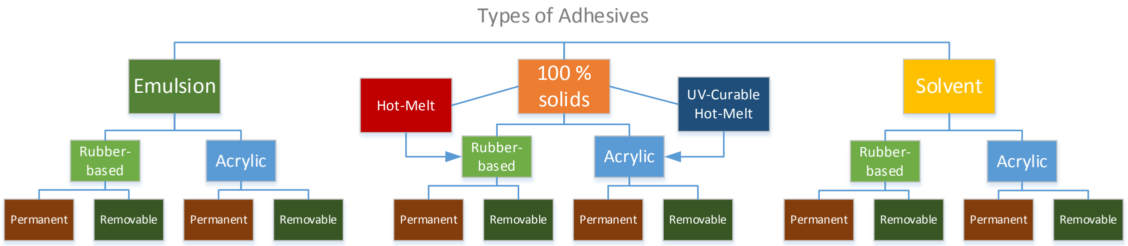


Figure 4. *Types of adhesive solutions used by the PSA industry. Larger version can be found from Appendix B.*

Out of the above, UPM Raflatac mostly utilizes water-emulsion and rubber-based hot-melt adhesives. UV-curable hot-melts are also used, although their current usage is lower. Adhesives' typically comprise of 95 % of polymer and resin, of which 70-80 % is base polymer and 20-30 % is resin, the remaining 5 % comprises additives. During the processing phase the additives are required to modify adhesives' adhesion and release properties and whether the adhesive will come out to be removable or non-removable. [9][10][11][12]

Emulsion Adhesives

Emulsion adhesives are polymer based adhesives suspended in water, making them safe to handle and environmentally friendly. Water-emulsion adhesives were the game changer during the mid-70's in the PSA industry. Water-emulsion adhesives became the trademark of the UPM Raflatac for being an early pioneer in the field. [9][10][11][12]

One of the founding principles of UPM Raflatac was to avoid the use of solvent-based adhesives altogether within their processes. The choice was made to promote occupational safety, health and environment. Therefore, to this date UPM Raflatac does not use any solvent-based adhesives. [10][12]

100 % Solid Adhesives

The 100 % solid adhesives are initially made in solvent but stripped to resin and cured to near 100 % – meaning, there is no solvent component in the adhesive system. Such adhesives require only re-heating or UV-initiation, thus making the adhesive drying unnecessary. However, the adhesive has to be cooled down by using chill rollers or low temperature air. Currently, low-viscosity 100 % solid adhesives are being developed to utilize existing hot-melt equipment at higher coating speeds. The aim is to achieve adhesive performance on par or better than the emulsion adhesives. [6][9][10][11][12]

Rubber-based hot-melts, which are mostly based on styrenic block copolymers, require only heating in the adhesive application phase. This type of adhesive requires oils, plasticizers and tackifiers to be added in order to achieve performance criteria. [9][10][11]

UV-initiated adhesives utilize hot-melt equipment, but the adhesive itself is composed of highly viscous polymers, making it non-flammable and solvent free. This enables creation of thick films, including foam-like adhesives, resulting in very high molecular weight fractions, which cannot be cast from solvent or emulsion based adhesives. [9][10][11]

Solvent-Based Adhesives

Solvent-based adhesives are polymer based adhesives in a petroleum-based solution or solvent. This was the common technology before water-emulsion adhesives broke through in the PSA industry. The solvent-based adhesives still have their uses, especially as the attainable adhesive performance is unrivalled. [9][10][11][12]

3.3 Release Coating

The release coating’s function is to release the facestock during waste matrix removal, and label during label dispensing from the release liner. There are several types of release materials which can be classified into migratory and non-migratory. Migratory release materials are, for example: fluids or powders. Non-migratory materials which do not transfer to the released material to any significant degree include polyacrylates, carbamates, polyolefins, fluorocarbons, chromium stearate complexes and silicones. [13][14][15][16][17]

Out of the aforementioned release materials, silicones have been adopted as de facto standard by the PSA industry. The benefits of silicones are that their structure is flexible and their surface energy is very low, thus yielding substantially lower release forces compared to many other substances. Additionally, the silicones can be applied on various types of release liners. Silicones can be cured into polydimethylsiloxane (PDMS) network, which adheres to the release liner surface, further restricting migration of the release coating. [13][14][15][16]

Like the adhesives, the silicones come in as water emulsions, 100 % solids or solvent based designs (Figure 5). Aforementioned systems utilize heat for curing and can be addition or condensation driven. There are also radiation cured 100 % silicone solids, which can be either cationic or free-radical cured systems. [13][14][15][16]

Industrial release liner coating applications mostly utilize two-part system for curing. Such systems have reactive ingredients initially separated, enabling high-speed cure. The two-part system's reactive components have to be mixed together in order to initiate the curing process. After the initiation, heat can be used to further speed up the curing process. [13][14][15][16]

In this work, condensation reaction refers to all reactions, where the functional groups of the reactants react and form a covalent link between the reactants. In polymer chemistry, this word has been traditionally used for the step growth mechanisms, whether producing condensates or not. Step growth is preferred in more modern presentations. Respectively, addition reaction refers to all reactions where the reactants are added to the unsaturated bond, usually a double bond. In polymer chemistry, this word has been traditionally used for the chain growth mechanisms, term preferred nowadays.

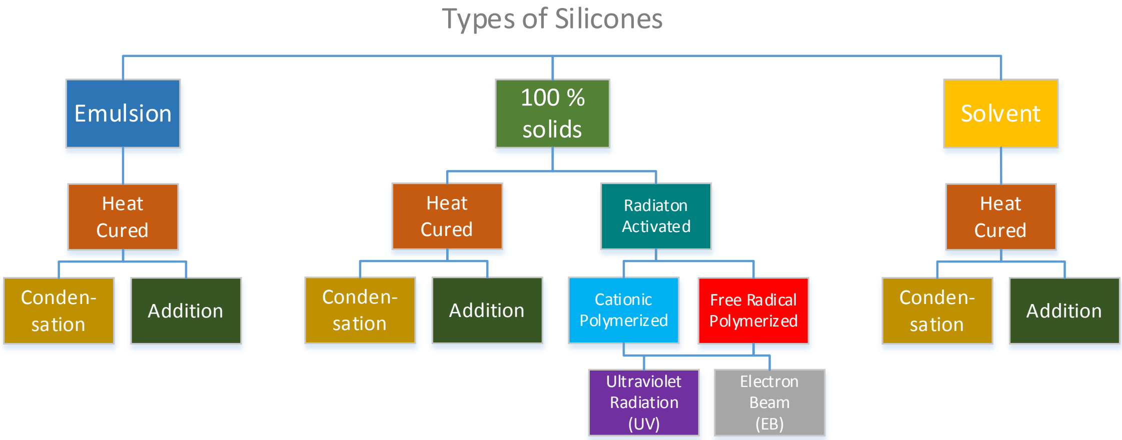


Figure 5. *Types of two-part silicone curing solutions used by the PSA industry. (Modified from [13][16]) Larger version can be found from Appendix B.*

Addition systems are based on SiOH/SiH chemistry, utilize platinum or rhodium as catalyst and are cured with heat. Condensation systems are also based on SiOH/SiH chemistry, but use tin salts or titanium alkoxide as catalysts and are also cured with heat. Free radical and cationic systems are cured by radiation, which can be ultraviolet (UV), electron beam (EB) or within the limits of special applications infra-red (IR) radiation. [13][14][15][16]

Curing chemistries are explained in more detail in Chapter 4. In the scope of this thesis the focus is kept on thermally cured 100 % solid silicone systems.

3.4 Release Liner

The release liner's main function is, first, to protect the adhesive until label application, secondly it acts as a carrier for the release coating and adhesive, before it is joined with the facestock. Later in the value chain, the release liner acts as a support for the die cutting after which it becomes the sole carrier of the actual label. Release liner material is often paper, but PET and PP films are gaining popularity. Recycling-wise the paper is the easiest to recycle followed by PP, and PET. [6][13][14][15][17]

The ideal release liner should have a high tensile strength to withstand high tension peaks at labelling line, smooth and closed surface retaining the silicone from penetrating the release liner. Furthermore, it would have minimal variation within thickness and compressibility, as these factors are critical for successful die cutting processes. [6][13][14][15][17]

3.4.1 Paper Liners

The paper liners are either glassine or kraft based. The grammage of the used paper varies from 45-100 g/m^2 and the paper thickness varies from 45-150 µm. [6]

The glassine liners have high density, smooth surface and are somewhat transparent. They are commonly used in an automated machine applications, where labels are transferred from label reel to the side of the product. Label dispenser's sensors can distinguish spaces between labels through transparent glassine liner which enables precise positioning of the label to the product. [6][11][13][14][15][17]

The kraft liners usually have a high grammage i.e. they are considerably thicker, more porous and have a rough surface. These liners aren't transparent and the laminates made using them don't curl as easily as those made with glassine liner. Therefore, the kraft liners are preferred in manual applications and used for making A4 sheet products for laser and inkjet printers whereas larger format sheets are used for sheet offset printing. [6][11][13][14][15][17]

3.4.2 Synthetic Liners

Most commonly used synthetic liner is PET due to a good heat resistance (T_m 165-255 °C) [18] and mechanical properties. Occasionally PP is used but its uses with current hot air silicone curing ovens are more limited due to weaker heat resistance (T_m 130-171 °C) [19] and mechanical properties. PP's biggest limitation is that it elongates somewhat easily due to used web tension during coating, printing or labelling processes. The higher the used temperatures the more elastic the PP structure becomes. To effectively use the PP liners, the elongation caused by the temperature should be minimized by using special UV-curable silicones and UV-curing ovens within the laminating process. As a material the PP is more environmentally friendly as it is easily recyclable compared to the PET liners. [6][14][15]

Plastic film's advantages over paper include: faster machine processing speeds and better durability due to high tensile strength. Since plastic films have very smooth surface, its benefits include: low silicone coat weights and most importantly, texture free adhesive layer – enabling visually pleasing non-label look. The PET and the PP usage as liner material is partly determined by their market price, if the PET price is becoming too high the PSA industry shifts to the PP and vice versa. [6][11][14][15][17]

4. THE LAMINATION PROCESS OF THE PSA

In short, the lamination process in the coating machine (Figure 6) occurs as follows: the release liner is siliconized at the silicone station and it is cured in the drying ovens; then the adhesive is applied on the siliconized release liner at the adhesive-coating station; finally, the adhesive is cured in the drying ovens or activated via UV-light. When necessary, the release liner can be moisturized before the facestock is combined with the backing at the lamination nip to produce laminate. [6][7][11][13][14][15]

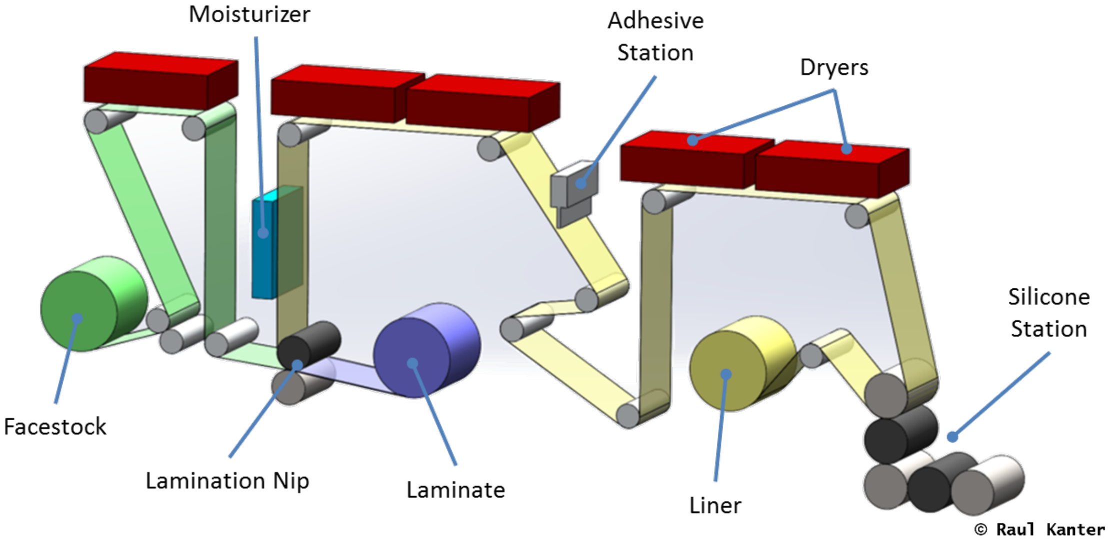


Figure 6. *Coating machine and its main components. (Re-illustrated from [8])*

The siliconizing can be done "in line" meaning that the siliconizing of the release liner is integrated *within* the lamination process, or "off line" meaning that the release liner is siliconized *separate* from the lamination process. Off-line siliconizing is usually done using separate silicone coating machine or running conventional lamination machine only with siliconizing unit. [6][7][11]

The off- and in-line siliconizing methods have both their benefits and drawbacks. The off-line siliconizing method enables to use longer curing times and more inexpensive silicone curing systems, because the silicone curing can continue even (up to months) in storage before usage. The biggest drawback is the possible contamination of the release liner's back side and also the required storage time and space. The in-line silicones are costlier, yet cured very fast – just in a few seconds. In addition, they enable silicone release level adjustment on the go. The UPM Raflatac utilizes both siliconizing methods as some of the legacy coating machines do not have their own siliconizing unit. [6][7][11][14][15]

4.1 In-line Solventless Silicone Application

The aim in the siliconizing process is to use as little silicone as possible, while reaching sufficient silicone coverage, release values and dispensability. Minimum necessary amounts vary depending on the material of the release liner. Small deviations in the silicone coat weight should have minimal impact on the release value. Plastic films may require only 0.1-0.2 grams per square meter (g/m^2) to reach perfect silicone film coverage while exhibiting required release properties. Glassines typically require 0.7-1.3 g/m^2 whereas machine calendered krafts need 1.0-2.2 g/m^2 for complete coverage. Differences are result of a different surface topographies. Closed and smoother surfaces require considerably less silicone to reach the perfect coverage than rougher liner textures. Typically a coating of 1 g/m^2 is almost of 1µm thick. [6][13][14]

The coating system used in UPM Raflatac's modern coating machines' is *multi-roll smooth roller coater*, it is a nip-fed system and all the nips are silicone film splits. The rollers alternate between rubber and steel throughout the multi-roller system (Figure 7).

