TAMPEREEN TEKNILLINEN YLIOPISTO
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PRACTICAL ADHESION OF SILICONIZED RELEASE LINERS

Master of Science thesis

Examiner: Jurkka Kuusipalo and Ali Harlin
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ABSTRACT

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Release liners are used in various self-adhesive applications such as hygiene products (feminine care and diapers), envelopes, labels, etc. The main function of the release liner is to protect the adhesive layer in the product. Release liner has to stick to the adhesive, but also be easily removed from it. Therefore, the optimal level of release force needed to peel off the release liner is important for the proper performance of the liner. Release liner consists usually of base paper, precoating, and silicone coating. Silicone offers easy release, but it is the most expensive part of the release liner. Precoating makes the paper surface smoother and allows the use of a thinner silicone layer. The properties of the base paper, such as roughness and porosity, as well as the properties of the precoating and silicone coating, such as coating coverage, affect the final performance of the release liner. In addition to the factors directly related to the release liner, the release performance is affected by other factors such as the adhesive, the face stock material and the peel speed and angle. For a release liner manufacturer, it is important to know well all the factors that affect the performance of the release liner in the final product. In this work, influence of base paper porosity, precoating and silicone amount of the release liner as well as impact of different adhesives on the release force were investigated.

In the theoretical part of the work, the phenomenon of adhesion is introduced with the help of general adhesion theories, continued with the concept of practical adhesion, or the practical strength of the adhesive bond, with contributions of fundamental adhesion and energy dissipation in the peeling process. Then, the materials involved in the study are introduced starting from the base paper, precoating and silicone, and continuing with pressure-sensitive adhesives. For the experimental part of the work, release liner samples were prepared with a base paper of 3 different levels of porosity coated with a hand coater using 2 levels of precoating and 3 levels of silicone coating. Air permeance values (closely related to the porosity), coat weights, water contact angles, and surface roughness were determined for the release liner samples. Six commercial adhesives intended for release liner applications were then characterized by their rheological properties. Release tests were then performed for the 18 different release liner samples and 6 different adhesives. It was found that the porosity of the base paper at the porosity level used did not have strong influence, but paper with lower porosity would allow the use of lower level of precoating. The level of precoating and silicone coating expectedly had a significant influence on the release performance with a higher level of precoating allowing less silicone to be used. Unexpectedly, a clear correlation between the rheological properties of the adhesive and the release force was not found. Commercial adhesives intended for the same purpose (hygiene products) gave similar release forces.

TIIVISTELMÄ

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Avainsanat: irrokepaperi, silikonipäällyste, paineherkkä liima, käytännössä havaittu adheesio, irrotusvoima, repäisylujuus

Irrokepapereita käytetään monissa erilaisissa tuotteissa kuten terveyssiteissä, tarrakirjekuorissa ja itsestään kiinnittyvissä etiketeissä. Irrokepaperin tärkein tehtävä on suojata liimakerrosta tuotteessa. Irrokepaperin täytyy tarttua liiman pintaan, mutta olla myös helposti irrotettavissa siitä. Irrokepaperin hyvän toimivuuden kannalta on tärkeää löytää optimaalinen taso irrotusvoimalle, joka irrokepaperin repäisemiseksi tarvitaan. Irrokepaperi koostuu yleensä pohjapaperista, esipäällysteestä ja silikonipäällysteestä. Silikoni mahdollistaa helpon irrotuksen, mutta silikoni on irrokepaperin kallein osa. Esipäällyste tasoittaa paperin pintaa ja mahdollistaa ohuemman silikonikerroksen käyttämisen. Sekä pohjapaperin ominaisuudet kuten karheus ja huokoisuus, että esipäällysteen ja silikonipäällysteen ominaisuudet kuten päällystepeitto vaikuttavat irrokepaperin lopulliseen toimintaan. Irrokepaperiin suoranaisesti liittyvien tekijöiden lisäksi myös mm. käytetty liima, hygieniatuotteen pintamateriaali, nk. face stock, johon liiman on tarkoitus tarttua, sekä repäisynopeus ja -kulma vaikuttavat irrotusvoimaan. Irrokepaperin valmistajan on tärkeää tuntea hyvin kaikki tekijät, jotka vaikuttavat irrokepaperin toimintaan lopputuotteessa. Tässä työssä tutkittiin irrokepaperin pohjapaperin huokoisuuden, esipäällyste- ja silikonipäällystemäärän sekä eri liimojen vaikutusta irrotusvoimaan.

Työn teoriaosassa adheesio ilmiönä esitellään yleisten adheesioteorioiden avulla, josta jatketaan käytännössä havaitun adheesion käsitteeseen, joka sisältää adheesion lisäksi energiahäviön vaikutuksen repäisyprosessissa. Sen jälkeen työhön liittyvät materiaalit esitellään alkaen pohjapaperista, esipäällysteestä ja silikonipäällysteestä, ja jatkaen kuumasulatettavilla paineherkillä liimoilla. Työn kokeellisessa osassa valmistettiin käsipäällystyksellä irrokepaperinäytteitä kolmella pohjapaperin huokoisuustasolla, kahdella esipäällystemäärällä ja kolmella silikonipäällystemäärällä. Irrokepaperinäytteille määritettiin ilmanläpäisevyys (läheisesti yhteydessä huokoisuuteen), päällystemäärä, veden kontaktikulma ja pinnan karheus. Kuusi kaupallisesti saatavilla olevaa hygieniatuotteisiin tarkoitettua liimaa karakterisoitiin niiden reologisten ominaisuuksien avulla. Irrotustestit suoritettiin kaikille 18:lle irrokepaperinäytteelle kuuden liiman kanssa. Huokoisuuden vaikutus irrotusvoimaan käytetyillä huokoisuustasoilla oli pieni, mutta alhaisempi huokoisuus sallisi hieman pienemmän esipäällystemäärän käytön. Esipäällystemäärillä ja silikonimäärillä oli odotetusti merkittävä vaikutus irrotusvoimaan, ja suurempi esipäällystemäärä sallii alhaisemman silikonimäärän käytön. Odotusten vastaisesti liimojen reologisten ominaisuuksien ja irrotusvoiman välillä ei havaittu selvää yhteyttä. Samaan sovellukseen (hygienia-tuotteet) tarkoitetut liimat antoivat hyvin saman suuruisen irrotusvoiman.

PREFACE

This work was carried out at the Department of Materials Science at the Tampere University of Technology (TUT) in collaboration with Mondi Štětí in Czech Republic. The main part of the experimental work was performed at Mondi Štětí with some of the measurements at TUT.

First I would like to thank Professor Jurkka Kuusipalo (TUT), Professor Ali Harlin (VTT), Product Manager Katja Jokiaho (Mondi Štětí), and Quality and Development Manager Tuomas Leppänen (Mondi Štětí) for offering me this great opportunity of MSc thesis work. Special thanks go to my main supervisor Tuomas Leppänen for all the help with both planning the literal part of the work as well as carrying out and reporting the practical work. I also want to thank the following people at Mondi Štětí for their help: Riku Liukkonen, Heikki Mäläskä, Zuzana Urbanová, and the helpful laboratorians at the PM 6 laboratory. At TUT, I want to thank Jurkka Kuusipalo for guidance, Pekka Laurikainen for the rheometer measurements, Jarmo Laakso for profilometer measurements, and Hilkka Koivuniemi-Mäkinen and Petri Johansson for help with other laboratory work questions.

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Tampere, 30.6.2016

Henna Ruuska

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
CCK	Clay coated paper
Cobb60	Water absorptiveness of paper/board (100 cm^2) in 60 seconds
CMC	Carboxymethyl cellulose
δ	Phase lag (between stress and strain), see tan δ
ε	Strain
EB	Electron beam
γ	Surface energy
γ_{ij}	Interfacial energy/tension between materials i and j. Materials i and j can be solid (S), liquid (L) and vapor (V)
Φ	Energy dissipation term or viscoelastic loss function
G*	Complex shear modulus
G’	Storage modulus (in shear)
G’’	Loss modulus (in shear)
G	Energy release rate
G	Gurley
h	Thickness of adhesive layer
HEC	Hydroxyethyl cellulose
HRA	High release agent
HMPSA	Hot-melt pressure-sensitive adhesive
ISO	International Organization for Standardization
JKR theory	Johnson-Kendall-Roberts theory
L	Liquid
LWC	Light-weight coated
MD	Machine direction

MG	Machine-glazed
MWC	Medium-weight coated
π_e	Equilibrium spreading pressure
PCK	PE-coated paper
PDMS	Polydimethylsiloxane
PE	Polyethylene
PSA	Pressure Sensitive Adhesive
PVA	Polyvinyl acetate
PVOH	Polyvinyl alcohol
Ra	Average roughness profile or arithmetic mean roughness
Rq	Root mean square roughness profile
Rz	Mean peak to valley height of roughness profile
σ	Stress
S	Solid
Sa	Average height of selected area
Sq	Root mean square height of selected area
Sz	Maximum height of selected area
SBC	Styrenic block copolymer
SBS	Styrene-butadiene-styrene
SCK	Supercalandered kraft paper
SC%	Solids content percentage
SD	Standard deviation
SIS	Styrene-isoprene-styrene
θ	Contact angle
Tan δ	Tangent δ; ratio of G’’and G’
T	Temperature
T_g	Glass transition temperature

t	time; time scale
TTS	Time temperature superposition
TUT	Tampere University of Technology
UG	Unglazed
UV	Ultraviolet
V	Vapor
ν	Rate of debonding; rate of peeling
W_A	Adhesion work
W_{coh}	Cohesion work
XRF	X-ray fluorescence
ω	Angular frequency

1. INTRODUCTION

Release liners are used in various applications, including labels, tape products, fibre composites, hygiene products (feminine and diaper), graphic arts, medical care and sealants [1, 07]. Main function of the release liner is to protect the adhesive layer of the product before use [2, p. 7:38–7:40][3]. Release liner should provide adequate adhesion to stick to the adhesive, but still be easily removable from the adhesive surface. Level of release should be tailored according to the requirements of the end product [4, p. 535]. Several factors affect the release performance of the product [5]. These factors can be related to the release liner, the adhesive, and the face stock of the product, and also to the process of removing the release liner (stripping). In addition, the way of application of the adhesive (spray, or narrow or wide strips either lengthwise or across) has influence on the release performance.

For the release liner manufacturer, it is important to know all the factors affecting release performance, in order to provide suitable release liners for their customers. In addition to the release liner related factors, it is good to know the behavior of the adhesives that the customers may use together with the release liner. There are several different commercial adhesives available. Therefore, both release liner properties (base paper, precoating and silicone coating) as well as adhesive properties are of interest in this study. Different face stock materials, which can be e.g. nonwoven or paper, were not considered, although they also influence the release performance of the product.

Release liners are usually paper based, but can also be polymer film or nonwoven [6]. Several types of papers are used as release liners, and different paper types are suitable for different applications. In the present study machine glazed (MG) kraft paper is of interest. Release liners of MG paper are used for feminine hygiene products (sanitary napkins and panty liners), document pouches (of polyethylene, PE) and self-adhesive envelopes and also labels. Properties of the base paper such as porosity and roughness are important for the quality of the final product [7, p. 13].

Silicone is the most common release coating [8, p. 9:2]. Good release performance is due to low surface energy (resulting in incomplete wetting of the adhesive and thus weak adhesion) and interfacial slippage (reduces energy dissipation effect in peel). Silicone is expensive, so the silicone coat weight is tried to keep as small as possible [9]. Base paper is first precoated with precoating including clay or polyvinyl alcohol (PVOH) containing mixture. Precoating increases the smoothness of the paper [7, p. 13] and precoating provides good silicone holdout (silicone stays on the surface) and enables thinner silicone coat weight [9]. After precoating, the paper is silicone coated. Silicone can be delivered solvent-based, solventless or emulsion [10, p. 609]. After application, silicone is cross-linked with heat or ultraviolet (UV) light. Degree of silicone coverage of the paper and thus silicone coat weight affects the release performance of the coating [11].

Adhesives used in release liner products are pressure-sensitive adhesives (PSA). PSAs are a special type of adhesives, which in dry form are aggressively and permanently tacky, and adheres firmly with only light pressure, and can removed from smooth surfaces without leaving a residue [12]. The nature of the adhesive, including chemical composition, thickness of the adhesive layers, and the viscoelastic properties affect the performance of the release liners [2, p. 7:39]. Many studies have shown correlation of energy loss property, loss modulus G’’ of the PSA and release force [13][14]. Thickness of the adhesive layer has also influence on the release force.

When the consumer uses release liner product, he/she peels off the release liner from the rest of the product. Resistance of peeling is called *peel force*, *release force*, *peel adhesion*, or *practical adhesion* and it is measured in *release* or *peel tests* [2, p. 10:29][13][15, p. 77-79]. *Adhesion* is phenomenon where two materials form contact region which is able to sustain or transmit stress [15, p. 76] (or in other words, adhesion means clinging/sticking of two materials or surfaces together). Several *adhesion theories* are used to describe the adhesion phenomenon, one of the most common is *wetting theory*, explaining the adhesion to be due to intermolecular forces between two materials brought in intimate contact with each other [16]. According to this theory, *surface energy* and *surface roughness* of the substrate have influence on the adhesion. Practical strength of an adhesive bond, or just practical adhesion, which is measured with peel tests or experienced by peeling by hand, includes the contribution of the adhesion due to interfacial forces, but also contribution of energy dissipation due to the adhesive and adherend [15, p. 76–79]. Practical adhesion is therefore always greater than the fundamental or thermodynamic adhesion.

