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SILICONE MISTING IN PRESSURE SENSITIVE LABEL PRODUCTION

Master's Thesis
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ABSTRACT

Adalmiina Viitaniemi: Silicone misting in pressure sensitive label production
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Silicone misting occurs when silicone release coatings are applied on multi-roll coaters on liner substrates at a high speed and pressure sensitive label materials are produced. Mist droplets are formed as the liquid silicone film splits between two rolls and produces fine mist. Misting can be reduced to some degree by using anti-misting additives when formulating silicones but especially at higher speeds it is nearly impossible to prevent misting totally. The effects of silicone misting are related to production, such as the more often occurring cleaning requirements of the equipment and to human health which is the main concern.

The objective of this thesis was to study misting of different silicone formulations by monitoring aerosol concentrations during the production of label materials and conducting laboratory measurements for the silicones, siliconized liners and laminate materials consisting of a face, an adhesive, a silicone release coating and a liner. The aim was to find correlations between laboratory measurements and misting observed in production and to find out if the measurements done in the laboratory could be used in predicting the extent of misting phenomenon. The effect of coating speed and properties of the silicones on misting were also studied.

The measurements included aerosol monitoring, viscosity and differential scanning calorimetry measurements of the silicones, contact angle and surface energy studies as well as topographic imaging of the siliconized surfaces, rub-off and release profile measurements. Differences between misting of the silicones and the properties of the silicones were observed. The differential scanning calorimetry measurements were able to be combined with the aerosol monitoring results by comparing the curing behaviour of the silicones. The effect of increasing line speed was verified to increase mist formation. Based on the measurements it seemed that the addition of release modifier could increase misting. The higher viscosity of the silicone did not correlate with higher aerosol concentrations observed at the coating station. All studied silicones produced mist, but the amounts were much lower than a common industry threshold level considers acceptable. The other measurements were not easily combined with the misting phenomenon depending on the test method or the laminate materials consisting of different faces, adhesives and liners making it difficult to make conclusions regarding the silicones only.

For being able to examine the misting phenomenon and compare different silicone formulations further, the line speeds and other conditions should remain constant. When studying laminate materials, the silicone should be the only variable while the other components would remain the same. The trend of how the amount of mist increases with increasing line speed and the effect of the use of modifier could be further studied as well as the effect of viscosity of the silicone on misting could be verified by making sure that the bath lives of the silicones would be the same as well as the other previously mentioned conditions.

Keywords: silicone misting, silicone release coating, pressure sensitive label

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TIIVISTELMÄ

Adalmiina Viitaniemi: Silikonin pölyäminen paineherkkien etikettien valmistuksessa
Diplomityö
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Silikonin pölyämistä havaitaan, kun paineherkkien etikettimateriaalien taustalle applikoidaan silikoninen irrokepäälyste monisyylinterisellä päällystykoneella. Pisaroita muodostuu päällystysprosessissa erityisesti korkeilla nopeuksilla, kun silikonifilmi halkeaa kahden sylinterin välissä. Pölyämistä voidaan vähentää jonkin verran lisäämällä silikonireseptiin pölyämistä estävää lisäainetta, mutta erityisesti korkeilla päällystysnopeuksilla pölyämistä on lähes mahdotonta estää kokonaan. Pölyämisen haittoja havaitaan tuotannossa esimerkiksi lisääntyneenä laitteiden siivoustarpeina, mutta merkittävin huolenaihe liittyy pölyämisen terveysvaikutuksiin.

Tämän diplomityön tarkoituksena oli tutkia erilaisten silikonireseptien aiheuttamaa pölyämistä mittaamalla ilmassa olevien aerosolien määrää etikettimateriaalien valmistuksen aikana sekä tehdä laboratoriomittauksia tutkittaville silikoneille, silikonoiduille taustamateriaaleille sekä laminaateille, jotka koostuivat pintamateriaalista, liimasta, silikonipäälysteestä sekä taustamateriaalista. Tavoitteena oli löytää korrelaatioita laboratoriomittausten ja tuotannossa havaittavan pölyämisen välillä sekä selvittää voisiko laboratoriossa tehtävien mittausten perusteella ennustaa pölyämismäärän laajuutta. Myös linjanopeuden ja silikonin ominaisuuksien vaikutusta pölyämiseen tutkittiin.

Työssä tehtävät mittaukset sisälsivät aerosolimittauksia, silikoneille tehtäviä viskositeettimittauksia ja differentiaalista pyyhkäisykalorimetriaa hyödyntäviä mittauksia, kontaktikulma- ja pintaenergiamittauksia, silikonoidun pinnan topografian tutkimista, silikonin ankkurointiin liittyviä mittauksia sekä irrokeprofiilien tutkimista. Tutkittujen silikonien ominaisuuksissa ja pölyämisessä havaittiin eroja. Differentiaalisen pyyhkäisykalorimetrian tuloksia pystyttiin yhdistämään aerosolimittauksiin vertailemalla silikonien ristisilloittumiskäyttäytymistä. Mittaukset vahvistivat sen, että ratanopeuden nostaminen johtaa pölyämisen lisääntymiseen ja tulosten perusteella vaikutti siltä, että irrokevoiman modifiointi lisäisi pölyämistä. Silikonin korkeampi viskositeetti ei vaikuttanut korreloivan silikonin päällystysasemalla havaittavan pölyämisen määrän kanssa. Kaikki tutkitut silikonit pölysivät, mutta määrät olivat paljon toimialalla yleisesti käytettyä raja-arvoa alhaisempia. Muita testimenetelmiä ei pystytty helposti yhdistämään pölyämiseen riippuen testimenetelmästä tai laminaateista, jotka koostuivat eri pinnoista, liimoista ja taustoista, minkä takia johtopäätösten tekeminen vain silikonien perusteella oli vaikeaa.

Jotta eri silikonireseptien pölyämistä voitaisiin tutkia ja vertailla jatkossa enemmän, ratanopeudet sekä muut olosuhteet tulisi pitää muuttumattomina. Tutkittaessa laminaatteja, silikonipäälysteen tulisi olla ainoa muuttuja ja muiden komponenttien pysyä samoina. Trendiä, joka kertoisi miten pölyämisen määrä kasvaa linjanopeuden kasvaessa sekä irrokevoimaa modifioivan lisäaineen käytön vaikutusta pölyämiseen voitaisiin tutkia lisää, kuten myös silikonin viskositeetin vaikutusta. Tällöin tulisi varmistaa, että silikonien sekoittamisesta kulunut aika pysyy vakiona kuten myös muut aiemmin mainitut olosuhteet.

Avainsanat: silikonin pölyäminen, silikoninen irrokepäälyste, paineherkkä etiketti

Tämän julkaisun alkuperäisyys on tarkastettu Turnitin OriginalityCheck –ohjelmalla.

PREFACE

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LIST OF SYMBOLS AND ABBREVIATIONS

–CH = CH ₂	Vinyl group
–COOH	Carboxyl group
CW	Coat weight
DNEL	Derived no-effect level
DSC	Differential scanning calorimetry
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6	Dodecamethylcyclohexasiloxane
ECHA	European Chemicals Agency
EDXRF	Energy Dispersive X-ray Fluorescence Spectrometry
FINAT	Fédération INTERNATIONALE des fabricants et transformateurs d'Adhésifs et Thermocollants sur papiers et autres supports, the European association for the self-adhesive label industry
FTM	FINAT Test Method
L2	Hexamethyldisiloxane
L3	Octamethyltrisiloxane
L4	Decamethyltetrasiloxane
L5	Dodecamethylpentasiloxane
L6	Tetradecamethylhexasiloxane
mol %	Mole percent
MQ resin	Methyl-treated silicate resin
–OH	Hydroxyl group
OWRK	Owens, Wendt, Rabel and Kaelble
PDMS	Polydimethylsiloxane
PE	Polyethylene
PET	Polyester, polyethylene terephthalate
PM	Particulate matter
PM1	Particles ≤ 1 μm in diameter
PM2.5	Particles ≤ 2.5 μm in diameter
PM10	Particles ≤ 10 μm in diameter
PM Total	Particles between 0.1 and 15 μm in diameter
PP	Polypropylene
PSA	Pressure sensitive adhesive
PSL	Pressure sensitive label
Ra	Average roughness
RH	Relative humidity
SCK	Supercalendered kraft
SEM	Scanning electron microscope
SiH:Vi	Ratio between the crosslinker and the polymer
TDS	Technical data sheet
UV	Ultraviolet
wt-%	Weight percent
XRF	X-ray fluorescence spectrometry
2D	Two-dimensional
3D	Three-dimensional
<i>Ca</i>	Capillary number
<i>η</i>	Viscosity
<i>γ_{lv}</i>	Liquid-vapor interfacial tension
<i>γ_{sl}</i>	Solid-liquid interfacial tension
<i>γ_{sv}</i>	Solid-vapor interfacial tension

H	Total heat flow
σ	Surface tension
T_g	Glass transition temperature
T_m	Melting temperature
t_1	Onset time of reaction
t_2	Time when the maximum heat flow is reached
t_3	Time when curing is complete
θ	Contact angle
V	Mean roll speed

1. INTRODUCTION

Pressure sensitive labels (PSLs) are used in numerous everyday applications such as packaging of foods, medicines, beverages and cosmetics. The four main components of the laminate structure are face material, adhesive, release coating and release liner. The basic structure of a PSL is presented in Figure 1 and more in-depth information can be found from multiple sources [1] [2] [3] [4, pp. 130–132].

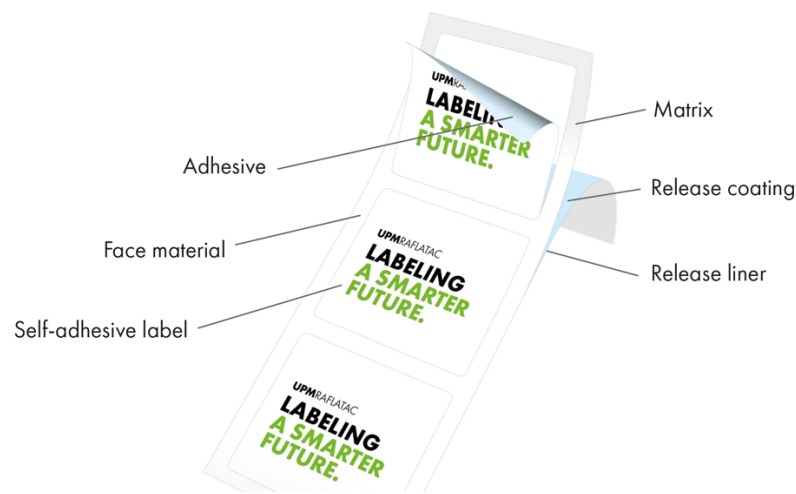


Figure 1. The structure and the components of a PSL [5]

This thesis was done at UPM Raflatac which is one of the leading suppliers of label materials [6]. The focus of the thesis was on silicone release coatings and silicone misting in production of pressure sensitive labels. Silicone is usually the chosen coating material for releasing pressure sensitive adhesives (PSAs) because of its exquisite physical and chemical properties [7, p. 92–1]. Those properties will be further explained in the following chapter.

Silicone misting is a phenomenon that appears especially in high-speed coating processes of silicones. The mist is generated because of film splitting as the coating passes from one process roll to the next. Anti-misting additives can be used to minimize the misting phenomenon. The effectiveness of these additives is affected by various matters related to the coating process as well as the properties of the silicone. [8, p. 12]

The aim of this thesis was to compare some silicone formulations used in the production of PSLs at UPM Raflatac and to try to find correlations between the properties of the

silicones and the extent of misting phenomenon. In the silicone industry it is acknowledged that different silicones produce different amounts of mist but reasons behind that could be examined further.

In the beginning, in Chapter 2, silicones, their properties and structure, components in silicone recipes as well as the curing reaction through which the silicone release coating is formed are introduced. Next the coating process, the phenomenon of silicone misting, and problems related to it are discussed, the focus being mainly on health effects. After that the tested materials and test methods are introduced, followed by the test results and analysis made based on them. The final part of the thesis includes the conclusions of the achieved results and some future areas of interest.

2. SILICONE

Silicones have such physical and chemical properties that make them ideal materials for release coatings of PSLs [7, p. 92–1]. Silicone release coatings are applied on the backing material to provide protection for the PSA during storage and transit under varying conditions and finally to release the adhesive without any damage. The force required to release the adhesive from the liner varies between different end use requirements set by customers. The coated silicone layer should be uniform, well anchored to the liner substrate and well cured to avoid interactions between unreacted silicone and the adhesive. A typical thickness of release coatings is below 1 μm , often less than 0.1 μm . [9] [10, p. 535] In this chapter, the main properties and the structure of silicones, components in silicone recipes, curing and silicone anchorage are discussed.

2.1 Properties and structure

The term silicone can be used to describe polymeric materials that are based on a backbone containing silicon and oxygen. There are also organic groups, typically methyl groups, attached to the silicon atoms [11, p. 1]. The structure of polydimethylsiloxane (PDMS) is presented in Figure 2.

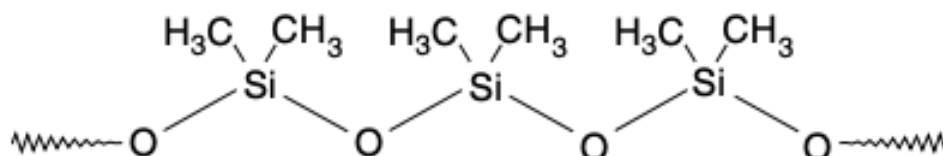


Figure 2. The structure of PDMS polymer [8, p. 3]

One of the most important properties of silicone is that it has a low surface energy which is due to the accumulation of non-polar methyl groups on the surface [11, p. 2]. The surface energy of crosslinked PDMS surface is usually about 22 mN/m, while the surface energies of PSAs can be about 30 mN/m or above that. Because of the low surface energy of silicone, it does not form a tight bond with the PSA enabling the easy release of the label from the siliconized liner. [7, p. 92–2] Silicones are fairly immiscible with many organic polymers used in PSAs and release of the PSA from the silicone is easy because not much interdiffusion or entanglements occur. [10, p. 547] Release forces and release profiles including varying release speeds can be tuned to provide a suitable release for different applications, because not always the lowest possible release force is wanted [8, p. 15]. Release profiles describe how easily the adhesive and the face material are

released from the silicone coated liner at different speeds and will be further discussed in the following chapters. Release forces are mainly tuned by modifying the rheology of silicones by adding release additives to silicone formulations [10, p. 548]. Controlled release additives will be discussed more later.

PDMS has a very low glass transition temperature (T_g) of about $-123\text{ }^\circ\text{C}$ indicating high flexibility of the polymer backbone chain. The high flexibility of PDMS polymer makes silicone stand out as a release coating material. Its flexibility provides low friction and interfacial slippage. Interfacial slippage is seen when peeling the PSA from the PDMS layer. Large displacements of particles occur at the crack tip minimizing shear dissipation and resulting in low release forces. The flexibility of the PDMS chain is also influenced by the small size of methyl groups and the backbone consisting of alternating small unsubstituted oxygen atoms and larger substituted silicon atoms. [10, pp. 542–548] [11, pp. 2–3]

The flexibility also allows easier release compared to other organic release material options which also have low surface energies and are inert. Fluoropolymers are one example of a material being able to provide very low energy surfaces, but the molecule flexibility may not be as good. The fluoropolymer coatings are also very expensive and are used in quite limited applications. [10, pp. 548–549] There are also concerns related to the effects fluoropolymers have on the environment as well as on human health which is why their production and usage should be limited to essential applications only [12].

PDMS is a semicrystalline polymer but because of having a melting temperature (T_m) of about $-45\text{ }^\circ\text{C}$, at normal use temperatures the structure is amorphous. After crosslinking the PDMS polymer chains, the free mobility of the polymer segments between crosslinks provides high elasticity to the silicone coating. Due to its elasticity, the coating is able to store energy and return it after the energy source is removed. [8, p. 14]

When the silicone network is properly cured, chemical interactions are prevented by the PDMS backbone meaning that the silicone surface remains fairly stable over time. Chemical interactions between the PSA and the silicone may happen only through the unreacted crosslink sites. Some increase in release force with aging is possible when epoxy or acrylate containing silicones are used in contact with acrylic PSAs. [10, pp. 546–548]

2.2 Silicone recipes

Silicone release coatings can be solventless, or dispersion coatings based on a solvent or an emulsion [13, p. 9]. The preferred release coating technology in the PSL industry

nowadays is addition cured solventless system. Solventless silicone release coating formulations include a base polymer, a crosslinker, a catalyst and an inhibitor. Additives that can affect for instance silicone misting, release values and anchorage may also be included in the formulation. All components in silicone recipes have multiple effects on processing and the final properties of the coating. [8, pp. 9–16] Formulation of coatings is a complex process where balancing between different properties and making the right trade-offs suitable for each application are required [14].

2.2.1 Polymer

The polymer in a silicone release coating has the greatest effect on release performance which is the main function of a release coating. That is why the polymer is the first component to be chosen. [8, p. 9] A typical structure of a polymer used in silicone release coatings is presented in Figure 3 where there are vinyl groups ($-\text{CH} = \text{CH}_2$) in addition to the methyl groups along the polymer chain.

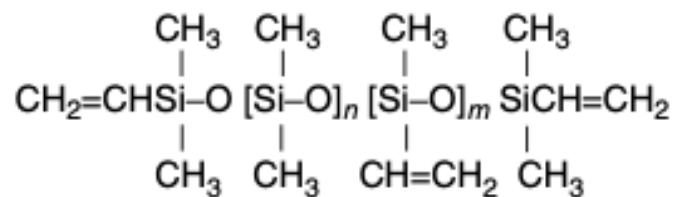


Figure 3. Basic polymer structure where $n + m$ is between 100 and 5 000 and $n/(n + m) = 0.96-1.0$ [8, p. 8]

Polymers used in solventless coatings can be classified as end-blocked, multifunctional, pendant or branched. Differences between the polymer types originate from the locations of the vinyl groups in the polymer chain. The first three types are linear polymers, whereas the last one has a branched structure. In an end-blocked polymer, the vinyl groups are located at the ends of the polymer chain, whereas in the case of a multifunctional polymer there are vinyl groups along the chain in addition to the chain ends. Pendant refers to a polymer where all the vinyl groups are located along the polymer chain. [8, pp. 9–10] In Table 1, the four polymer types and some of their features related to release profiles and curing are listed.