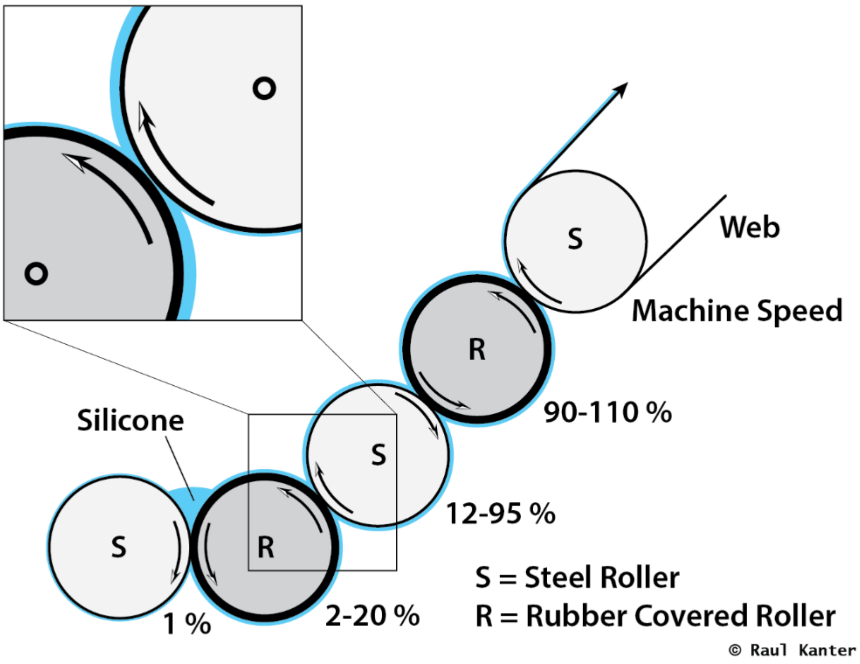


Figure 7. *Multi-roll smooth roller coater. (Re-illustrated from [14])*

The silicone application in brief is as follows: the silicone mixture is fed between two metering rollers, from where the silicone layer is split onto a steel transfer roller. From the transfer roller the silicone film is split onto rubbery application roller, from where silicone is transferred onto liner material. Splitting the silicone-film at *rubber-steel roller interfaces* several times (Figure 7) has a benefit of having an evenly spread silicone layer with minimum amount of silicone used, in comparison to applying silicone straight onto the web. After the siliconizing the liner with uniform, wet film of coating continues into curing ovens. [6][13][14]

The coating system is speed dependent, meaning that the coat weight changes as the machine speed changes. Therefore, the coating system's roller speeds and nip pressures have to be adjusted in relation to used speed to obtain the desired coating weight, typically used speed ranges are shown in Table 1. Other speed configurations will work well, as long as the speed differentials are kept less than 4:1 between contacting rollers. The backing roller runs at machine speed, thus defining the web tension after the silicone station. The speeds and nip adjustments have direct impact on the transferred silicone amount and evenness of the silicone film. The nip positions in relation to each other can be adjusted to a precision of 0,001 mm. [6][13][14]

Table 1. *Typical roller speeds used at silicone station. [13]*

Roller	**Speed**
1st Metering	a few rounds per minute
2nd Metering	2-20 % of the machine speed
Transfer	12-95 % of machine speed
Applicator	90-110 % of machine speed
Backing	machine speed, thus adjusting the web tension

The benefits of multi-roll system include low coat weight, good surface coverage and no engraved rollers which may clog. The system's drawbacks are that it requires time to be optimized in terms of nip pressures and roller speed differentials. Furthermore, it is somewhat complicated and expensive. In conclusion, this type of coating system is the best option for big PSA producers or release liner suppliers who have significant output volumes. [14]

4.2 Temperature Activated Silicone Curing

Shortly after silicone coating the release liner has to be cured. Curing is usually done using hot air, IR-, UV-radiation or a combination of the aforementioned methods. To give an idea of different oven types in PSA industry, common oven types are presented in Figure 8. These include arch dryers for maximizing web tension, air flotation ovens for minimizing web scratching and straight through ovens for minimizing moisture loss. Two of the mentioned designs apply hot forced air from both sides of the web, whereas the latter of the three applies heat only from top. Ovens range typically from 5 to 90 m and may have one to eight heating zones. [6][7][13][14][15]

***Figure 8.** Different types of curing ovens: a) Arch dryer b) Straight through oven c) Air flotation oven. [20][21][22]*

Below, the curing process is explained in detail for water-emulsion based silicone systems cured by hot air. It applies with slight modifications to the solvent and 100 % solid silicone systems as well. Generally the coating machine's siliconizing lines are run at 300-900 m/min which translates into a few seconds of curing in the zoned ovens. UPM Raflatac mostly uses 100 % solid silicone systems. [6]

4.2.1 General Principles and Water Emulsion Silicone Curing

The curing begins as the siliconized release liner with wet film of silicone coating enters the curing oven. The first oven zone uses relatively low temperature (90-100 °C) to initiate the water evaporation. As the web progresses into hotter oven zones (120-170 °C) the silicone polymer (PDMS) particles in the water-emulsion will start to coalesce. During this curing phase, the silicone polymers must coalesce into oil, migrate to the surface before they begin to gel or they risk being trapped beneath the film-forming organic material. [6][14]

Such stratification of the organic material will substantially hinder the silicone migration to the surface. This, in turn, leaves the surface covered in too much organic material and results in undesired release properties. Additionally, too high temperatures may cause a race between the catalyst evaporation and the curing process – meaning, if all the catalyst is evaporated, the curing reaction can’t complete as intended. [14]

When everything goes as planned the silicone-rich surface forms as the topmost layer. Next, the silicone needs to be cured. Applying too much heat in this phase, results the cure progressing faster than intended by not allowing the absorbed water to be fully evaporated from the moist paper liner. The evaporating water, will instead, be trapped under the formed silicone web. Later, this trapped water will explode holes into the silicone web as it has nowhere to go when the heat forces it to volatize. [14]

For the aforementioned reasons a zoned oven heating is required. The first oven zones utilize relatively low temperatures to slowly evaporate the water and initiate the silicone particle fusing. The later oven zones have somewhat higher temperatures to evaporate the residual water and enhance the silicone mobility. The final curing phase utilizes high temperatures to fully cure the silicone and to completely harden the organic matter. [6][14]

4.2.2 Solvent Based Silicone Curing

For the solvent-based silicone coating, the process is simpler and requires much lower temperatures to initiate the curing process as the organic solvents are readily evaporated in the room temperature. Since there is no water to evaporate, it is only required to evaporate the solvent and, in some cases, volatile components such as catalysts, crosslinkers or additives before they become trapped under the formed silicone coating. Again, too much heat early on may cause a race between curing process and catalyst evaporation, for example in condensation systems; it is quite easy to evaporate the tin salt catalyst too fast, leading to tin oxide deposits in cooler parts of the oven. [6][14]

4.2.3 Solventless Silicone Curing

In the solventless silicone systems (100 % solids), as there is no solvent to evaporate, the curing is initiated by evaporating the inhibitor. Namely, the silicone coating is often slightly uneven due to film splitting effects, as the siliconized liner leaves the silicone nip’s application roller, and due to higher viscosity compared to the aforementioned systems. Therefore, it takes some time to level out the inconsistencies. The levelling can be accelerated by introducing elevated temperatures. As learned before, ramping up too much heat in the beginning may trigger the evaporation of critical components, such as inhibitors, crosslinkers or additives. [6][14]

4.3 Adhesive Coating Process

The adhesive coating can be applied onto release liner by different methods, discussed in more detail below. Once the adhesive coating is applied, the emulsion adhesive goes through curing in zoned drying ovens, while UV-hotmelts require UV-radiation for cure. When using rubber based hotmelts, only cooling is needed. [8][9][10][13]

The adhesive coating quality is monitored during the process via special apparatuses, which measure the momentary coat weight profile of the adhesive coating. The measured data from the apparatuses is displayed as a trend in machine direction and the profile in cross direction is illustrated by graphs. The adhesive coating is also visually inspected from the finished laminate by peeling facestock from the release liner and checking the adhesive coating's texture. [7][10][13]

The quality of the adhesive coating is essential as it has great impact on the final product performance and it determines the PSA's converting properties: adhesion, release printability and outlook. Therefore, it is essential that adhesive profile is even, especially in the cross direction or the formed reel may become tapered or lopsided. The adhesive's coat weight determines label's adhesion properties, so it is critical for coat weight to be within tolerance limits to ensure that label can fulfill its requirements. Furthermore, it is important that adhesive coating is smooth, free of holes and defects. This is especially important when using transparent facestock, as the adhesive coating becomes part of the labelled product's visual outlook. Unevenness and holes in the adhesive layer would be copied into the print image, rendering the transparent labels hazy and visually displeasing. [6][7][10][13][13][14]

4.3.1 Curtain Coating with Water Emulsion Adhesives

The curtain coating adhesive application method is literally based on the creation of "curtain" or "waterfall" out of the water-emulsion adhesive, Figure 9. The curtain coating station has no rollers in its construction. The adhesive is distributed on the release liner through a slot die, located several centimeters above the web, utilizing only gravity to produce the curtain. The adhesive coating's thickness is controlled by the machine speed or by adjusting the nozzle diameter of the slot die itself. [6][7][10][13][24]

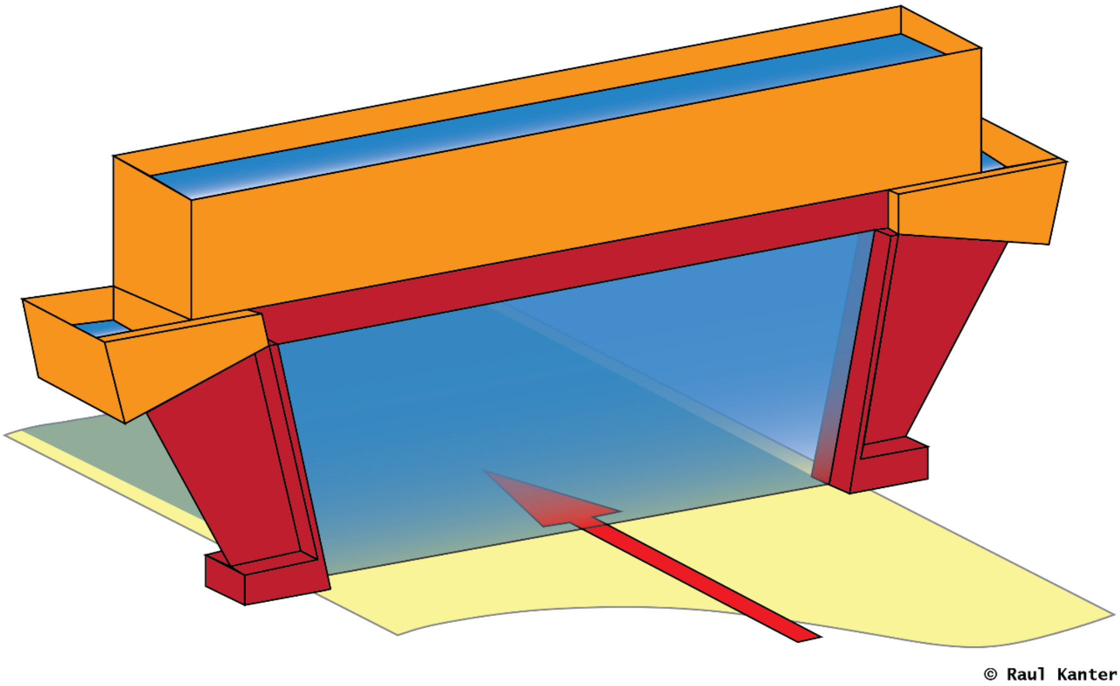


Figure 9. *Curtain coater principle illustrated. (Re-illustrated from [23])*

This coating method's benefits include: consistent adhesive layer of same thickness throughout the whole web, high coating speeds without misting rollers, good quality coating and low maintenance costs. On the contrary, this method requires sufficient adhesive drying capacity, minimum machine speed of 100 m/min. The coating method becomes optimal at speeds of 300-500 m/min or above. [6][10][13][24]

Furthermore, the adhesive has to meet certain criteria to be applicable for curtain coating. Namely, the adhesive is required to have; high shear stability and good filtering characteristics within a pump, a low dynamic surface tension and an excellent wetting characteristics. A proper adhesive viscosity is crucial when forming uniform curtain, maintaining desired coat weight, while avoiding adhesive curtain ruptures initiated by air bubbles in the adhesive curtain. The presence of too many air bubbles may disturb the curtain in such a way that it collapses altogether. [6][10][13]

When applying water-emulsion adhesive via curtain coater its viscosity is lowered by excess emulsifying water. Before the release liner and facestock are joined at the laminating nip, the excess water must be evaporated from the adhesive emulsion to activate the adhesive. The excess water is evaporated within the drying ovens; leaving the release liner with 'floating' adhesive coating on top of a non-sticky silicone web. Usually, the adhesive is slightly over-cured to avoid leaving the adhesive wet, as overly wet adhesive is runny and oozes out from the finished roll's sides. [6][7][10][13]

When using paper liners, over-curing the adhesive may dry the paper too much. Dry paper liner draws moisture from the ambient air and also from the adhesive. As paper fibers absorb moisture the paper swells and its dimensions change, increasing compression and pressure in the final roll. The increasing pressure can cause the adhesive to be pressed out from the finished roll. To counteract excess laminate dryness, the paper liner is re-moisturized post-oven, in order to better control final laminate's moisture content and swelling. If proper moisture conditions are not met within laminate there is a chance of laminate curling. [6][7][10][13]

4.3.2 Hot-Melt Adhesive Application

The hot-melt adhesives come from the supplier as a viscous liquid, solid or paraffin packed in casks. At the coating station the adhesive is melted or heated in the casks with a special drum melter. Liquefied hot-melt is pumped into the temporary adhesive reservoir where it is further heated. From where the hot-melt is pumped to a coater nozzle and applied on the release liner. The hot-melt the adhesive is subsequently cooled by chill rollers or cool air. The UV-curable hot-melts, of course, require UV-cure and then cooling. [6][7][10][13]

The UV-hot-melt-coated release liner travels under UV lamps which cure the adhesive. Exposure to the UV radiation initiates the adhesive curing by triggering photoinitiators in the polymer chain. As the photoinitiators react to the radiation they induce crosslinking in the polymer chains, i.e. adhesive is cured. The intensity of the UV radiation is adjusted accordingly to each adhesive as their polymerization energies vary. After the curing process the adhesive layer is cooled down and joined together with facestock in the lamination process. Adhesive cooling is done by the regular curing ovens, which now operate at cool temperatures or using chill rollers. [6][7][10][13]

4.4 Laminating

Laminating nip combines the facestock and backing into final product, the laminate. The laminating nip consists of smooth, parallelly positioned top roller (rubber) and bottom roller (steel), positioned on top of each other. Rollers must have equal pressure on both ends to ensure uniform pressure for proper adhesive contact and bond strength or unnecessary wrinkling and steering of the web will occur. The used nip pressure depends heavily on adhesive and laminated materials, for example lower pressure is used for softer adhesives and fragile substrates and vice versa. [6][7][13][24][25]

Usually, before the nip, there are slightly convex rollers which slightly stretch the facestock and release liner, helping to keep connecting faces in-line with each other. Furthermore, it is essential that lamination nip is clean and smooth as any dirt particles leave imprint into the print surface. Lastly, the finished laminate is rolled into a reel, put in storage and further processed into smaller coils. The smaller, more easily handled coils are sent out to label converting businesses. [6][7][13]

5. SILICONE (PDMS)

The most widespread release coating technology in the PSA field is based on polydimethylsiloxane (PDMS). Solvent-based silicone systems were industry standard from late-1950s until mid-1970s. As the environmental pressure against solvent and emulsion systems grew, it led into development of the 100 % solid silicone systems. Today, the PSA industry mostly utilizes 100 % solid silicone systems. Regardless, the solvent and emulsion based systems have their special applications and are used to date. [6][7][8][12][13][14][26][27][28][29]

Worldwide, major silicone suppliers are: Bluestar Silicones, Dow Corning, Momentive, and Wacker. In more special, UV-cured silicones, major suppliers are Evonik and Shin-Etsu. Obtaining detailed information about silicone components is difficult as they are trade secrets. [6][14][26][27][28][29]

In following sections a closer look is taken on silicone components and curing chemistries. The focus is on thermally cured 100 % solid addition systems. First, the basic PDMS polymer properties are discussed, followed by discussion about the release values. Next, properties of crosslinker, catalyst, inhibitor and additive are reviewed. Finally, after all the components have been described, curing chemistries are briefly explained for thermal and radiation cured silicone systems.