In the present study, MG kraft paper of 35 g/m^2 was used as base paper. Base paper was first precoated with pigment (clay) precoating and then with Pt-catalyzed silicone coating in emulsion, which was cross-linked with heat. Coatings were made by hand coating. Three different porosity levels of the base paper, two levels of precoating and three levels of silicone coating were used in release liner samples. Contact angle measurements (which tell about the surface energy) and surface roughness measurements were performed for the samples. Six different commercial PSAs were used, and their rheological properties were examined. Release tests were performed for release liner samples with the PSAs. Paper was used as a “model” face stock and the effect of face stock material on the release performance was not considered here. The type of application of adhesive was one strip, and the other types (spray, or narrow/wide strips either lengthwise or across) were not considered, although this has a strong influence on the release performance for hygiene applications. Clear differences in release forces were found between different precoating and silicone coating levels, but porosity at the chosen level did not have (strong) influence. There were no differences in contact angles between the release liner samples and differences in surface roughness values were also negligible. Different commercial PSAs for hygiene applications gave slightly different release value (~ 30–35 N/m for release liners of lowest coat weights), but an adhesive for envelope applications gave significantly higher value (140 N/m). However, a clear correlation between the rheological properties of the PSAs and the release performance was not found.

The theoretical part of this thesis starts by introducing adhesion theories and practical adhesion, as well as polymer viscoelasticity. After that, components of release liners (base paper, precoating and silicone) and pressure sensitive adhesives are presented. All factors affecting release performance are then collected to a short summary chapter. In the experimental part, release liner samples and the used adhesives are shortly presented, and the experimental methods described. Fabrication and characterization of release liner samples, as well as adhesive rheological measurements are then considered. Finally, release tests results are presented and the influence of base paper porosity, precoating and silicone coating coat weight as well as different adhesives on the release force are discussed.

2. ADHESION AND POLYMER VISCOELASTICITY

Release liner has to adhere to the adhesive, but it also has to be easily removable from the adhesive surface. Adhesion can be described as attraction between two substances due to intermolecular forces between them [17, p. 4]. Phenomenon of adhesion includes two phases [15, p. 76−77]: in *the bonding phase*, the materials (e.g. release liner and adhesive surface) are brought into close contact with each other, and bond is formed between them. In *the debonding phase* two materials are separated under induced stress (e.g. release liner is peeled from the adhesive surface). All the energy used for peeling does not go to breaking the bond, but some part of it is dissipated, due to deformation of the adhesive and adherend. Total energy needed to break the assembly and separate the two substances− including both the contribution of interfacial forces and energy dissipation in the deformation – is called practical strength of adhesive bond or practical adhesion. Bonding and debonding phases of adhesion are controlled by separate physical processes and material properties: The bonding phase is controlled by the interfacial processes which occur between the two surfaces forming contact. The debonding phase is controlled by both interfacial and bulk processes which occur in the adhesive and adherends when they are separated, and it strongly affected by adhesive rheology (viscoelastic properties). This chapter presents some selected topics of adhesion science, surface science and polymer science, which are needed to understand practical adhesion in silicone–PSA (pressure-sensitive adhesive) systems. These topics are theories of adhesion, terms and definitions related to work of adhesion, practical strength of an adhesive bond as well as (linear) viscoelasticity of polymers.

2.1 Adhesion

2.1.1 Theories of adhesion

In adhesion, two materials form a contact area which can sustain or transmit stress [15, p. 76]. Several mechanisms contribute to formation of adhesive bond, most important being according to Mangipudi [15] van der Waals and other non-covalent interactions across the interface, interdiffusion of polymer chains across the interface and chemical bonds at or across the interface. In a real situation, one or more of these mechanisms are responsible for the adhesion.

Pocius [18, p. 132] states (in his book Adhesion and Adhesives Technology) that a unifying theory which would make a connection between the physical and chemical properties of materials, adhesion, and the practical strength of an adhesive bond does not exist. Instead, there are several theories (with experimental evidence) which are specifically related to certain observed phenomena. Pocius also states that the goal of adhesion science, which is predicting adhesive bond strength from first principles, can be reached by a proper combination of these adhesion theories and proper description about strain energy dissipation in the adhesive and adherend. The adhesion theories as described by Pocius are presented in Table 1, and considered in more detail below, supplemented with Kinning's [4] considerations regarding release coatings and PSAs. Table 1 presents also magnitudes of intermolecular forces concerning adhesion. Adsorption theory and always present van der Waals interactions are valid in the case of release coatings – PSA systems, but stronger, chemical interactions should be avoided for easy release [4, p. 541] [13, p.3][19, p. 47]. Electrostatic theory is not considered important for polymers and diffusion theory is valid for similar polymers (e.g. in silicone PSA – silicone coating systems) and mechanical theory explanation can have a role [4, p. 539–540][20, p. 2553].

Table 1. *Adsorption theories and intermolecular interactions responsible for adhesion.*

Adsorption theories [18, p.132–163]	Magnitude of interaction energy* [kJ/mol] [21, p.52]
1. Adsorption or wettability theory	
➢ Van der Waals forces -Dipole-dipole -Induced dipole -Dispersion (London)	1 – 40
➢ Hydrogen bond	10 – 40
2. Chemical interactions theory	
➢ Covalent forces	200 – 800
3. Electrostatic theory	
4. Diffusion theory	
5. Mechanical interlocking theory	
6. Weak boundary layers	

* Values of energies vary in different sources. Values from [21, p. 54].

Thermodynamic adsorption theory (wettability theory)

Most widely used adsorption theory is the thermodynamic adsorption theory or wettability theory [18][22]. This theory states that for achieving good adhesion, the adhesive and the adherend have to come into intimate contact at molecular level so that the intermolecular interactions can affect between them [18, p. 146]. Intimate contact is achieved when the adhesive spreads spontaneously over the surface (process called wetting) and maximizes interfacial contact. Wettability (extent of wetting) is determined by the balance between *cohesive forces* (forces between molecules of the same substance) of the liquid and *adhesive forces* (forces between molecules of two different substances) between the liquid and the solid surface [17, p.4][23, p.1][24, p. 15]. When adhesive forces are stronger, liquid spreads out over the surface (good wetting), and when cohesive forces are stronger, the liquid stays as almost spherical droplets on the surface with minimal contact with surface (poor wetting).

Surface energy: Wettability and spreading of a liquid drop (e.g. an adhesive) on a solid surface is related to *the surface energy* of the surface and *the surface tension* of the liquid [25, p. 15]. Surface energy or surface free energy is the energy needed to bring bulk molecules of a material to the surface and overcome the attraction by the bulk molecules when a surface is formed, and its magnitude depends on the intermolecular forces of the substance [22, p. 17, 89]. For liquids, the surface energy is equal to the surface tension [22, p. 92], the resistance to the deformation of the surface (tendency to minimize the surface area). The surface tension at which a liquid just completely wets (spontaneously spreads on) a solid is called critical wetting tension or critical surface tension of the solid. Good adhesion and wettability is obtained when the adhesive has lower surface tension than the critical wetting tension of the surface material [18, p. 147]. Materials having low surface energy (such as silicone) have poor adherability, and they are *release surfaces*. Low surface energy is prerequisite for a release material (easy release requires poor adhesion), although it is not enough alone for good release performance [4, p. 536–538]. Surface energy will be discussed more in Chapter 2.1.2. and contact angle methods which are be used for studying wetting/spreading of a liquid is described in Chapter 6.5.

Forces involved in adhesion: Whenever there is contact between two materials at molecular level, there will be adhesion [26, p. 39]. When two materials are in contact with each other, attraction forces affect between them. The type of these forces depends on the chemical nature of the two materials. The types of interaction forces and also the adhesion mechanisms are classified in somewhat different ways in the literature. The main classification of intermolecular forces is short-range, strong chemical bonding (including ionic, covalent or metallic bonding) also called *primary bonding*, and long-range, weak physical bonding or *secondary bonding*. The secondary forces generally known as van der Waals forces are due to molecular dipoles. These forces include dipole-dipole (or Keesom orientation) forces between permanent dipoles (Figure 1), dipole-induced dipole (or Debye induction) forces between a permanent and an induced dipole and dispersion (London) forces between transient dipoles (Figure 2).

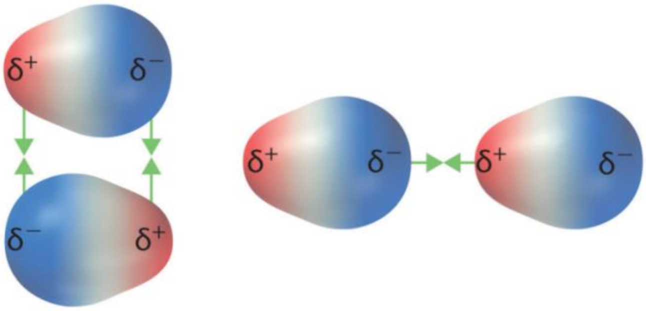

Figure 1. *Attractive dipole-dipole interaction, which occur between polar molecules having permanent dipole-moments. Picture adapted from [27].*

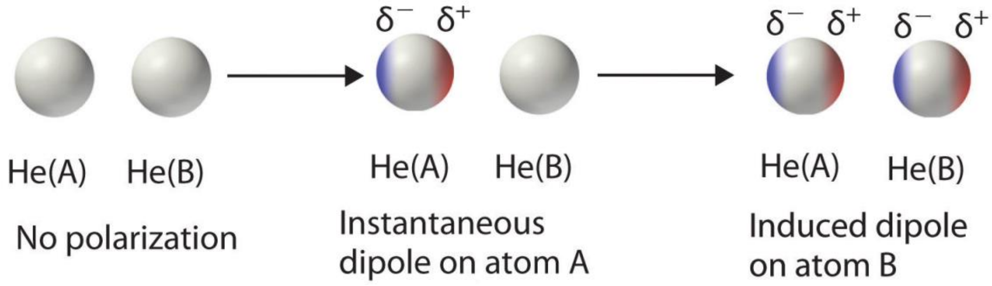

Figure 2. *Attractive London dispersion forces caused by temporary fluctuations in electron distribution in otherwise nonpolar atoms or molecules, here Helium atoms. Picture adapted from [27].*

In some sources only dispersion forces are included under the term van der Waals forces and the other two are called polar (polarization) forces [24, p. 15–18]. Covalent bonding is usually discussed as a separate adhesion theory (like in this text) and acid-base interactions are sometimes treated under a separate heading, sometimes under wettability theory together with van der Waals forces. Acid-base interactions include hydrogen bonding (a special case of dipole-dipole bonding), which occur with materials containing hydroxyl groups, and have both dipole-dipole and covalent properties [22, p. 17]. These interactions occur when an electron pair from one of the molecules is partially shared by another molecule [18, p. 85].

Potential energy curves for covalent, van der Waals and hydrogen bond forces shown in Figure 3 indicates that there is an optimum interatomic distance for each forces where the attraction is highest [22, p.17][28]. Covalent, short-range forces have strength of hundreds of kJ/mol, whereas the long-range van der Waals forces are only a few or a dozens of kJ/mol (see Table 1). Hydrogen bond has strength between covalent and van der Waals forces. The van der Waals forces are present in all situations between all atomic and molecular species and these determine surface and interfacial energies of materials and therefore the wetting process [15, p. 77][22, p. 17]. In most cases in pressure-sensitive adhesion, physical adsorption is the only adhesion mechanism [13, p.3][19, p. 47].

Rough surfaces: Above in the adsorption theory, the surfaces are assumed smooth although in practice they are always rough to some degree. Significant surface roughness may reduce the wetting and therefore adsorption and fundamental adhesion. The effect of roughness on wetting depends on the roughness features such as shape of the pores (“ink bottle” type pores are more difficult to wet than cylindrical) [17, p. 19]. Roughness of a substrate surface may inhibit the contact with adhesive, due to either thermodynamic equilibrium factors, or kinetics of adhesive penetration into a pore, and lead to poor adhesion [29, p. 333]. In other circumstances surface roughness can lead to increased spreading of the adhesive and good contact and thus high adhesion. Surface roughness is also dealt with under *mechanical interlocking theory* below (p. 18–19).

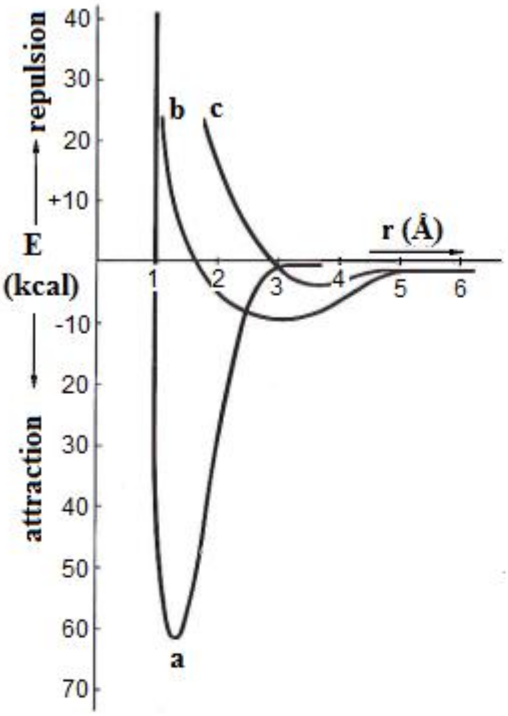

Figure 3. *Potential energy curves as a function of interatomic distance r for different types of interatomic forces: a) covalent bond, b) hydrogen bond and c) van der Waals bond. Picture adapted from [28, p. 12].*

Chemical interactions

In different sources, it alternates which intermolecular forces are included under term *chemical interactions*. Pocius [18] includes only acid – base interactions and covalent bonding to chemical interactions, and Kinning [4] polar (dipole-dipole and dipole-induced dipole) interactions together with acid-base interactions (including hydrogen bonding), which means any other or any stronger force than the always present dispersion force between nonpolar substances.