Table 1. Polymer types where *Vi* indicates the vinyl groups, adapted from [8, p. 10]

$\text{Vi} \text{ ————— } \text{Vi}$	<p>End-blocked polymer</p> <ul style="list-style-type: none"> • Rising release profiles
$\begin{array}{c} \text{Vi} \text{ ————— } \text{Vi} \\ \quad \quad \\ \text{Vi} \quad \text{Vi} \quad \text{Vi} \end{array}$	<p>Multifunctional polymer</p> <ul style="list-style-type: none"> • Flat release profiles • Fast cure
$\begin{array}{c} \text{—————} \\ \quad \quad \\ \text{Vi} \quad \text{Vi} \quad \text{Vi} \end{array}$	<p>Pendant polymer</p> <ul style="list-style-type: none"> • Flat release profiles • Slower cure
$\begin{array}{c} \quad \quad \quad \text{Vi} \\ \quad \quad \quad \\ \text{Vi} \text{ ————— } \text{Vi} \\ \\ \text{Vi} \end{array}$	<p>Branched polymer</p> <ul style="list-style-type: none"> • Flattest release profiles • Very fast cure

The chosen polymer greatly affects cure speed. Multifunctional and branched polymers are more reactive and cure faster because they have more opportunities to react than end-blocked type of polymers. Pendant polymers cure more slowly because the pendant vinyl groups are less reactive than the vinyl groups at the ends of the chain. Polymers that react faster usually have a shorter bath or working life. Bath life can be modified to some extent with the choice and amount of inhibitor. Polymer types that exhibit faster cure leading to higher crosslink densities can show poorer anchorage to the liner substrate. In solventless systems that are coated on roll coaters, the preferable polymer chain length is 100 to 200 siloxane units to ensure good coatability. [8, pp. 9–17]

The release values and profiles of silicone coatings also vary based on the chosen polymer. In the case of an end-blocked polymer, there is a more significant increase in release force when peel rate is increased. Release forces at low peel rates are higher when pendant or multifunctional polymers are used compared to end-blocked polymers. The increase in release forces as the peel rates are increased is not as significant with pendant polymers compared to end-blocked polymers, and release curves of multifunctional polymers remain fairly stable as the peel rate increases. [8, p. 17] Multifunctional

polymers produce a higher crosslink density and behave more glass-like than end-blocked polymers which produce a lower crosslink density [13, p. 15].

2.2.2 Crosslinker

There are two types of crosslinkers that are used in the formulations of silicone release coatings: homopolymers and copolymers. Their structures are presented in Figures 4 and 5. The homopolymer type of crosslinker provides rapid gelation and better anchorage of the coating to the liner substrate, whereas the copolymer type provides longer bath life and more rapid cure. Often both types of crosslinkers are used to achieve an optimized balance between cure speed and silicone anchorage. [8, p. 7]

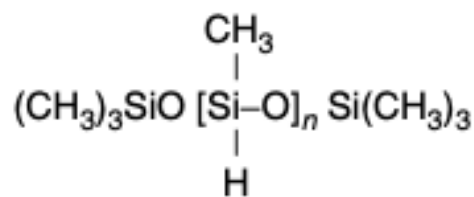


Figure 4. The structure of a homopolymer crosslinker where n is between 5 and 60 [8, p. 8] [13, p. 19]

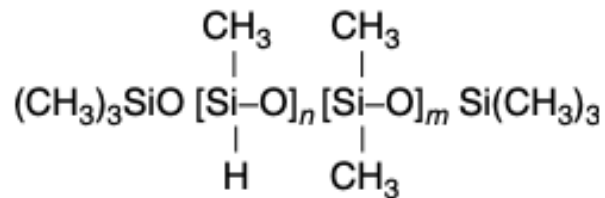


Figure 5. The structure of a copolymer crosslinker where $n + m$ is between 5 and 60 and m is between 50 and 90 mole percent (mol %) [8, p. 8] [13, p. 19]

The ratio between crosslinker and polymer (SiH:Vi) is of high importance in silicone formulations. An excess amount of crosslinker is needed for the curing reaction to occur at a desired rate. Higher ratios may improve anchorage of the silicone coating to some substrates, while lower ratios are usually used in situations where interactions with reactive adhesives must be minimized. The ratios usually vary between 1.1:1 and 2.5:1. [8, p. 12]

2.2.3 Catalyst

Platinum is the most commonly used catalyst in solventless systems. The amount of platinum catalyst mainly affects curing and bath life but may also have an effect on how well the silicone covers the surface of the liner substrate and anchors to it. Rhodium is

an alternative for platinum but is quite rarely used. It requires higher temperatures to activate and thus is not suitable for most plastic liner substrates. [8, p. 10]

The usage of platinum has been tried to minimize because of its high cost. A platinum amount of 100 ppm is a common industry benchmark and 50 ppm or less is considered a low amount of platinum. Temperature sensitive substrates may require platinum amounts from 150 to over 200 ppm to obtain an adequate cure. [14] That is, the coating speed, the silicone formulation and the coating system mainly dictate the curing and thus the platinum needs.

2.2.4 Additives

Inhibitors are used to separate the vinyl groups from the platinum catalyst to prevent the crosslinking reaction from happening prematurely. When temperature is raised, the inhibitor evaporates, dissociates from the platinum, or reacts with the silicon hydride and becomes a part of the cured silicone matrix. Inhibitors used in addition cure chemistries can be for example acetylenic alcohols, unsaturated dicarboxylic acid esters, or materials containing double and triple carbon-carbon bonds. Some inhibitors provide long, stable bath lives and require higher initiation temperatures, while for others the initiation temperature is lower and bath lives are shorter. [8, pp. 4–8]

The release force of silicone liners can be tailored by modifying the rheology of the silicones. Methyl-treated silicate resins (MQ resins) can be used as controlled release additives. MQs have a very high T_g and a usual molecular weight of a few thousand g/mol. Usually, little effect is noticed at low concentrations of MQ, but often as the MQ level is raised above about 30 weight percent (wt-%) there is a sudden increase in release forces. The effect of increasing release forces is mainly caused by increasing the dissipative character of the otherwise elastic silicone. That happens because by adding MQ resins to the formulation, the T_g of the silicone release coating shifts closer to the use temperatures. There is a reduction in flexibility of the silicone network leading to higher friction and to a more rigid surface which can sustain increased stress levels. It has been noticed that adding MQ to the silicone network results in a reduction or even elimination of slip. [8, pp. 18–20] [10, pp. 548–549] When interfacial slippage is hindered, the adhesive deformation is increased during delamination resulting in higher release forces [1]. The use of release additives has been noted to affect the cure rate in a way that as the amount of release additive is increased, the cure reaction occurs more slowly [14].

Anti-misting additives are often used to minimize silicone misting which is generated in high-speed processing of solventless silicone coatings. A common method to minimize

misting is to change the silicone formulation by reducing the number-average degree of polymerization which reduces the viscosity of the coating and limits mist density [15]. By using anti-misting additives, it is possible to prevent formation of silicone aerosols during the coating process even at high coating speeds. These additives can be included in the polymer or the catalyst. The use of agents reducing mist allow higher processing speeds, but their effectiveness may be affected by many factors related to the coating and process parameters. [8, p. 12] [16]

Other additives may be used to improve processing and performance of the silicone release coating. Anchorage is affected by many factors, but it can be adjusted by including anchorage additives in the formulation. [8, p. 12]

2.3 Curing

Silicone release coatings can be cured thermally or by radiation. Thermally cured systems can be divided into condensation curing and addition curing, also known as hydrosilylation. [9] Curing of silicone release coatings through a condensation reaction was the main system used in production of silicone release liners from the late 1950's to the mid 1970's. Its advantages are fast cure at low temperatures and easily controllable release performance by varying the polymer molecular weight. Some of the disadvantages are that there is no possibility for a 100% solid coating, migration issues and blocking in case of liners coated with silicone on both sides. [8, p. 4] Blocking is caused by bonding of two contacting surfaces resulting in unwinding resistance [17, p. 38].

Addition cure is nowadays the most dominant cure chemistry and can be applied to solventless, solvent-based and emulsion systems. In the addition cure reaction, a silicon hydride group is added to a vinyl group and a crosslink network is formed as presented in Figure 6. Inhibitors are used to control bath life by excluding the vinyl groups from the platinum catalyst. When temperature is raised above 80 °C, the inhibition effect ends and curing reaction occurs rapidly. [8, pp. 4–5]

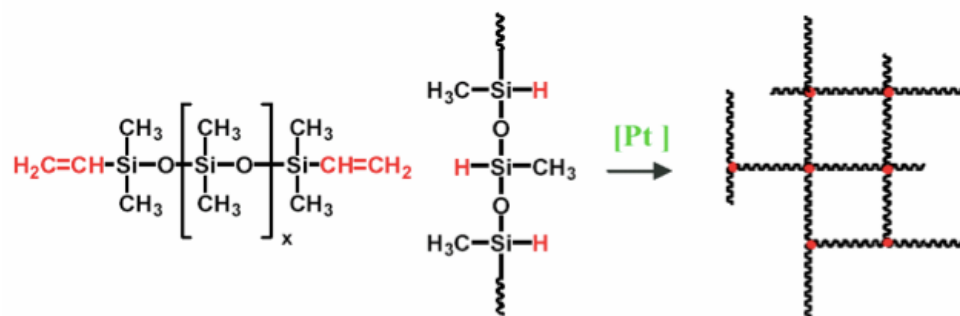


Figure 6. The mechanism of addition cure reaction [14]

In the scanning electron microscope (SEM) images presented in Figure 7, a cluster of silicone particles gathered from the siliconizing station is presented next to thermally cured silicone. On the left side a particle agglomerate cluster before thermal curing process is presented whereas the right side depicts fractured thermally cured silicone.

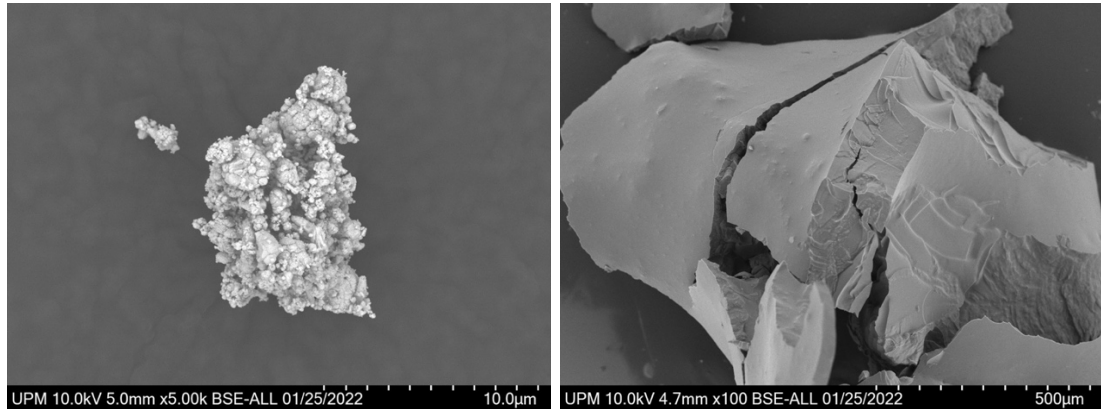


Figure 7. SEM images of an uncured silicone particle cluster (left) and a fracture of cured silicone film (right) (courtesy of UPM Lappeenranta research centre)

In addition to the main reaction in which a vinyl functional silicone polymer and a silane-hydride functional crosslinker react, secondary reactions that are slower than the crosslinking reaction may occur. These secondary reactions are called post-cure reactions and they occur especially in cases where an excess of crosslinker has been used. [9]

One of the main advantages of addition cure chemistry is that the manufacturing of polymers is very easy. The vinyl groups can be placed terminally as well as anywhere along the polymer chain. The polymers also stand heat treatment well and can be devolatilized to remove polymers with lower molecular weights enabling the creation of migration-free coatings. Through controlling the polymer chain lengths as well as the number and placement of vinyl groups in the polymer chain, elasticity of the cured silicone network can be adjusted. In the case of addition cured systems, there are no blocking issues which is a disadvantage of condensation cured systems. The addition cure chemistry is very sensitive for contamination by the liner substrate or any foreign materials. [8, p. 5] Plastic liners are an example of substrates which may contain additives that could be detrimental to the curing reaction [1].

Thermally cured silicone release coatings are the preferred system, but ultraviolet (UV) radiation cured silicone release coatings can be used to avoid exposure to high temperatures when temperature sensitive thermoplastic liners including polyethylene (PE), polypropylene (PP) and polyester (PET) are coated. In addition to their low temperature resistance and the possibility of being harmful to the crosslinking of the silicone release coating, there are also difficulties in silicone adhesion to plastic liners and maintaining

anchorage over time. The problem of silicone anchorage occurs particularly in the case of PET films. The use of more expensive, special grades of films can help overcome some of the issues. One example is coextruded or primed PET in which case there are no anchorage issues occurring over time. [1]

Through the crosslinking reaction, silicones cure into a solid silicone rubber. After curing, the silicone surface is no longer oily, and no silicone should be able to transfer to the adhesive. Extraction test with an organic solvent can be used to test how well the silicone has cured. Often the silicone surface is considered well cured if less than 5% of silicone can be extracted from the surface. [8, pp. 2–3]

2.4 Silicone anchorage

Silicone release coatings anchor to a substrate through mechanical interlocking and chemical reactions. Mechanical interlocking takes place when silicone is applied to a porous surface, such as paper. Silicone forms a mechanical bond with the paper substrate as it flows on the surface and penetrates into the porous surface. Surface penetration and thus the use of silicone is decreased by using specifically designed paper grades, such as glassine and supercalendered kraft (SCK) which minimizes penetration to the paper surface and keeps the silicone coating on it. The use of these substrates also improves surface coverage. [9]

Although mechanical interlocking accounts for some part of the stable silicone anchorage, majority of it occurs because of the chemical interactions between the silicone and the substrate. Chemical reactions occur as the silicone crosslinker reacts with the unreacted hydroxyl ($-OH$) or carboxyl ($-COOH$) groups in the cellulose and surface sizing agents. These reactions are slower than the primary crosslinking reaction between the vinyl functional silicone polymer and a silicon-hydride functional crosslinker but take place by the time the coated liner is quality tested. By then the anchorage of the silicone to the substrate is settled, and usually no improvements are seen over time. [9]

3. SILICONE COATING PROCESS

Typically, the production of PSLs is a coating and laminating process. It includes applying the release coating on the liner substrate, applying the PSA on the coated liner and laminating it together with the face material to form the PSL material. [2] The process of coating the liner with silicone is introduced in more detail because of the focus of this thesis.

Coating a liner substrate with silicone can be done using a five-roll smooth roll coater presented in Figure 8. The coater is a nip fed system where rubber covered rolls and steel rolls are alternating. The typical rolling speeds increase from the bottom where the silicone is fed into the system up towards the web. Coat weight changes as the rolling speeds are altered and time is needed to optimize the speeds and nip pressures to achieve a desired coat weight. [13, p. 9] The roll settings are also affected by the viscosity of the silicone [3].

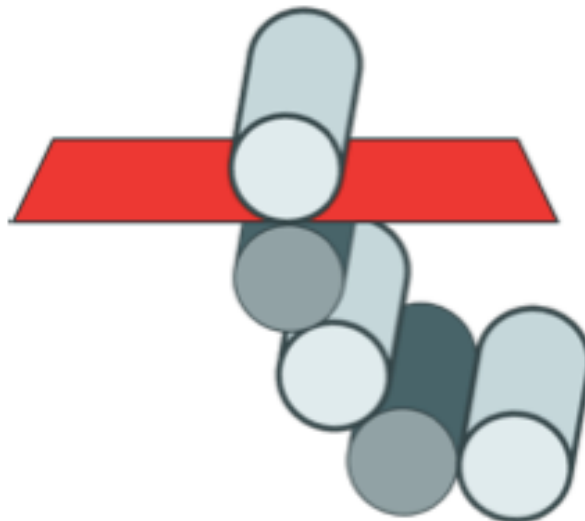


Figure 8. A five-roll coating system consisting of alternating rubber and steel rolls [3]

Immediately after coating the web, the silicone needs to be cured. As the web leaves the coating head, uniformity of the coating is often poor which is a result of film splits occurring at all nips. The coating needs to be levelled which is accelerated by heat. A combination of time and temperature results in proper curing of the silicone release coating.

Temperature is needed to deactivate the effect of the inhibitor and to speed up the reaction but adding too much heat too early may lead to the evaporation of the crosslinker. Two to three seconds in the ovens should be enough to reach a full cure with web temperatures between 150 and 190 °C when paper substrates are coated. Web temperatures of 100 to 120 °C are common for temperature sensitive substrates, such as PE and PP, but in those cases time in the ovens must be increased or the chemistry modified in order to properly cure the coating. Time and temperature needed to achieve a properly cured and well anchored coating can be found but they would be valid for only that specific oven system. [13, p. 10] [14]

Usually, the ovens are air flotation ovens that apply heat to the web from both sides and thus are very efficient heaters. The best oven system for curing silicone release coatings is a zoned oven that is cooler at the front, ranging from a single-zone to an oven consisting of up to eight zones. [13, pp. 9–10]

Curing of the coating occurs at temperatures above 80 °C, after the inhibitor no longer excludes the vinyl groups of the polymer from the platinum catalyst [8, pp. 4–5]. Those temperatures are reached at the beginning of the oven system and the curing reaction should be finished by the end of the ovens. There are some differences in curing behaviour of different silicone formulations, including the temperature at which the silicone starts to react and how long the crosslinking reaction takes. Studying those factors was a part of the work of this thesis where silicone misting was mainly considered as the mist produced in the roll coating process but also as the mist observed at the oven system as the inhibitor evaporates, the silicone reacts, and a uniform coating is formed on the liner substrate. Misting at these stages of the process was studied by monitoring the aerosol concentration in the surrounding air. The misting phenomenon will be further discussed in the next chapter.

4. SILICONE MISTING

Decades ago, the line speeds of machines applying silicone release coatings ranged from 100 to 200 m/min and silicone misting did not appear regularly. Nowadays the line speeds are much higher, and the occurrence of silicone mist is nearly impossible to avoid. Different methods can be used to reduce the formation of mist and to remove the mist that is generated. Generally, misting increases as the coating speed increases. Reducing silicone misting is important in order to minimize contamination of the plant environment, equipment and materials, but the main concern is worker exposure. [18] A typical aerosol threshold level in a working environment used in the industry is 5 mg/m^3 [16].

Next, the misting phenomenon is introduced, followed by the discussion on how mist can be reduced and what are the problems related to silicone misting. Health effects are given higher value than problems in production because they are considered to be of higher importance.

4.1 Misting phenomenon

During the coating operation, the liquid film splits multiple times, once between two successive cylinders. This way it is possible to coat a thin film on a substrate moved by the last cylinder. At high speeds, the films break-up leading to generation of fine and often visible mist. [8, p. 12] [19] The mist can be observed to follow the web to the ovens, flowing outward horizontally and spraying from the back of the coating head [18]. The generation of silicone mist is presented in Figure 9 and visible mist at a coating station in Figure 10.

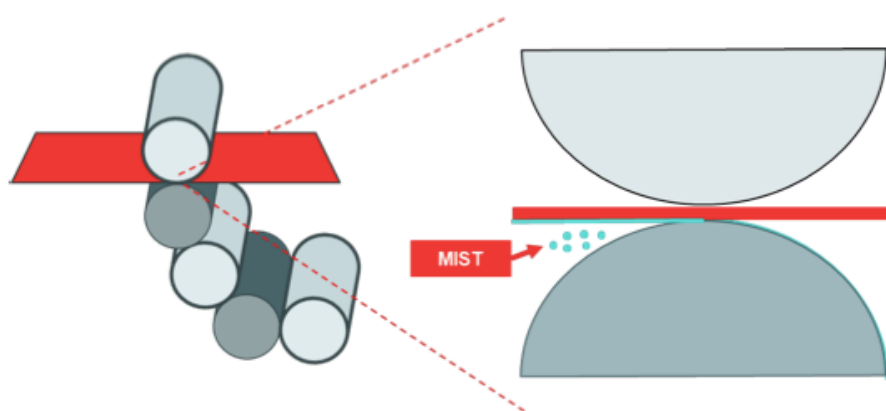


Figure 9. Formation of silicone mist in multi roll coating [3]

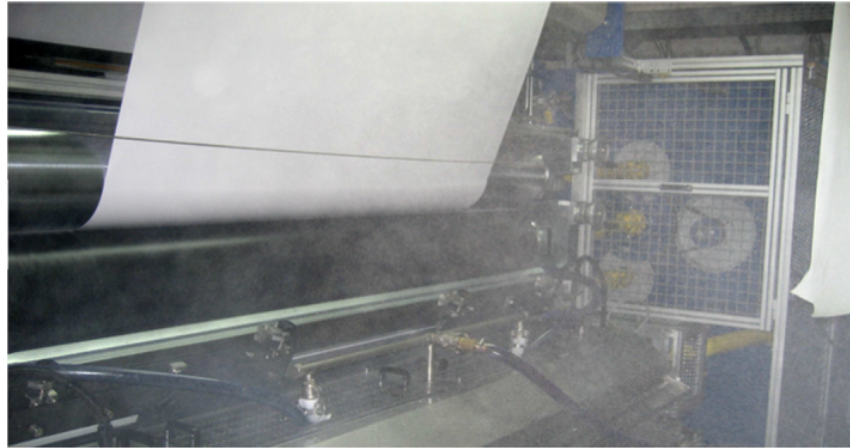


Figure 10. *Misting at a silicone coating station [16]*

Studies related exactly to silicone misting in production of PSLs were not found but misting of Newtonian liquids in forward roll coating has been studied. One of the materials used in the measurements of the study was PDMS which is why it is used for the introduction of misting phenomenon in this thesis. The PDMS solution as well as the other studied solutions showed Newtonian behaviour at shear rates from 1 to 1000 s^{-1} . [20] Fluids exhibit Newtonian behaviour when their viscosity remains constant with varying shear rates [21, p. 43].