5.1 Polymer

The basic polydimethylsiloxane (PDMS) molecule structure is modified based on what type of curing system is used. The changes are made to the reactive groups of the base-polymer. The reactive groups dictate the possible chemical reactions and the curing mechanisms cure. For example, the reactive groups may form crosslinked structures through thermal or radiation cure. [6][13][14][26][27][28]

All of the used silicone polymers have common characteristics of good spreading and film forming properties. They also have capabilities of producing a three dimensional silicone network which is relatively elastic and hydrophobic after cure, Figure 10.

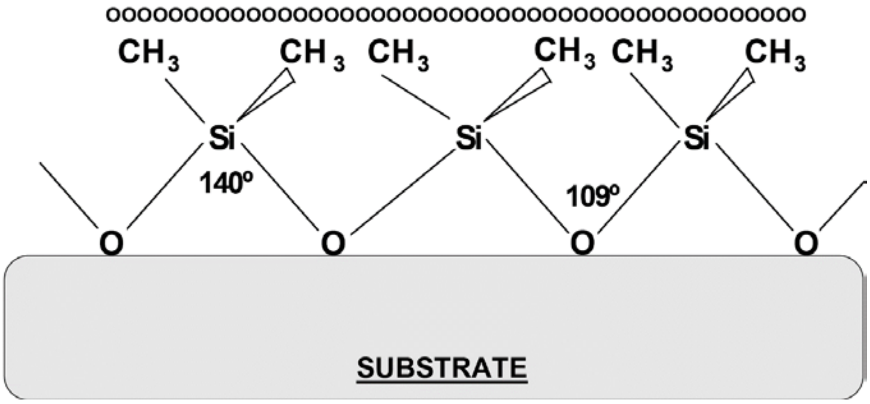
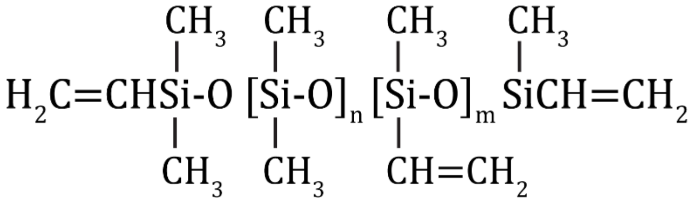


Figure 10. *A substrate with polydimethylsiloxane network. Non-polar dimethyl groups give the surface low surface energy. Extremely flexible siloxane backbone makes the whole structure resilient. [26]*

As UPM Raflatac mainly uses thermal addition cure we will take a closer look on 100 % solid silicone systems used in this type of curing reaction. The solventless silicones use much lower molecular weight polymers and they can be either terminal-only or multi-functional vinyl polymers. Terminal-only polymers have only two reactive terminal groups, whereas multifunctional polymers have up to six reactive groups within the polymer chain, Figure 11. In order to cure, one of the reactive groups has to react. Meaning, in multifunctional polymers one out of six has to react, whereas in terminal-only polymers one in two has to react. The amount of reactive groups gives different characteristics to each polymer type. [6][13][14][26][27][28]



$$H_2C{=}CH\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\ [\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O]_n\ [\underset{CH{=}CH_2}{\overset{CH_3}{Si}}\text{-}O]_m\ SiCH{=}CH_2$$

n+m ranges from 100 to 5000

Figure 11. *Multifunctional vinyl PDMS pre-polymer, displaying three reactive vinyl groups. [14]*

For example, number of reactive groups directly relate to the percent extractable material at various states of curing, and multifunctional polymer will always show less extractable content. Extractable content is directly related to cure rate. However, terminal-only polymer cures reach completion faster than multifunctional polymers. [6][13][14][26][27][28]

As usual, different functional characteristics are required for different purposes, therefore both polymer types have their place and neither is necessary better or worse. Furthermore bath life, coatability, current equipment and cost are major factors determing polymer selection. Differences between polymers can be seen in coverage efficiency, leveling speed and in the development of a fine mist or spray around the final transfer nip where silicone is actually laid onto the substrate. Aforementioned differences arise from polymer molecular weight and their architecture; multi- and terminal-functional polymers exhibit clear differences. Chosen silicone polymer is also the component which dictates the release values, release profile and silicone anchorage. [6][13][14][26][27][28]

5.2 Silicone Release Values

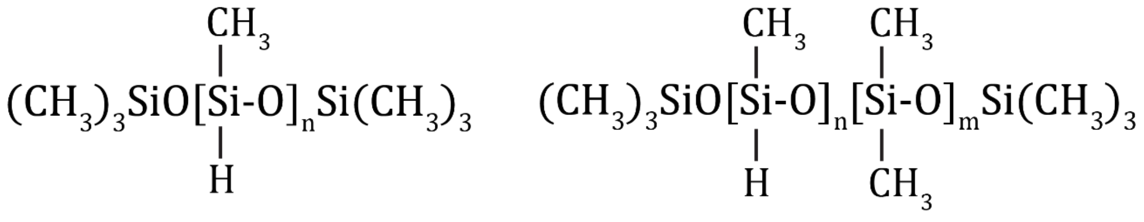
The silicone release coatings have different properties to control release forces, depending on the customer’s needs being either low or high release. Release values are defined by following low and high speed release tests: Low speed release is defined to have 0.3 m/min peel rate when removing the face from backing. High speed release’s peel rate is 100-200 m/min when removing backing from the face. [6][13][14][26][27][28]

High speed release values are mostly determined by used silicone type. Linear end-blocked silicone pre-polymer forms springy silicone net, which absorbs a lot of energy during label peel off, increasing especially the high speed release values. Branched silicone forms tight inelastic web, with almost constant release independent of used peel speeds. [6][13][14][26][27][28]

Release values are also affected by adhesive properties, release liner properties, silicone quantity, facestock properties, moisture and temperature. Additives make it easy to increase release values, but lowering is done through changing silicone system’s cross linker properties. Release properties have a tendency to change over time, especially when certain combinations of adhesives and silicone are used. At times, varying release values are desired. Most often not, as the time independent release is preferred in the PSA industry for its predictableness. [6][13][14][26][27][28]

5.3 Crosslinker

Crosslinkers are short chain polymers. They bond substantially longer pre-polymer chains by forming bridges i.e. crosslinks between pre-polymer chains, see Figure 3, crosslinks in dark blue. For addition cured polymers, the crosslinkers can be either homo- or copolymers, as shown in Figure 12. [6][13][14][26][27][28]



$$(CH_3)_3SiO[\overset{CH_3}{\underset{H}{Si}}\text{-}O]_nSi(CH_3)_3 \qquad (CH_3)_3SiO[\overset{CH_3}{\underset{H}{Si}}\text{-}O]_n[\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O]_mSi(CH_3)_3$$

Homopolymer, n = 5-60

Copolymer, n+m = 5-60

Figure 12. *General crosslinker structures for addition cured reaction. [14]*

Hompopolymers are used for rapid gelation of polymer network. They also enable good anchorage to the release liner and give a good cohesive strength in crosslinked web. Copolymers on the other hand give better bath life and final cure properties. As both types have their benefits, different mixtures of homo- and copolymers are used to reach desired properties depending on the used release liner, adhesive, face material or end-use. [6][13][14][26][27][28]

5.4 Catalyst

Which catalyst is being used, is determined by possible solvent, oven temperature, the type of polymer used and regulatory status, as food industry has strict laws. To improve solubility of the catalyst in solventless 100 % silicone systems Pt or Rh oragnosilicone complexes are used. The catalyst is the most expensive part of the silicone system. Due to increased costs, the catalyst content has decreased in few years from 50-150 ppm to 20-40 ppm of total silicone content. [6][13][14][26][27][28]

5.5 Inhibitors

Inhibitors are used to extend the bath life of mixed silicone. They function by forming coordination complexes with noble metal catalysts, thus preventing the catalyzation of the curing reaction. In curing process, the inhibitors are either vaporized or the coordination bonds between inhibitor and noble metal complexes are broken, enabling catalysis to take place. There is a big difference between how the addition and the condensation systems can be inhibited; the addition systems are in fact too easily inhibited due to platinum catalyst poisoning, the condensation systems on the other hand tend to be difficult to inhibit effectively. [6][13][14][26][27][28]

Inhibitors come in many varieties, ranging from strong inhibitors with long and stable bath life accompanied with higher initiation temperatures, to a weak inhibitors with barely adequate bath life but low initiation temperatures. Inhibitors which form very weak and easily reversible coordination bonds can be packed together with the noble metal catalysts without fear of damaging catalyst. [6][13][14][26][27][28]

For addition cured systems inhibitors are required to form a weak coordination bonds with the platinum. Such weakly bound compounds are commonly vinyl siloxane dicarboxylic acids, acetylenic alcohols and ketones. In condensation systems, compounds such as; alcohols, amines, carboxylic acids and amino-polysiloxanes are commonly used. [6][13][14][26][27][28]

However, the inhibitor solubility in 100 %-silicone system has its challenges as low storage temperatures may cause the inhibitors coming out of the solution, forming their own phase. Solvent based systems have wider temperature range and enable greater inhibitor concentrations making it possible to combine good curing performance with good bath life. To reach desired levels of solubility, the bath life and good enough curing performance; strongly and weakly binding inhibitors are blended to combine their properties. [6][13][14][26][27][28]

5.6 Additives

Additives are used to modify many of the silicone properties, including release value, anchorage, curing properties, misting and silicone component solubility. Release additives control the silicone release values mostly by affecting the low-speed release. High-speed release is more dependent on silicone structure itself, but can be somewhat modified by additives. Anchorage additives are occasionally necessary on some silicone substrates with paper liners. However, they are critical when siliconizing PP and PET surfaces because film surfaces are smooth and non-polar. Curing additives affect silicone curing speeds. Anti-mist additives are used to control or completely remove the effect of silicone misting at the silicone station's application roller. Additives controlling the component solubility are mostly used with solvent based silicone-systems. [6][13][14][26][27][28]

5.7 Curing Chemistries

As the liquid silicone is applied on the release liner it has to be cured in order to produce crosslinked release surface, which is supple and has adhered to release liner. Therefore, in the silicone coating phase it is beneficial for liquid silicone to slightly penetrate the release liner's surface. When fully cured, a secure adhesion is formed between two components, reducing silicone migration.

When silicone is wrongfully mixed, cured or applied, silicone may migrate through the release liner. In the later processing phases, the migrated silicone may weaken the ink adhesion or adhesive's tack to an applied surface. There are various ways how curing can be done chemically, below is a detailed description of the most common methods which utilize either thermal or radiation cure. [6][13][14][26][27][28]

5.7.1 Thermally Cured Systems

Thermally cured systems can be divided into condensation and addition cured processes. Condensation refers to a chemical reaction where two functional groups react, forming a large and a small molecule as a byproduct. Addition refers to a chemical reaction where the polymer chain grows via addition to multiple bonds of vinyl (C=C) groups present at the chain ends of the PDMS. [6][13][14][26][27][28]

An example of thermally cured addition reaction in two-part system between vinyl and hydrogen (SiH) containing silicone groups carried by functional oligomers, Figure 13:

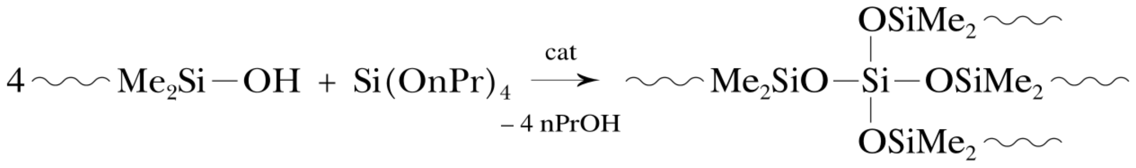
$$\sim\sim\sim\ \mathrm{OMe_2Si - CH = CH_2 + H - Si \equiv} \xrightarrow{\text{cat}} \sim\sim\sim\ \mathrm{OMe_2Si - CH_2 - CH_2 - Si \equiv}$$

Figure 13. *Crosslinking of addition cured silicone, where ≡ represents remaining valences of Si. [28]*

The addition cured reaction is usually catalyzed by Pt metal complexes, although other noble metal complexes such as Rh can be used. However, two-part system catalyst complex can be easily inhibited when it comes in contact with electron donating substances. The addition cure has no byproducts, therefore the formed silicone web retains its original dimensions. [13][14][24][26][27][28]

Although this reaction can occur at the room temperature, it is significantly faster with proper thermal input and evaporation of the inhibit, requiring only few seconds to fully cure. Fast cure enables the use of in-line siliconizing technique and reduces silicone transfer significantly. [13][14][24][26][27][28]

An example of thermally cured condensation reaction in two-part system between hydroxyl end-blocked polymer and alkoxysilane, here, tetra n-propoxysilane i.e. $Si(OnPr)_4$, Figure 14:



$$4 \sim\sim\sim \mathrm{Me_2Si - OH} + \mathrm{Si(OnPr)_4} \xrightarrow[-\,4\ \mathrm{nPrOH}]{\text{cat}} \sim\sim\sim \mathrm{Me_2SiO - \overset{\displaystyle OSiMe_2 \sim\sim\sim}{\underset{\displaystyle OSiMe_2 \sim\sim\sim}{Si}} - OSiMe_2} \sim\sim\sim$$

Figure 14. *Crosslinking of condensation cured silicone. Alcohol is formed as byproduct. [28]*

The curing starts as two components are mixed. The reaction is further catalyzed by organometallic tin salt and applied heat. As the condensation cured reaction releases n-propanol as a byproduct, the silicone webbing’s dimensions slightly change. [13][14][24][26][27][28]

The condensation cure reaction is relatively slow as full cure may take several days. Therefore, the siliconized release liner rolls are kept in storage before use. As the partly cured silicone is rolled into a roll the chance for silicone transfer is fairly high as uncured silicone can attach itself to the release liner’s back. [6][13][14]

5.7.2 Radiation Cured Systems

Radiation curing is carried out in free radical or cationic chain reactions. The stimulus for cure can be ultraviolet (UV), electron beam (EB) or infra-red (IR) radiation.