With PSA−release coating systems, physical adsorption is usually the only mechanism of adhesion, but chemical bonding may contribute in some cases [19, p. 47]. For good release performance of PSA– release coating system, the chemical interactions should be minimized by proper design of the release material and selection of the PSA/release material pair [4, p. 541]. Most release coating materials are multi-segment materials with one segment of low polarity and low surface energy (e.g. silicone, alkyl, fluoroalkyl) and other segments of higher surface energy and higher polarity or acid-base character. These higher surface energy segments are used e.g. to increase the mechanical strength of the coating and they are buried under the coating surface to be separated from the PSA. Reconstructing of the polymer surfaces may lead to increased release force with increasing temperature and time for aging. [4, p. 541][30][31]

Electrostatic theory

Electrostatic theory explains the adhesion as a formation of electrical double layer and attraction across the double layer, when two materials are brought in contact [22, p. 16-17]. According to Pocius [18, p. 135], electrostatic interactions can control the strength of the adhesive bond but only in cases when the electronegativities of the two materials differ significantly. For adhesion between polymers, electrostatic explanation is unsatisfactory [20, p. 2553].

Diffusion theory

If the two materials which are brought into close contact are soluble in one another, they form an interphase – a solution of the two materials – and ultimate adhesion is obtained [18, p. 135–137]. In polymer-to-polymer adhesion, diffusion occurs when the polymers are identical or compatible [22, p. 16]. According to Pocius, cases where the adherend and adhesive are soluble in one another and diffusion plays a significant role in adhesion are rare. The solubility can be estimated from the solubility parameters of the materials: materials with nearly equal solubility parameters are soluble in one another. In the case of release coating and PSAs, identical/compatible polymers occur with silicone release coatings with silicone PSAs [4, p. 540]. Otherwise the role of diffusion is small. However, the low molecular weight additives of PSAs (tackifiers, oils, surfactants) may diffuse to the PSA/release coatings interface and thus affect the adhesion. The role of this depends on the chemical nature of the PSA additives and the release coating.

However, Abbot [32, p. 169–183] claims that intermingling of polymer chains across the interface occur somewhat at the surface even for otherwise immiscible (bulk-immiscible) polymers. According to Abbot, diffusion theory is important but better described with words *intermingling* and *entanglement*. Figure 4 present intermingling of polymer chains as presented by Abbot. More about Abbot's view on adhesion at p. 19.

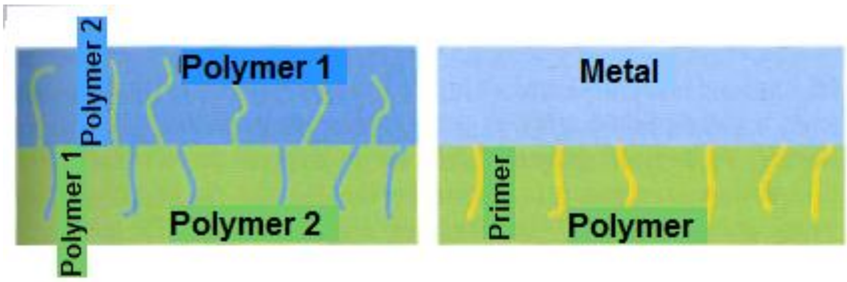

Figure 4. *Intermingling of polymer chains across the interface causes significant adhesion according to Abbot [32, p. 51], which can be two ways as in the case of two polymers, or one was as a primer on a metal. Picture adapted from [32, p. 51].*

Mechanical interlocking theory

Mechanical interlocking theory states that surface roughness improves adhesion by 1) providing more physical area of contact 2) by interlocking effect (solid adhesive in a pore on the surface cannot move apart from the pore without plastic deformation) and 3) by providing more complicated crack propagation with energy dissipation [18, p. 141–145]. The pore radius and the viscosity of the adhesive have effect on the pore penetration and mechanical interlocking. In the release coating–PSA system, contact area of the interface is influenced by roughness of the two surfaces, stiffness of the PSA and the method to bring the materials together [4, p. 539].

Scale of roughness: Scale of roughness can be macro (0.1–1 mm), micro or molecular (nm) scale and these can have different influence on the adhesion [29]. Roughness of the surface can either decrease or increase the adhesion compared to a smooth surface [24, p. 20–21]. Good wetting may be difficult to achieve on a rough surface together with a viscous adhesive. Joint at rough surface may have voids at the interface and asperities act as points of stress concentration lowering the practical adhesion (with brittle adhesives). In some cases, good wetting is obtained with rougher surfaces and with ductile adhesives stress concentrations can increase the practical adhesion (local plastic deformation, increases energy dissipation during failure). Also many successful pretreatments produce rough, microfibrous or microporous surfaces and enhances practical adhesion and there are many examples where roughness plays an essential role in adhesion and interlocking theory is valid [24, p. 20–21]. For example, Kowalski and Czech [33] found that the substrate surface energy is critical for tack properties (see concepts *tack* and *peel* in Chapter 3.3.5) with acrylic PSAs on rough surfaces. The tack performance was controlled by the adhesive's viscoelastic properties on rough substrates, but the final tack performance was strongly affected by the level of substrate roughness. Sun et al. [34] conclude in a review on mechanical properties of PSAs, that surface roughness affects strongly the adhesion properties of PSAs.

As already mentioned, surface energy is the excess energy in the surface of the material compared to the energy in the bulk material [24, p. 21], which is needed to break bonds in the bulk to produce the surface. Surface energy is expressed as energy per unit area. The unit area is interpreted to mean the nominal geometric area and thus roughness of the surface increases nominal area and also the surface energy and work of adhesion, according to e.g. Packham [29, p. 424]. Effect of rough surface on surface energy is presented Figure 5. Bulk atom B (of a close-packed array of spherical atoms) is bonded to six nearest neighbor atoms, and surface atom S only to four neighbors. On a (very) rough surface, an asperity A has even higher surface energy than surface atom S, which explains the higher surface energy of (very) rough surface compared to a smooth one. In addition, fracture energy is expressed per unit area, and for a rough surface the true area is higher than for a smooth one. However, the practical adhesion will not become indefinitely large with extremely rough surfaces due to cohesive failure in some other region [24, p. 21–23].

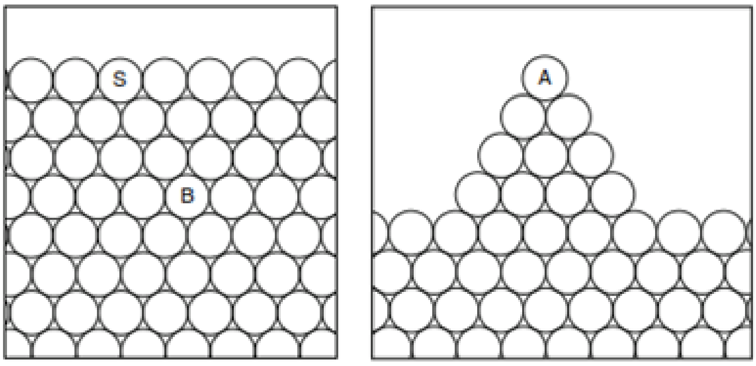

Figure 5. *Local environment of an atom in the bulk of a material (B), on a plane surface (S), and on an asperity on a rough surface (A). Picture adapted from [17, p. 2].*

Steven Abbot's view on adhesion: Abbot [32] states in his book Adhesion Science: Principles and Practice (2015) and at his web page [35] that abovementioned mechanical explanation is wrong and that the role of mechanical interlocking for adhesion is insignificant. Rough surfaces are believed to give extra adhesion because of extra surface energy, but according to Abbot this is not important in adhesion because the influence of the surface energy in general is small for adhesion. Also chemical bonds are too weak on their own to affect adhesion. Instead, he states that (strong) adhesion is due to entanglement of polymer chains across the interface together with energy dissipation, and also intermingling of polymer chains (which occur somewhat at the surface even for immiscible polymers) across the interface. The message of Abbot is described in brief with help of his schematic pictures in Figure 6.

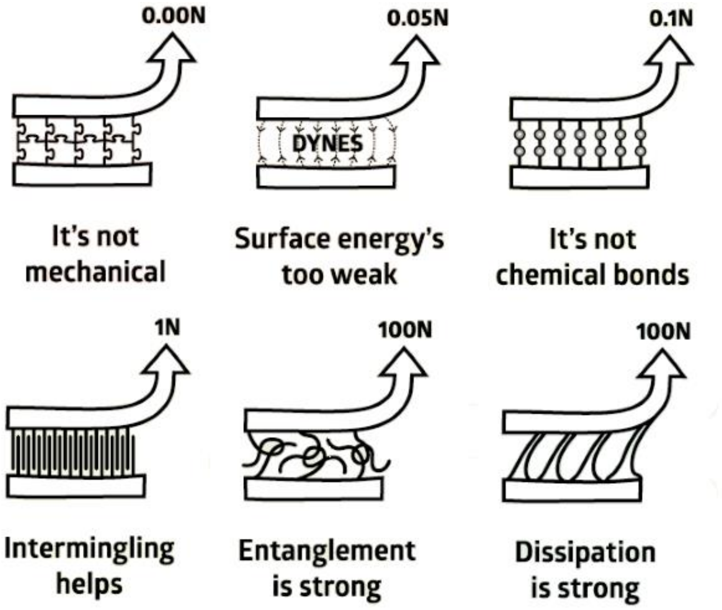

Figure 6. *According to S. Abbot [32][35], entanglement of polymer chains across the interface together with energy dissipation mainly determines the adhesion, and intermingling of polymer chains has also some contribution. Surface energy and chemical bonds instead are too weak on their own (without entanglement and dissipation) to have importance and mechanical explanation is wrong. Picture adapted from [35].*

Weak boundary layer theory

Loss of adhesive strength can occur either due to adhesive or cohesive failure [36, p. 697]. Loss of adhesion occurs at the interface of the two materials, and loss of cohesion inside one of the materials. *The weak boundary layer theory* is often referred under the adhesion theories, but it is actually a mechanism of *loss* of adhesion. This theory states that if a proper adhesive bond is made, but it is weaker than expected, a weak boundary layer theory can explain this difference since the bond fails due to cohesive failure of adherend or adhesive [18, p. 159]. The presence of mechanically weak boundary layer at the surface of release coating can contribute to low release force [4, p. 541]. Since the weak boundary layer results in transfer of the release coating materials to the adhesive, which may result in an undesirable loss in re-adhesion, the weak boundary layers is not a preferred method to achieve low adhesion with PSA release coatings.

2.1.2 Work of adhesion

If an entirely elastic material (does not absorb or dissipate energy) is subjected to a tensile force and broken, creating two new surfaces of the same material, the work done is called *work of cohesion* and it is twice the surface energy of the material [18, p. 90]:

$$W_{coh} = 2\gamma, \tag{1}$$

where γ is the surface energy already introduced earlier. In the case of two dissimilar materials, that are in intimate contact, the work required to reversibly separate the interface of the two bulk materials is called *work of adhesion* (J/m^2), and is given by the Dupré equation [18, p. 91][26, p. 49]:

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12}. \tag{2}$$

γ_1 (γ_2) is the surface energy of material 1 (2) and γ_{12} is interfacial energy between materials 1 and 2. The stronger the interfacial attraction, the stronger is the work of adhesion and the smaller is the interfacial free energy between the two materials. Figure 7 presents a case of solid–liquid (S–L) interface, where θ is the contact angle at three phase contact point, and γ_{ij} are the interfacial tensions between solid (S), liquid (L) and vapor (V).

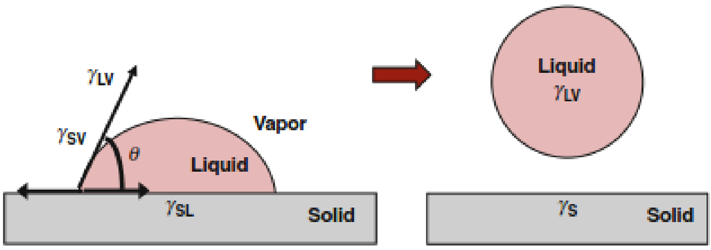

Figure 7. *Work of adhesion is the work required to separate two interacting materials [26, p. 50].*

The Young equation gives the relationship between γ_{ij} of solid, liquid and vapor:

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}, \tag{3}$$

where the solid–vapor interfacial energy γ_{SV} is the surface free energy minus equilibrium spreading pressure π_e, which describes the energy which is released when vapor is adsorbed to the solid surface:

$$\gamma_{SV} = \gamma_S - \pi_e \ . \tag{4}$$

Equilibrium spreading pressure is important (only) when a low surface energy liquid wets high surface energy solid, and can be otherwise ignored [18, p.95–96].

Substituting the Young equation (3) into the Dupré equation (2, 5)

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \tag{5}$$

gives Young–Dupré equation:

$$W_A = \gamma_{LV}(1 + \cos\theta). \tag{6}$$

In equation 6, the quantities θ (contact angle) and γ_{LV} (liquid–vapor interfacial tension) are easily determinable. W_A has its highest value when cos θ = 1 and thus θ = 0, which means complete wetting. E.g. for water, which has the γ_{LV} of 72 mJ/m^2 [18, p. 89], the maximum W_A in the case of complete wetting would be 144 mJ/m^2. This is very small quantity, and the practical work of adhesion is much higher, as will be discussed in Chapter 2.3.