In the study, standard and high-speed cameras were used to visualize misting in the area of film splitting of two counter rotating rolls. One studied roll configuration consisted of two cylinders where the top cylinder was chrome-plated, and the bottom cylinder was rubber covered. The studies made using that configuration included visualization of misting and for instance mist drop size, drop count and mass concentration measurements as a function of roll speed and the viscosity of PDMS. [20]

Flow instability referred as ribbing occurs in forward roll coating. Viscous forces destabilize the free surface that is generated in the area where the film splits, whereas surface tension forces act against any instabilities. These two forces compete with each other resulting in ribbing. The ratio between the two forces is referred as the capillary number (Ca) which is defined with the equation

$$Ca = \frac{V\eta}{\sigma} \quad (1)$$

where V is the mean roll speed, η is the viscosity of the liquid and σ is the surface tension of the liquid. [20]

In Figure 11, the events that lead to the formation of mist droplets with PDMS having a viscosity of 460 cP at a Ca of 44.6 are presented. There is a septum near the cylinder ends which is first at a stable state after which the septum extends further away from the

nip. At the next phase there are some instabilities occurring at the septum rim. At the final state the septum rim breaks and mist droplets are generated after 7 ms from the first image. [20]

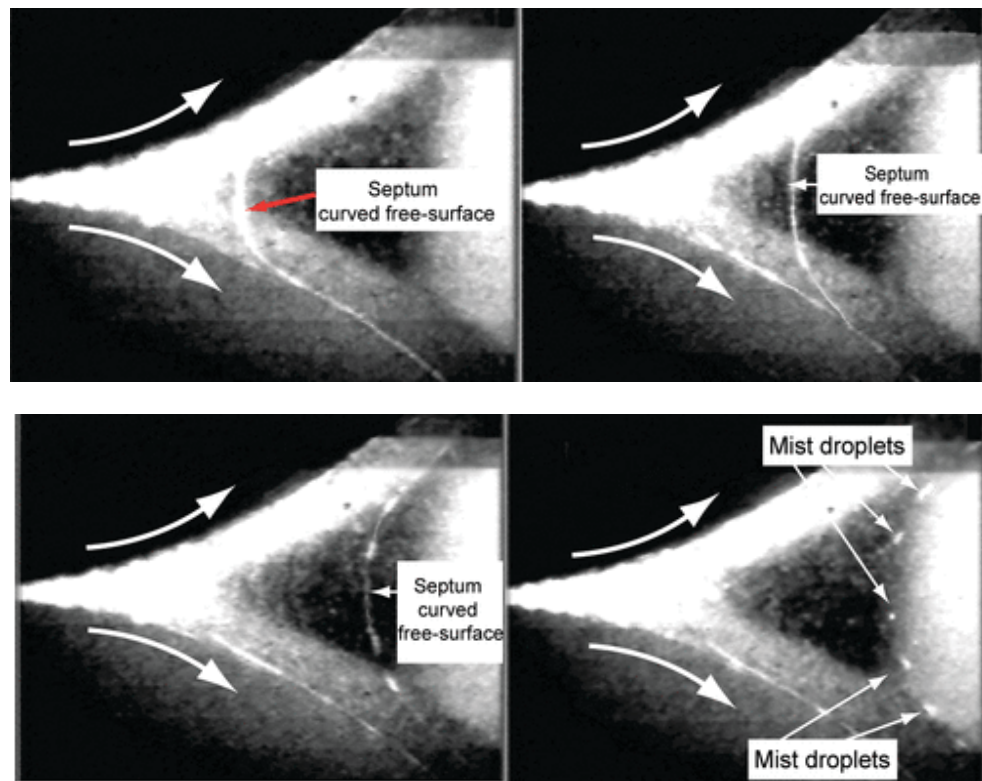


Figure 11. Images taken from a high-speed video where the septum is first stable (top left), the septum extends and instabilities evolve (top right and bottom left) and finally the rim of the septum breaks into mist droplets (bottom right) [20]

The effect of viscosity on mist droplet count with varying roll velocities is presented in Figure 12. Different PDMS oligomers were used in the studies and it can be seen that the droplet count increased linearly at roll velocities between 115 and 172 m/min. It seems that as viscosity is increased there are viscous forces destabilizing the septa towards break-up, but the forces also allow more PDMS liquid to pass through the nip. In the study it was thought that when roll speeds are higher, the septum extends downstream but also becomes thinner. The thinner septum is more likely to rupture and generate mist droplets which is why more droplets are generated with increasing roll speeds. Higher viscosity has the same effect of leading to the septa extending more downstream and becoming thinner because of the viscous forces, resulting in the generation of a higher number of mist droplets. [20]

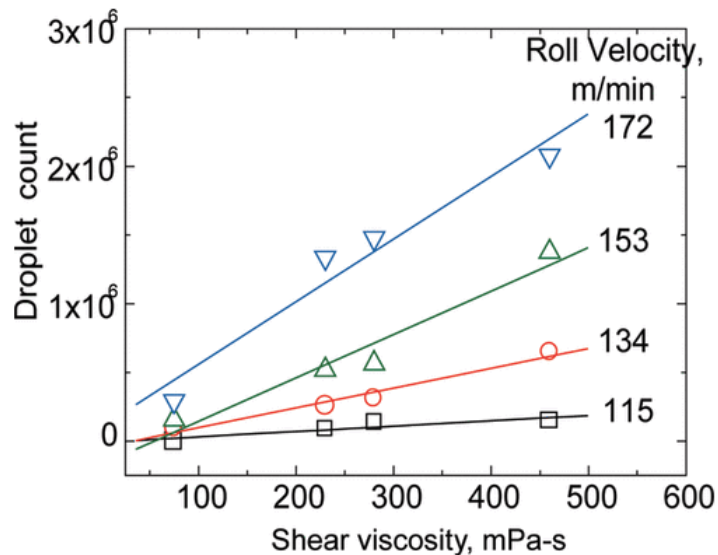


Figure 12. The effect of increasing PDMS viscosity and roll velocity on mist droplet count [20]

The measurements done in the study showed that as viscosity was raised from 74 cP to 460 cP and the roll velocity was kept at 134 m/min, the droplet diameter increased from 1.6 to 2.24 μm , the droplet count from 122,500 to 671,600 and the mist concentration from 0.4 to 8.5 mg/m^3 . The effect of increasing roll velocity was seen when PDMS viscosity was kept at 74 cP but the roll velocity was raised from 134 to 192 m/min. In that case the droplet size ranged from 1.6 to 1.72 μm , the droplet count from 122,500 to 907,500 and the mist concentration from 0.4 to 3.4 mg/m^3 . [20]

Line speed seems to be the most significant factor in the extent of misting phenomenon, but other factors related to the nip, silicone coat weight and roll ratios have also been examined [18]. In the measurements done for this thesis, the effect of line speed as well as the effect of viscosity of the silicone formulation on misting was studied and the effects described above were expected to be seen.

4.2 Ways to reduce silicone mist

Additives to minimize misting can be used allowing processing speeds of solventless silicone coatings to be about 1000 m/min. Mist generation and the effectiveness of the anti-misting additives are influenced by the viscosity of the coating, polymer structure, and many process parameters including silicone coat weight, roll speeds and roll diameters. [8, p. 12] To reduce mist formation, line speed may be lowered leading to lower productivity, a coater design that reduces circumferential velocity of the rollers may be used and the pressure between the coating and press rolls may be increased [15] [16].

The effect is seen as less operator exposure, improved coating hygiene, reduced cleaning requirements, increased productivity and a smaller amount of waste [18].

Exhaust tubes or channels can be placed at the coating head and used to reduce the exposure of operators to silicone mist. The mist is directed through filters from where it goes into or outside the plant. The filters need to be changed often because they will become clogged by heavy misting. This method only moves the already generated mist elsewhere in another form and the main focus should be on reducing mist generation. [18]

4.3 Problems related to silicone misting

Silicone misting has become a more significant issue as the production line speeds have increased over the years. The main concern is the worker exposure to silicone mist but minimizing contamination of equipment and materials is also necessary. [18]

4.3.1 Effects in production

Silicone misting has been a problem in the industry for a long time. It lowers the efficiency of production of silicone release liners by causing downtimes and higher maintenance costs [19] [22]. Cleaning the ovens and other equipment is required because the equipment and the surrounding area become coated with silicone. Misting may also result in slipping hazards posing a risk to the workers. Mist particles, usually of larger size, may originate from the back of the coating setup and contaminate the backside of the liner. This may lead to problems later in the converting phases. [18]

4.3.2 Health effects

Particle size, molecular weight, shape and chemical groups present in silicone polymers determine their physicochemical properties. These properties strongly affect the ability of silicones to interact with the human organism and to pass cell membranes and skin barriers. As the silicone particle size decreases so does the safety of the application. [23, pp. 1–2] It is possible for silicones having low molecular weights to accumulate in the human organism and have long-term effects on the organs [24]. Cyclic siloxanes and linear low molecular weight siloxanes are known to pose the most significant risk to human health [25] [26] [27] [28] [29]. Those types of siloxanes may be able to enter the organism through the respiratory system [28] [29] [30] [31].

Particles having a diameter $\leq 10 \mu\text{m}$ are small enough to be inhaled and thus could affect human health. Particles with a diameter $\leq 10 \mu\text{m}$ are able to reach the lungs, whereas

particles with a diameter $\leq 2.5 \mu\text{m}$ are able to penetrate the lungs and might reach the alveoli. [32, p. 1]

Siloxanes are produced through a synthesis reaction which leads to formation of chains having different structural units in the molecule. The obtained blend consists of different molecular weight compounds with different chain lengths. A predominant fraction of a certain degree of polymerization exists but so does the possibility of contamination by low molecular weight linear and cyclic siloxanes. [23, p. 4] [33] Cyclic siloxanes having low molecular weights may have toxic effects on the immune system and proteins conformation, irritate skin, increase intraocular pressure and be cancerogenic, genotoxic and teratogenic [24] [33]. Low molecular weight linear siloxanes that are formed in the synthesis of siloxanes might not be efficiently removed during the purification process and remain as contaminants. Short-chained, low molecular weight siloxanes and cyclic siloxanes may become trapped by longer chains preventing their distillation. In the cross-linked silicone network there exists so-called free permeable channels which can close the short chain linear or cyclic structures in the network. [23, pp. 3–5]

The cyclic low molecular weight silicones include hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6). These compounds fulfil the so called Lipinski's rule of five which is used to assess bioavailability of different compounds. [33, pp. 244–246] Structures of the four cyclic PDMS molecules are shown in Figure 13.

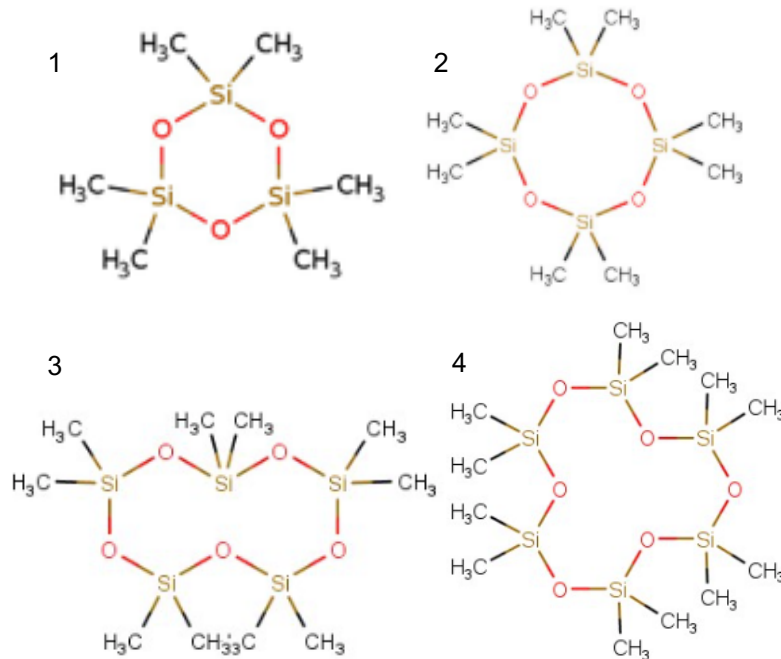


Figure 13. Low molecular weight cyclic structures of PDMS molecules: 1. D3, 2. D4, 3. D5, 4. D6 [34] [35] [36] [37]

The inhalation route of exposure to the low molecular weight substances is considered the most relevant for the topic of silicone misting. In addition to the inhalation route, substances at workplaces may come into contact and enter the human body by contact with the skin or by swallowing [38, p. 10]. European Chemicals Agency (ECHA) provides some toxicological information on the substances, including the threshold values of worker exposure by inhalation. The information is divided into systemic and local effects, both further divided into long-term and short-term effects. [34]

Properties of inhaled particles determine the most probable location in the respiratory system and in most cases the possible health effects. Particles having systemic effects are such that they are soluble in human fluids and can be absorbed in the respiratory system. Local effects are caused by particles accumulating in a specific area of the respiratory system. Acute or short-term exposure is referred to in case of rapid exposures causing acute effects such as narcosis or irritation. Long-term exposures refer to repeated or continuous exposure lasting for months or years and having chronic effects on human health. [38, pp. 11–12]

The derived no-effect level (DNEL) is the exposure level which should not be exceeded in human exposure [34]. The DNELs of the four low molecular weight substances having cyclic structures are shown in Table 2. The identified DNEL values of two low molecular weight linear molecules are also included in Table 2.

Table 2. *The DNEL values of long-term worker exposure by inhalation of the low molecular weight cyclic and linear PDMS molecule structures [34] [35] [36] [37] [39] [40]*

Structure	Systemic Effects, Long-term (mg/m ³)	Local Effects, Long-term (mg/m ³)	Local Effects, Acute / Short-term (mg/m ³)
D3	64	-	-
D4	73	73	No identified hazard
D5	97.3	24.2	No identified hazard
D6	No identified hazard	1.22	6.1
L2	53.4	-	-
L3	78	-	-

In addition to the identified DNEL values of exposure by inhalation, the most sensitive endpoints of the exposure to the substances are told. In case of the low molecular weight cyclic substances, exposure to D3 could affect fertility and in case of D4, D5 and D6, toxicity of repeated dose is told to be the most sensitive endpoint. [34] [35] [36] [37]

Linear low molecular weight PDMS molecules that fulfil the Lipinski's rule of five include hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5) and tetradecamethylhexasiloxane (L6) [33, p. 246]. The structures of the molecules are presented in Figure 14.

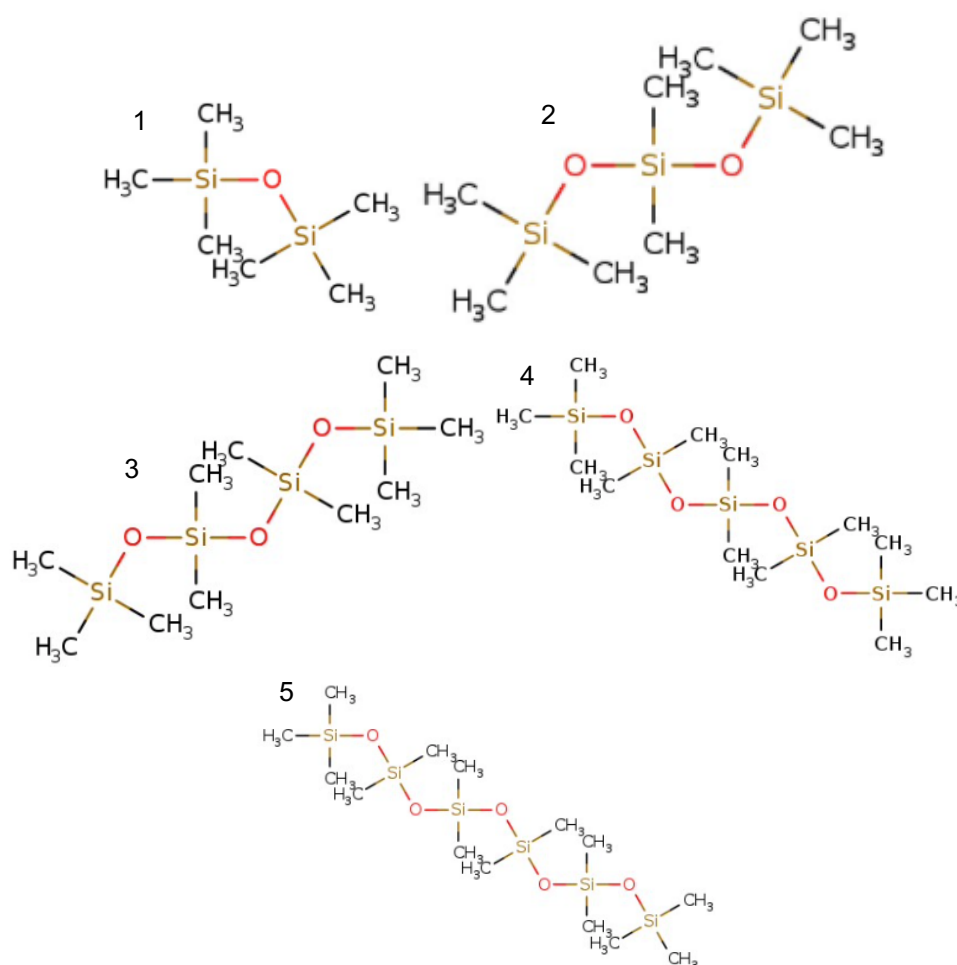


Figure 14. Low molecular weight linear structures of PDMS molecules: 1. L2, 2. L3, 3. L4, 4. L5, 5. L6 [39] [40] [41] [42] [43]

ECHA has identified DNEL threshold values for long-term systemic effects of worker exposure by inhalation for L2 and L3 which are listed in Table 2. Toxicity of repeated dose is told to be the most sensitive endpoint of exposure to L2 and L3. In the case of the other low molecular weight linear PDMS molecule structures no such hazard has been identified according to ECHA. [39] [40] [41] [42] [43]

5. MATERIALS AND TEST METHODS

In this thesis, five different laminates and especially silicone formulations were tested using varying methods that provide information on the chemical aspects of the silicones as well as their mechanical behaviour. In addition to the other methods, aerosol monitoring was used to track the quantity of particles in the surrounding air during the production of the laminates and the results were compared to a situation where no production was ongoing.