Specific chemical groups when attached to silicone polymer, commonly acrylates in PSA industry, can crosslink via free radical curing. In addition to acrylates, epoxy siloxane and mercaptosiloxane systems for curing exist. Aforementioned chemical groups can be cured by UV or EB radiation. Biggest benefit of the radical system is that it has very fast curing times, usually less than one second. [26][27][28][29]

Free radical UV cure is usually carried out in the presence of a shielding gas such as nitrogen or helium, due to a fact that free radical type reaction is easily inhibited by the presence of oxygen. In the case of the UV radiation cured processes a photoinitiator is required to initiate the curing process. The photoinitiator breaks down in presence of UV-light to produce free radicals. These free radicals then “steal” an electron from the acrylate group’s double bond producing free radical in the acrylate. Newly formed acrylate-radical will interact with other acrylate groups in the silicone polymer thus initiating crosslinking. [26][27][28][29]

Free radical EB cure doesn’t require photoinitiator or shielding gas. Instead, the silicone coating is bombarded with high energy electrons which collide and scatter with present electrons. Thus creating free radicals in the polymer chain and initiating the crosslinking. This method is not yet in widespread use, mainly due to high capital cost of coating equipment compared to other systems. [26][27][28][29]

In cationic cure system, the UV radiation is used to produce strong acids i.e. protons, H^+ from photoinitiators. Formed protons drive cationic reaction, causing polymerization at the epoxy groups in the silicone polymer chain. The produced protons initiate cationic propagation by seeking and bonding with polymer epoxide ring’s oxygen, forming an intermediate, protonated epoxide functional group $R–Epoxide=O–H^+$, in the base silicone polymer. [26][27][28][29]

The protonated epoxide can bond with second epoxide ring attaching two polymer chains together while propagating the positive charge forward to the next epoxide ring forming intermediate: $R–Epoxide=O^+$. This propagation continues until growing chain is terminated. Termination can occur via impurities quenching the free protons, growing epoxy chain cyclizing or chain transfer agents terminating the chain growth while initiating the new chain. [26][27][28][29]

Cationic curing is relatively slow process but once the reaction is initiated by UV-radiation it continues to the end even after the UV-exposure ends. Again this requires some storage time to fully cure the silicone and therefore increases the silicone transfer risk. However as this type of silicone is used in the in-line siliconizing processes the residual monomers can react with the adhesive and can therefore affect the release values over time. [26][27][28][29]

6. FACTORS IN SILICONE TRANSFER

Even the best cured and aged silicone coating may be put against an adhesive and on separation the silicone can be detected on the adhesive surface. This can be problematic, as large labels can tolerate relatively high amounts of silicone transfer when applied on a clean, marginally curving surface, whereas small and stiff labels, can tolerate very little transfer when applied onto curved surfaces. [6][13][14][24][26][27][28]

The following sections focus on explaining challenges presented by the printing surface contamination by silicone i.e. silicone transfer.

6.1 Factors Contributing to Printing Surface Contamination

A fine silicone mist is formed at the silicone nips whenever the silicone film splits. When the film splits at high speeds, it is torn apart with high kinetic force, providing enough kinetic energy for some silicone molecules to become suspended in the air. The misting increases in conjunction to roller speeds. At the application roller, the silicone mist may attach itself to the back of the release liner. However, the silicone mist effectively only reaches the release liner sides. [6][7][13]

A silicone vapour may form in the oven, when the wet silicone receives enough thermal energy to evaporate from the rest of the silicone film. The vaporized silicone is readily cured in the hot air becoming solid aerosol, i.e. dust suspended in the air. The dust particles form a white powder, presumably SiO_2. Over time, the oven insides get covered with silicone powder as the solid dust particles condense. The formed silicone powder may be set afloat, enabling the powder to be attached at the back of the release liner, from where, the powder may be easily transferred onto facestock, contaminating the printing surface. [6][13]

6.2 Factors Leading to Silicone Transfer in Paper Liner

There are various process variables which may play a part in silicone migration and transfer, for example:

- Silicone abrasion in the nip; a high pressure forces the silicone through a porous paper liner.
- Too low drying energy in relation to used coating speed, leaving parts of silicone uncured.
- Rubber rollers and seals in pumps; possible chemical interactions and catalyst poisoning.

- Water in 100 % solid silicone system; inducing possible reaction with crosslinker, resulting in deactivation of crosslinker.
- Mismatching amount of base polymer to crosslinker to catalyst ratio; results in reaction imbalance i.e. bad or impartial cure.

In the silicone manufacturing process non-reactive hydrocarbon ring structures are formed, which, to some extent, are distilled from the final batch. Regardless, a small percentage of such rings are left in the silicone. Even after prolonged curing, a polyfunctional system has a significant amount of reactive groups uncured, due to a lack of required reagents needed to complete the chemical reaction. For example, a steric impediment may prevent reactive groups from reacting with the crosslinker. Meaning, no matter how well the film is cured, it still remains somewhat reactive and not fully inert. In turn, enabling chemical reactions with contacting materials, causing release level instability. [6][13][14][24][26][27][28]

The unreacted hydrocarbon rings and non-reactive silicone polymer components may migrate through the adhesive or the release liner. Especially, when an external pressure is applied. Such external pressure is present at the lamination nip and in the finished label stock roll. By definition, the silicone transfer occurs when the silicone penetrates the release liner and attaches to the facestock, contaminating the printing surface. A low surface energy silicone components hamper the print ink adhesion to the facestock. Furthermore, when liquid silicone is applied to the paper release liner, given enough time the silicone components would migrate through the paper liner if not cured. The above can be explained by paper’s porous structure which contains polar groups, which can attract silicone components. [6][13][14][24][26][27][28]

7. REVIEW OF GPC AND GC-MS FOR SILICONE RESEARCH

The benefits, drawbacks and feasibility of gel permeation chromatography (GPC) and gas chromatography–mass spectrometry (GC-MS) are evaluated from the UPM Raflatac's point of view by keeping the silicone research in mind.

7.1 Gel Permeation Chromatography (GPC)

The gel permeation chromatography (GPC) is a type of size exclusion chromatography (SEC), where analytes are separated by their size. The GPC is one of the most versatile analytical techniques available for analyzing and characterizing polymers and their complete molecular weight distribution (MWD). Basic setup of the GPC illustrated, Figure 15. [30][31][32][33]

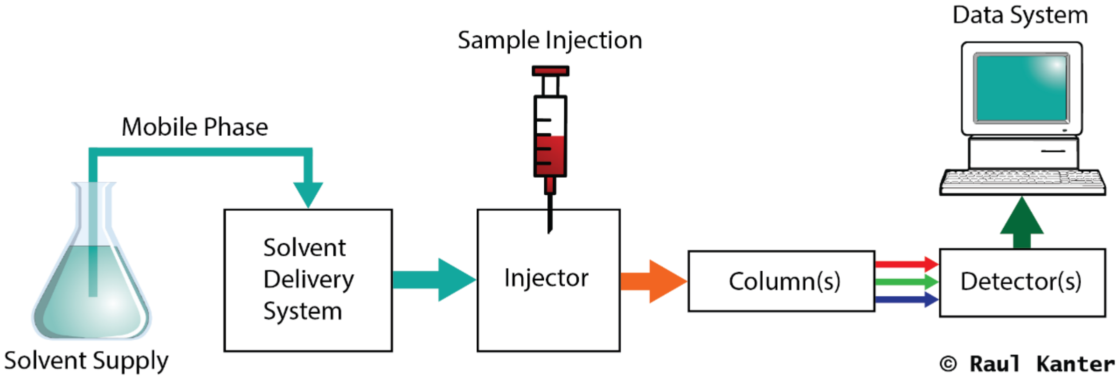


Figure 15. *Basic setup of GPC. (Modified from [30])*

The mobile phase is drawn from external container and pumped by the solvent delivery system through the GPC. The actual sample is injected in to the mobile phase flow through the injector. The sample component separation takes place at the temperature controlled column(s). Retention times are recorded by data system when analytes reach the detector. From the recorded data it is possible to identify original sample constituents by comparing them to known substances. [30][31][32][33]

The column is packed with porous beads i.e. gel particles, see Figure 16. The small analytes can enter the pores and therefore spend more time in the gel, increasing retention time. Conversely, the larger analytes spend less time and flow through the column faster. Separated components are analyzed by the detector unit, which sends the acquired data to the data system i.e. computer software which calculates, records and reports numerical values for given analytes. [7][30][31][32][33]

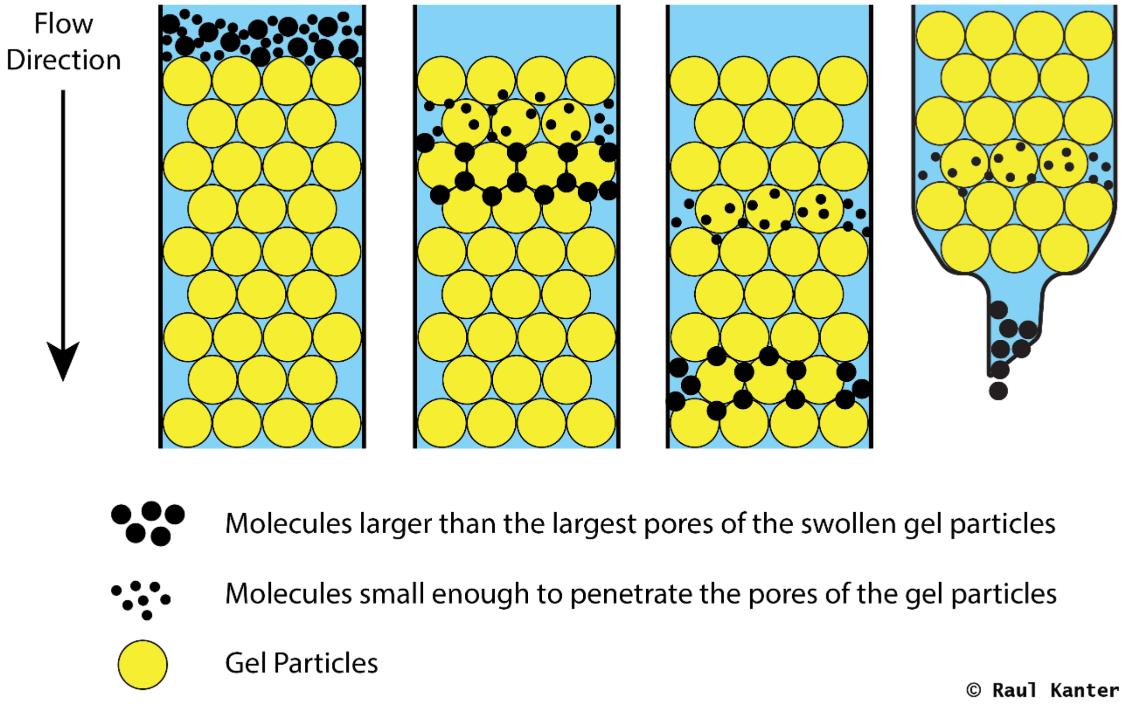


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***Figure 16.** GPC principle illustrated. (Re-illustrated from [32])*

7.1.1 The Pros and Cons of the GPC

With the GPC it is possible to characterize different polymeric materials to understand the makeup of a single polymer batch or complex polymeric compound consisting of poly-, oligo-, monomers and additives. Furthermore, the GPC is accurate enough to measure subtle batch to batch differences of several important parameters defining polymer physical properties. [30][31][32][33]

The MWD is a "fingerprint of the polymer" out of which other parameters can be determined. Other parameters include: number average molecular weight (M_n), weight average molecular weight (M_w), dispersity index ($Đ_M$) i.e. M_w/M_n, size average molecular weight (M_z) and viscosity molecular weight (M_v). All of the aforementioned parameters define the polymer's characteristic physical properties. Thus, minor batch to batch differences in these parameters may have drastic effects over the material properties, even though other tests (e.g. tensile strength, melt viscosity) give identical results between batches. [30][31][32][33]

To measure a wide range of polymers, the GPC requires different solvents for mobile phases depending on used columns and examined polymers. The solvents may be costly, toxic or carcinogenic depending on application. Also different columns with different type and sized gel particles are required for wider range of applications. All of the GPC samples require preparation as they must be in liquid phase before the examination. As the GPC is delicate and sophisticated instrument, a knowledgeable staff is required to operate and maintain it. If only certain type of polymer characterizations are done with the GPC then the operating costs and initial investments are reduced considerably as less columns are needed for example. [30][31][32][33]

The GPC accuracy, reported by many analytical laboratories is < 5 % for M_w and 10-15 % for M_n depending on the complexity of the samples. Furthermore, the accuracy of the molecular weight is limited by the need to calibrate against reference compounds. Therefore, absolute molecular weight determination by such technique is not possible. [30][31][32][33]

In conclusion, the GPC could add value to the UPM Raflatac R&D and/or quality control. With the help of GPC equipment it would become possible to verify the quality of each incoming silicone component batch. This novel information would enable to fine tune the silicone component mixing ratios on the coating machine based on the used batch. Which, in turn, may lead to better silicone adhesion and less silicone transfer. Obtained information may also provide better understanding whether or not the silicone extractable values correlate with different silicone batches.