Surface free energy and work of adhesion can be determined either using contact angle method (see Chapter 6.5) or with contact mechanical approach based on so-called JKR (Johnson–Kendall–Roberts) theory, which utilizes surface force apparatus [18, p. 94–102]. Contact mechanics is a study of the behavior of solids that are in contact with each other under an external load [15, p. 75–76]. The JKR theory relates the interfacial-force-induced contact deformation to the thermodynamic work of adhesion, and provides theoretical basis for experimental measurements of surface and interfacial energies. For determining surface energy of a solid with contact angle methods, contact angles are determined using at least two liquids (e.g. water and ethylene glycol) and surface energies are then calculated using various approaches, which are however debatable (see for example reference [37]). In the present study, contact angle measurements were performed for the release liner samples and water, but surface energies were not calculated since the same information could be obtained from only contact angle results.

2.2 Viscoelasticity of polymers

Both pressure-sensitive adhesives and silicone are polymers, and thus viscoelastic materials, and their viscoelastic behavior has a significant role in the performance of the release liners [4, p. 542]. Concepts needed to understand this viscoelastic character are briefly described below.

Viscoelastic materials behave both as a viscous liquid and as an elastic solid, and their performance depends on the viscoelastic response to a cyclic strain [18, p. 26**].** Figure 8. presents the response of a viscoelastic solid to a sinusoidal stress

$$\sigma(t) = \sigma_0 \sin(\omega t), \tag{7}$$

where $\sigma(t)$ is stress, t = time and ω = angular frequency of the applied stress. The corresponding strain is

$$\varepsilon\,(t) = \varepsilon_0 \sin(\omega t). \tag{8}$$

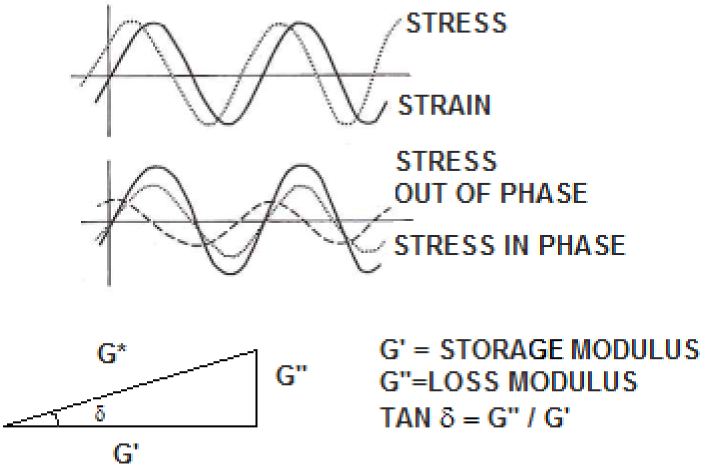

Figure 8. *Stress and stain response of a viscoelastic material. Stress (σ) and strain (ε) are out of phase by an angle less than 90°. The response can be divided to elastic (in-phase with the strain) and viscous (90° out of phase) components called storage modulus G' and loss modulus G''. The ratio G''/G'', tan δ, is called loss factor. G', G'' and tan δ, are important parameters which have an important role in the release performance of PSAs [13][18, p. 29][38, p. 158–160]. Picture adapted from [38, p. 160].*

For a totally elastic (Hookean) solid the stress and strain are in phase and for a totally viscous liquid (Newtonian liquid), the stress and strain are out of phase 90 °. For a viscoelastic material, there is phase-lag (δ) of less than 90°:

$$\sigma\ (t) = \ \sigma_0 \sin(\omega t + \delta). \tag{9}$$

The viscous part dissipates energy in each cycle, whereas the elastic part stores it. The stored energy is measured by storage modulus G’, in-phase component of the complex shear modulus G*, and the dissipated energy by out-of-phase component, loss modulus G’’. The ratio of energy lost to energy stored is called *tan δ:*

$$\tan \delta = \frac{G''}{G'}. \tag{10}$$

All the quantities G’, G’’ and tan δ are important for describing behavior of polymers in adhesive problems. These parameters are also important for the release performance of PSAs [13][18, p. 29][38, p. 158–160], which will be discussed more in Chapter 3.3.6.

2.3 Practical strength of adhesive bond

Term (practical) strength of an adhesive bond or just practical adhesion means the adhesive strength of a joint that is measured in a defined adhesion test geometry (see peel test /release test in Chapter 5.2.4). The strength of an adhesive bond depends on the geometry of the joint, mechanics of the test method, rate and temperature of debonding as well as bulk material properties of the adhesive and adherend.[15, p. 77][36, p. 693]

The practical strength of adhesive bond, or *energy release rate* G (J/m^2) is usually orders of magnitude higher than the thermodynamic work of adhesion (W_A) due to the fundamental intermolecular forces [15, p. 79] described above. This difference is due to energy dissipation in the (irreversible) bulk deformation of the adhesive and adherend in the debonding phase. In the case of release liners, both release coating and the backing can be deformed, in addition to the adhesive [4, p. 536]. This energy-dissipation process in a peel test is described in Figure 9. The magnitude of the energy dissipation depends on the viscoelastic properties of both the adherend and adhesive, and local stresses and strains near the crack tip, which in turn depend on the peel angle in the test [15, p. 79]. However, the interfacial characteristics are important in determining the strength of the adhesive bond.

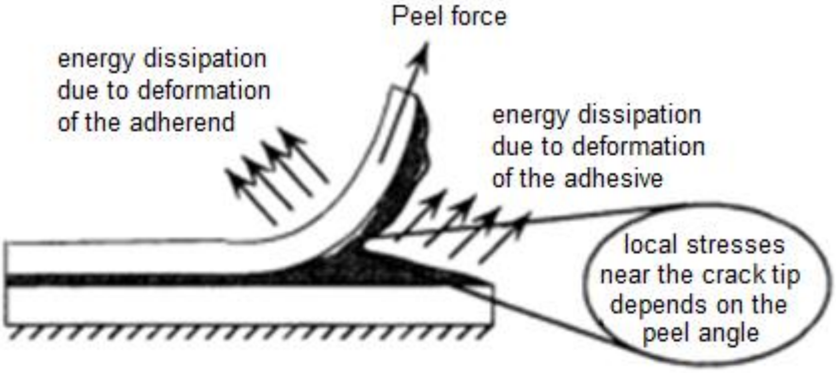

Figure 9. *Energy dissipation in a peel test can occur due to deformation of the adherend or the adhesive, and it depends on viscoelastic properties of the materials and local stresses and strains near the crack tip. Picture adapted from [15, p. 79].*

Practical strength of adhesion and thermodynamic work of adhesion are interrelated with the following empirical equation [15, p. 79][36, p. 693]:

$$G = W_A[1 + \Phi\ (v, T)], \tag{11}$$

where Φ is the energy dissipation term or viscoelastic loss function that depends on the rate of debonding v and temperature T. This means that also the peel force depend on the v and T. When the interfacial and bulk factors are separated as in equation 11 shows, two main approaches for controlling the practical adhesion can be presented according to Parbhoo [36, p. 693]. One is changing W_A through interface modification, which is called *adhesion promotion*, and the other is altering Φ by modifying the bulk properties of the materials, called *cohesion promotion*

Kinning [4, p. 536] presents the relation between practical adhesion and adhesion in a slightly different form: He presents the work required to peel (a PSA tape from a release coated substrate) using the following equation

$$\text{Work to peel} = W_A \times f\ (v, T), \tag{12}$$

where W_A is the work of adhesion from equation, and $f\ (v, T)$ is a function, which describes energy which is dissipated in peeling.

The deformation of the PSA has thus both elastic, non-dissipative component and viscous dissipative component [4, p. 537]. According to Kinning [4], several authors have proposed that when the stored elastic strain energy of the PSA exceeds the work of adhesion, the PSA will separate from the release coating at the peel front. Thus a more viscous PSA, which dissipaters more energy, has higher peel force than a more elastic one. Also, higher work of adhesion allows more dissipation within the PSA before the release, causing higher peel force than with lower adhesion work.

Kinning [4] states that, it would seem that for a given PSA, the work of adhesion (and thus peel force) should decrease systematically as the surface energy of the release coating decreases. This does not often hold in practice, because of other factors affecting the system, such as interfacial dynamics and rheological considerations. Low surface energy is a prerequisite for the release material, but it is not enough alone. Abbot [32][35] states that dissipation is the only factor that provides strong adhesion for PSAs and that the surface energy of the system has no significance here, but the good release properties of silicones is because of "fluid" character of the silicone surface that allows no dissipation. This phenomenon is often called *interfacial slippage* and will be discussed more in Chapter 3.2.3.

Molecular view on Pressure-Sensitive Adhesion / Rheological theory: Feldstein and Siegel [39] have written a review of molecular and nanoscale factors governing adhesion strength of pressure-sensitive adhesives. They state that although adsorption/wetting theory has the widest applicability, none of the common adhesion theories can be seen adequate in describing adhesion strength in the case of pressure-sensitive adhesion. Contribution of interfacial interactions to the debonding strength of PSA in a peel test is around 1 %, and major part comes from the viscoelastic deformation of the adhesive during failure of the bond. Thus peel test characterizes the viscoelastic properties of the adhesive rather than tack. Adhesion strength can instead be predicted considering rheological behaviour (viscoelastic deformation) of the PSA, which they call "rheological theory". Rheological view gives best understanding of pressure sensitive adhesion, although it is different than the classical view of adhesion dealing with only bond formation. According to rheological theory, important factors in determining the strength of adhesive joint are high cohesive strength, high diffusion coefficient and long relaxation time of the PSA material. At the molecular level, high strength of the adhesive joint is a compromise between two generally conflicting factors (and thus difficult to combine in a single polymer material), high energy of intermolecular cohesion and large free volume. The ratio between these two can be expressed with parameters such as glass transition temperature, diffusion coefficient, relaxation time, elastic modulus and tan δ. Influence of viscoelastic properties of PSA are discussed more in Chapter 3.3. For example, study of Taghizadeh and Ghasemi [40] about rheological and adhesion properties of acrylic PSAs show similar results than the "rheological theory". In their study, different PSAs were synthesized, and their viscoelastic parameters as well as surface energies of PSA tapes (using contact angle methods) were measured. Strong dependence between peel strength and viscoelastic energy dissipation (G'' at higher frequency) was found, and that the effect surface energy and work of adhesion on peel strength was found to be so small that it can be neglected.

3. MATERIALS

This chapter presents the materials used in the study. First, products using release liners are introduced and then components of a release liner are presented. Both properties of the base paper, as well as properties and amount of precoating and silicone coating are important for the performance of the release liner. Surface properties of paper relevant to release performance are considered, as well as function and components of pigment coating of the paper. Properties of silicone and components and performance of silicone coating and different silicone systems (solvent-based, emulsion, solventless) are also discussed. Finally, pressure-sensitive adhesives are presented. The composition of PSAs, their performance tests (peel, tack and shear) as well as the effect of rheology on their behavior are considered.

3.1 Release liner products

3.1.1 Structure and requirements of release liners

Release liners are sheet-like, thin, paper-based (sometimes polymer film based) solid state components having a special polymer coating, usually silicone, which gives the good release property [2, p. 7:38–7:40][3]. Functions of release liners are to serve as a carrier sheet for the adhesive, protect the adhesive, serve as a functional support for die cutting and printing and the transport material for the labels, carry useful product information, and release from the adhesive leaving it undamaged.

Release liners have various applications, including labels, tape products, fibre composites, hygiene (feminine and diaper), graphic arts, medical care and sealants [1, 07]. As earlier mentioned, feminine hygiene products, document pouches (of PE) and paper envelopes (where siliconized MG kraft paper is used as release liner) are considered in this study. Examples of these products are shown in Figure 10. Feminine care hygiene products are described in more detail below.

Figure 10. *Applications of MG kraft paper release liner are feminine hygiene products, document pouches and envelopes [41].*

A typical release liner product includes face stock, adhesive and siliconized release liner [1, 06][6], as presented in Figure 11 (this figure presents a “laminate”; dimension of the face stock is larger in hygiene products).

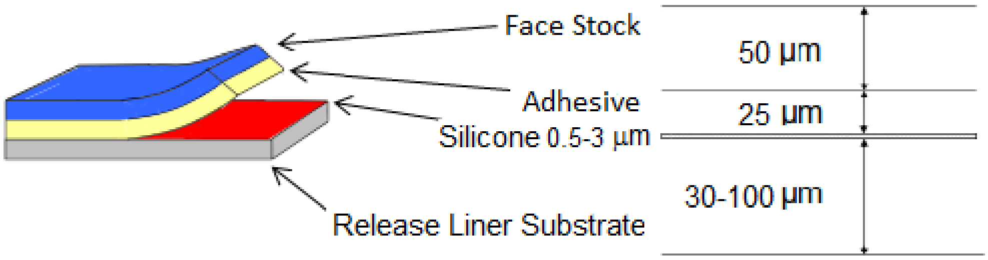

Figure 11. *Typical PSA product / release liner product with dimensions. Release liner substrate is typically paper (can also be polymer film or nonwoven). Face stock depends on application: in hygiene products it is nonwoven, in labels (as in figure) it is paper. [1, 06][6] Picture adapted from [1, p. 06:3*–*06:4].*

The release liner consists of substrate in web form and a non-sticking surface. The substrate or base paper is first precoated and then coated with silicone. Precoating can be clay coating or PVA (polyvinyl acetate) coating. The layer structure and weights of the components of clay precoated and siliconized MG paper based release liner is presented in Figure 12. Paper grammage (mass per unit area) varies between 30–100 g/m^2, clay coating coat weight 1–10 g/m^2, and silicone coat weight 0.5–1.5 g/m^2. [1, 02][6][9]

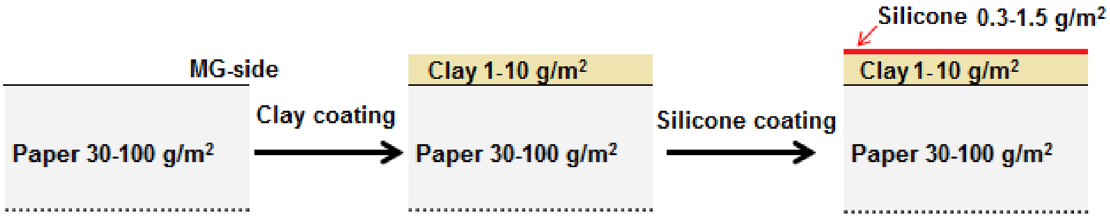

Figure 12. *Machine glazed side of MG kraft paper is precoated and siliconized for release liner applications. Paper grammage is in range 30-100 g/m^2 (typically 30–60 g/m^2) in hygiene and envelope applications. Precoating (clay) coat weight can be between 1–7 or even 10 g/m^2, and silicone coat weight 0.3–1.5 g/m^2. [1, 02][6][9]*

The basic requirement of release liner is to provide desired peel force from the adhesive [42, p. 2]. The level of release must be optimized according to the end-use requirements [3, p. 1]. Factors that affect the release force are the nature of the base paper and the silicone coating of the release liner, (dealt with in this Chapter), the nature of the adhesive (considered in Chapter 3.3), the end use product characteristics and the matrix stripping operation (speed, angle, physical dimensions) [10, p. 604].