The main interest related to silicone misting phenomenon was on aerosol monitoring and differences in aerosol concentrations between the studied silicone formulations. Differential scanning calorimetry (DSC) was chosen because it allows studying the curing behaviour of silicones. Siliconized surfaces were able to be studied by measuring surface energies and imaging the siliconized surfaces. The anchorage of the silicone to the liner was also examined as well as the forces needed to peel the adhesive and face material from the silicone coated liner. The aim was to use these measurements to gather data and information of the studied silicones, compare them and hopefully be able to combine the laboratory measurements with the extent of the misting phenomenon observed in production.

5.1 Test materials

Five laminate materials of which PSLs are produced were tested. The laminates composed of different face materials, adhesives, liners and silicone release coatings which were the main interest of this thesis. The five silicone formulations all had the same catalyst, but the other components differed from each other. All laminates were produced on the same production machine to eliminate the machine related variables.

The laminate compositions could not be affected in a way that the only variable would have been the silicone formulation. The laminate composition is designed for a certain application and that is why it was not possible to compare the silicone coatings only. One silicone was applied on a PET liner while the others were applied on paper liners. The aim was to choose laminates with the face materials having similar thicknesses to minimize the effect of their stiffness on the measurements done for the whole laminates. Most of the tests were done for the silicone layer coated on the liner after removing the face and the adhesive and only one test type included the whole laminate where the face

and the adhesive had an effect on the results. It was assumed that the adhesive and the face material did not affect the results of the other measurements.

5.1.1 Silicone A and silicone A + modifier

The silicone A formulation includes a polymer, a crosslinker, a modifier and a catalyst. The polymer is fast curing, has a branched structure and is told to provide very stable low release values by the supplier. In the technical data sheet (TDS) it is mentioned that the polymer provides very good mist reduction and minimizes the mist effect at high coating speeds. Viscosity of the polymer at 25 °C is below 200 cP. The crosslinker used in the formulation provides fast cure, can be used with low catalyst levels and has a viscosity below 100 cP at 25 °C. The catalyst is used to accelerate the cure at a given temperature and to reduce the temperature that is required for curing which may provide energy savings and allow the cure of temperature sensitive liners. The catalyst is a reactive organo-platinum complex dispersed in polysiloxane and its viscosity at 25 °C is in the range of a few hundred cSt. A quite high amount of release modifier is used in silicone A + modifier. The modifier provides efficient modification of release values at low peel speeds. Its viscosity at 25 °C is multiple times the viscosity of the polymer. Silicone A is identical to silicone A + modifier with the exception that silicone A does not contain any modifier. It was expected that the addition of modifier would be seen as differences in the properties of the silicone and the behavior of the silicone release coating as a part of the laminate structure.

5.1.2 Silicone B

The polymer used in the formulation of silicone B also has a branched structure and is fast curing, provides stable release and has a slightly rising release profile. It provides very good mist reduction, minimizes the misting effect at very high speeds and has a viscosity between 200 and 500 cP at 25 °C. It is designed for polyester substrates and to be used with an anchorage additive when it provides excellent long-term anchorage to substrates. The crosslinker used in the formulation provides excellent anchorage and stable release values. Its viscosity at 25 °C is between 100 and 300 cP. The anchorage additive improves the anchorage of the silicone release coating to unprimed polyester films and has barely any impact on cure and release. Its viscosity at 25 °C is also in the range of 100 to 300 cP. In this formulation, no release modifier is used, and the platinum catalyst is the same as with silicone A.

5.1.3 Silicone C and silicone C + modifier

The polymer in the silicone C formulations is fast curing, provides stable release values and can be used when low release force is required at high-speed peeling. The polymer has a multifunctional structure, can be cured at low temperatures, and has a viscosity between 200 and 400 cP at 25 °C. The crosslinker is fast curing and enables curing at low temperatures. Its viscosity at 25 °C is below 100 cP. The platinum catalyst used in this formulation is the same as in the previously introduced silicone formulations. Silicones C and C + modifier are the same with the exception that a low amount of modifier is included in silicone C + modifier. The modifier used in this silicone formulation provides efficient modification of release values at low peel speeds and its viscosity at 25 °C is multiple times the viscosity of the polymer.

5.2 Aerosol monitoring

The aerosol monitor used in the measurements of this thesis is a multi-channel light-scattering laser photometer that collects a gravimetric sample and provides real-time mass and size fractions. The aerosol concentration range possible to measure with the device is 0.001 to 150 mg/m³. [44] The monitor is able to measure mass fraction concentrations corresponding to size fractions of airborne particulate matters (PMs) PM1, PM2.5, respirable, PM10 and PM Total. PM1 corresponds to particles having diameter ≤ 1 μm, in PM2.5 all particles with diameters ≤ 2.5 μm are included, the respirable PM includes particles having diameters ≤ 4 μm and in PM10 particle diameters ≤ 10 μm are included. PM Total includes all particles with diameters ranging from 0.1 to 15 μm. [44] [45]

The logged data can be viewed and analysed on the monitor screen or with a data analysis software. The results of mass fractions corresponding to only one, some or all the size fractions can be presented at the same time.

For this thesis, data was gathered from the siliconizing station, around the oven system where the silicone was cured and other places around one coating and laminating machine at UPM Raflatac's production facility. The measurements were conducted when no production was ongoing and during the production of the five studied laminates. The chosen measurement time for each spot was three minutes and the data was saved every 10 seconds, giving in total 18 measurement points for each spot of which the average aerosol concentration value was used in the results.

5.3 Viscosity

Rheology can be used to characterize the structure of polymer melts, solutions, suspensions and gels. The measurement of viscosity is the most basic rheological measurement and can be done using various techniques and geometries [46, pp. 125–126]. The viscosity of a fluid describes the way it flows and characterizes the internal resistance of a fluid to an external load. [21, p. 42] Fluid temperature and molecular mass have a distinct effect on viscosity. An increase in molecular mass results in an increased viscosity whereas temperature has an opposite effect. Also pressure influences viscosity but the effect becomes significant only at high pressures. [21, p. 46]

In Chapter 4.1 the effect of viscosity on misting was discussed and to see if the effect would be seen also in the measurements of this thesis, viscosity measurements of the studied silicones were decided to be included in the work. Samples of the studied silicones were collected from production and their viscosities were measured using a rotational viscometer. The measurement parameters were kept the same at all measurements.

5.4 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a method for testing the thermal properties of polymers. It is based on simultaneous heating of two trays according to a selected temperature program. One tray holds a studied sample and the other one is used as a reference. Usually, the inert reference is air. There are two principles which can be used in the measurements. Heat-flux calorimetry refers to a method where the sample and the reference are placed in a cylindrical oven and there is no temperature difference between the trays as the oven is heated. In a case where the specific heat capacity of the studied sample changes as the temperature is increased, a temperature difference between the trays occurs. Theoretically, this temperature difference is proportional to the specific heat capacity. The other possible measurement principle is power compensation calorimetry, in which the sample and the reference have their own heaters and temperature sensors. They are both heated at the same rate in a way that no temperature difference occurs. When the specific heat capacity of the studied sample changes, the amount of heating power needed to avoid a temperature difference is changed. When the specific heat capacity of the studied sample changes, the amount of heating power needed to avoid a temperature difference is changed. More power is needed in case of an endothermic process, whereas less power is needed if an exothermic process takes place. [21, p. 293]

Melting and evaporation are examples of endothermic processes, whereas crystallization and curing are exothermic processes. These processes are seen as peaks in the DSC curve. Glass transition is an exception because it is not seen as a peak but as a shift in the curve. [21, p. 295]

Curing of silicones can be studied with DSC. In Figure 15, DSC measurements of a terminal functional and a multifunctional polymer are shown. It can be seen that a terminal functional polymer reaches a complete cure faster than a multifunctional polymer. [13, pp. 19–21]

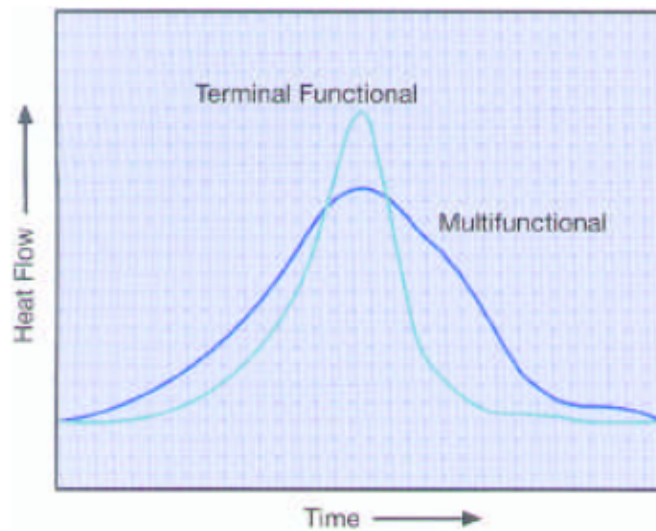


Figure 15. DSC curves presenting curing reactions of a terminal functional and a multifunctional polymer [13, p. 19]

In Figure 16, t_1 is the onset time of the reaction, t_2 is the time when the maximum heat flow is reached and t_3 is the time when the curing is complete. Also, the corresponding temperatures can be seen from the graph. H indicates the area under the curve corresponding the total heat flow of the exothermic reaction. A smooth and quick decline from t_2 to t_3 indicates that the cure is finished. [13, p. 21]

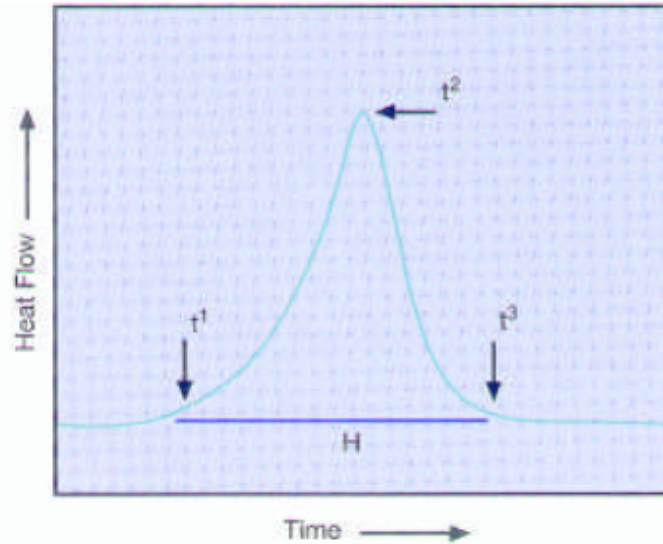


Figure 16. Times, corresponding temperatures and total heat flow describing the curing reaction [13, p. 20]

DSC is good method for studying curing and determining the optimum SiH:Vi ratio for a silicone system. The ratio is increased until the peak width at half of the peak height is ≤ 3 °C and the heat of reaction has become steady. DSC is a useful method for comparing silicone systems but the results must be verified on the coater because the oven systems and surface inhibition of different substrates may have an effect on the actual performance. [47]

DSC measurements for this thesis were done for the five different silicone formulations to compare their curing behaviour. The measurements were done in a nitrogen atmosphere by raising the temperature at a constant rate of 10 °C/min from the ambient temperature up to 160 °C. Other heating rates and their effect on the results were also studied.

5.5 Contact angle and surface energy

A solid material aims at forming a common interface with a liquid that it is in contact with. This feature is called wettability. [48] When wettability is studied, measurements of contact angles are used to indicate the degree of wetting. High wettability leads to the liquid spreading on the surface and contact angles being below 90°, whereas over 90° contact angles indicate poor wettability and formation of a compact liquid droplet. In Figure 17, contact angles formed by liquid drops on a solid surface are presented. θ represents the contact angle, γ_{lv} is the liquid-vapor interfacial tension and γ_{sv} is the solid-vapor interfacial tension. [49, pp. 3–4]

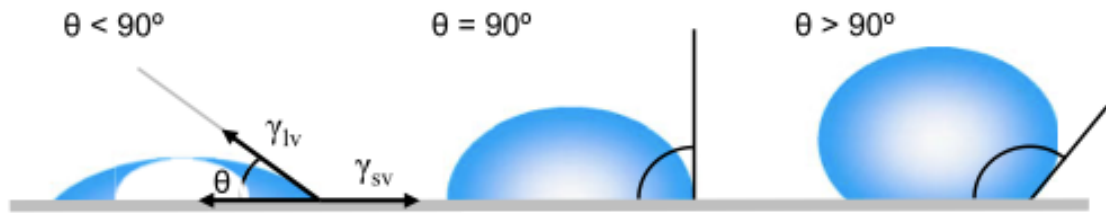


Figure 17. Contact angles formed by liquid drops on a smooth solid surface [49, p. 4]

Surface tension of the used liquid together with external forces, such as gravity, define the shape of the liquid droplet. In a liquid, neighbouring molecules pull each molecule in the bulk equally but the molecules at the surface of the liquid do not have neighbouring molecules in all directions. The surface molecules are pulled inwards, and an internal pressure is created. Surface tension refers to the intermolecular force which contracts the surface area of the liquid. [49, pp. 4–5]

The most common technique to measure a contact angle is to determine the two-dimensional (2D) profile of a sessile droplet and measure the tangent angle at the three-phase contact point. The measurement equipment consists of a horizontal stage where the sample is mounted, a micrometre pipette with which the liquid droplet is formed, a source of illumination and a telescope. The method is simple, uses only a small amount of liquid and requires a small surface substrate. There is a risk for impurity impacts because of small sizes of the liquid and the sample. Significant errors and differences between measurements and operators may occur because the tangent line is assigned by the operator. The drop may be unsymmetrical which is why contact angles should be measured on both sides of the drop profile and use the average of those as the contact angle. Multiple measurement points should be used for larger substrates in order to get a value that represents the whole surface. [49, pp. 7–8] In Figure 18, contact angles of a water droplet on a silicone surface are presented.

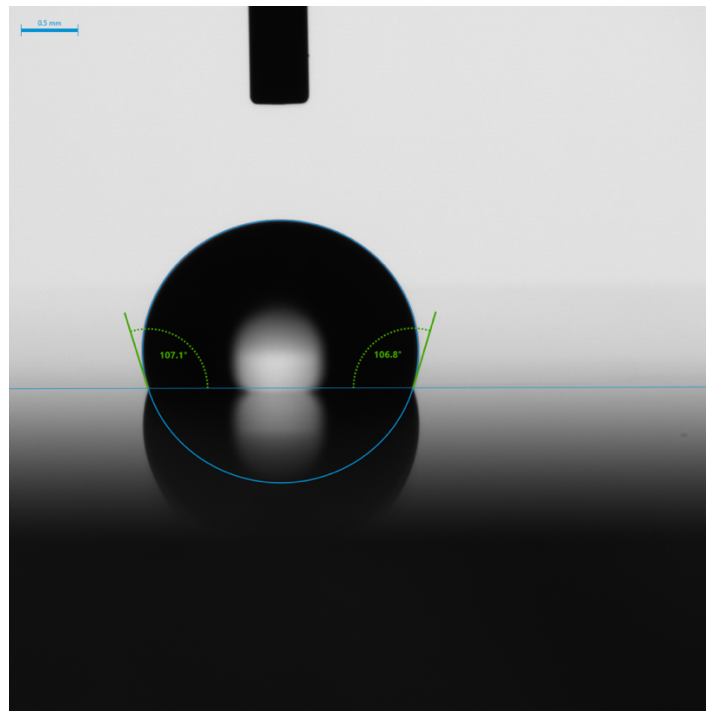


Figure 18. Contact angles of a water droplet

Measuring only one static contact angle to study wetting behaviour of a surface is not adequate in case of heterogeneous surfaces where there are domains presenting barriers to the contact line motion. The three-phase contact line is in motion and the contact angle produced is a dynamic angle. The contact angles formed as the liquid droplet is expanded and contracted are called advancing and receding contact angles which are presented in Figure 19. The advancing contact angles approach a maximum, while the receding contact angles approach a minimum value of the contact angle. [49, pp. 5–6]

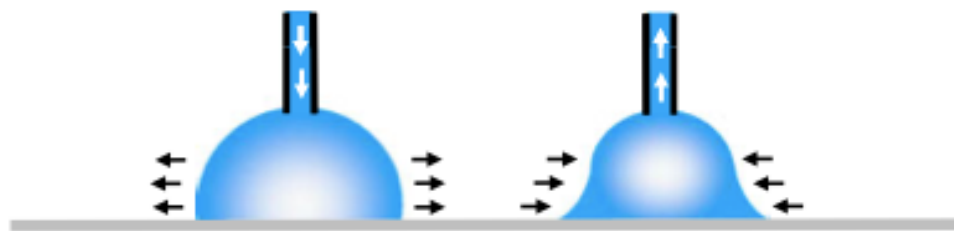


Figure 19. Advancing and receding contact angles [49, p. 6]

Surface energy describes the work needed to increase the surface area of a solid and can be expressed in mN/m. Surface energy of a silicone surface is about 22 mN/m, whereas for instance surface energy of a PET film is 42 mN/m. Contact angle measurements using two or more liquids can be used to determine surface energies of solid materials. There are different models that can be used to calculate the surface energy.

Commonly surface energy and surface tension are divided into polar and disperse fractions. Permanent and localized asymmetries of electron densities in molecules cause polar interactions that are quite strong. The weaker disperse interactions are caused by fluctuations of electron density distributions in molecules. These fluctuations lead to temporary charge differences resulting in electrostatic attraction between molecules. [14] [50]

The liquids used in the contact angle and surface energy studies of this thesis were pure water, diiodomethane and benzyl alcohol. Surface energies were calculated according to a method of Wu. It is a method mostly used for polymer surfaces with low surface energies up to 40 mN/m [51]. Other example of a method that could be used to determine surface energies is the method of Owens, Wendt, Rabel and Kaelble (OWRK). It is commonly used when studying contact between surfaces of different polarities and how a change in polarity affects surface energy, for instance [52].

Methods used to calculate the surface energy of a solid are based on contact angle measurements with several liquids and dividing the surface energy into polar and disperse parts. The methods are based on Young's equation which can be expressed as

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (2),$$

where γ_{sl} is the solid-liquid interfacial tension. [51] [52] [53]

Before the surface energy can be calculated from the contact angle, γ_{sl} needs to be determined. The way it is determined can be slightly different between methods but at least two test liquids with known disperse and polar parts of surface tension are needed. [51] [52] Water is a polar liquid, while diiodomethane is dispersive [53]. By adding the third test liquid, benzyl alcohol, accuracy of the results can be improved.

5.6 3D optical profilometry

A three-dimensional (3D) optical profilometer can be used to study surface topographies by utilizing the interference of light. The shape of the studied surface can be determined with very high precision including the surface curvature and roughness values, for instance. [54]

Together with contact angle and surface energy measurements, optical profilometry provides good information on the siliconized surface. If contact angle hysteresis is observed, the surface can be studied with an optical profilometer where unevenness of the surface can be studied. In the studies of this thesis, images of the siliconized surfaces as well as

the average surface roughness (Ra) values were compared to gain a better understanding of the studied surfaces.