7.2 Gas Chromatography–Mass Spectrometry (GC-MS)

The gas chromatrography-mass spectrometry (GC-MS) combines features from two analytical methods (Figure 17) to identify broad spectrum of substances within a tested sample. The gas chromatograph (GC) is utilized for separating and analyzing compounds that can be vaporized without decomposition. Typically, the GC is used to test the purity of the sample, or for separating mixture into its components and defining their relative amounts. The mass spectrometry (MS) is used to measure masses within the sample by ionizing chemical substances, and sorting the formed ions by their mass to charge ratio. [34][35][36][37]

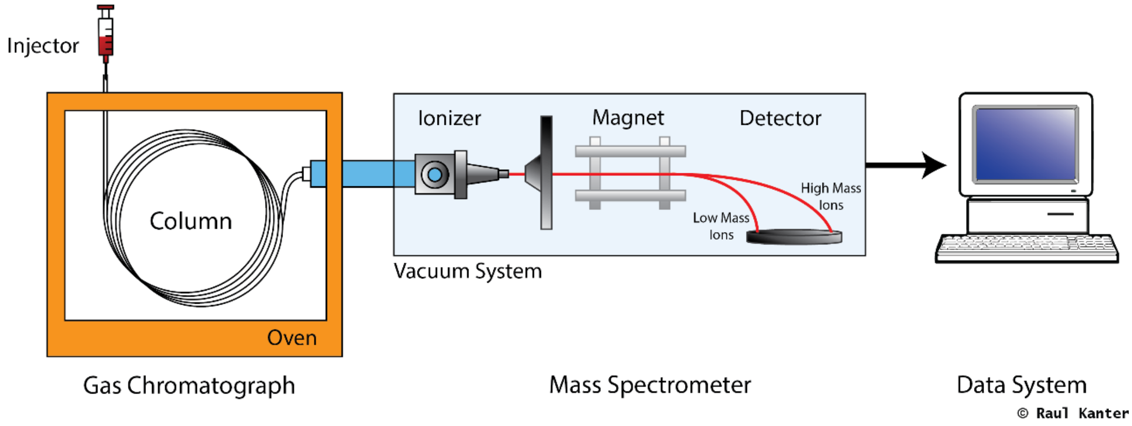

Figure 17. *Basic setup of GC-MS equipment. (Re-illustrated from [38])*

The combined GC-MS unit enables the separation and identification of even trace amounts of substances with great accuracy. The liquid sample is injected into the GC column within a temperature-controlled oven. In the column, the sample is vaporized and separated into compounds, revealing their relative amounts. Next, the separated compounds are ionized for mass analysis. The compounds' masses are measured in vacuum system by MS. The compounds are then sorted by their mass to charge ratio. The acquired data is sent to the data system for further processing. [34][35][36][37]

7.2.1 The Pros and Cons of the GC-MS

The GC-MS equipment with sufficient resolution is highly reliable and sensitive, making possible to detect even trace amounts of substances. Thus, GC-MS excels at separating organic compounds into various compounds. High precision also enables the determination of absolute molecular weights of specific oligomers of polymers. [34][35][36][37]

The GC-MS accuracy is highly dependent on technician's competency in interpreting the results. The MS feed may suffer from background "noise" i.e. impurities if GC instrument does not completely separate examined sample. Volatile solvents are required to prepare the sample as the GC samples must be gaseous, thus non-volatile samples require additional preparation. Additionally, different types of solvents are required for different sample compounds as they exhibit different solubilities. The used, highly volatile solvents may exhibit toxic or carcinogenic properties. [34][35][36][37]

In conclusion, the GC-MS is very useful tool for chemical analysis, especially when used in conjunction with other analyzing equipment. The GC-MS could add significant benefit to the UPM Raflatac R&D and/or quality control. The GC-MS would also make possible to check the quality of each incoming silicone component batch. With the gained knowledge, it would be possible to fine tune silicone component mixing ratios based on the used batch. These small adjustments may lead to better silicone adhesion and less silicone transfer through better curing. Obtained information may also provide better understanding whether or not the silicone extractable content correlates with different silicone batches.

8. RESEARCH METHODS AND MATERIALS

Initially, the ultimate goal was to differentiate between unique silicone recipes by determining baselines for characteristic extractable contents. Such tests were meant to be conducted in completely idealized laboratory settings, in order to eliminate all the process factors and to ensure the full cure. The approach included making use of existing laboratory equipment, and coating silicone onto aluminum to eliminate silicone absorption and variable kaolin levels present in paper. Namely, the kaolin contains elemental silicon in its structure, thus contributing to Si-peak intensity when examined with XRF. Furthermore, the new method was to be derived from existing extractable measurement method. Once the characteristic extractable content baselines had been identified, they were to be compared to the extractable content baselines acquired from the process conditions. This would have given means to evaluate the processes capability.

For practical reasons silicone was never mixed at lab scale. Rather it was extracted directly from the coating machine’s tank, as it was inaccurate to mix silicone from bulk components meant to produce tens of litres silicone. Doing so also saved time and experimentation could be started straight away. Whenever possible the specific “silicone A” was extracted fresh for each experiment. However, as different silicone recipes are used at the coater machine, the surplus silicones were stored in the freezer to be used with the next similar batch. In practice the required “silicone A” for the tests was virtually always available.

8.1 X-Ray Fluorescence (XRF)

The X-ray fluorescence (XRF) was the primary characterization method used during studies. It is a non-destructive analytical method to determine the chemical composition over a wide range of substances. Notable manufacturers include: PANalytic, Bruker, Oxford, Rigaku, and SPECTRO Analytical Instruments.

The basic principle of the XRF equipment is illustrated in Figure 18. The XRF is fast, accurate and requires only a little sample preparation as analytical method. Its applications include broad range of industries from mining, metal, oil, polymer, plastic, pharma and food industries. [39][40]

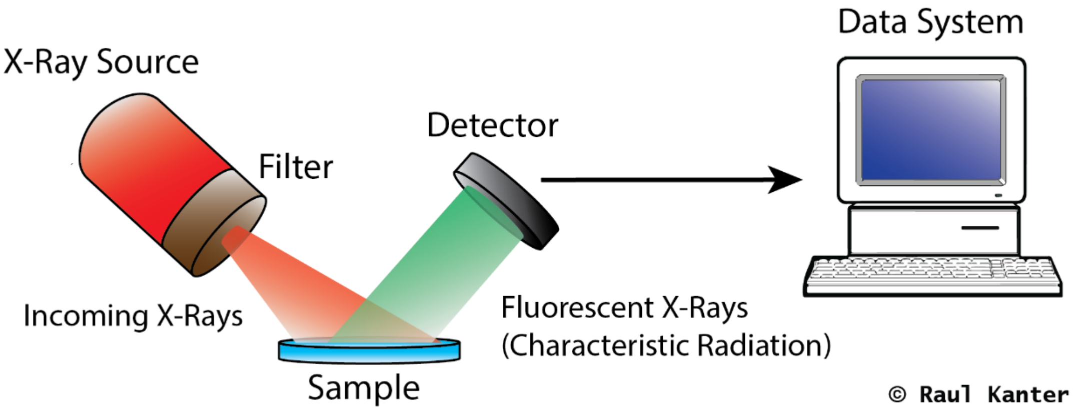

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Figure 18. *Simplified illustration of the XRF measurement equipment.*

The X-ray source, using a set voltage and current, produces electromagnetic radiation with very short wavelength defined as X-rays. When necessary, for certain element detection, the X-rays may be filtered before they irradiate the sample. The filtering is done to increase characteristic radiation intensities for specific element(s). As the sample is irradiated by X-rays some of its electrons become excited and will emit characteristic radiation specific to the material as the excitation discharges. This characteristic radiation is picked up by a detector which counts photons and their energy. Acquired raw information is fed into data system which displays acquired spectra and enables its further manipulation and data extraction. [39][40]

The XRF enables analysing solid, powder, granular or liquid samples. Although, the sample preparation is relatively easy, precautions should be taken in order not to contaminate the samples. Careful sample handling is needed as the sensitivity of the modern XRF spectrometers is high enough to detect fingerprints. [39][40]

When analyzing the sample, only atoms within an analysis depth are analyzed. Therefore, samples should be homogenous, and representing the whole measurable body as well as possible. The approximate analysis depths in various materials for three elemental lines with their respective energies are shown in Table 2.

Table 2. *X-ray penetration into selected materials for selected elemental lines. (Modified from [39] pp. 19, Section 3.5).*

		Penetration Depth [µm]		
Material	**Density [kg/m^3]**	**Mg Kα** (1.25 keV)	**Cr Kα** (5.41 keV)	**Sn Kα** (25.19 keV)
Pb	11 340 [41]	0.7	4.5	55
Fe	7 870 [41]	1	35	290
SiO_2	2 200 – 2 650 [41]	8	110	9 000
$Li_2B_4O_7$	2 440 [42]	13	900	46 000
H_2O	1 000 [41]	16	1 000	53 000

The analysis depth and absorption varies between the measured materials. Generally, the denser the material, the less the X-rays can penetrate it. Dense materials also absorb more of the produced characteristic radiation, therefore reducing the analysis depth. [39][40]

8.1.1 Characteristic Radiation

When the examined material is being irradiated, the high energy X-rays excite electrons, enabling higher energy states. The excited electrons leave behind an empty orbital. Any electron from higher energy state may now fill this vacant orbital, Figure 19. [39][40]

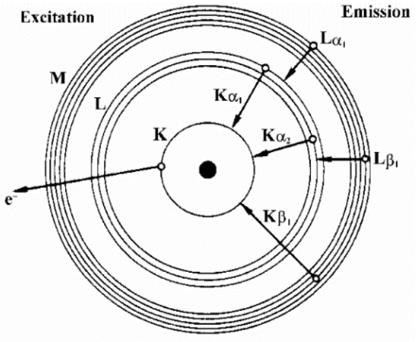

Figure 19. *Bohr's atomic model, shell model. Electron excitation and emission. [43]*

When the vacancy is filled, energy is released in a form of a photon i.e. characteristic radiation. Each known element has its characteristic energies for respective electron orbitals. There are limited number of ways how this can happen, mainly transitions are from: L→K i.e. Kα transition; M→K i.e. Kβ; M→L i.e. Lα, and so on. Each of these transitions have unique characteristic energies which equal the energy differences between the initial and the final orbital. [39][40] Wavelength of the released fluorescence radiation can be calculated from Planck's Law:

$$\lambda = \frac{hc}{E}$$

The measured fluorescent radiation can be analyzed in energy- or wavelength-dispersive manner. Meaning, the radiation is sorted either by energies or by wavelengths. UPM Raflatac utilizes energy-dispersive equipment in their labs. [39][40]

8.2 Experimental Research Methods

UPM Raflatac has been utilizing silicone extraction test to monitor free silicone levels in their products. The test is done to the final label stock produce right after a roll has been completed on the coating machine.

From the finished roll, a sample sheet of few meters is sent to the laboratory for various tests, inspection and to the archive. One of the measured entities is silicone extractable content [%]. It is analyzed by measuring the silicone coat weight before and after the silicone extraction process with X-ray fluorescence (XRF). The percent difference in coat weights [g/m^2] defined as extractable-%, see section 8.4 for the formula. This percent value tells how much silicone has been dissolved by the solvent compared to the original amount of silicone in the sample. An industry standard for acceptable extractable content is < 5 %. In the siliconizing processes the average is around 1.5-2.5 %, the lower the value the better. Extractable-% can be higher or lower depending on the used curing conditions, silicones and backing materials.

The biggest difference to the used method was that samples were manually manufactured and cured onto non-absorbing material, in practice, aluminium sheet or PET film. The coat weight measurements were done using R&D laboratory's XRF. Possible candidates for non-absorbing material were: moisture analyzing scale's aluminium containers, regular cooking aluminium foil, thick aluminium sheet used as facestock, or regular non-siliconized PET film. Possible application options included applying silicone manually with doctor blade [44], using hand-held flexo proofer, meter bar coater machine or pilot coater machine. For curing, two options were available: moisture analyser scale's heating function or using larger adhesive drying ovens. The right curing temperature and time were found by simply testing different temperatures and curing times.

The very first samples were made by manually applying the silicone onto the moisture analyzing scale's test cup (Figure 20) using the doctor blade. The silicone was cured by using moisture analysing scale's built in heating function. The goal was to replicate a coat weight of 1.0 g/m^2 used in real life processes. As the cup's effective diameter was less than 70 mm, only one XRF sample (⌀ 35 mm) could be obtained per cup. The sample had to be cut out by scissors as the aluminium was 100 µm thick.

Figure 20. *Moisture analyzing scale's sample tray.*

As above described sample manufacturing was very slow and tedious, the cooking aluminium foil was evaluated. Spreading the silicone with the doctor blade yielded scratches and tears in the 16 µm thick foil. After few tries, it was clear the material was too fragile to be coated with used method.

Next, the thick aluminium facestock was tried. The sheet was 40 µm thick with a glossy varnish on the label side, back being untreated matte aluminium. Such properties yielded very good abrasion and tear resistance over cooking aluminium. At first the aluminium sheet samples were coated using the existing doctor blade. As very small area could be covered with the 5 cm doctor blade reliably, either longer blade or some other method was required. It was to be experimented with semi-automatic bar coating machines. These machines were originally made to spread adhesives onto siliconized release liners. First tests were promising as the silicone coat weight was close to 1.0 g/m^2 and the sheet withheld without breaking. At first, the coating was done atop of the varnished face, but to ensure the silicone only came from the applied coating, the matte side of the sheet was used.

8.3 Coating of the Sample Sheets

The initial sample sheets varied in dimensions but were roughly 48x16 cm, Figure 21. As the sheet was thin, yet mechanically durable, it enabled the use of a circular cutter to produce XRF samples from the aluminium sheet. The used bar coater machines weren't without issues either, as they were originally intended to spread adhesive disregarding the exact coat weight demands.