3.1.2 Release liners in hygiene applications

Hygiene products include sanitary napkins and panty liners [43]. Face stock material of hygiene products is non-woven fabric. The main purpose of the release paper in these applications is to protect the adhesive, but also in some cases to keep wings of the napkin folded (Figure 13).

Figure 13. *An example of a sanitary napkin where the release liner protects the adhesive but also keeps the wings folded [43, p. 2].*

In some hygiene products, adhesive is first applied directly to the release liner, which is then applied to the nonwoven, and in other cases adhesive is applied on the non-woven face stock and then the release paper on the adhesive [43]. In the latter case, the paper does not have to endure the direct adhesive application. The release paper has to also have enough strength (machine direction (MD) tensile and tear strength) to withstand cutting. It also has to withstand vacuum without breaking. The higher the speed of the product line is, the more demanding it is for the release paper.

General requirements for release liners for hygiene applications are the followings: The release liner should have as low release value as possible, and the release should be smooth – not “zippy” [43]. For good runnability at the machine, the release liner must also have sufficient tensile and tear strength. The porosity of the liner should be low, to prevent the transfer of silicone to the backside of the liner, and to prevent too high absorption of adhesives. In addition, bending stiffness and curling of the liner has to be appropriate, and the liner has to be printable.

3.2 Components of release liners

3.2.1 Base paper

Several types of papers are used as release liners, and different paper types are suitable for different applications [1, p.02:12 – 02:38]. These paper types are glassine = supercalendered kraft paper (SCK), clay coated paper (CCK), PE-coated paper (PCK) and machine-glazed (MG) paper. Yankee cylinder (Figure 14) used for MG paper glazing and drying improves paper surface smoothness [44, p. 142]. MG kraft release paper is used for hygiene and envelope applications and also for labels [1, 02][6]. Typical MG paper grammage is 35–40 g/m^2 (the whole range 30–100 g/m^2). MG paper has high tensile and tear strength. Only one side (MG side) of the paper is smooth and siliconisable, and precoating is necessary before silicone coating (see Figure 12).

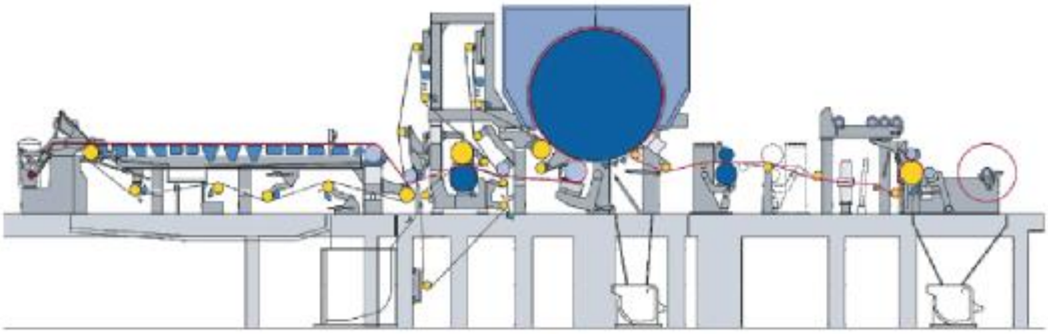

Figure 14. *MG machine with shoe press and large-diameter Yankee cylinder (original source Voith, cited in Holik [45, p. 1152]).*

The structure of the paper surface varies significantly depending on the raw materials as well as process used for paper production [9]. Although important properties can be obtained by coating the paper, the properties of the base paper especially porosity and surface roughness – are still crucially important to the properties of the final product [7, p. 13].

Paper surface should be as tight and smooth as possible for good silicone holdout [9]. Silicone holdout is the ratio of coating volume remaining on the surface to the coating volume which penetrates into the paper, and it is also affected by the viscosity of the coating mixture in addition to the paper surface properties [44, p. 142]. General requirements for good base paper for pigment coating are 1) high and uniform strength, 2) no defects or contamination and uniform thickness and formation of the base paper, as well as 3) optimal surface properties (smoothness, porosity, permeability, pore size, absorption properties) and pore structure [46, p. 46].

Sufficient *smoothness* (opposite to roughness) of the coated paper ensures the quality of the final product [46, p. 49]. Macro roughness (0.1 – 1 mm) is the results of paper formation (fibre bundles), and micro roughness (1–100 μm) is due to shapes and positions of individual fibres and fines (= furnish ingredients small enough to pass through a forming fabric) in the paper network structure [47, p. 94–95][48, p. 200]. Optical roughness (< 1 μm) is due size and arrangement of fines and pigment particles and surface properties of pigment particles and pulp fibres, and it affects paper gloss and absorption of fluids. Both macro and micro roughness affect paper gloss and uniformity, but printing and coating properties depend more on macro roughness. Rough base paper requires more coating to cover the surface than a smooth one, although some roughness is needed for good adhesion of the coating. Roughness measurements give the topography (roughness height variation) of the paper surface [48, p. 157].

Porosity, permeability and pore size distribution (mainly) determine the coating holdout [46, p. 49]. Porosity is the ratio of pore volume to total volume of paper [49, p. 20]. Permeability, which is characterized by the flow rate of air through a defined area of paper, is closely related to the porosity of paper [50, p. 274]. In the paper making process, these three surface properties are affected by pulp refining (= mechanical treatment), forming, press section dewatering and furnish composition. With wood free paper grades (such as MG Kraft release paper), refining has the strongest influence on the structure of the base paper surface. Increased refining gives denser paper and smaller pore size. The formation of the base paper is also influenced by softwood fibre. E.g. paper with 100% softwood fibre content is strong, but rough and porous, whereas paper with 100% hardwood fibre content is smooth but not very strong [1, p. 02:7–02:8]. Refining of fibres in paper making increases tensile and internal strength, and decreases porosity, but decreases also tear strength. *Absorption properties and sheet pore structure* determines how fast the coating color consolidates [46, p. 50]. These two properties are affected by surface chemical properties of the fibres as well as internal sizing of the paper with sizing agents.

3.2.2 Precoating (pigment coating)

Both papers and boards can be coated with pigment coating [51, p. 30]. Papers can be either mechanical (wood-containing) paper which are made mainly of mechanical pulp, or fine (wood-free) paper made of only (or >90%) of chemical pulp. LWC (light-weight coated) and MWC (medium-weight coated) papers are typical coated mechanical papers and printing papers typical coated fine papers. MG kraft release paper is wood-free paper.

Pigment coating fills the cavities and covers the surface of the base paper, and thus increases smoothness of the paper (Figure 15) [7, p. 12–13]. In general, pigment coating improves the quality of the paper. Improved properties are surface strength, gloss, opacity, and decreased dusting and ink absorption. On the other hand, mechanical strength and stiffness of the paper decreases when it is pigment coated (when compared to a non-coated paper with same grammage). In the case of release paper, the main purpose of the precoating is to achieve good silicone holdout [9]. The precoating closes the paper surface by reducing the web porosity and reducing the penetration of the expensive silicone coating into the paper, and thus affects the economy of the release liner. The precoating also modifies the physical and chemical properties such as surface energy, smoothness and strength of the paper surface, and thus provides even and controlled quality for the paper.

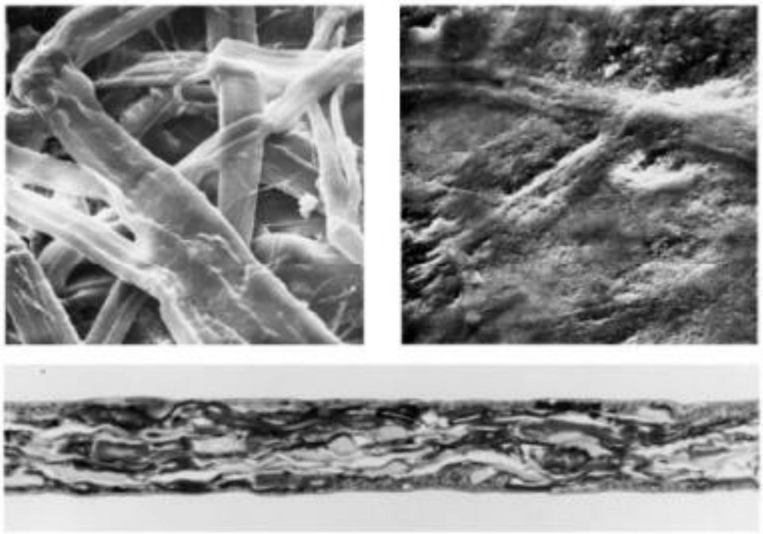

Figure 15. *Scanning electron microscope image of uncoated and coated paper as well as a cross-section of coated paper [7, p. 14].*

Pigment coating materials: Pigment coating materials include pigments, binders, co-binders, additives and water [7, p. 14–15]. Pigments are main component (80–95 w% of solids) of the coating color [7, p. 14–15][52, p. 60] and common pigments are minerals such as kaolin clay, calcium carbonates and talc as small (< 10 μm) particles. The binding component of the coating color usually contains two or more binders and the amount of binders is 5-20 w% of the amount of dry pigment [7, p. 14–15]. Binders bind pigment particles to the base paper and to each other, and also partly fills voids between pigment particles. Binders also affect viscosity and flow properties of the coating. The role of binders is described in Figure 16. Common binders are various polymer dispersions such as latexes (non-soluble in water), starch, carboxymethyl cellulose (CMC) and other derivatives of natural (water-soluble) polymers, as well as fully synthetic polymers such as polyvinyl acetate (PVA) and polyvinyl alcohol (PVOH) [52, p. 66–68]. Thickeners, which are natural or synthetic polymers such as CMC or PVOH, are used to affect the rheology of the coating and to increase water retention. Thickeners also act as binders (co-binders) [7, p. 14–15]. Thickeners are used a few percent of the amount of pigments. In addition, various additives are used in the coating (<2w% of the total solids), such as dispersing agent for pigments, pH adjuster, microbiocides, defoamers, lubricants etc. Water in the coating colour enables mixing the other coating components, so that pigment particles are separated from each other. Water also allows applying the coating to the base paper so that the coating colour remains dispersed. After applying the coating, water is evaporated so that the coating layer consolidates and the binder forms bridges between pigment particles and base paper.

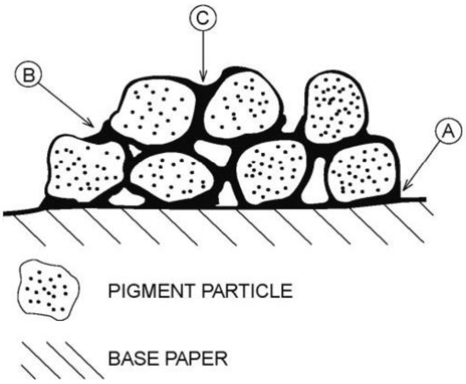

Figure 16. *Roles of binder (black in figure) in the pigment coating layer are binding of pigment particles to base paper (A) and to each other (B), as well as partly filling of voids between the pigment particles (C). [52, p. 65].*

Coating process: Coating process includes applying the coating color (aqueous suspension of pigments, binders and additives) on to one or both sides of the base paper, metering the coating (before, during or after its application), drying (often with IR radiators and then air dryers) it and possibly finishing e.g. by supercalendering or soft calendaring [7, p. 18–23]. Metering after application can be done with blade, roll or air-knife coater. Coating can be done on-line or off-line.

3.2.3 Silicone coating

The release coating, which gives the desired release properties for the release liner, is usually silicone, although some organic polymers (fluorocarbons, urethanes, carbamates, vinyl acetate copolymers, acrylics) are sometimes used e.g. when toughness of the surface is more important than easy release [8, p. 9:2]. Silicone coating gives good release properties by decreasing adhesion forces 90–100% [9]. Silicone is the most expensive material in the release liners, and the silicone coat weight is tried to keep as small as possible. Determining factors of silicone coat weight are the properties of the silicone coating (solids content and rheology) and also porosity and coating coverage of the precoated paper [6].