5.7 Rub-off

Silicone rub-off can occur immediately after coating or as the silicone coated substrate ages. Silicone anchorage or adhesive failure, or cohesive failure of the cured silicone result in silicone rub-off. These issues can be caused by crosslink density of the silicone network, having a wrong type or a too low amount of crosslinker, and poor cure which are all related to the silicone formulation. Possible reasons for rub-off related to the substrate material are too smooth or not enough porous surface, surface inhibition, surface energy and lack of surface treatment. Post-curing reactions, reorientation of the silicone network, migration and changes in surface energy can lead to rub-off resulting from ageing of the silicone coated substrate. [55]

In the rub-off tests of this thesis, anchorage of the silicone to the substrate was studied quantitatively. The method is somewhat based on the European association for the self-adhesive label industry's (FINAT's) test method 7 (FTM 7) "Silicone coat weight by energy dispersive X-ray fluorescence spectrometry (EDXRF)". Silicone coat weight is the amount of cured silicone coating on a standard area of a release liner and is expressed in g/m². Using EDXRF it is possible to measure coat weights from 0 to 4 g/m² when properly calibrated. [56, p. 18] The rub-off test is based on measuring silicone coat weight of the sample using EDXRF after which a mechanical stress according to an in-house standard is applied on the sample and then the coat weight is measured again. Based on the difference between coat weights prior and after rubbing the rub-off percent can be calculated using the equation

$$Rub - off (\%) = \frac{CW_{after}}{CW_{before}} \times 100 \% \quad (3)$$

where CW is the coat weight. The equation indicates that the closer the result is to 100 %, the better is the silicone anchorage.

For silicone coat weight measurements, several samples should be taken from a laminate, or a silicone coated release liner. The area from where the samples are taken should be representative and include the area along and across the web because variations in silicone coat weight may occur. The samples are cut into discs with a sample cutter onto a clean surface and are handled with tweezers on the edge. No pre-conditioning of the samples is required. The samples are put into a sample holder which is making sure that a flat reproducible surface of the sample is measured by the analyser. In the analyser machine, the samples are moved into a measurement chamber where

the analysis is done using X-rays. As a result, the software provides the silicone coat weight directly in g/m^2 . [56, p. 18] The rub-off tests of this thesis were done using three parallel samples and their average rub-off value.

5.7.1 X-Ray fluorescence spectrometry

In X-Ray fluorescence spectrometry (XRF), X-ray radiation is used to ionize the inner shells of atoms of the studied sample. When a photon having higher energy than the binding energy of an inner electron orbital of an atom is targeted to the atom, part of the photon's energy can be absorbed. This leads to an electron being ejected from its position creating a vacancy. Because a vacancy exists, the atom is in an unstable state. The atom can achieve its original state through rearrangement, or the vacancy can be filled by an electron from the outer atom orbitals, for instance an L orbital electron drops to K orbital. The first leads to emission of Auger electrons and the latter generates secondary (or fluoresced) X-rays. [57, p. 1] [58, p. 344] Atom ionization and emission of Auger electrons and X-rays are presented in Figure 20.

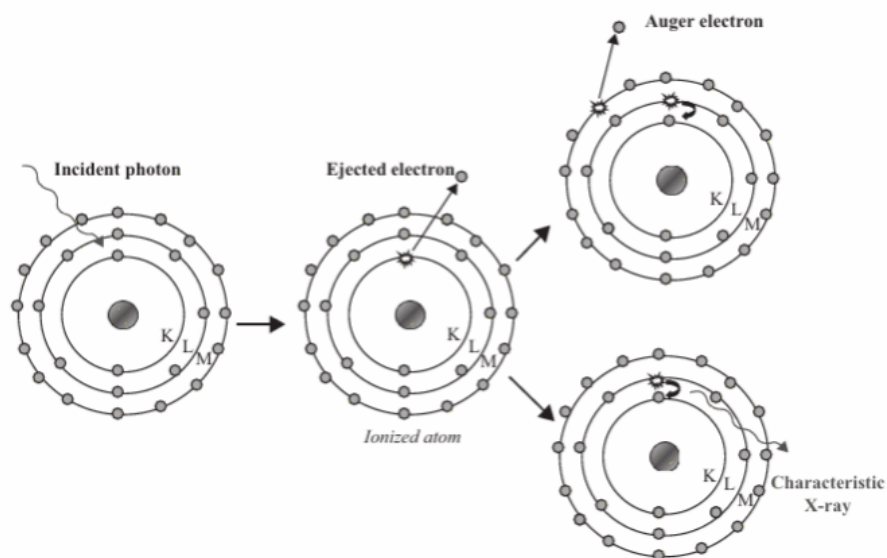


Figure 20. The generation of Auger electrons and X-rays [57, p. 2]

The energy of an X-ray photon is the energy difference between the initial and end states of the electron that is filling the vacancy. When an electron from the L orbital drops to the K orbital, it loses energy which can be measured as K_{α} and K_{β} X-rays. The number of generated fluoresced X-rays and their intensities increase as the atomic number increases. In EDXRF, the energy and the intensity of the fluoresced X-rays are measured by the detector, and it is best suitable for analysing elements having atomic numbers between 20 and 41. Depending on the instrument it is possible to analyse elements with atomic numbers ranging from approximately 11 to 92 with suitable excitation voltage,

filters and preparation of the sample. [58, pp. 344–345] When silicone release coatings are studied, the fluoresced X-rays characteristic to silicon are measured [56, p. 18].

5.8 Release profile

Release profile of a laminate can be used to estimate how the material will behave in conversion [56, pp. 12–13]. In Figure 21, examples of release profiles of three polymer types are presented. In chapter 2.2.1 different polymer types were discussed based on which polymer A is likely to be branched, pendant or multifunctional since their release profile are usually quite stable and the flattest in case of branched polymers. Rising release profiles are seen when end-blocked polymers are chosen.

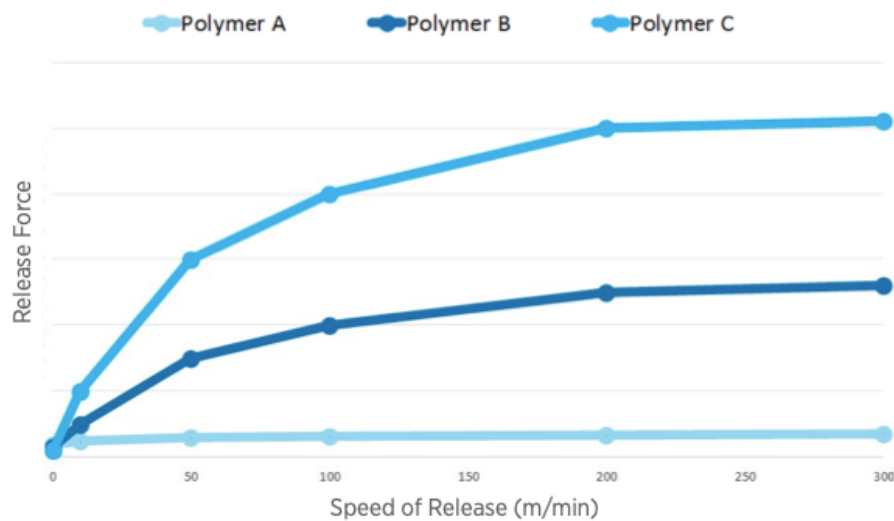


Figure 21. Release profiles of different polymers [55]

To obtain a release profile of a studied laminate, low and high speed release force measurements are done. Both methods include separating the face material and the adhesive from the silicone coated liner, but the separation is done at different speeds [56, pp. 12–13]. In addition to the peel speed, the release force is dependent on the peel angle, coat weights of the silicone and PSA, silicone coverage and rigidity of all components of the laminate [3] [59]. Release values are higher and not as stable with time if the silicone coverage is poor. If there are uncoated areas on the release liner, the adhesive will become in contact with it and releasing the adhesive from the liner will require larger forces. As the thickness of the PSA layer or the silicone increases, their capability to absorb energy when stretched increases resulting in higher release forces. [59]

5.8.1 Low speed release force

Low speed release force describes the force required to separate the adhesive coated material from the release liner or vice versa. The method can be used to evaluate how the laminate will behave in converting. Very low release forces may lead to label fly during label application, whereas high release forces may result in dispensing failures when labels are applied automatically. [56, p. 12] The test assembly used to test low speed release forces is presented in Figure 22.



Figure 22. Test assembly for measuring low speed release force [56, p. 12]

According to the FINAT test method FTM 3, the samples are stored under pressure for 20 hours at $23\text{ °C} \pm 2\text{ °C}$ to assure good contact between the adhesive and the backing. After that the samples, cut to 50 mm wide and minimum length of 175 mm in the machine direction, are taken out of the pressure and stored at standard test conditions of $23\text{ °C} \pm 2\text{ °C}$ and 50 % relative humidity (RH) $\pm 5\text{ % RH}$ for 4 hours before testing. A tensile tester or similar is used to peel the laminate open. The separation is done at an angle of 180° and at a rate of 300 mm/min with an accuracy of $\pm 2\text{ %}$. The peeling angle is maintained by attaching the test piece to a back plate using a double-sided tape. The samples should be taken from a representative laminate and be clean and straight. Low speed release force is expressed as the average of the tested samples in centiNewtons per 50 mm width (cN/50 mm). [56, p. 12] In the tests of this thesis, five parallel measurements were made and the average value was used in the release profile of the laminate.

5.8.2 High speed release force

FTM 4 is used to measure high speed release forces which provide better assessment of how the laminate will behave in conversion. As in low speed release force tests, the pressure sensitive adhesive coated material is peeled from the release liner or vice versa

at an angle of 180°. The speeds used in high speed release force tests were between 10 and 300 m/min and are better comparable to the speeds often used when the material is converted and dispensed. [56, p. 13] In Figure 23, a machine used for high speed release testing is presented.

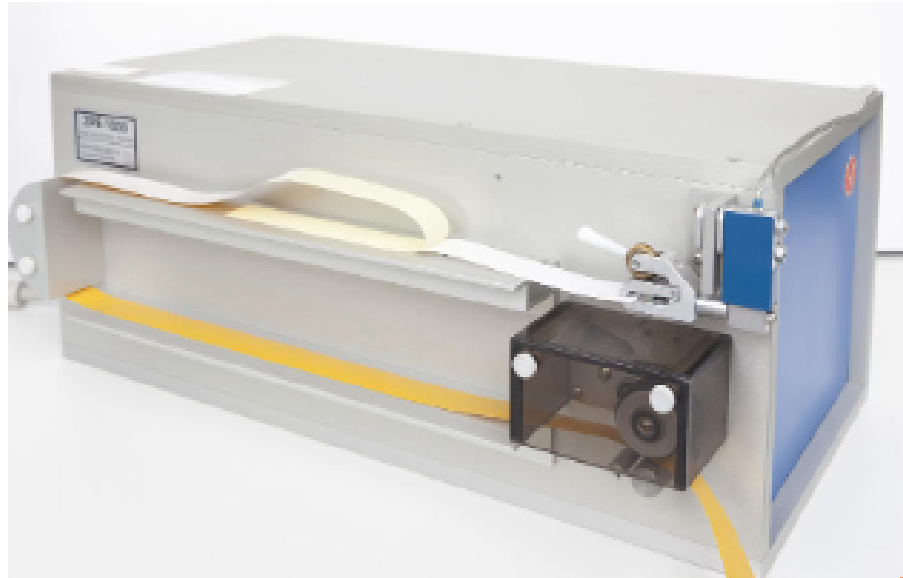


Figure 23. High speed release tester [56, p. 13]

According to FTM 4, the material to be tested is kept under pressure for 20 hours at $23\text{ °C} \pm 2\text{ °C}$, after which they are stored at the standard conditions of $23\text{ °C} \pm 2\text{ °C}$ and $50\text{ \% RH} \pm 5\text{ \% RH}$ for 4 hours. The tested samples should be 25 mm wide and have a minimum length of 300 mm in the machine direction. They should be damage-free, clean and taken from a representative laminate material. High speed release force is expressed as centiNewtons per 25 mm width (cN/25 mm), either as the peak or average value of the samples tested. [56, pp. 13–14] For the tests of this thesis, five parallel samples were measured using peeling speeds of 10, 30, 60, 80, 100 and 200 m/min.

6. RESULTS AND DISCUSSION

The testing phase of this thesis included aerosol monitoring around one coating and laminating machine at UPM Raflatac as well as viscosity and DSC measurements of the studied silicone formulations. Laminate material consisting of the silicone coated liner, adhesive and face material was also gathered from the same production run of which the other measurements were conducted. Release profiles, rub-offs, surface energies and surface topographies were studied using the laminate material. In this chapter, results of the measurements for different silicones are compared and results from multiple measurements are combined to gain a better understanding of the materials and conclusions are made based on them.

6.1 Aerosol monitoring

The aerosol concentration of the surrounding air was monitored when no production was ongoing which was used as a reference, and when the five silicone formulations were coated on liner substrates and laminate materials were produced. The measurements were conducted at ten locations around the machine and five of them were included in the final results: siliconizing station (1), beginning of the oven system (2), middle area of the oven system (3), end of the oven system (4) and area near the laminate closing roll further away from the silicone end of the machine (5). Those five locations were considered the most relevant as the first four measurement points were places where misting was expected to occur, and the last measurement point was included because it was further away from the silicone end of the production line and silicone misting should not have been observed there. Because this measurement method had not been in wide use before, the accuracy and the deviation of the results was not known. To study that, five subsequent measurements were made at the siliconizing station. The standard deviation of the aerosol concentrations observed there was 0.01 mg/m^3 .

It was expected that the reference measurements would give the lowest aerosol concentration values and that some differences between the silicone formulations would be observed. The results are presented in Figure 24. Particles with diameters ranging from 0.1 to $15 \text{ }\mu\text{m}$ were decided to be included in the results.

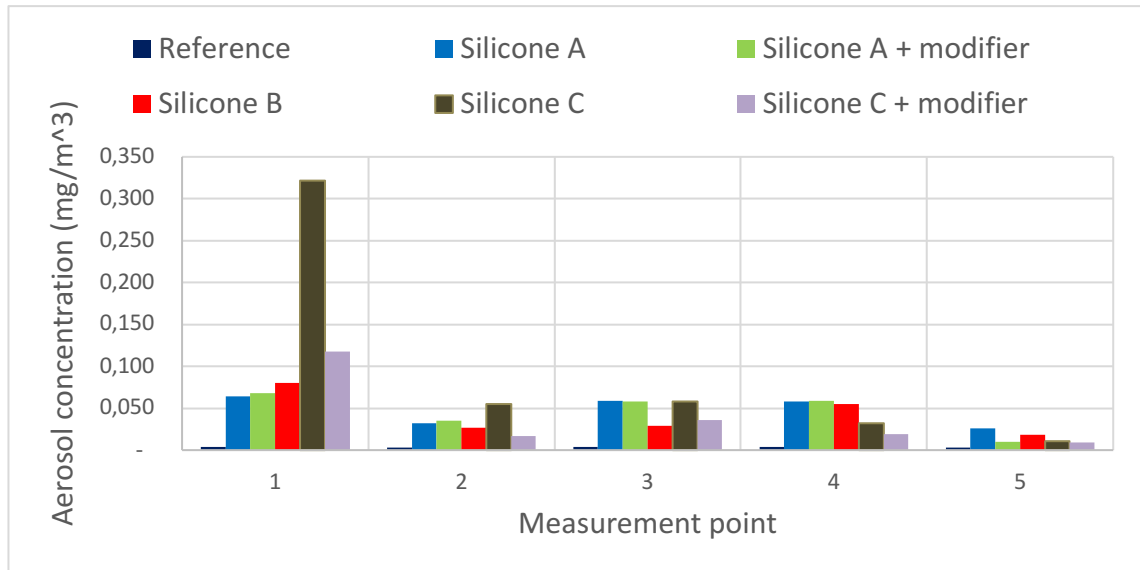


Figure 24. *Aerosol monitoring results including the particles with diameters between 0.1 and 15 μm*

Misting is said to be the generation of droplets having a diameter of less than 50 μm [60]. The size of the silicone mist particles was not known, and the monitor used in the studies of this thesis was able to detect particles with diameters only up to 15 μm . That is why the total particle size range of the monitor was chosen to be included in the results. Other possible range would have been the PM10 including particles with diameters between 0.1 and 10 μm because as discussed previously in Chapter 4.3.2, those particles are inhalable and thus could affect human health. Aerosol concentrations were very similar for PM10 and PM Total. That is why it can be concluded that almost all particles observed in the studies were small enough to be inhaled and based on their size could cause health effects.

As expected, the aerosol concentrations of the reference measurements were significantly lower at every measurement point compared to a situation where any of the studied silicones were coated. The highest aerosol concentrations were observed at the silicizing station where silicone C produced the highest amount of particles, followed by silicone C + modifier where the only difference between the two silicones was the low amount of modifier. When silicone B was coated, the aerosol concentration was the next highest, and silicones A and A + modifier produced the lowest concentrations, slightly lower when silicone A was coated.

When looking at the aerosol concentrations and how they evolved throughout the oven system at measurement points 2, 3 and 4, differences in how the aerosol concentrations changed when moving from the beginning of the ovens towards the end can be seen. In the case of silicones A and A + modifier the aerosol concentration was at its lowest at

measurement point 2, increased by measurement point 3 and remained practically the same at the end of the ovens. Aerosol concentration in the beginning and in the middle of the oven system was nearly the same when silicone B was coated but the highest at the end of the ovens. Silicone C + modifier produced an aerosol concentration that was the lowest of all silicones at measurement points 2 and 4. The concentration increased slightly at the middle of the oven system and then decreased to nearly the same value as at the beginning. When silicone C was coated, the aerosol concentration was the highest of all silicones at measurement point 2, remained nearly the same at measurement point 3 and decreased almost by half by the time it reached the measurement point 4.

At the final measurement point further away from the silicone end of the coating and laminating machine, where no silicone misting should be observed, the aerosol concentrations were quite low. There were some differences between the measurements but those can most probably be explained mainly by the presence of other particles such as dust originating from the face materials, especially paper. Misting occurred in the case of all silicones, but all concentrations were significantly lower than the common industry threshold level of 5 mg/m^3 or threshold levels told by ECHA which were discussed in Chapter 4.3.2.

6.1.1 The effect of line speed

Line speeds during the aerosol monitoring were not the same when all silicones were coated which most probably affected the results and how well they can be compared. Line speed during the measurements was low when coating silicone A + modifier, medium in the case of silicones A, B and C + modifier and high when silicone C was coated. The difference in line speeds when coating silicone A + modifier and silicone C was 100 m/min and could at least partly explain the much higher aerosol concentrations observed with silicone C at measurement points 1 and 2.

Aerosol monitoring was conducted for the second time when silicone C + modifier was coated at a higher line speed. Comparison of the two results is presented in Figure 25 including the ratios between the aerosol concentrations observed at each measurement point.