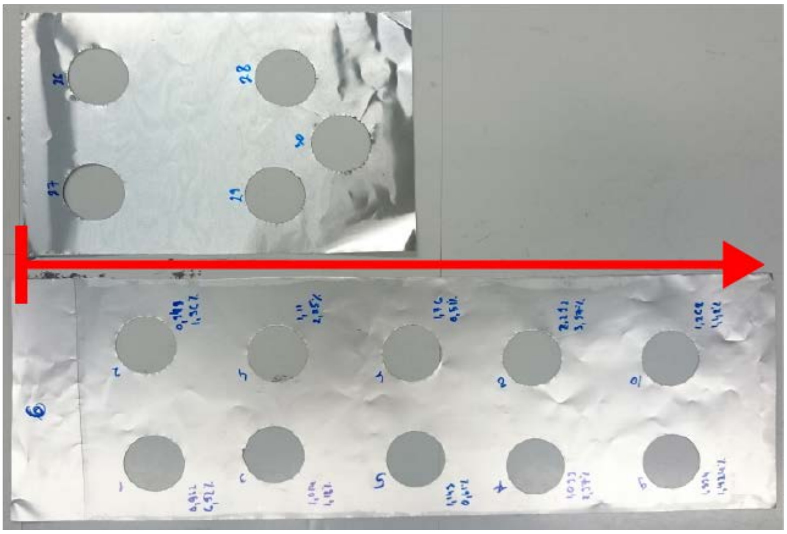

Figure 21. *The 24x15 cm and 48x16 cm sample sheets side by side. Red arrow demonstrates the coating direction.*

The coating procedure was prepared by deploying a protective plastic film atop of the bar coater's mat. The aluminium sheet was then taped onto protective plastic film. The protective film and the coatable aluminium sheet were then properly positioned and fastened to the coating machine. Next, the applicator bar was inserted few centimeters away from the adhesive tape's edge. When set at correct position, the bar was fastened and adjusted for the desired height. The height adjustment determines the applied pressure and coat weight.

After everything was set, about 5 ml of silicone was applied onto aluminium sheet as a horizontal line in front of the applicator bar. By the press of a button the applicator bar moved forward, what should have been the constant speed. The silicone was then spread onto the aluminium sheet by motorized action of the application bar.

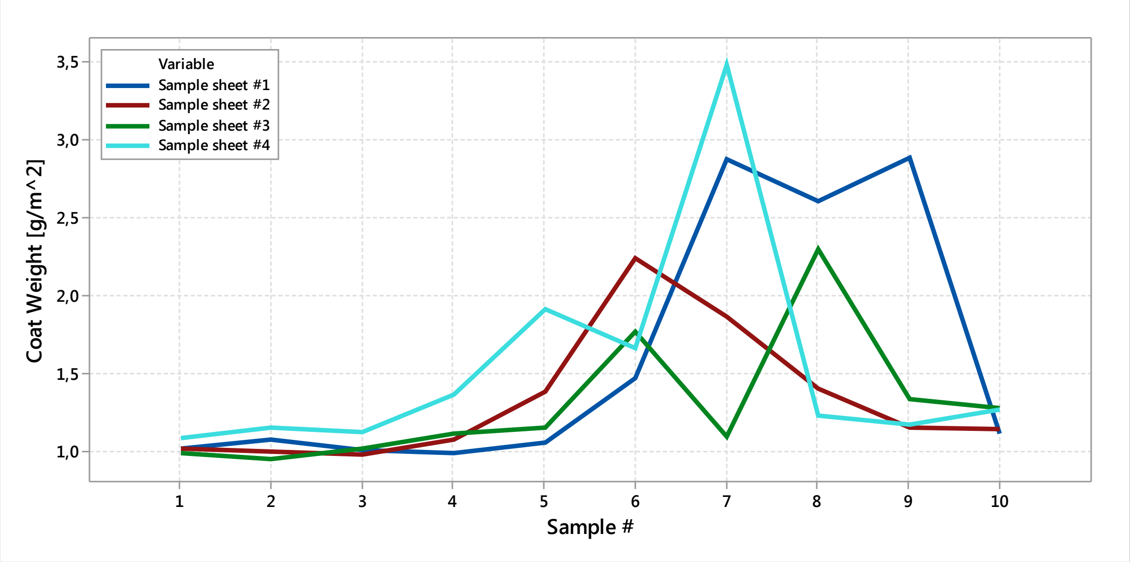

Figure 22. *Illustration of how coat weight changes within the sample sheet. The latter part of the sample sheet yields higher coat weights as the pressure build up releases.*

It became quickly evident that the soft mat underneath the applicator bar made the bar's speed uneven. The mat was compressed by the moving bar due to its restricted height. This resulted in lower coat weight at the beginning, and higher coat weight after the pressure build up released at the end of the soft mat and sample sheet. This effect can be clearly seen in the Figure 22. Four of such sample sheets made it into the final sample pool.

To mitigate the rising coat weights, it was decided to cut the aluminium sheet length into half. The standard dimensions became to be 24x15 cm, five XRF samples were cut out of each sheet (Figure 23).

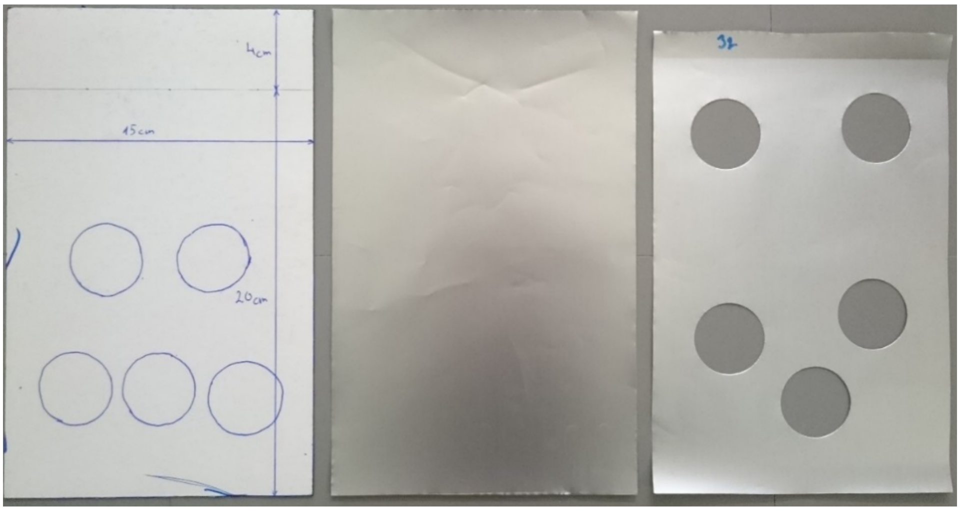

Figure 23. *Left: Sample sheet template. Middle: actual sample sheet cut out. Right: Coated sample sheet from where five XRF samples have been cut out.*

The sample sheets were manufactured by dividing a 2x1 m piece of aluminium sheet into 24x15 cm tiles by using the sample sheet template, a ruler and a marker. The outlined aluminium sheet was then cut into 24x15 cm tiles with scissors. The effective coated area of such aluminium sample sheet was about 22x15 cm. The few centimeters went into attaching the sample sheet onto the bar coater’s protective film and for markings. Before coating, the sample sheets were cleansed from the markings and fingerprints using laboratory-grade ethanol and lint-free cloth.

Figure 24. *Uneven silicone coverage of the aluminium sample sheet as not enough pressure was applied to the coating bar.*

When trying to obtain too high coat weights with existing coater machine the result looked much like in Figure 24. Furthermore, few sample sheets with 30 µm thick PET films were made, to evaluate whether the extractable-% would yield different results from the aluminium sheet. As there were no measurable differences in the extractable-%, the use of the PET film was discontinued. Transparent and flexible PET film was also difficult to handle, further encouraging the use of aluminium sheets.

Simulating the process conditions, the siliconized sample sheets were cured using 110-140 °C temperatures. The sample sheets were placed onto an oven tray, near to the heating elements. At first it was experimented with curing times 30 s to 30 min, to see whether the cure time would have relation with silicone extractable-%. As expected, the addition cure was very fast and curing samples over 30 s had no effect. However, to keep constant workflow, the sample sheets averaged few minutes in the oven as it took few minutes to prepare the next sample.

8.4 Measuring Coat Weight

The silicone coat weight was measured using XRF (X-ray fluorescence) equipment. The XRF samples were cut out from the cured sample sheets using provided circular cutter. From the first 48x16 cm sheets ten and later from 24x15 cm sheets five XRF samples were cut out, the XRF tray held ten samples and a sample spinner was used. Measuring full tray took about 30 min.

After initial coat weight determination the samples were put into methyl isobutyl ketone (MIBK) solution to dissolve unbound silicone. Under fume hood, samples were put into separate containers containing 25 ml MIBK. The MIBK solutions were used four times before replaced with fresh. The containers were put for 30 min onto a rocking table ensuring the solutions were not sitting still. After dissolvation, samples were placed onto paper towels to dry off MIBK, before re-measuring the coat weight.

After pre- and post-dissolvation coat weights (CW) had been determined it was possible to calculate the percent value of extracted silicone. The calculations were done using the following formula:

$$Ex\text{-}\% = \frac{CW_{Pre} - CW_{Post}}{CW_{Pre}} \times 100\ \% = \frac{[g/m^2]}{[g/m^2]} \times 100\ \% = \%$$

The formula gives positive extractable-% values when silicone is dissolved from the sample and negative values when it is deposited on the sample.

9. RESULTS

9.1 Experimental Results

The overall picture of all 173 measured samples, and different variables present in measurements is shown in chronological order in Figure 25. It is seen two different silicone recipes, at times taken from freezer (❄), four different coat weight ranges, two coater machines, and three sample materials were used in the measurements. The first four sample sheets were 48x16 cm, yielding ten XRF samples each i.e. #1-40, from #41 onwards all the sample sheets (24x15 cm) had five XRF samples, Figure 21. X-axis: sample number. Y-axis: coat weight (gsm i.e. g/m^2) and extractable-%. For easier referencing, the coat weight ranges are labelled into sections from A-F.

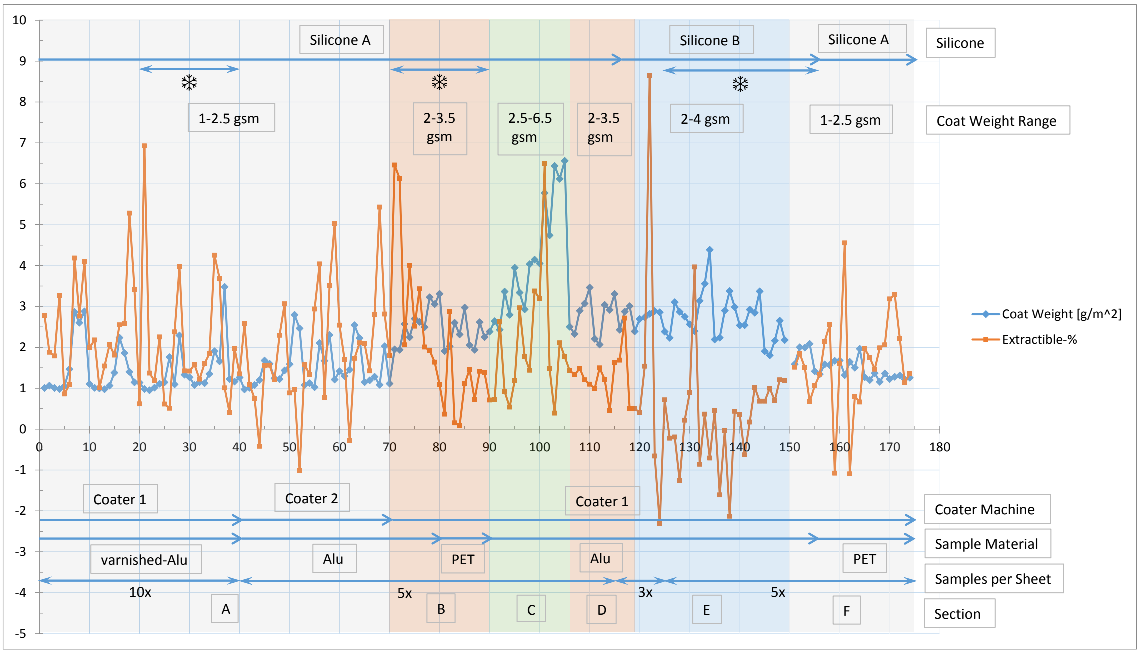

Figure 25. Overview of the measurements for quick reference. Bigger figure can be found from Appendix A.

Generally, the coat weight values consistently rose to the end of the sample sheet, explaining the fluctuations throughout the measurements. Seemingly coat weight had no correlation with the extractable-%. Section A: after few initial measurements, it was speculated the varnish (v-Alu) might contain elemental Si. To rule it out, the remaining samples were coated on the matte side of the sample sheet (Alu). Furthermore, as fresh silicone was not always available, it could be obtained from a freezer, where any meaningful surplus was kept. No difference between fresh and surplus silicone was found. Briefly, another coater machine was used instead of the original as it was forgotten to be reserved, no observable difference between coaters were found. Section B: it was experimented with 2-3.5 gsm coat weight range, whether correlation with extractable-% would appear, PET was tried without noticeable change. Section C: PET being much harder to handle it was resumed using Alu sheets. Next, even higher coat weights, 2.5-6.5 gsm were experimented. Again, results were inconsistent. Section D: it was resumed using 2-3.5 gsm range as obtaining uniform silicone spread was much easier, see Figure 24 for uneven silicone coverage. Section E: out of options, "Silicone B" was tried with 2-4 gsm coat weight. The obtained results were confusing. The extractable-% spread was the highest observed, and low or negative results were quite common. Section F: in vain, PET sheets were coated using both silicones with the 1-2.5 gsm range. The situation changed very little. As expected, no correlation was found.

Half of the experimentally obtained coat weight values fell roughly into 1-2 or 2-7 gsm range. In comparison, the actual process values fell into 1.25-1.5 gsm range, resulting in minimal spread, Figure 26.