Polydimethyl siloxane (PDMS) is the basic functional unit of silicone coating [8, p. 9:3]. Characteristic properties of PDMS, which makes it an effective release material are the high flexibility of the polymer backbone, and small barrier to bond rotation, which allows the methyl groups to point out from the surface [8, p. 9:14][53, p.1]. Low intermolecular forces of methyl groups and chain flexibility causes *low surface energy* of magnitude 20 mN/m, which is significantly lower than surface tensions of typical PSAs (30–40 mN/m) [8, p. 9:14][10][36][54]. This difference in surface energies results in incomplete wetting of the surface, and easy release.

Another reason for easy release of silicone is the rheological behavior of the PDMS. The mobility of the polymer segments makes the silicone coating very *elastic* and enables efficient storing of energy and returning if after energy source is removed [13]. This reduces energy dissipation (which increases practical adhesion as discussed in Chapter 2.3) and leads to low release force. This phenomenon is also called *interfacial slippage* (or low friction): local slip at the silicone-adhesive interface concentrates the shear forces at the interface and reduces energy dissipation [55]. Interfacial slippage is the main reason why PDMS has lower release forces than fluorocarbon polymers, which have lower surface energy, but higher friction than PDMS.

The silicone coating layer has to be uniform and well cured (cross-linked) to avoid interaction between unreacted silicone species and the adhesive, and to minimize silicone transfer to the adhesive surface [3, p. 1]. Contamination of the adhesive surface might lead to poor tack and adhesion [8, p. 9:2]. As coating in a PSA product, silicone must have strong adhesion to the substrate at which it is cured (*anchorage*), but the cured silicone surface has to provide sufficiently weak adhesion (good release) with the PSA [36, p. 704–705].

Anchorage: Anchorage of silicone to the substrate is especially important if the release liner is stored before use, since long storage time may lead to degradation of the anchorage (particularly with film substrates) [3, p.2]. Mechanical interlocking and chemical interaction mechanisms are used to explain the silicone anchorage to substrate. Mechanical interlocking is particularly important for porous substrates such as paper. However, mechanical interlocking becomes less important when supercalendering, machine-glazing or coatings are used to minimize the porosity and silicone penetration to the paper. In addition, mechanical interlocking does not provide long-term anchorage, and therefore chemical interactions have major role in silicone anchorage. In some cases, chemical and/or mechanical mechanisms are sufficient for good adhesion to the substrate (unprimed silicone) [36, p. 689–692]. This is the case e.g. with silicone release coating based on hydrosilylation reaction (see below) where adhesion of silicone to paper substrate is achieved so that silicone first penetrates to the paper and after that gets cross-linked. Reactive groups at the paper surface as well as chemical cross-linkers can also have a role in the chemical bonding mechanism. If chemical and/or mechanical mechanisms are not sufficient, an *adhesion promotion* can be used by adding a coupling agent (primer) to the silicone system or by pre-treatment of the substrate.

Silicone coverage and coat weight: Major factor affecting release performance is the degree of silicone coverage of the paper [11]. Uncoated or incompletely coated areas allow adhesive to contact the base paper fibres, which lead to higher release value and also less stable release value with time. In addition, both adhesive and silicone coating thickness affect the release force, up to the point that coating thickness is large enough for good coverage. Higher thickness means higher energy dissipation and thus higher release force. This effect is different for different silicone systems, as can be seen from Figure 17. Point “A” is the silicone coat weight needed for total coverage.

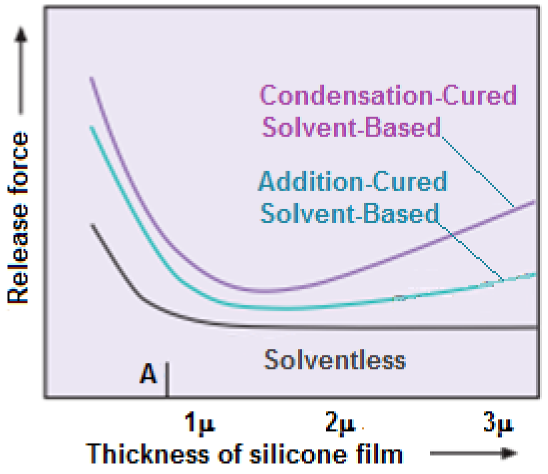

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Figure 17. *Effect of silicone film thickness on release force for condensation-cures solvent-based, addition-cured solvent-based and solventless silicone systems. "A" is the silicone amount needed for total coverage. Figure adapted from [11, p. 1].*

Controlling release force: Controlling release force of release coatings in an accurate way is challenging [8, p. 9:15]. Two main approaches for this are controlling cross-link density of the silicone coating and addition of silicate resin-base high-release additives (HRA). Changing molecular weight of the PDMS chains, which can be controlled by degree of polymerization (of the silanol-terminal PDMS component), was the main tool for release force control in (tin-catalyzed) solvent systems, which were earlier popular. Nowadays more popular are solventless systems (such as addition-cured solventless system), which use shorter PDMS chains which leads to narrower range of achievable release forces, and therefore, HRA may be needed [8, p. 9:15–9:18]. Traditional HRA "freezes out" interfacial slippage and results in increased adhesive deformation, and thus higher energy dissipation and higher release force [56].

3.2.4 Silicone systems

The term *silicone* usually refers to polydimethylsiloxane (PDMS) (Figure 18), which is a polymer with "inorganic" backbone and "organic" methyl side groups [57, p.1]. The methyl group could be replaced with e.g. phenyl, vinyl or other groups.

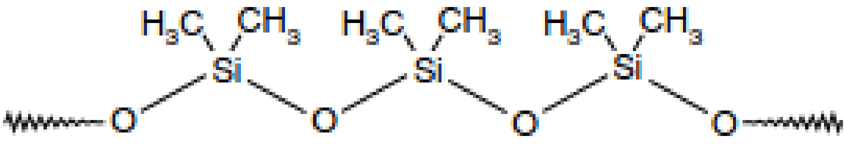


Figure 18. *Polymer structure of PDMS [8, p.9:37].*

In addition to the silicone polymer, silicone coating includes a cross-linker and a catalyst, as well as different additives, such as inhibitors, thickener (e.g. HEC or CMC) or sometimes high-release or fast-cure additives [8, p. 9:6–9:7][9]. The coating is done by mixing the components, applying it to the paper surface, and then cross-linked e.g. by heating [10, p. 605].

Silicone can be applied in a form of *solvent*, *emulsion*, or *solventless (100% solid)* [10, p. 609-618]. Solvent system is most flexible and easy to apply, but the solvents possess the air-pollution problem. A problem with waterborne (emulsion) system is that water swells paper fibres. This can be controlled with additives, e.g. CMC. The properties of the release coatings obtained with these three ways differ in (at least) cure rate and release rate. With *solvent-borne release coatings* a wide range of release characteristics can be produced. Different additives can be used to help the processing, e.g. bath-life extenders, fast cure, high release or anchorage improving additives. A variety of substrates can be used and anchorage is good. Release force ranges from easy to tight and cure rate ranges from fast to slow. Either tin or platinum catalysts are used. *Emulsion release coatings* are limited to low or medium molecular weight polymers and the range of release force values available is more limited (from easy to medium tight) than with other methods. Cure rate ranges from medium to slow. Some emulsion coatings require post-cure. Either tin or platinum catalysts are used and curing is done at 130–175° C. After removing excess water, certain amount of heat energy is required for cross-linking, which is usually obtained in 10 - 40 seconds, depending on the system used, silicone amount, and temperature used. For *solventless coatings* the release force ranges from easy to tight and cure rate from fast to medium. Solventless coating avoids the problems of solvent (pollution) and emulsion (swelling the paper), but only addition cure (see below) is available.

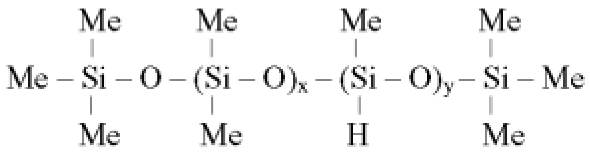
Cure chemistry and coating components

Silicone curing mechanism can be *condensation*, *addition* or *radical / cationic*, and curing energy either *heat* (thermal cure) or *radiation* (UV or electron beam). Condensation cure system uses heat as curing energy, addition cure systems utilize either heat or radiation and radical/cationic system radiation as curing energy. Condensation cure system uses the silicone in solvent form, addition cure system in solvent, emulsion or solventless and radical/cationic curing system in solventless form. [1, p. 01:9-01:10][36, p.682]

Addition cure: The most common cure chemistry nowadays is the addition cure with hydrosilylation reaction [8, p. 9:4][53, p.3]. It consists of vinyl-functional PDMS, hydrogen-functional PDMS and platinum catalyst (Figure 19). The hydrosilylation reaction can be written as:

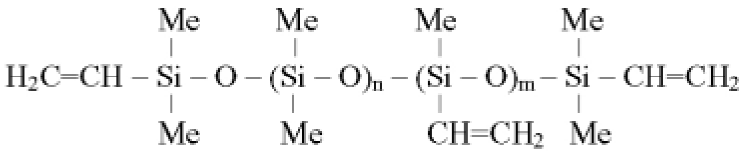
$\text{Si-CH=CH}_2 + \text{SiH} \rightarrow \text{Si-CH}_2\text{-CH}_2\text{-Si}$

a) hydrogen-functional siloxane



$$\mathrm{Me}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-(\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O})_x-(\underset{\mathrm{H}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O})_y-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{Me}$$

b) vinyl-functional siloxane



$$\mathrm{H_2C{=}CH}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-(\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O})_n-(\underset{\mathrm{CH{=}CH_2}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O})_m-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{CH{=}CH_2}$$

Figure 19. *Structures of silicone polymers with hydrogen and vinyl functional groups [53, p. 3].*

The role of Pt catalyst for the mechanism is described in Figure 20, where a silicone hydride group (-H) is added across a vinyl group ($-CH=CH_2$) [8, p. 9:5]. The addition happens rapidly in the presence of Pt catalyst, and heat is evolved. Advantages of addition cure system is that polymer manufacturing is easy. Vinyl groups can be placed anywhere along the polymer chain (not only terminally as the silanol groups in the condensation cure system). Advantage is also good resistance to heat treatment, so that lower-molecular-weight species are easily devolatilized, which helps getting migration-free coatings.

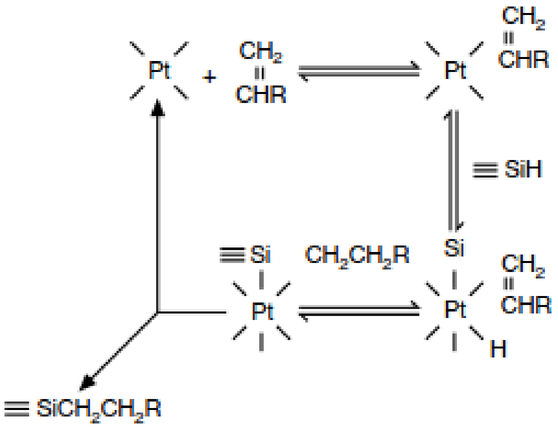
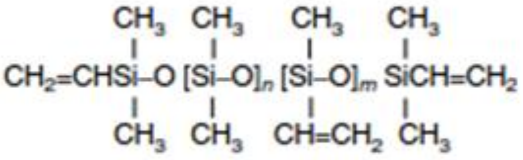


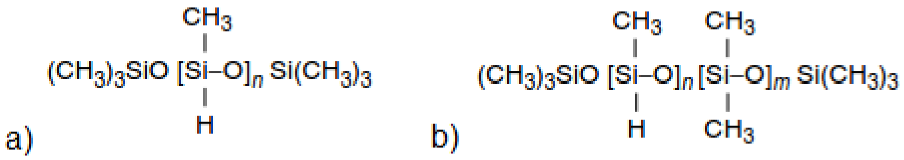
Figure 20. *Addition cure mechanism of silicone with Pt catalyst. (≡ represents the remaining valences of SI) [8, p. 9:5].*

Typical silicone polymers that are used in addition cure are shown in Figure 21. High molecular weight polymers are used in solvent products, and much lower molecular weight polymers in solventless and emulsion products [8, p. 9:7]. In addition to the basic polymers and the catalyst, cross-linkers (homo- and copolymers of SiH functionality; Figure 22) are used in the formulation. Also inhibitors (in solventless system) and high-release additives may be used.



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

Figure 21. *Typical silicone polymers used in addition cure. n+m ranges from 100 to 5000 [8, p. 9:8].*



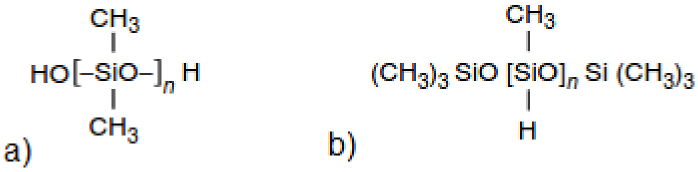
$$\text{a)}\ (CH_3)_3SiO\,[\overset{CH_3}{\underset{H}{Si}}{-}O]_n\,Si(CH_3)_3 \qquad \text{b)}\ (CH_3)_3SiO\,[\overset{CH_3}{\underset{H}{Si}}{-}O]_n[\overset{CH_3}{\underset{CH_3}{Si}}{-}O]_m\,Si(CH_3)_3$$

Figure 22. *SiH functional a) homopolymer and b) copolymer cross-linkers for addition cure system. Figure adapted from [8, p. 9:8].*

Condensation cure: condensation cure reactions can be written as [8, p. 9:3]:

1. Si-OH + SiH → Si-O-Si + H_2
2. Si-OH + Si-OH → Si-O-Si + HOH

where the first reaction is the primary cross-linking mechanism and the second reaction secondary but still important mechanism. The basic siloxane polymer for condensation cure system (Figure 23) range from low-viscosity gums (n = 20) to thick gums (n = 6000).



$$\text{a)}\ HO[-\overset{CH_3}{\underset{CH_3}{Si}}O-]_n\,H \qquad \text{b)}\ (CH_3)_3\,SiO\,[\overset{CH_3}{\underset{H}{Si}}O]_n\,Si\,(CH_3)_3$$

Figure 23. *a) Basic siloxane polymer (n = 20–6000) and b) cross-linker for condensation cure. Figure adapted from [8, p. 9:7].*

Sn catalyst as a form of organotin salt is used for condensation cure [8, p. 9:3–9:6]. Condensation cure system with silanol-functioning polymer, H-functional cross-linker, Sn-catalyst and alkoxy-functional accelerator is presented in Figure 24. Condensation cure coating can also include fast-cure additives, anchorage additives and high-release additives.