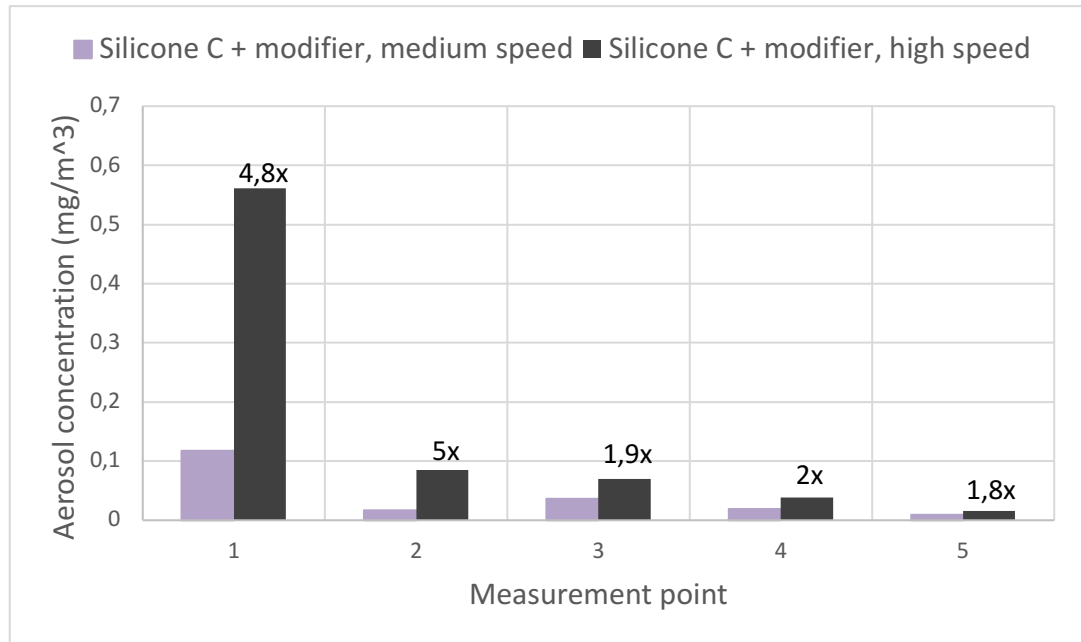


Figure 25. A comparison of the aerosol monitoring results of silicone C + modifier being coated at two different line speeds and the ratios of the aerosol concentrations

During the two measurements the silicone formulation was the same and there should not have been any other major differences between the two production runs but the line speeds. These measurements showed that an increase in line speed results in much higher aerosol concentrations which was also acknowledged in Chapter 4.1 where misting phenomenon was discussed.

6.1.2 Properties of the silicones and their effects

Viscosities of the silicones were measured to study if a higher viscosity of the silicone would be seen as higher aerosol concentrations measured at the siliconizing station. In Chapter 4.1 the effect of viscosity on misting was discussed and based on the theory there should be a significant increase in aerosol concentration with increasing viscosity. The aerosol concentration measured at the siliconizing station as a function of viscosity of the silicone formulation is presented in Figure 26.

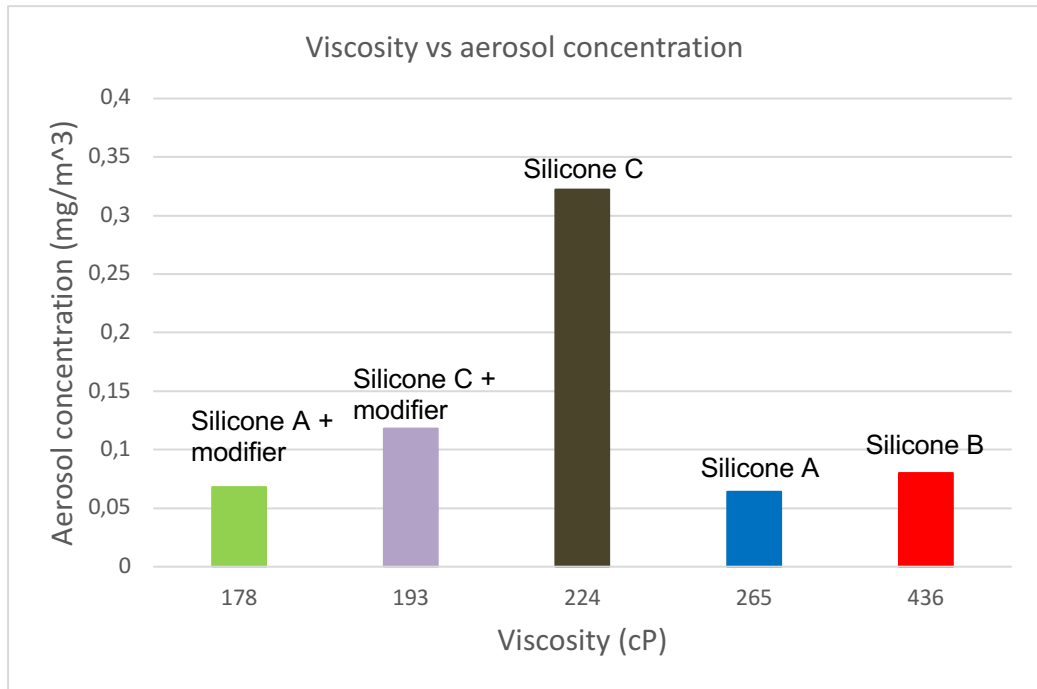


Figure 26. *Aerosol concentration at the siliconizing station as a function of the viscosity of the silicone*

As seen from Figure 26, there seems to be no correlation between the viscosity of the silicone and the amount of particles in the air at the siliconizing station based on the results of these measurements. Silicone A + modifier had the lowest viscosity and the second lowest aerosol concentration, very close to the aerosol concentration of silicone A which had the second highest viscosity. Silicones A, B and C + modifier were coated at medium line speed and could thus be better compared with each other but the effect of viscosity seems to be the opposite to what was expected. The viscosity of silicone C + modifier was the lowest of the three silicones, but the aerosol concentration was the highest. The viscosity of silicone B was clearly the highest, but the aerosol concentration was only 67% of the aerosol concentration of silicone C + modifier.

The polymer type used in silicones A, A + modifier and B was branched, whereas in silicones C and C + modifier a multifunctional polymer type of polymer was used. By comparing the three silicones coated at the same speed range it seems that a multifunctional polymer structure could produce more mist than a branched one. The aerosol concentration at the siliconizing station in the case of silicone C + modifier was 48% higher than the aerosol concentration when silicone B was coated and 84 % higher compared to when silicone A was coated. It is difficult to evaluate how much the other differences between the silicone formulations have affected the mist concentrations.

The effect of modifier use could not be easily analysed because the line speeds were not the same for the same silicones with different modifier contents. The aerosol concentrations for silicones A and A + modifier were very close to each other at the siliconizing station as well as throughout the oven system even though the difference in modifier content was very significant. If silicone A + modifier would have been coated at the same line speed as silicone A, the aerosol concentrations would most probably have been higher with the silicone including the modifier. That would indicate that the addition of modifier leads to heavier misting. In silicone C + modifier only a small percentage of modifier was added compared to silicone C but the aerosol concentrations were very different at the measurement points mentioned earlier, much higher in the case of silicone C where no modifier was added. The difference in line speeds between silicones A and A + modifier as well as C and C + modifier was nearly the same, but the speeds were higher when silicones C and C + modifier were coated.

Based on these results it seemed that the use of modifier did not greatly affect misting but affected the viscosity of the silicone by lowering it. The viscosities of the components in silicone formulations were discussed in Chapter 5.1 and it could have been expected that the addition of modifier would have been seen as an increase in viscosity because the viscosity of the release modifier added in the formulations of silicones A and C was multiple times the viscosity of the polymers used in those formulations.

The viscosities of silicones A and A + modifier and silicones C and C + modifier were all within 87 cP, whereas the viscosity of silicone B was over 170 cP higher than the viscosity of silicone A which was the highest of the first four silicones mentioned. Silicone B had the highest viscosity, but the aerosol concentration was not much higher than in the case of silicones A and A + modifier. The highest aerosol concentrations at the siliconizing station were when silicones C and C + modifier were coated and distinctly the highest with silicone C.

The viscosity and aerosol concentration measurements were not conducted at the same time but in most cases within an hour or two from each other. That may also have affected the results as the bath life indicating the time from mixing the components of the silicone formulation to the viscosity measurement was not the same in all cases. Ambient conditions, for instance temperature might have also been different at the times of the measurements and could have affected the results.

6.1.3 Comparison according to aerosol particle size

In Chapter 4.3.2 health effects related to silicone misting were discussed. PM_{2.5} and PM₁₀ were mentioned to be able to reach or even penetrate the lungs. The aerosol

concentrations corresponding to PM_{2.5}, PM₁₀ and PM Total which was used in the previously introduced results are gathered in Table 3.

Table 3. *Different particle size concentrations observed at the siliconizing station*

PM	Silicone A (mg/m ³)	Silicone A + modifier (mg/m ³)	Silicone B (mg/m ³)	Silicone C (mg/m ³)	Silicone C + modifier (mg/m ³)
2.5	0.049	0.036	0.072	0.291	0.098
10	0.064	0.066	0.08	0.320	0.117
Total	0.064	0.068	0.08	0.322	0.118

As mentioned before, there were close to no differences between the aerosol concentrations of PM₁₀ and PM Total indicating that nearly all observed particles had a diameter of $\leq 10 \mu\text{m}$. As discussed in Chapter 4.3.2, particles included in PM₁₀ are small enough to be able to reach the lungs. A significant difference is seen when comparing the PM_{2.5} results to PM₁₀ or PM Total. With all silicones, the amount of particles corresponding to PM_{2.5} was more than 50% of the total aerosol concentration, 53% at its lowest in the case of silicone A + modifier and the highest with silicones B and C where the percentage was 90. A significant share of the particles present at the siliconizing station were so small that they are able to penetrate the lungs, but the aerosol concentration when all silicones were coated was much lower than the threshold levels discussed in Chapter 4.

6.2 Differential scanning calorimetry

DSC measurements were done for all studied silicones by heating the samples at a rate of 10 °C/min up to 160 °C. The DSC curves are presented in Figure 27. The curves of silicones C and C + modifier were very much the same which seems reasonable because the only difference between them was the low amount of modifier in silicone C + modifier. Silicones A and A + modifier were the same except the quite significant amount of modifier in silicone A + modifier. Differences were seen at least in peak height and the temperature at which the crosslinking reaction began. Silicone B was the slowest to activate and also had the lowest peak.

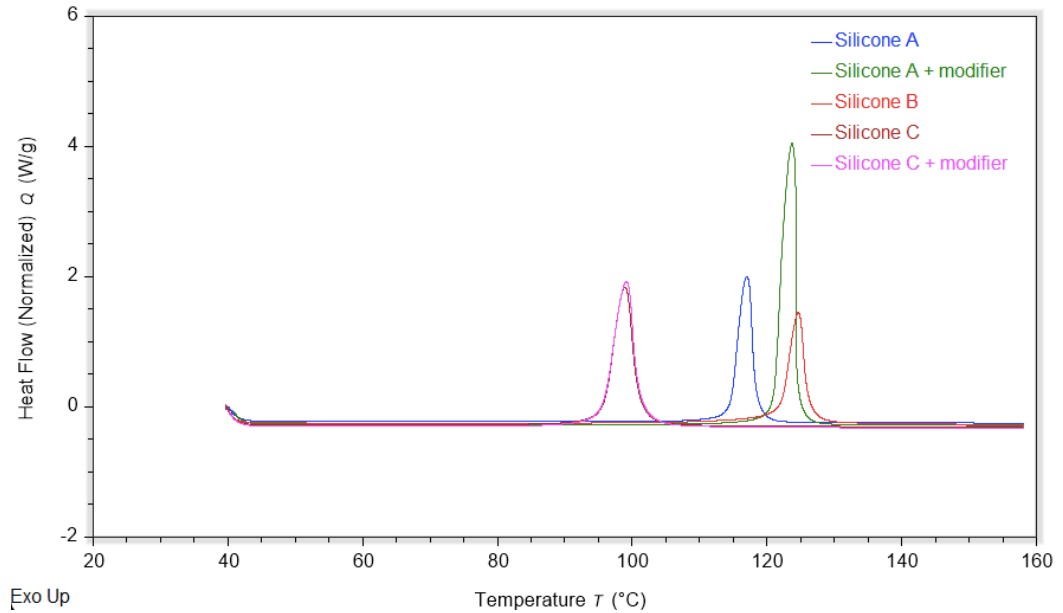


Figure 27. DSC curves of the five silicone formulations

In Table 4, temperatures at which the crosslinking reactions started, peak temperatures, peak heights and reaction enthalpies are listed. Based on them, the curing behaviour of the silicones could be compared.

Table 4. Temperatures, peak widths, peak heights and enthalpies gathered from the DSC measurements

Silicone	Onset temperature (°C)	Peak temperature (°C)	Peak height (W/g)	Peak width at half height (°C)	Enthalpy (J/g)
A	115	117	2.2	2.4	35.5
A + modifier	121	124	4.3	2.3	54.3
B	122	125	1.7	2.5	35.3
C	96	99	2.1	3.2	48.9
C + modifier	96	99	2.2	3.3	54.2

The effect of modifier can be seen when comparing silicones A and A + modifier. All values listed except width of the peak at half of its height are higher in the case of silicone A + modifier. The addition of modifier to the silicone formulation shifts the curing reaction to higher temperatures meaning that the reaction requires more energy, and it takes longer for the silicone to activate. The DSC measurements at the heating rate of 10

°C/min took minutes whereas the time the silicone spends in the oven system in the process of laminate production is only a few seconds as discussed in Chapter 3. In production the temperature is increased much faster, and the few seconds are enough to crosslink the silicone network.

Because there is a slight difference in the peak width it can be said that the crosslinking reaction of silicone A takes a little longer to go through than crosslinking of silicone A + modifier. Peak height in the case of silicone A + modifier is nearly double the height of the peak of silicone A indicating a higher vinyl content which is also seen as an increase in enthalpy. In Chapter 2.2.4 release additives were discussed and it was told that their use results in cure occurring later than it would without the additive.

The only difference between silicones C and C + modifier was the low amount of modifier. The amount of modifier in silicone C + modifier was so low that no significant differences were seen in the temperatures but the peak temperature as well as peak height, peak width at half height and enthalpy were higher in the measurement of silicone C + modifier. This was in line with the conclusions made on the effect of modifier based on silicones A and A + modifier. In Chapter 5.4 it was discussed that the peak width at half of its height should be ≤ 3 °C but in the case of silicones C and C + modifier it was slightly above that. Based on the measurements it can be said that the crosslinking reaction of silicones C and C + modifier began a lot earlier than the reactions of the other silicones, but the reaction took slightly longer to go through.

Silicone B had the highest onset and peak temperatures, really close to the ones of silicone A + modifier. These two silicones took the longest time to activate based on the results of these measurements. Peak height was the lowest with silicone B and its peak was slightly wider compared to silicones A and A + modifier but narrower compared to silicones C and C + modifier. The enthalpy of silicone B was very close to the enthalpy of crosslinking of silicone A.

Silicones A, A + modifier and B had a branched polymer structure, whereas silicones C and C + modifier were multifunctional. The different polymer structure might have been the reason for why silicones C and C + modifier began to react earlier. In Chapter 2.1.1 different polymer types were discussed and that both branched and multifunctional polymers are fast to react because due to their structure they have many opportunities to react. In the case of branched polymers, the reaction seems to go through faster based on peak widths, but the multifunctional polymers would affect curing in a way that the reaction occurs at lower temperatures.

As discussed earlier, when silicone is coated in the coating machine, the speeds are naturally many times higher leading to the silicone heating up and activating much faster. The effect of changing the heating rate on DSC curves is commonly acknowledged but was also studied in this thesis by heating one silicone also at lower rates than 10 °C/min.

In a study of composites based on PDMS matrices their curing behaviour was examined with DSC by heating the materials at different rates. In the DSC measurements of neat PDMS it was noticed that as the heating rate was decreased the reaction shifted to lower temperatures and a decrease in reaction enthalpy was also observed. [61]

The DSC measurements were done for silicone C + modifier also at heating rates of 3, 5 and 7 °C/min and the curves are presented in Figure 28 including the curve from Figure 27. For comparison, the values determined from the curves for silicone C + modifier at different heating rates are listed in Table 5.

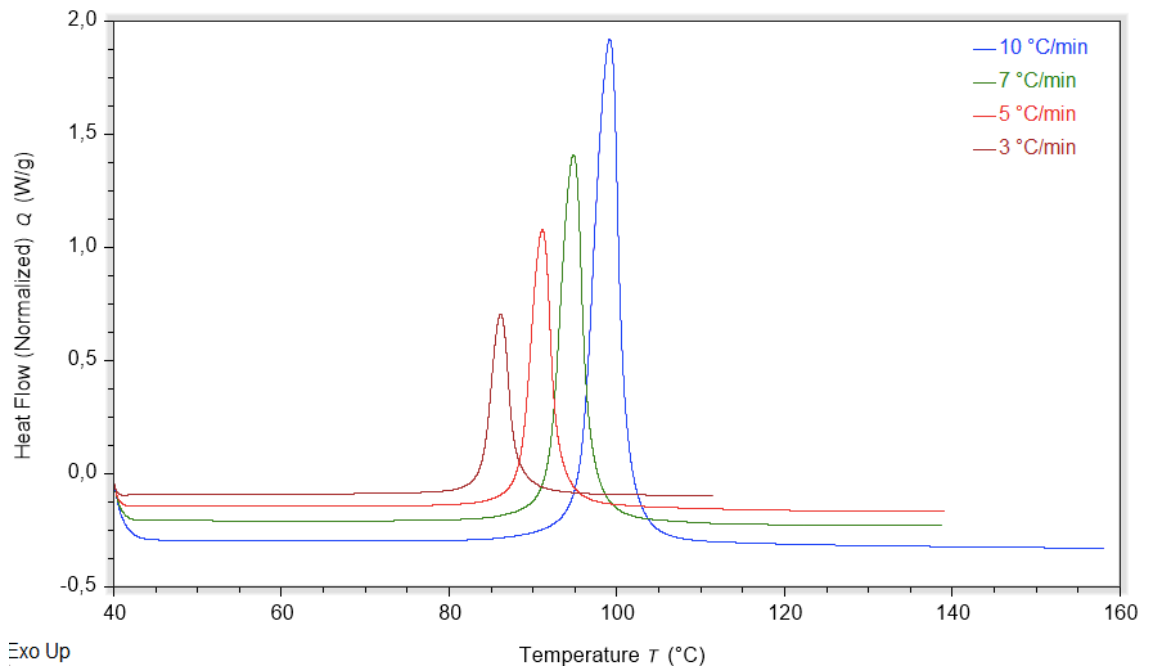


Figure 28. DSC curves of silicone C + modifier heated at different rates

Table 5. *Temperatures, peak heights, peak widths and enthalpies gathered from the DSC curves in Figure 28*

Heating rate (°C/min)	Onset temperature (°C)	Peak temperature (°C)	Peak height (W/g)	Peak width at half height (°C)	Enthalpy (J/g)
10	96	99	2.2	3.3	54.2
7	92	95	1.6	3.0	51.7
5	88	91	1.2	2.7	54.5
3	84	86	0.8	2.4	52.8

Based on the values listed in Table 5 it can be seen that as the heating rate was decreased, the reaction occurred at lower temperatures and the peak height as well as peak width at half of the peak height decreased. No significant differences were observed in reaction enthalpies, but they were not always decreasing with decreasing heating rate. At the coating and laminating machine, the direction is the opposite and the reaction occurs at much higher temperatures. In that case the peak would be much higher and wider at half of its height and the enthalpy should be significantly higher.

6.2.1 Results combined with aerosol monitoring

The DSC measurements were used to study curing of the five silicone formulations. At the coating and laminating machine, curing of the silicone occurs in the oven system. That is why it seemed reasonable to analyse the results of the DSC measurements together with the aerosol monitoring results gathered around the oven system. Based on the DSC measurements, silicones C and C + modifier were the fastest to activate, followed by silicone A, while silicones A + modifier and B took the longest time. In Chapter 5.1 the silicone formulations were discussed, and the polymer used in silicones C and C + modifier was told to be able to cure at low temperatures which was also seen in the DSC results.