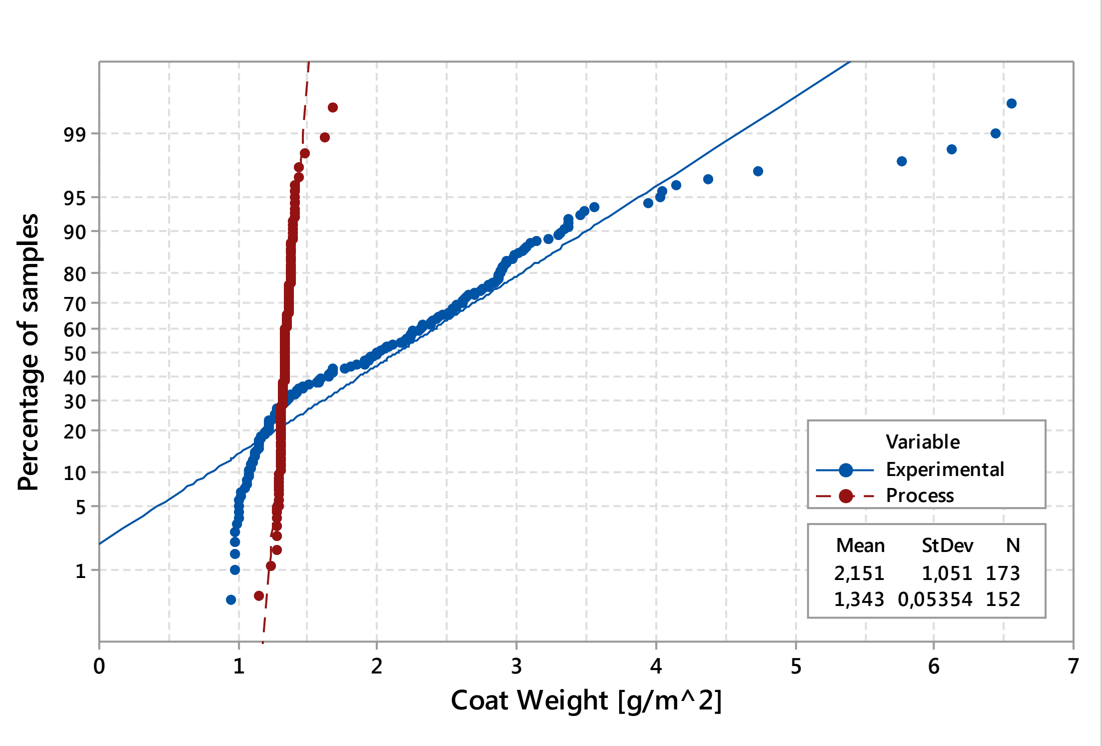

Figure 26. Experimental and production values of coat weights compared.

In conclusion, it is possible to replicate the process values with present laboratory equipment, however, adjustments are needed to reduce the spread. Surprisingly, the extractable-% values were rather similar given the big differences between the experimental and process coat weight values. Negative extractable-% values shouldn't theoretically exist, but are kept to represent all the data, Figure 27.

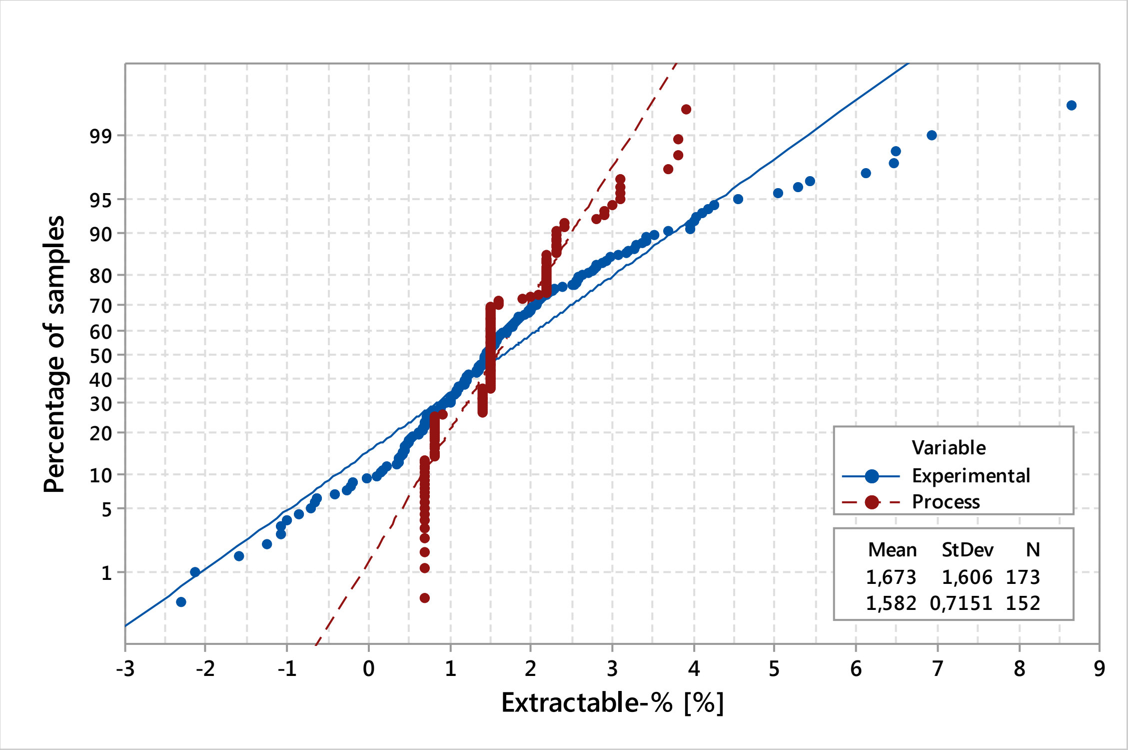

Figure 27. *Experimental and production values of extractable-% compared.*

Rather interesting findings were made as the real process extractable-% data seemed to be grouped after every 0.75 %, whereas the experimental data was analogous. Based on the above, no correlation between the coat weight and extractable-% was exhibited.

9.2 Importance of Decimals in the Extractable-% Calculations

As the “grouping” anomaly in extractable-% values was found to be caused by low measuring accuracy of the QC lab’s XRF equipment, the quality control XRF was set to measure at four decimals. Although, the differences are not big when measuring coat weight, e.g. 1.34 vs. 1.3444 as shown Figure 28.

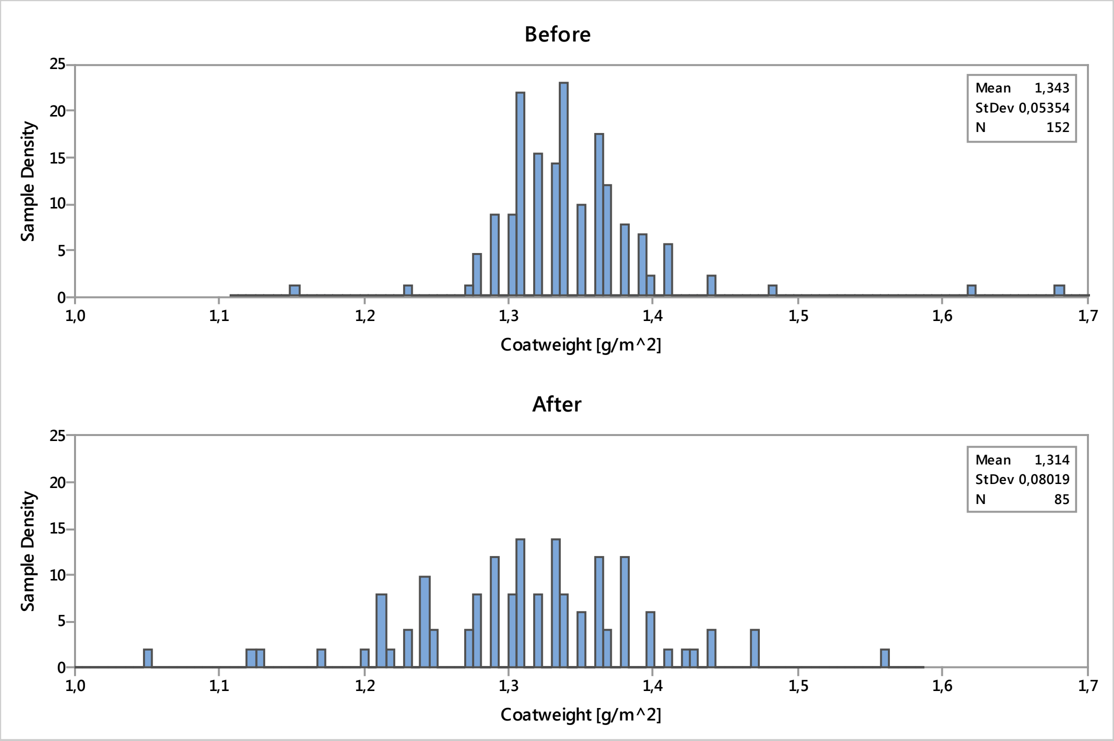

Figure 28. *Measured coat weight values before and after the XRF adjustment.*

The insufficient accuracy piled the extractable-% values in separate groups. The additional decimals had substantial impact in further calculations, yielding continuous results and improving accuracy from ± 0.75 to ± 0.078 %, Figure 29.

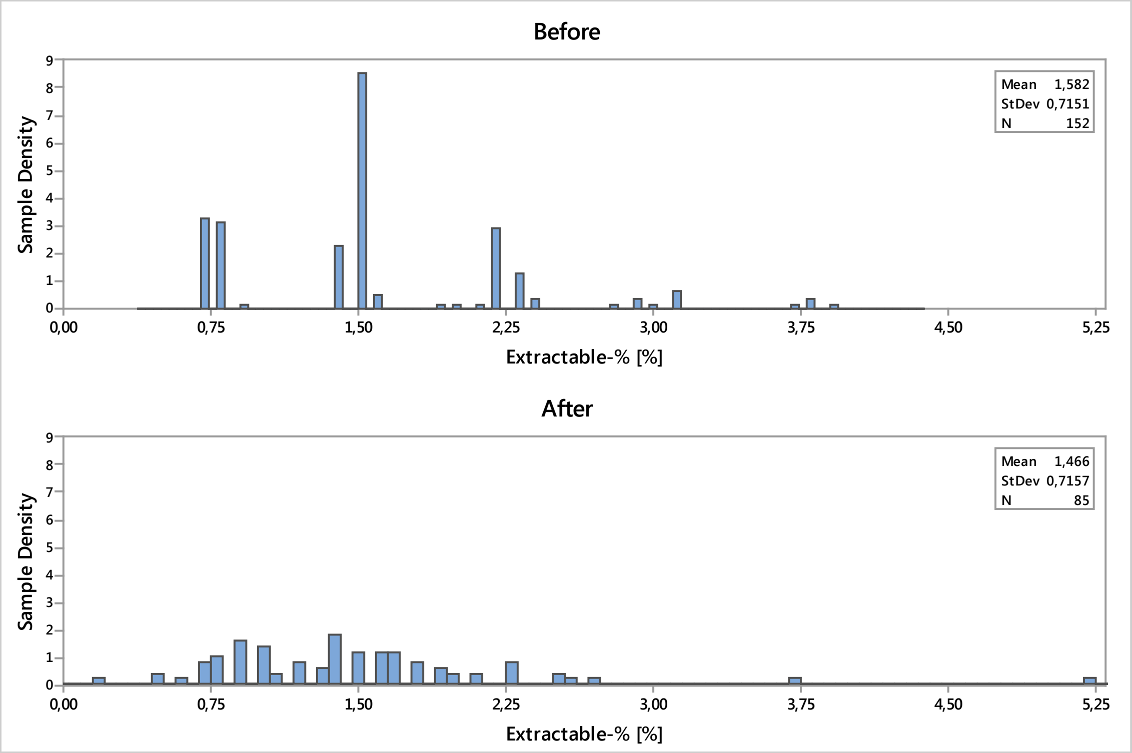

Figure 29. *Calculated extractable-% values before and after the XRF adjustment.*

The coat weight accuracy improvement, using more than two decimals can be seen in Figure 30. Later, the same is found to be true for extractable-%. For this measurement the R&D lab's XRF was used to measure a single sample 10 times in two separate runs. Doing so revealed an unexpected undulating pattern. Additional experiments are needed to find the reason. While the undulations are within the XRF's accuracy limits, the deviations are enough to produce near zero or even negative extractable-% values, this phenomenon is explored later on in this section.

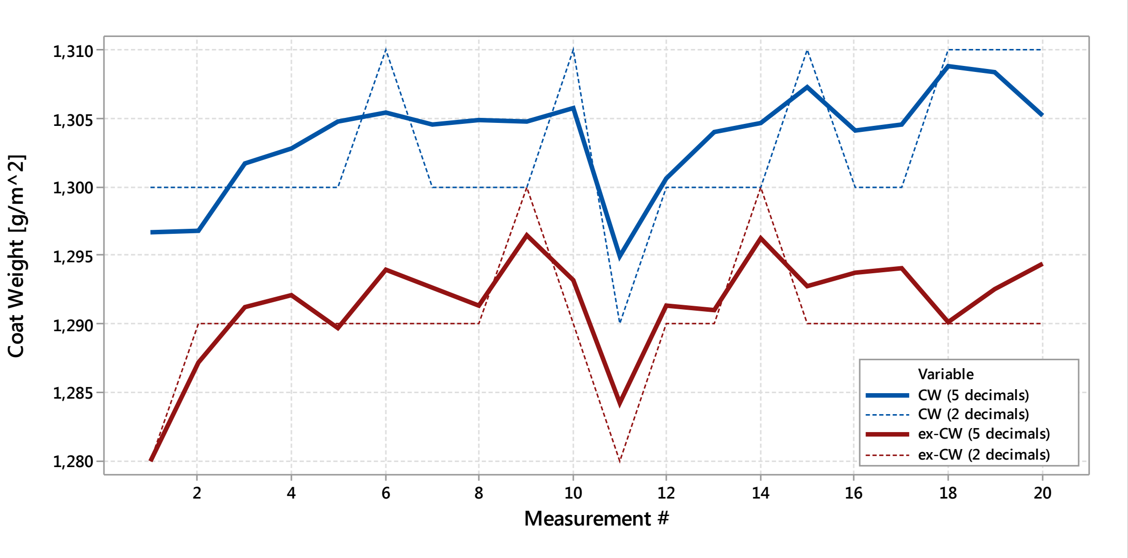

Figure 30. *Coat weights of a single sample before and after extraction, measured 20x with two and five decimal accuracy.*

Measuring coat weight with two decimal accuracy is enough to monitor and adjust the silicone amounts on the coater machine, Figure 30. However, it is not enough for actual quality control, especially when further calculations are made from the measured data. A closer look is taken on how additional decimals affect the calculated extractable-%. For example, using 2 decimal accuracy, for measurement #1 yields

$$Ex\text{-}\% = \frac{CW_{Pre} - CW_{Post}}{CW_{Pre}} \times 100\ \% = \frac{1.30 - 1.28}{1.30} \times 100\ \% = \ 1.53846\ \%\,,$$

as extractable-%. However, using 5 decimal accuracy for measurement #1, it is obtained

$$Ex\text{-}\% = \frac{CW_{Pre} - CW_{Post}}{CW_{Pre}} \times 100\ \% = \frac{1.29666 - 1.28001}{1.29666} \times 100\ \% = \ 1.28406\ \%\,.$$

Such calculations are made for every data point with 2, 3, 4 and 5 decimal accuracy. Obtained extractable-% values are presented in the Figure 31 below.