Advantages of condensation cure are low costs and that the system is not suspected to (catalyst) poisoning. Condensation cure also allows wide range of release by control of polymer molecular weight. Disadvantages are that 100% solids alternative is not possible, and relatively slow cure. [8, p. 9:4][36, p. 685]

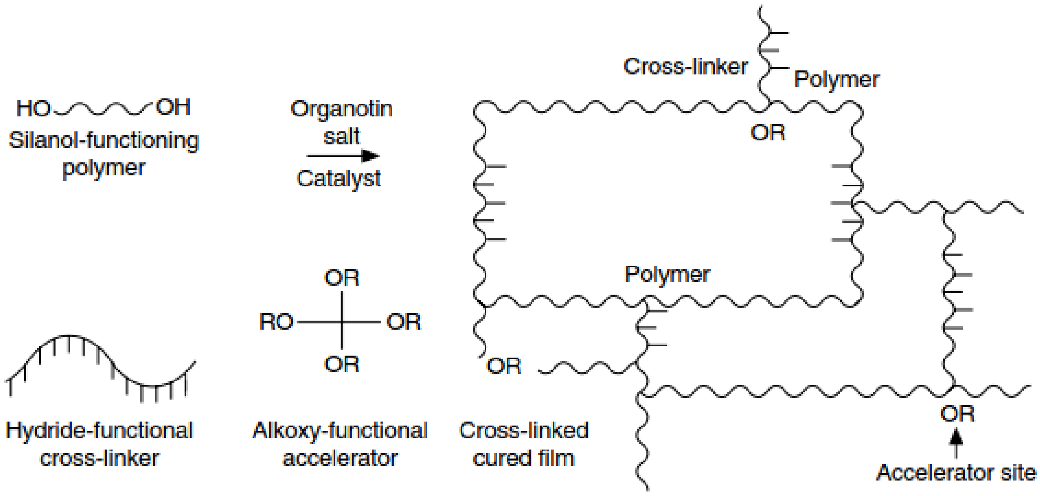


Figure 24. *Sn-catalyzed condensation cure system [8, p. 9:4].*

Radiation cure: Radiation cure can be done with electron beam (EB) or UV light [8, p. 9:5]. In radiation cure system, also the methyl groups of the siloxane polymer are replaced by functional groups that will participate in cross-linking reactions. Examples of radiation cure are shown in Figure 25. In EB cure example, silicone acrylate is subjected to high-energy EB and radicals are created, which due to their unstable nature leads to propagation reactions and radical formation to other available reactive groups. In the UV curing mechanism, UV light causes radical formation in the initiation reaction step. This can be helped with a catalyst that absorbs a certain frequency of UV energy. The radicals then propagate to reactive groups. The range of release performance of radiation cured systems is not as good as thermal cure systems, but advantage is complete cure at low temperature.

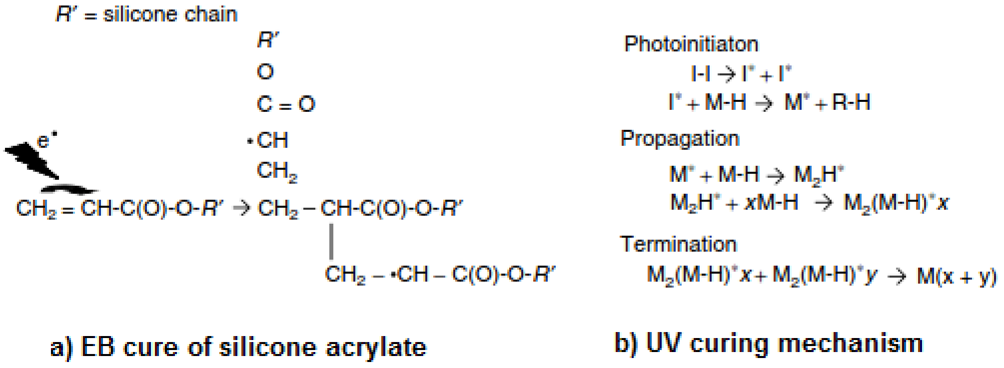


Figure 25. *Examples of radiation cure: a) Electron beam cure of silicone acrylate and b) UV curing mechanism with initiation, propagation and termination steps. Figure adapted from [8, p. 9:6].*

3.3 Adhesives

3.3.1 General about adhesives

Adhesives used with release liner applications are pressure sensitive adhesives (PSA). The name comes from the property of PSAs that they bond under (very light) pressure [25]. In general, adhesives can be classified according to the manner which they harden, which can be loss of solvent, cooling or chemical reaction [19, p. 23]. Pressure-sensitive adhesives are different than other adhesives, since they do not harden, but remain permanently sticky. PSAs are used above their Tg (glass transition temperature), in the rubbery state of the polymer (whereas e.g. structural adhesives are used below Tg). PSA:s are relatively weak adhesives, but the benefits of PSAs are e.g. that no mixing or heat is needed when the adhesive is used [58, p. 467].

Adhesives in general should behave like liquids for bonding process (when applied) but like solid to resist debonding (when the product is used), and this is usually achieved by a change in physical or chemical state [25, p. 502–404]. For example, hot-melt adhesive (e.g. in hot melt glue gun) changes after its application form low viscous melt to crystalline solid upon cooling, or two phase epoxy adhesive from two liquid components to cured, hard solid. PSAs are different to other adhesives in that they do not undergo this kind of change in physical state, but they achieve the liquid-like behavior for bonding and solid-like behavior to resist the debonding only due to their viscoelastic properties. Viscoelastic materials respond more like liquids for slow deformations, and more like solids for rapid deformations. The natural time scale for bonding for PSA products is longer than the time scale for debonding in e.g. peel tests. In that sense, the name of PSAs could be “time-scale sensitive adhesive”.

3.3.2 Pressure-sensitive adhesives

According to Pressure Sensitive Tape Council [12], a pressure sensitive adhesives (PSA) are adhesives, which in dry form are aggressively and permanently tacky, adheres firmly with only finger or hand pressure, do not require activation by water, solvent or heat but exerts strong adhesive holding force, and in addition has sufficient cohesive strength and elasticity that they can be handled with fingers and removed from smooth surfaces without leaving a residue.

PSAs can be applied in organic solvent (solvent-based PSA), in water dispersion or emulsion (water-based PSA) and solvent-free (e.g. hot-melt, warm-melt and photoreactive UV cross-linkable prepolymers) [59, p. 51]. Solvents are necessary for application of natural rubber PSA. In this study, the interest is in hot-melt PSAs (HMPSA).

HMPSAs are 100% solid thermoplastic compounds, which are applied in hot liquid form [12][59, p. 51]. Hot-melt PSAs have to be fluid (low viscosity) at the coating temperature, but at the use (lower) temperature the viscosity has to be high. The melting point of the adhesive has to be lower than the thermal degradation temperature of the components. The processability of the adhesive is thus important in designing the composition of the hot-melt adhesive. Conventional elastomers (e.g. natural rubber) are not suitable for HMPSAs, and therefore thermoplastic elastomers are used. Most commonly used polymers are linear SIS (styrene-isoprene-styrene) block copolymers, and also SBS (styrene-butadiene-styrene) copolymers. The adhesive, coating and end-use properties are controlled by changing the viscoelastic properties of the adhesive components. Benefits of hot-melt PSAs according to Czech [59, p. 51] are their application properties and environmental friendliness compared to solvent-based adhesives.

PSAs can be classified according to their chemical composition / base polymer (next chapter), application form (as above in the text) or according to the types of PSA products. PSA products can be permanent (labels, packaging tapes), removable (labels, Post it ® notes, hygiene products), repositionable (wider format graphic arts, or specialties (low temperature applications, medical care, food contact) [1, p. 06:10]. PSAs for permanent products have higher peel value (> 10 N/25 mm) than PSAs for repositionable and removable applications and they also have high shear strength. In repositionable products, the adhesive force of the PSA increases over time whereas in removable applications the adhesive force is stable. Specialty products have some special character/demand for the PSA, e.g. low temperature performance. Classification of PSAs according to their peel resistance and removability as presented by Czech [60, p. 887] is shown in Table 2. Removable and excellent removable PSAs, which are of interest in this study, have 180° peel values under 160 N/m.

Table 2. *Classification of PSAs versus peel adhesion.*

PSA type	180° peel adhesion	
	[N/2.5 cm]	[N/m]
Excellent permanent	>14	560
Permanent	10 – 14	400 – 560
Semi-removable	6 – 8	240 – 320
Removable and repositionable	2 – 4	80 – 160
Excellent removable	< 1	< 40

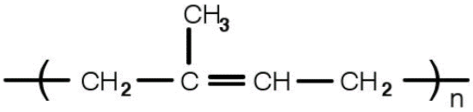
Source: Czech [60]. Czech gives peel adhesion values only in units N/2.5 cm.

3.3.3 Composition of PSAs

Common base polymers of PSAs are natural rubber, styrene butadiene rubber, block copolymers, amorphous poly-a-olefins and acrylics, and common additives in PSAs are tackifiers (resins) and antioxidants [19, p.34]. In this text, the classification of base polymers follows that of Everaerts [58]. Some of the PSA:s, such as polyalkylacrylates and its copolymers are inherently tacky, and others need tackification to meet the Tg and modulus criteria of PSA:s (see Chapter 3.3.6). Rubber-based adhesives, either natural or synthetic rubber, need tackification [58, p. 478]. Rubber based adhesives (rubber-resin adhesives) are most cost-effective PSAs [1, p.06:11].

Natural rubber based PSAs

Natural rubber (Figure 26) based PSAs are not used in the applications which are of interest in this study, but since it is the first polymer used to PSAs [58, p. 472], it is mentioned here. Natural rubber needs tackification and slight cross-linking [58, p. 472]. Natural rubber is compatible with different tackifiers and adjusting the adhesion/cohesion balance of the natural rubber based adhesives is thus easy [2, p. 5:4]. In addition to traditional rubber/resin adhesives, natural rubber is also used as latex form in emulsion-based SBR/tackifier resin PSAs (for permanent label stock applications) to modify the adhesive properties.



$$-\!\left(CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2\right)_n\!-$$

Figure 26. *The repeating unit of natural rubber (polyisoprene) [61, p. 77].*

Block copolymer based PSAs

An important group of PSAs are block copolymers, which have the largest volume of PSAs in the industry [58, p. 479]. The most common are styrene block copolymers. These are of ABA –type, where A (end-block) are styrene blocks and B (mid-block) is isoprene (SIS) or butadiene (SBS), where styrene content in is usually above 25% [19, p. 34]. The SBS (styrene-butadiene-styrene) and SIS (styrene-isoprene-styrene) structures are presented in Figure 27.

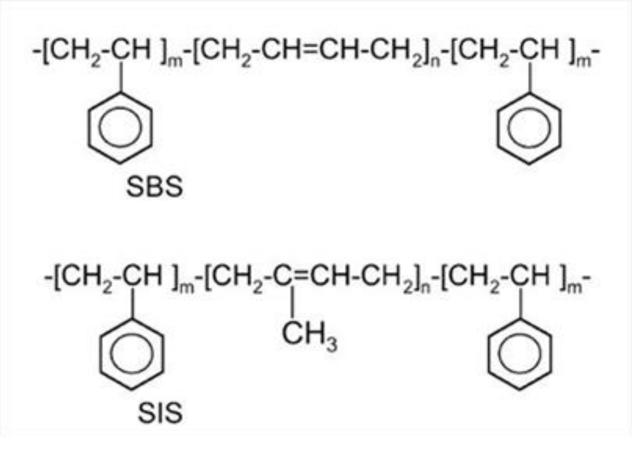


Figure 27. *SBS and SIS block copolymer structures [62, p. 7].*

Block copolymers are thermoplastic elastomers which means that they have elastomeric behavior at room temperature but they can be processed as thermoplastics [61, p. 106–107]. Elasticity of elastomers is due to reversibly deformable network structure, but with conventional, non-segregated elastomers the existence of the network does not allow viscous flow [2]. Both elasticity and viscous flow can be obtained with a segregated, two-phase system. For PSA this means that they can be applied as solvent-free, hot-melt adhesive. Figure 28. presents the two phase system of a common block copolymer SBS (and linear and radial types of it) [61, p. 106–107]. Polystyrene spheres (hard segments) are embedded in a continuous, elastomeric polybutadiene phase (soft segment). The hard segments act as pseudo cross-links, and the soft segments gives the elasticity to the material. The separate phases are due to the incompatibility of the two polymers. Both phases have a separate glass transition temperature. Above T_g of the soft segments, the domains soften and dissociate and the material can flow. Below the T_g of soft segment, behavior is elastomeric.