After the silicone is coated on the liner, it goes into the ovens where temperature is increased in a matter of seconds to temperatures between 100 and 200 °C, and the inhibitor should evaporate allowing the silicone to crosslink. The crosslinking reaction should

have finished by the end of the ovens, and it could be assumed that a decrease in misting would be seen after the reaction has fully taken place.

Looking at the aerosol monitoring results the aerosol concentration was not as high at the end of the oven system when silicones C and C + modifier were coated. That can be explained by the fact that these silicones activated at lower temperatures in the DSC measurements and the difference to the other silicones was quite significant. This indicates that the cure could have completed sooner compared to the other silicones which were seen to require more energy before the crosslinking reaction began. Peaks on the DSC curves were wider in the case of silicones C and C + modifier compared to others indicating that the curing reaction itself would last a slightly longer time, but it is assumed that all the studied silicones were fully cured by the end of the oven system and the peak width does not have much significance.

Silicone B had a rising aerosol concentration through the oven system, although the concentrations at the beginning and at the middle were very close to each other after which it was nearly doubled by the oven end, to a concentration corresponding to silicones A and A + modifier. Based on the DSC measurements, silicone B took the longest time before activation which could explain the increase in aerosol concentration towards the end of the oven system.

Although the onset temperature of the crosslinking reaction of silicone A was several degrees Celsius lower than the onset temperature of silicone A + modifier, practically no differences were seen in the aerosol monitoring results. In both cases, the aerosol concentration was at its lowest at the beginning of the ovens and increased to a level that remained basically the same by the end of the ovens. As mentioned earlier there was a difference in line speeds when the aerosol monitoring was done for silicones A and A + modifier which was coated at low speed while silicone A was coated at medium speed. The difference in line speeds might have excluded the effect of modifier which shifted the curing reaction to higher temperatures because more energy and time was needed to activate curing. With a lower line speed, the heating rate is also lower. As the DSC curves in Figure 28 showed, when the heating rate was decreased the curing reaction shifted to lower temperatures. That effect could be the reason for why the aerosol concentrations were so similar with silicones A and A + modifier. If the line speeds would have been the same, silicone A + modifier would most probably have produced more mist than silicone A and the aerosol concentration would have increased towards the end of the oven system similar to silicone B which also required a longer time before the reaction was activated.

6.3 Contact angle and surface energy

Surface energies of the studied silicones were examined, and the thought was that if clear differences were observed between the different silicone formulations, the results could possibly be combined with some other test methods and the misting phenomenon. Maybe a silicone with a higher surface energy could have produced less mist because the higher surface energy particles would have been more heavily attracted by the silicone surface than particles with lower surface energies.

Contact angles were measured from the five silicone surfaces using water, diiodomethane and benzyl alcohol. Based on the contact angle measurements including ten measurements with each test liquid, surface energies of the silicones were determined according to the method of Wu. The results are presented in Table 6. Contact angle hysteresis and thus the surface irregularity was studied by calculating the differences between contact angles of the left and right side.

Table 6. *Surface energies determined using the method of Wu*

Silicone	Surface energy (mN/m)	Contact angle hysteresis (°)
A	20.1 ± 5.0	0.05 ± 0.06
A + modifier	19.2 ± 7.3	0.06 ± 0.02
B	17.5 ± 8.8	0.02 ± 0.01
C	19.9 ± 3.3	0.06 ± 0.08
C + modifier	20.0 ± 6.2	0.16 ± 0.09

Silicone B had the lowest surface energy, whereas surface energies of the other four silicones were quite close to each other, the highest in the case of silicone A. Standard deviations of the results were quite high in case of all silicones, highest with silicone B. Rougher surface of paper compared to a smoother surface of PET can be seen in contact angle hysteresis. The hysteresis was the lowest with silicone B which was the only one coated on PET, while the other silicones were coated on paper substrates.

The surface energies were determined using a method which was based on measuring the contact angles of different test liquids dropped on the siliconized surfaces and the angles were then used in the surface energy calculations. Because the surface energy was not directly measured from the silicone surface, the substrate on which the silicone

had been coated did have an effect on the results. The surface energy of silicone B coated on PET liner was the lowest meaning that the contact angles were the highest. That was most probably affected by the smoother surface of PET, and it was not possible to conclude that the surface energy of silicone B would have actually been the lowest. Because of the effect of the liner material on the results, this method was not possible to be reliably used to compare the different silicone formulations and thus combined with the misting phenomenon.

The addition of modifier affects the chemistry of the silicone but there were no clear differences in the results. Surface energies of silicones C and C + modifier were nearly the same, but a slight difference was seen when comparing silicones A and A + modifier. The paper liners used with silicones A and A + modifier were the same and if it is assumed that the adhesive had not interacted with the silicone, it could be said the addition of modifier slightly decreases the surface energy of the silicone.

6.4 3D Optical profilometry

An optical profilometer was used to image the different silicone surfaces. The images are shown in Figure 29. To be able to compare the surfaces, all images are presented in the same scale. Silicone B had the smoothest surface which can be seen as the surface being purely green, whereas in case of other silicones there are other colours present as well to indicate that there were some differences in surface heights. In Figure 30, an image of silicone B with a different scale shows that there are also surface height differences with silicone B but much smaller compared to the silicone surfaces.

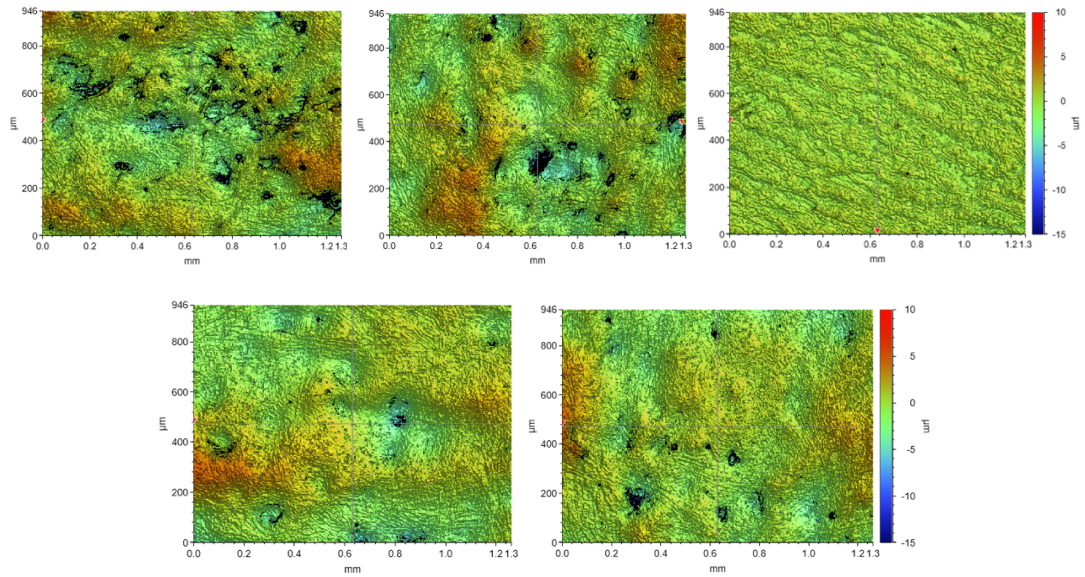


Figure 29. Silicone surfaces imaged with an optical profilometer. On the upper row from the left: silicone A + modifier, silicone A and silicone B, and on the lower row from the left: silicone C + modifier and silicone C

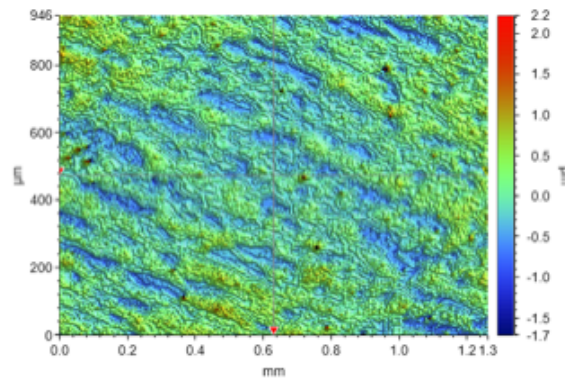


Figure 30. The surface of silicone B imaged on a different scale

Roughness average (Ra) values were also determined from the surface images. The Ra values are listed in Table 7.

Table 7. *The average Ra values of the siliconized surfaces*

Silicone	Ra (μm)
A	1.5 ± 0.3
A + modifier	1.4 ± 0.4
B	0.3 ± 0.0
C	1.2 ± 0.1
C + modifier	1.4 ± 0.1

As mentioned earlier, silicone B was coated on PET, whereas the other silicones were coated on paper which can be seen in the roughness values. In Chapter 5.5 contact angle hysteresis occurring in the surface energy measurements because of surface heterogeneity was discussed. These Ra values are in line with the results where there was the least contact angle hysteresis in case of silicone B. The standard deviation being the lowest with silicone B also indicates that the surface was really smooth compared to the silicone surfaces on paper substrates.

6.5 Rub-off

Rub-off was done to test how well the silicone was anchored to the liner substrate. It could be hypothesized that the weaker the silicone is holding itself together and is anchored to the liner substrate, the more it would mist. The rub-off percentages are listed in Table 8 where the closer the result is to 100% the better it is.

Table 8. *Results of the rub-off measurements*

Silicone	Rub-off (%)
A	95 ± 1
A + modifier	92 ± 2
B	96 ± 1
C	99 ± 0
C + modifier	99 ± 1

Based on the results it seemed that silicones C and C + modifier were the best anchored to the paper surfaces they were coated on whereas silicone A + modifier had the lowest result indicating that the anchorage was the poorest. Silicones A and B had quite the same rub-off values. In the rub-off test, the silicone surface was rubbed against a rough material and it could be thought that rubbing two rough surfaces together would result in more silicone rubbing off compared to a situation where the other surface is smooth. If this was true, the rub-off value of silicone B would have been the best because the silicone was coated on PET which had a lot smoother surface than paper on which the other silicones were coated. This was true with the first three silicones but not with silicones C and C + modifier where there was very little rub-off.

The hypothesis of more rub-off being in line with heavier misting did not seem to be true at least based on these measurements and rub-off would not be a useful tool in estimating the extent of misting phenomenon. The highest aerosol concentrations were observed with silicones C and C + modifier but their rub-off results were the best. In the case of silicone A + modifier the laminate material used in the measurements was not produced at the same time as the aerosol monitoring was done and the line speeds were different in those two situations. The laminate was produced at a high line speed, highest of all the studied laminates, and the difference was quite significant compared to the line speeds at the time of aerosol monitoring when silicone A + modifier was being coated. The higher line speed means that the time spend in the ovens was shorter which could have affected curing and how well the silicone anchored to the liner. This could be one reason for a poorer rub-off result of silicone A + modifier.

The addition of modifier to the silicone formulation might have affected the rub-off based on the results. Silicone C had no modifier, whereas a small amount of modifier had been added to silicone C + modifier but otherwise the two silicones were the same. In that case the difference in rub-offs was not significant. In the case of silicones A and A + modifier the difference in rub-offs was much clearer and so was the amount of modifier used in silicone A + modifier. It was anchored to the paper much poorer compared to silicone A. Paper liners used to produce laminates including the silicones A and A + modifier were the same, but the adhesive was different. It was expected that no interactions occur between the adhesive and the silicone. If that holds true, the addition of modifier to silicone A + modifier could be one reason for its poorer rub-off result.

Three parallel rub-off measurements were done for each siliconized material by taking the samples from the width of one A4 sized laminate. The standard deviations provide some idea of the consistency of the silicone layer and based on these results it seems

that the surface of silicone A + modifier was the most inconsistent. Taking more measurements or taking the parallel samples across the web width would have provided more reliable information of the material. Rub-off is also quite a rough method because as discussed in Chapter 5.7, rub-off can be caused either by adhesive failure meaning that the silicone detaches from the liner as a result of rubbing or cohesive failure where the silicone layer itself would break.

6.6 Release profile

Release profiles of the five tested laminates were gained by measuring the force needed to separate the face material including the adhesive from the silicone coated liner. The release speeds used in the measurements were 0.3, 10, 30, 60, 80, 100 and 200 m/min. The release profiles of the five tested materials are shown in Figure 31.

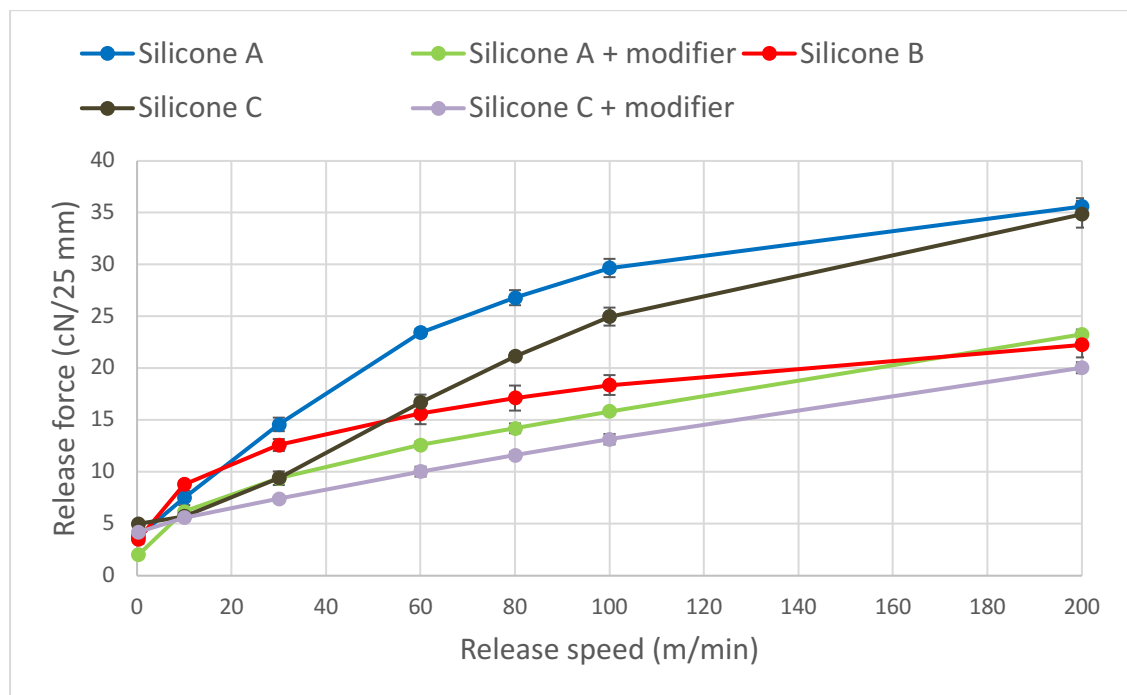


Figure 31. Release profiles of the tested laminates

All materials showed rising release profiles throughout the release speeds meaning that the release force always increased as the release speed was increased. Even though all profiles were rising there were differences in how steeply they rose with increasing release speed.

In Chapter 5.1 the studied silicone formulations were discussed and according to the supplier, silicones A and A + modifier provide very low release values, silicone B was told to produce a slightly rising release profile and silicones C and C + modifier were to be used in applications where low release forces at high release speeds were required.

That effect is seen in the case of silicone C + modifier which had the lowest release forces at higher release speeds. The release profile of silicone B also corresponds well with the information provided by the supplier and had a slightly rising release profile. Silicone A + modifier had low release values but slightly higher than silicone C + modifier nearly all release speeds. The release modifiers were told to provide efficient modification of release forces at low peel speeds.

The effect of modifier can be looked at by comparing silicones A and A + modifier as well as silicones C and C + modifier. Silicone A had no modifier and its release profile rose much steeper than the profile of silicone A + modifier. The effect of modifier as a flatter release profile can also be seen when comparing silicone C + modifier where a low amount of modifier had been added to silicone C. Based on these results, the effect of modifier could be seen as flatter release profiles and the effect seemed to be really significant. At all release speeds, release forces of silicone A were higher than in the case of silicone A + modifier and release forces of silicone C were higher than release forces of silicone C + modifier. The difference was much smaller at lower release speeds compared to higher speeds. It needs to be noted that the adhesives were not the same which made comparing release profiles of these laminates very difficult and the silicone release coating could not be considered the only variable.

Silicone B was used only without a modifier, but its release profile was similar to the silicones A + modifier and C + modifier. Release forces of silicone B increased as the release speed was increased but the shape of the profile remained fairly flat.

Silicones A and A + modifier as well as silicone B had a branched polymer structure, whereas silicones C and C + modifier had a multifunctional polymer structure. In Chapter 2.2.1 different polymer types were listed, and it was told that multifunctional polymers have flat release profiles, whereas branched polymers provide the flattest release profiles. Based on the measurements done for this thesis, the flattest profiles were seen in case of silicones A + modifier, B and C + modifier of which silicones A + modifier and B were branched and silicone C + modifier had a multifunctional polymer structure. Based on the difference between the highest and lowest speed releases, silicone C + modifier with the multifunctional polymer had the flattest release profile followed by silicones B and A + modifier with branched polymer structures. The situation might have been different without the presence of the other variables including the adhesives, face materials and liner substrates.

The combination of a face material, adhesive, silicone and liner are designed to fill certain end use requirements. Because the test materials were gathered from production as they

were produced and no special trials were arranged, it was not possible to test laminates where the silicone formulation would have been the only variable. As a result, the tested laminates consisted of different faces, adhesives and liners in addition to the different silicones. All other tests except release profiles were made for the siliconized liner after removing the face and the adhesive. It was assumed that the adhesive had not interacted with the silicone layer in a way that would have affected the results, but the face and the adhesive most probably had some effect on the release profiles because the release measurements were done for the whole laminate material.

It was possible to gather some laminates with faces of two different grammages while the adhesive, silicone and liner remained the same. That enabled studying the effect of the face material thickness on release values. Release profiles of silicones A + modifier and C + modifier with different faces are shown in Figure 32. Face 1 refers to the face that has been part of the laminate used in the results of Figure 31 and face 2 refers to a face of higher grammage.

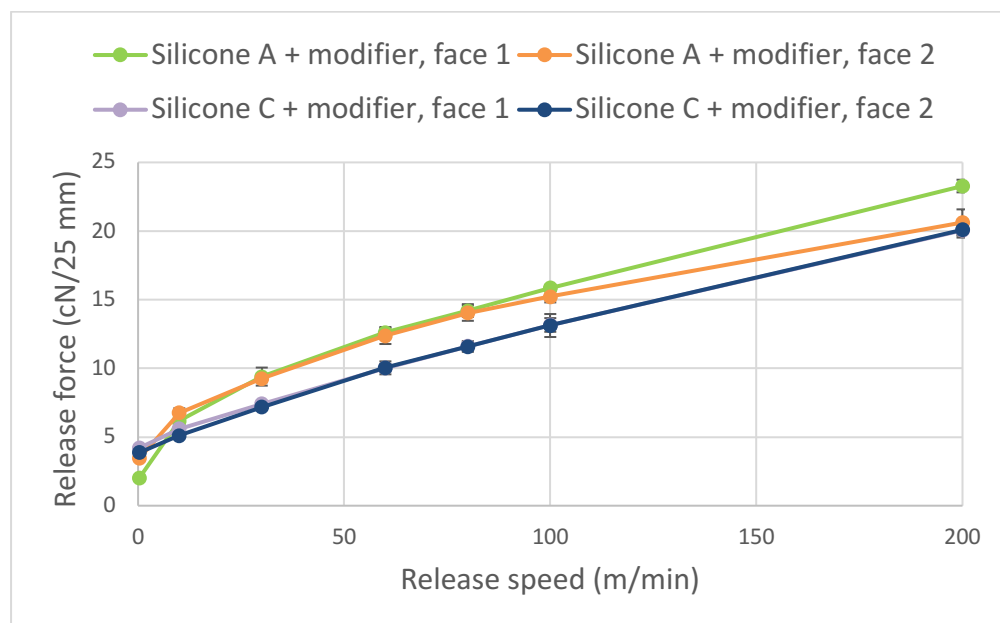


Figure 32. *The effect of the thickness of the face material on release values*

The thickness of face 2 with silicone A + modifier was over double the thickness of face 1 and the difference in release values was also much more significant than in the case of the two faces with silicone C + modifier. Face 2 with silicone C + modifier was only below 1.5 times the thickness of face 1 and practically no differences were seen in release values. The faces of the five laminates tested in this thesis were very close to each other in thickness and the effect of the face material thickness can thus be considered irrelevant. The effects of the other properties of the face materials and the adhesives still remained and were not studied further.