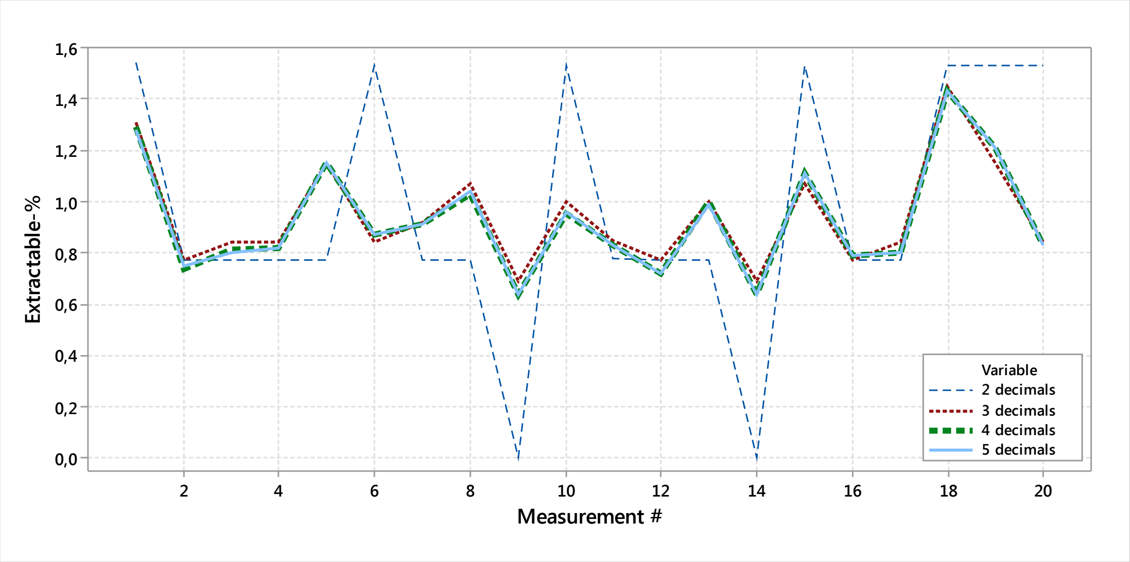

Figure 31. *Extractable-% when calculated with: 2,3,4 or 5 measured decimals.*

Even when using five decimals it is possible to obtain negative extractable values. This could be as XRF's accuracy's variability is higher than the obtained difference in coat weights before and after dissolvation, Figure 32.

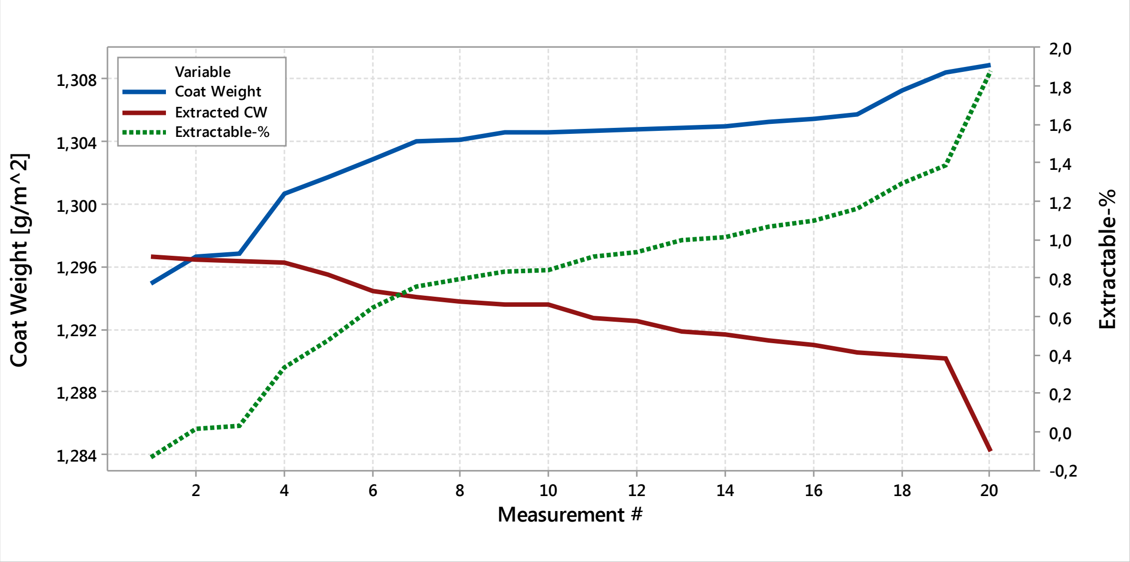

Figure 32. *Maximum theoretical spread of extractable-% within a single sample.*

Taking the original data from Figure 30 and plotting the pre-extraction coat weight values from min to max and post-extraction values from max to min yields maximal theoretical spread for extractable-%, Figure 32. Therefore, obtaining very low, negative or very large extractable-% values as outliers is possible during the routine quality control.

9.3 Discussion

As concluded in Figure 25, there are many variables to consider, therefore reasoning conclusions about the silicone transfer is impossible. On the bright side, much was learned about the extractable-% measuring process itself. Although, somewhat controlled coat weight values were produced, there seemed to be no correlation with the obtained extractable-%. This may be explained by solvent’s contamination, as the 25 ml solution is used to dissolve four samples before replacing. Therefore, it is possible the MIBK solution has become overly concentrated with the silicone.

Too much silicone may come into solution, as the siliconized samples are handled with regular tweezers. When the sample surface is accidentally scratched or gently rubbed making some of the silicone loose before dissolvation. When the sample’s silicone surface directs to the bottom of the dissolvation container it likely yields higher extractable-% as silicone is mechanically rubbed from the sample when using the horizontal shaker. If the MIBK finds its way under the silicone layer it very effectively dissolves the silicone. Presumably, when the solution’s silicone concentration reaches certain threshold, a chemical equilibrium is reached. Eventually, the silicone is not dissolved by the MIBK but is rather deposited onto the sample, resulting higher in the coat weight, thus producing negative extractable content.

10. FUTURE DEVELOPMENT SUGGESTIONS

It is possible to improve the accuracy of the existing method, but as found out earlier, the method has its limits. A short list of development suggestions is presented and later alternative methodologies are reviewed in this chapter.

10.1 Improving the Extractable-% Measurement Method

As it turns out, the currently used method to measure unbound silicone content has over the years become somewhat outdated and is lacking accuracy. As more precise method is desired, but the new method development does not occur overnight, an improvement to the existing method is needed to cover the transition period. Based on Chapter 9, the following improvements are suggested for the current measurement method:

0) Measuring using XRF equipment’s full potential, i.e. four decimals instead of two.
1) MIBK solutions should be used only once, the total volume could be halved from 25 ml. As solution is replaced, the container should be rinsed using organic solvent, or washed.
2) Multiple samples to have a control group.
3) Multiple measurements of one sample to calculate means. Minimum of 2, preferably 3 or more measurements to omit outliers; before and after MIBK dissolvation.
4) Investing into new XRF machine with digital data transfer, thus removing human error from typing and calculations.

Out of the above, 0) has been already implemented and extractable-% accuracy has improved alot as demonstrated in Chapter 9. Implementing 1) would make big impact with relatively low cost. Implementing suggestions 2) and/or 3) would add value but doing so adds diminishing returns, as significantly more effort and resources are required to carry out multiple sample measurements. Suggestion 4) would be most ineffective cost wise, although with great benefits. Obtaining such system is recommended in conjunction when replacing existing XRF equipment. It is advisable to develop new measurement method hand in hand with the new equipment procurement.

10.2 Alternative Extractable-% Measurement Methods

As the paper is made of fibers, its structure is porous and uneven, resulting in uneven thickness. The paper's surface is levelled and smoothed using surface sizing atop of the paper surface. The sizing contains kaolinite, $Al_2Si_2O_5(OH)_4$. Due to ever changing paper topography there can never be same amounts of sizing atop of paper surface. The XRF calibration curves are required to subtract the added elemental silicon from the kaolinite.

Paper surface's unevenness makes it challenging to accurately subtract added elemental silicon. Atop of that, the current XRF calibration curves are outdated. It is clear, the paper liners and films have evolved since then. Mostly, paper's basis weights have decreased, and various surface treatments have become common, yielding better performance at reduced costs. This, of course, adds uncertainty when measuring the extractable content. Therefore, it is advisable to emphasis R&D in this area.

To counter the above mentioned variabilities and challenges, it is possible to measure the amount of unbound silicone using the following strategies:

1. Measuring dissolved silicone directly from the MIBK solution. This necessitates for sensitive enough equipment as dissolved silicone concentrations constitute of µg/ml i.e. mg/l.
    a. A quick test revealed the existing XRF equipment to be unsuitable, as dissolved concentrations were hardly detected.
2. Measuring aluminium content of the paper sample, and calculating the amount of additional Si from kaolinite's chemical structure. Then, proceeding to measure total Si content of the sample and finally subtracting the baseline.

11. CONCLUSIONS

The main goal was to evaluate and compare the silicones' suitability before their use in production by assessing their properties in laboratory setting. Rather soon, it became clear the goal was unrealistic and unattainable within the set framework. Next, the goal became to determine whether the coat weight and extractable-% would exhibit relation.

Assumed relation was looked for by coating aluminium sheets with silicone and using XRF to measure the coat weights before and after the MIBK dissolvation. From the obtained coat weight values the extractable-% could be calculated. Throughout the experiments the coat weight was varied and compared to the extractable-%. In the end, the obtained data did not statistically support nor oppose the hypothesis. When comparing the obtained results with an actual process data the results were similar. Therefore, it would be interesting to repeat the experiment, especially as the methodology is now tried and tested, it is possible to reduce many unnecessary variables. Repeating the experiment with less variables could likely produce statistically viable data. Which, in turn, can enable to draw conclusions whether coat weight correlates with extractable-% or not.

When replicating the test, it is suggested to use 1-2 g/m^2 coat weight range, only one silicone (frozen or fresh) and a single coater machine. Only the matte side of the aluminium sample sheet should be coated. When using the PET, 50 µm or thicker film is recommended. It is suggested to manufacture 20-30 aluminium sample sheets, conducting coating and curing during the same day. Next, 100-150 XRF samples would need to be made and measured, samples with 0.9-1.3 g/m^2 would be selected to undergo MIBK dissolvation. The dissolvations would be done using fresh MIBK solutions and replaced after every use. Next, the samples would be measured for remaining coat weights to calculate the extractable-%. The described procedure would reduce variables and increase the accuracy of the measurements.

If there is a desire to reach the original goals, specialized equipment, and experienced personnel are required. An outsourced 3rd party laboratory team might be the best for the task. Even though the original goal could be reached, the question remains: is it economically viable to do so and does it add enough value to the process? Future development plans as discussed earlier in this chapter are currently under progress.

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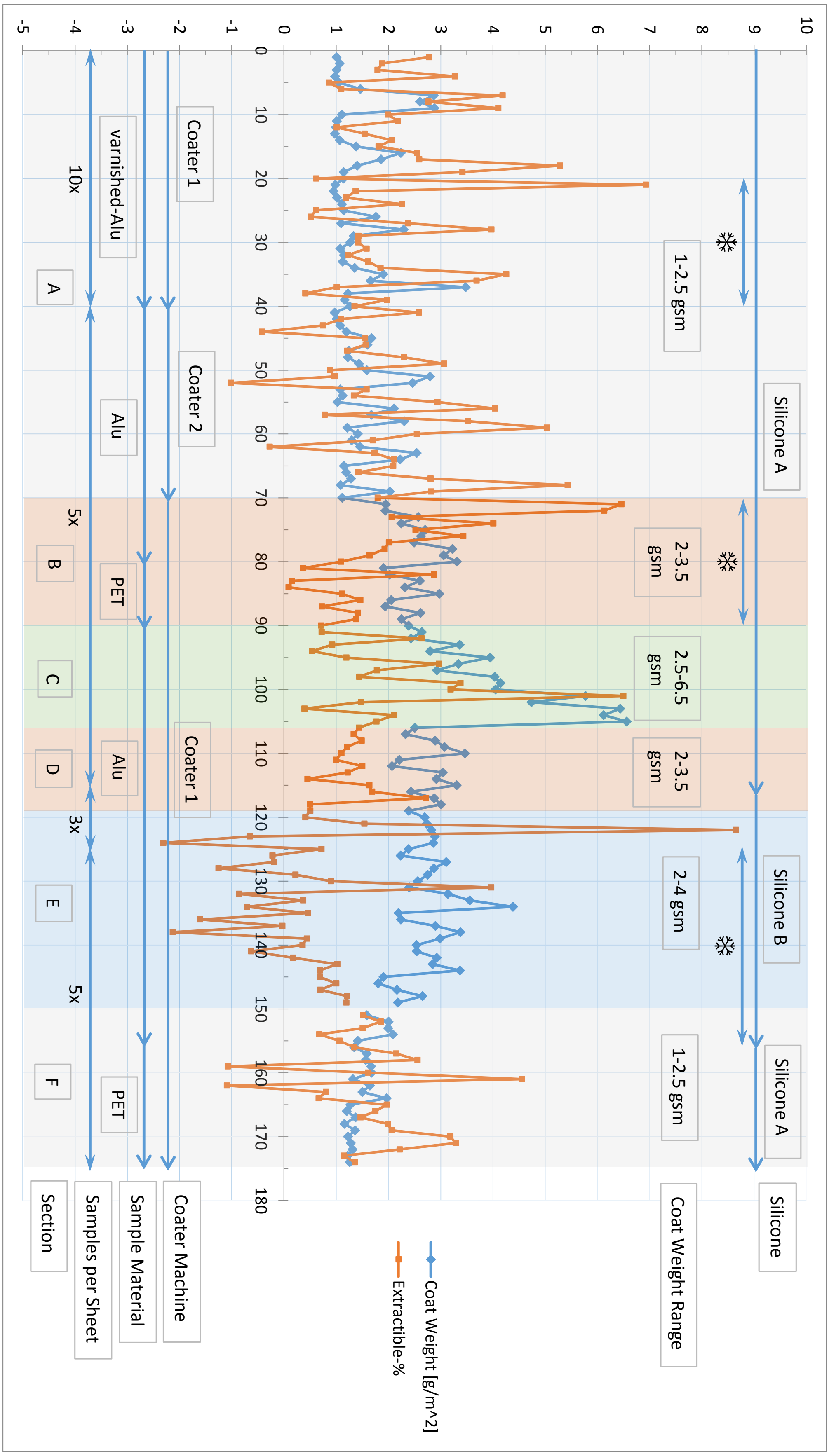
APPENDIX A: OVERVIEW OF THE MEASUREMENTS



Overview of the measurements.

APPENDIX B: TYPES OF SILICONES AND ADHESIVES