7. CONCLUSIONS AND FUTURE PROSPECTS

The aim of this thesis work was to study silicone misting when different silicone formulations were coated, and pressure sensitive label materials were produced. Misting of silicone is an issue occurring especially with higher line speed coating causing effects for human health as well as concerns in production. Misting can be prevented to some degree with the use of anti-misting additives and adjustments of the coating operation.

Misting is considered to occur mainly at the multi roll coating station but also in the oven system where the crosslinking reaction of the silicone occurs after the inhibitor evaporates. The tests made for this thesis included aerosol monitoring around one coating and laminating machine at UPM Raflatac, differential scanning calorimetry (DSC) and viscosity studies of the silicones as well as surface energy and topography, rub-off and release measurements. These methods provided information on the aerosol concentration present in the surrounding air during coating operations of the studied silicones, their curing behaviour, the siliconized liner surfaces and how the silicones behaved mechanically. The objective was to study misting of different silicone formulations, use certain laboratory measurements to compare the silicones and find out if those laboratory measurements could be used in predicting the misting phenomenon observed in production.

As a result, differences in misting of the studied silicones were observed. At the siliconizing station where the silicone was applied on the liner, silicones having a multifunctional polymer structure produced the highest mist concentration, while the ones with a branched polymer structure showed lower concentrations. The situation was no longer the same in the oven system where the aerosol concentrations evolved differently going from the beginning towards the end of the oven system. The differences were quite well explainable with the DSC results which provided information on the curing behavior of the silicones and allowed them to be easily compared. The idea of increased misting with increasing line speed was verified based on these measurements and it seemed that the addition of release modifier could lead to heavier misting. Based on the measurements there was no correlation between higher viscosity of the silicone and higher aerosol concentration observed at the coating station. The health effects of silicone misting were considered to be of high importance and based on the measurements done for this thesis, the aerosol concentrations were much lower than the threshold levels discussed in Chapter 4.

The other measurements were not able to be combined with the misting phenomenon. Rub-off was used to study anchorage of the silicones to the liner substrates and the results showed quite good anchorage in case of nearly all silicones. One silicone containing a significant amount of modifier showed poorer rub-off results which may have been caused by the addition of modifier or the high line speed when the laminate was produced. The assumption of more silicone rub-off being seen as higher aerosol concentrations did not hold true in these measurements. Contact angle measurements and imaging of the surface allowed studying the low surface energies and how the effects of the liner materials were seen in the surface energies as one of the silicones was coated on PET, while the others were coated on paper substrates. Release profiles of the laminates showed differences, but the results were difficult to compare reliably because the studied laminates consisted of different faces, adhesives and liners in addition to the different silicones. The effect of the face material was able to be minimized by choosing faces of similar thicknesses.

These results provided new information on misting of different silicone formulations and raised some ideas on what could be done next. The measurements verified the significant effect of increasing line speed to misting but the trend of how mist concentration increases with increasing line speed could be studied more in the future. Because the samples were gathered from production and the composition of laminates is always designed to suit a certain end use application, there were a lot of variables affecting the results. Being able to compare only the effect of the silicone formulation on misting and possibly finding better correlations with the laboratory measurements would require laminates consisting of the same face materials, adhesives and liners as well as line speeds, oven temperatures and other conditions in production remaining the same. The effect of silicone bath life and if it affects misting or properties of the final product could be further studied as well as the effect of modifier addition on misting as it seemed that the modifier addition could increase misting based on the studies of this thesis.

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APPENDIX A: CURVES OF THE DIFFERENTIAL SCANNING CALORIMETRY MEASUREMENTS

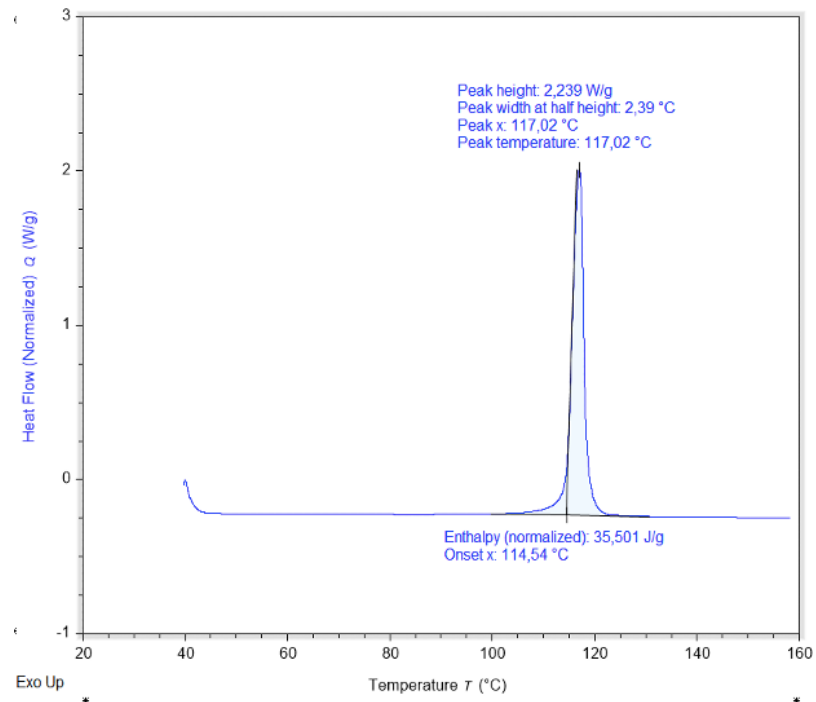


Figure 1. Silicone A

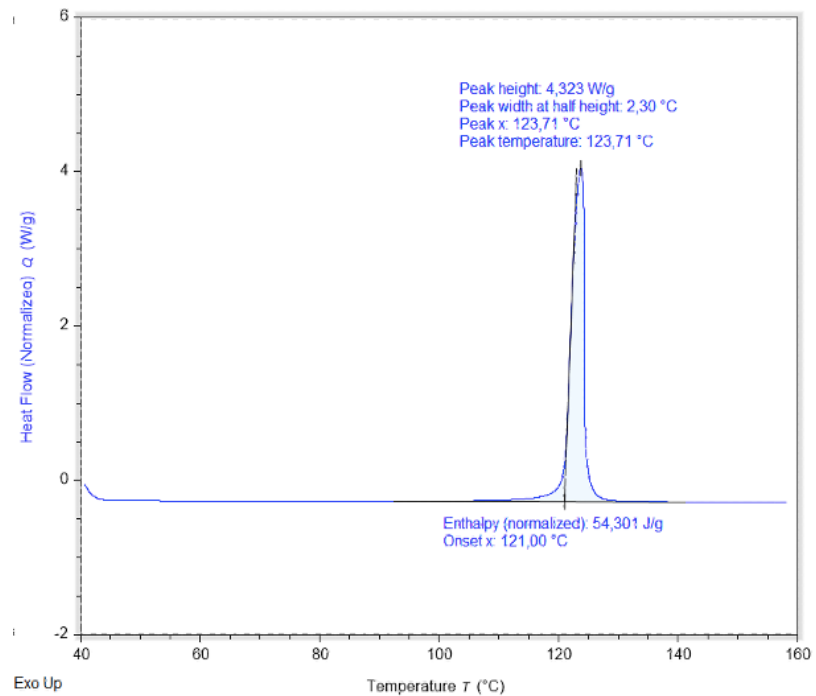


Figure 2. Silicone A + modifier

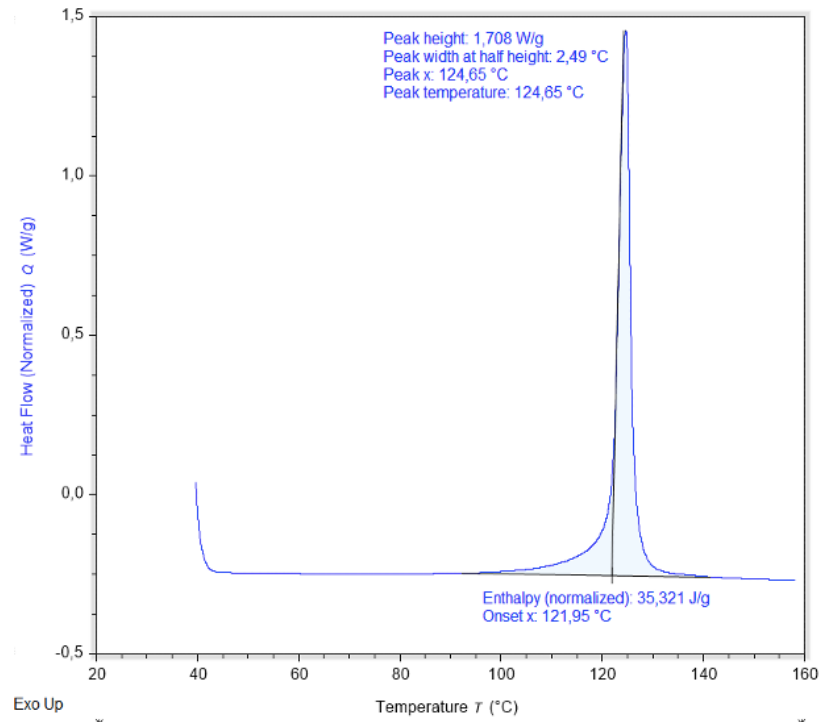


Figure 3. Silicone B

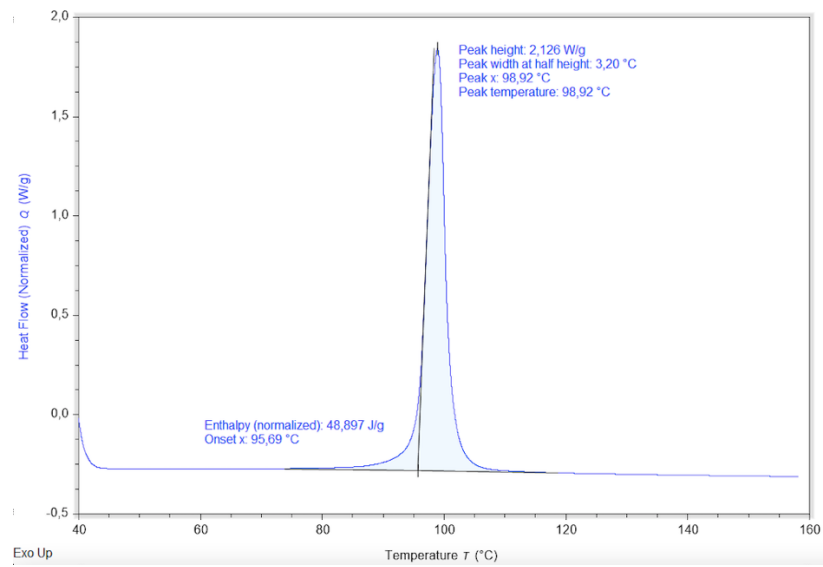


Figure 4. Silicone C

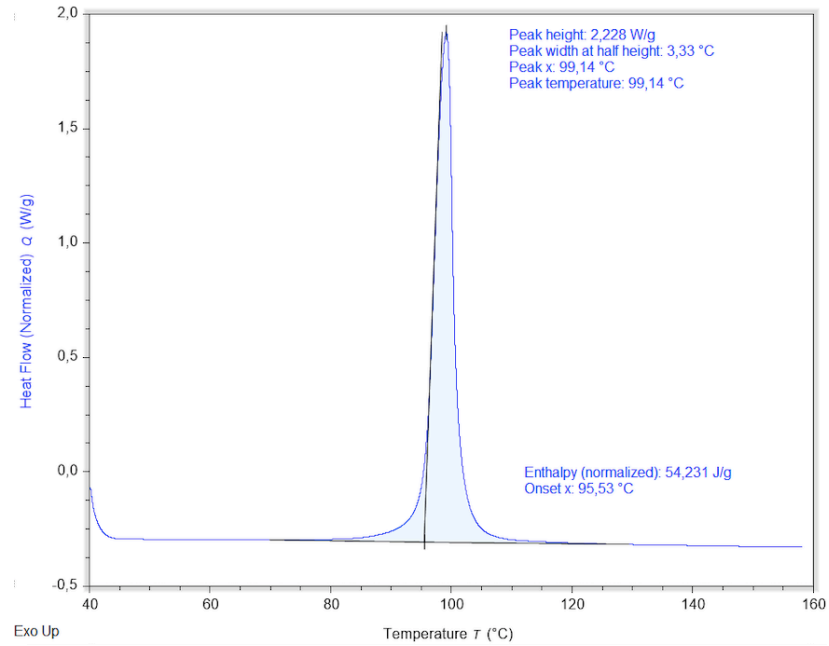


Figure 5. Silicone C + modifier

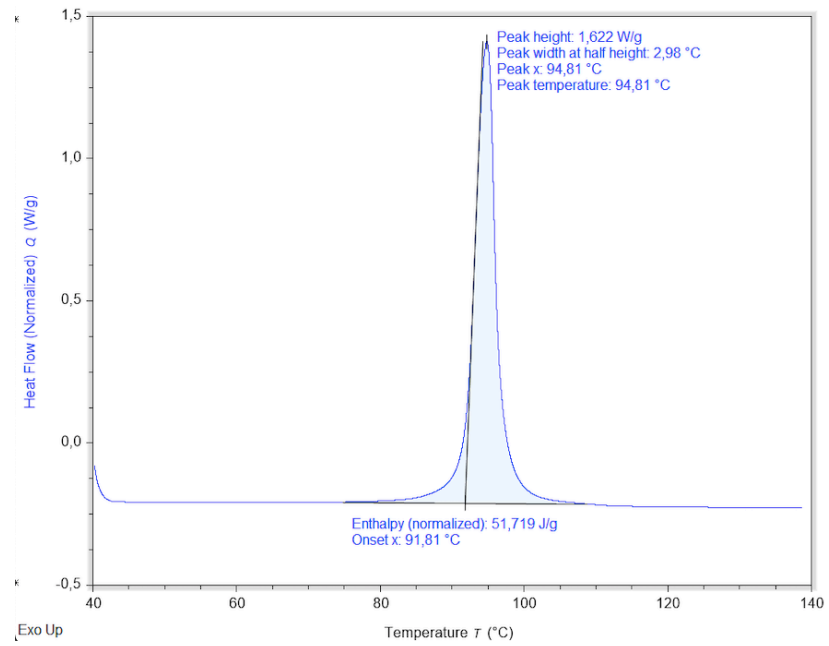


Figure 6. Silicone C + modifier heated at the rate of 7 °C/min

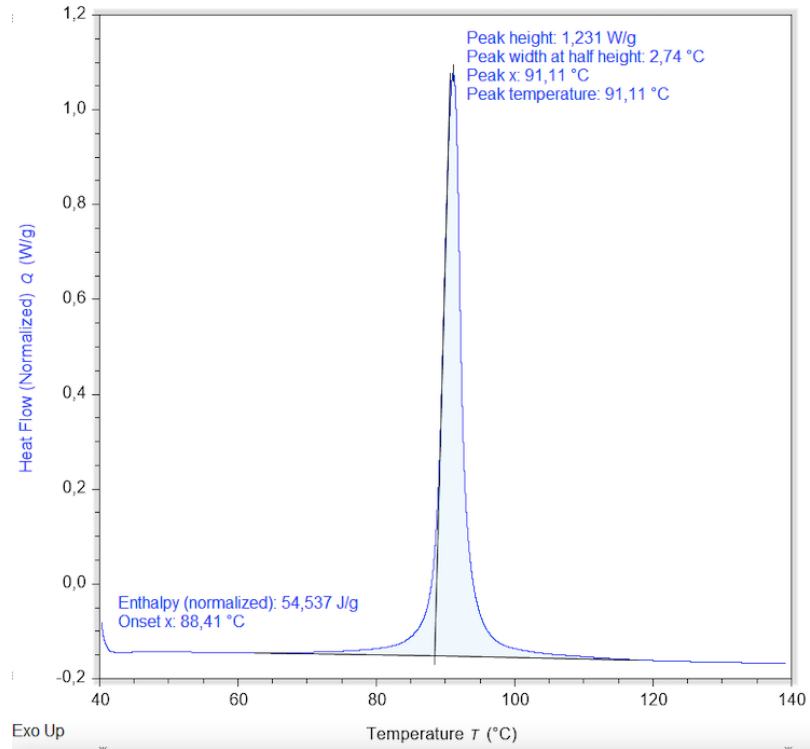


Figure 7. Silicone C + modifier heated at the rate of 5 °C/min

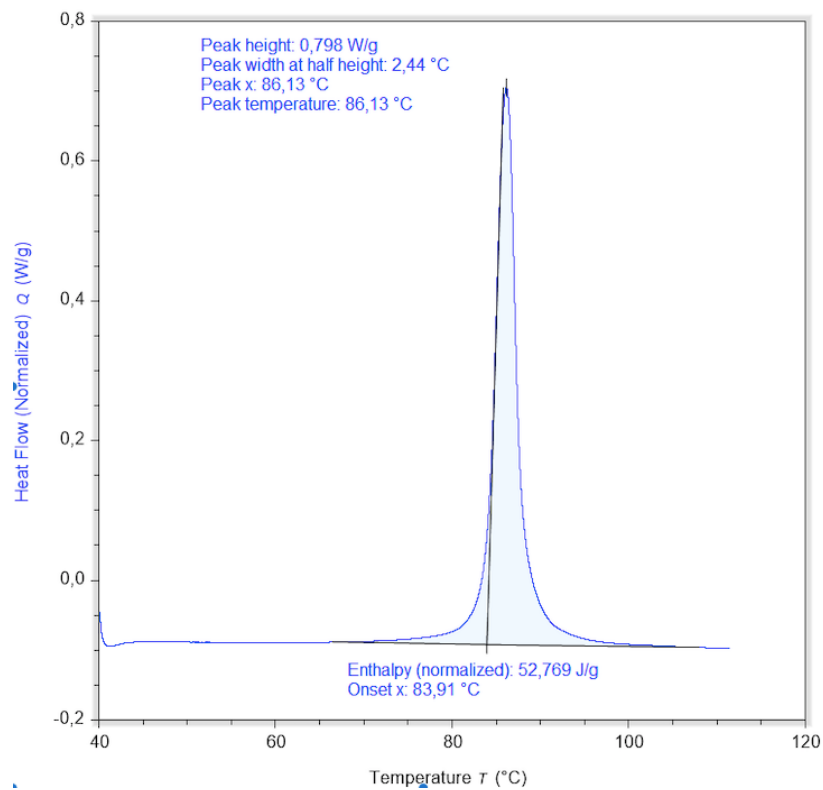


Figure 8. Silicone C + modifier heated at the rate of 3 °C/min