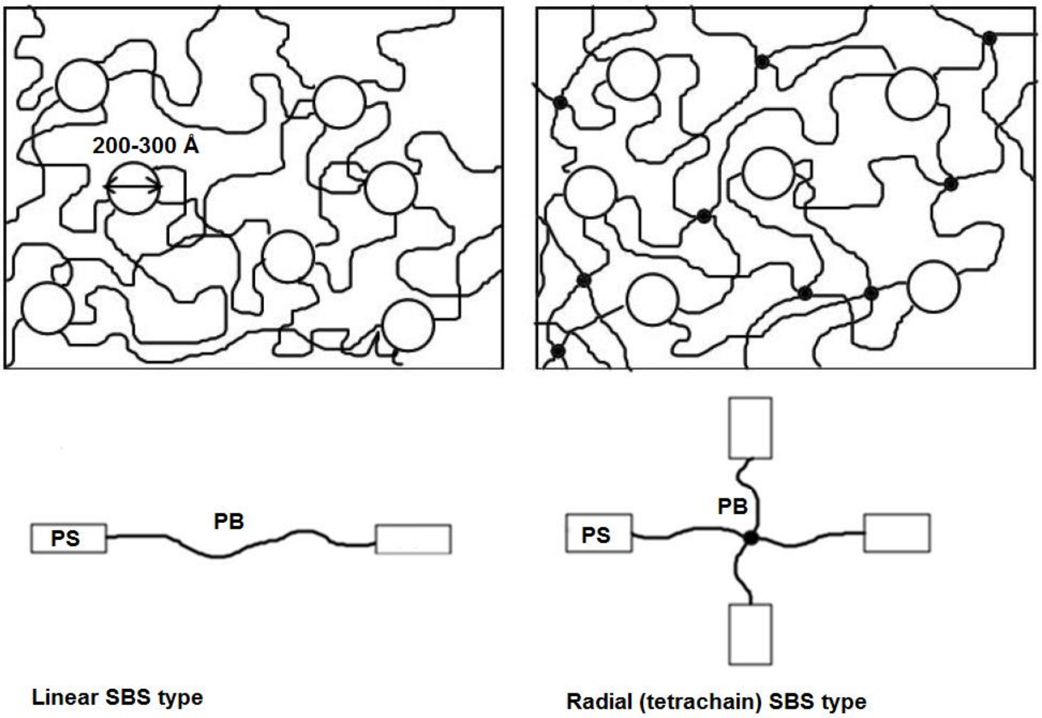


Figure 28. *Structures of SBS block copolymers. Hard polystyrene spheres are embedded in soft polybutadiene phase. The structure can be linear or radial. Picture adapted from [61, p. 106–107].*

There are many variations of styrene block copolymers PSAs with different grades with different physical properties suitable for various special applications [2, p. 5:52]. Most commonly used hot melt PSA polymers are linear SIS block copolymers (polystyrene content 10–25%), and also SBS copolymers. SIS copolymers are easier to tackify than SBS and they have relatively low modulus. They also have better tack, compatibility, and aging resistance. Styrene block copolymers are not the only two phase (segregated) elastomers used for PSAs, but also acrylic, polyolefin, silicone, polyurethane and polyester block copolymers are used. Formulation of SBC (styrenic block copolymer) based HMPSA includes base polymer, tackifying resins, plasticizers and antioxidants in the following proportions [63, p. 3-7]:

-SBC polymer	20–40%
-Tackifier resin	30–75%
-Plasticizers (oils)	10–25%
-Antioxidants	<2%

Polymer is the core of the adhesive formulation. Performance of the adhesive can be controlled by changing e.g. M_w (molecular weight), styrene content, radial and linear structures [63, p. 3-14]. *Tackifiers* are low M_w amorphous resins with high T_g, which usually composes the highest percentage in the adhesive formulation [63, p. 3-20]. The role of tackifier is to reduce the plateau modulus (magnitude of the modulus at the plateau region of the modulus curve), increase Tg of amorphous mid-block phase and reduce melt viscosity. They affect wet-out, tack, heat resistance and processability of the adhesive. *Plasticizers* are petroleum oils, polar plasticizers or natural oils. They are used to reduce melt viscosity so that the adhesive can be manufactured and applied below the degradation temperature of the SBC polymers. They can also be used to adjust mid-block T_g and they reduce raw material costs of the adhesive. *Antioxidants* are important to prevent thermal and UV light induced degradation of the SBC polymers [63, p. 3-29].

Acrylic PSAs

Acrylics are also common material in the PSA industry, and the dominant single component PSA [58, p. 485–487]. Acrylates are one of few materials that can be synthetized as inherently tacky, and compounding with tackifiers, oils or plasticizers is not needed. However, using tackifiers and plasticizers allows adjusting the rheological properties beyond what can be obtained with single component PSA. Advantages of single component PSA are the elimination of migration of low M_w compounds, easier maintaining of high cohesive strength at elevated temperatures, and less risks for skin irritation. Acrylic PSAs are made by polymerizing acrylate monomers, shown in Figure 29. R can be hydrogen (acrylate) or methyl group (methacrylate). The polymer backbone of the acrylate polymer is fully saturated, which makes it resistant to environment (oxygen, UV, chemicals).

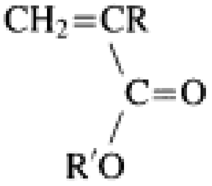


Figure 29. *Acrylate monomer. R can be H or CH_3. [58, p. 487]*

3.3.4 Wetting, bonding and debonding of PSAs

General requirement for all adhesives is that they must wet the substrate where they are applied, i.e. the adhesive must flow to allow molecular contact with the substrate [25, p. 500–504]. After bonding, however, the adhesive must behave like a solid to be able to bear a load and resist fracture and debonding. The interfacial interactions (mainly dispersion) provide the driving force for spreading of the adhesive, and the rheological properties control the resistance to the flow, which is needed for the spreading. For adhesives that are applied as liquid the resistance to flow is controlled by its viscosity. However, PSAs are different to other adhesives in that they are not low viscosity liquids, but more like soft solids and it is therefore the modulus (stiffness) of the PSA, which controls the wetting flow (lower modulus promoting wetting).

PSA has to have resistance to debonding from the surface, but it also should be removable with a moderate force in many PSA applications [25, p. 504]. Debonding the adhesive – substrate interface can only occur by deforming the adhesive itself. PSAs are very soft (compared to other adhesives) and they deform strongly during debonding. When the PSA is subjected to peeling stress, internal voids appear in the material, which then coalesce and create filaments of adhesive, which then elongates. Fibril elongation of rubber and acrylic PSAs is presented in Figure 30. The failure happens usually as detachment of the adhesive strand from the substrate (the adhesive should not fail cohesively and leave any residue on the substrate) [25, p. 504]. It depends on the strength of the interface, how much the adhesive must deform to separate the interface, and it depends on the adhesive mechanical properties how much work (peel force) is needed for this deformation.

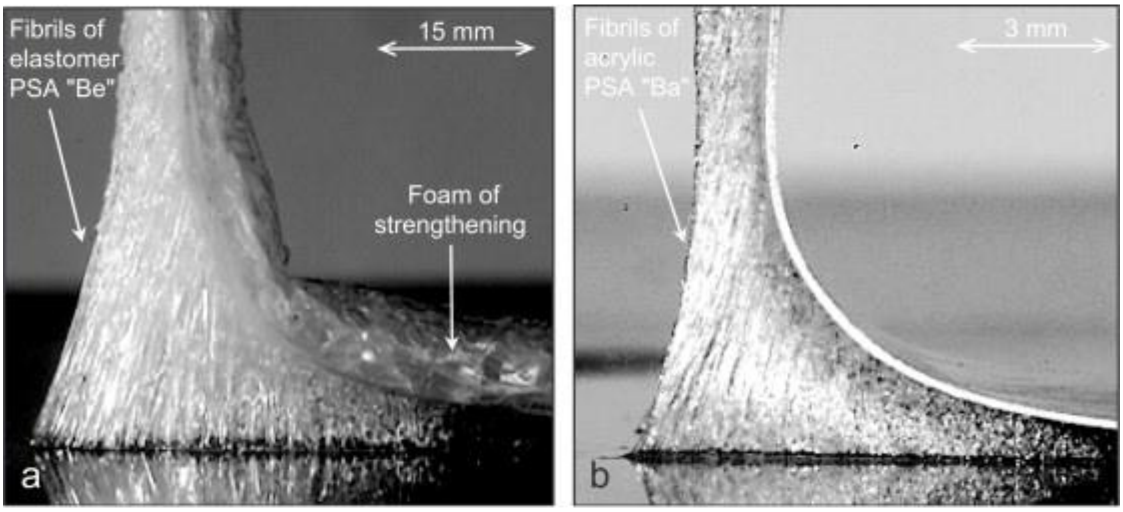


Figure 30. *Fibril elongation of rubber-based PSA(a) and acrylic PSA (b) in the peeling observed with a fast CCD camera [64, p. 663].*

3.3.5 Performance tests of PSAs: Tack, Peel and Shear

The behavior of PSAs can be reduced to three fundamental physical properties, which are interconnected: tack, adhesion or peel adhesion and shear strength or cohesion [59, p. 53–57]. Tack means the ability of the adhesive to adhere quickly under light pressure, peel adhesion means ability to resist removal by peeling and shear strength means the ability to maintain position under shear forces. These properties are not inherent properties of a PSA but they are a response to the bulk and surface properties of the adhesive [65, p. 24]. Tack, peel and shear performance tests have certain characteristic time scale, and requirements of the rheological properties at those time scales.

Tack

Tack, or initial adhesion or in every-day language “stickiness” is a property of a material, which allows it to form a physical bond immediately when it is brought to contact with another material [59, p. 53] and to provide significant resistance to debonding [25, p. 505]. After the adhesive is applied to the surface, it takes some time that wetting of the surface occurs and thus optimum contact and adhesion is achieved [59, p. 53–54]. This time varies between fractions of a second to weeks. Wetting can be accelerated by applying pressure. A subjective test of tack or stickiness is how well a PSA sticks to a finger, when only slight pressure and short dwell time is used. A common tack test is probe tack test, where a probe is brought into contact with adhesive for a certain dwell time (typically is order of 1 s) and the pulled away [25, p. 505]. Tack test can be considered to be a measure of the wettability of the PSA under controlled conditions [59, p. 54]. Tack increases when soft, viscous component is added to the adhesive formulation.

Kowalski and Czech [33] have studied tack of acrylic PSAs on rough surfaces. They found that the tack performance was controlled by the adhesive's viscoelastic properties and the final tack performance was strongly affected by the level of substrate roughness as well as PSA thickness.

Peel adhesion

As described in Chapter 2, the term adhesion can be understood as the process in which two materials are brought together and attached to each other as a results of all interfacial forces, and practical adhesion (or peel adhesion) is the energy needed to break the assembly and separate the two substances, and this is measured with peel tests. Peeling properties of a PSA product are determined by the surface properties of the adherend bulk rheological properties of the system and [34, p. 99]. When the PSA contacts the substrate under a light pressure, a bond is formed between them [59, p. 55]. First only small adhesion points are formed, but the number and size of these adhesion points are increased by elastic deformation, viscous flow and wetting of the substrate (bonding). In the following phase, the assembly is separated by tension force, and deformed in this process. High peel adhesion requires sufficient tack level for bonding and sufficient cohesion (shear strength) for debonding. Peel adhesion is also dependent on the ratio of elastic and viscous components of the adhesive.

Peel adhesion measurement (peel test)

Since peel test is an important part of this work, it is described here in more detail. Peel test is the most common method for testing the PSA strength [2, p. 10:29]. There are different versions of the peel tests with different peel angle, peel speed and substrate used. At least one of the adherends is flexible material and can be deformed plastically in the measurement [18, p. 70]. Figure 31 presents a typical T-peel test (described in ASTM D1876 [66], cited in [18]), and a 180° peel test (described in ASTM D903 [67], cited in [18]). In the T-peel test, two thin, flexible adherends are bonded with an adhesive. A variation for T-peel test is 90° peel test, where the lower flexible adherend is replaced with a thick, rigid adherend, and the flexible adherend is peeled away at 90° angle. Also in the 180° peel test (Figure 31 b), a flexible adherend is bonded to a rigid adherend, but the peeling angle is different. In this test, the flexible adherend has to be very flexible, so that it can be bended without yielding to fracture. 180° peel test is often used for films or sheets.

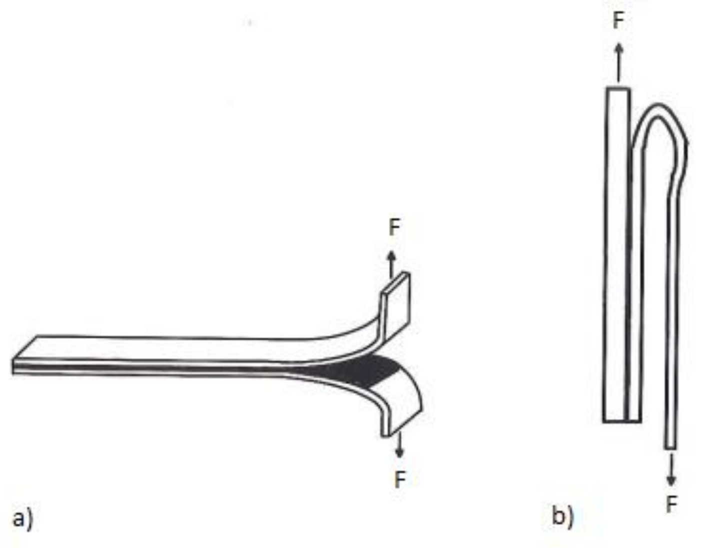


***Figure 31**. a) T-peel test and b) 180° peel test (figure adapted from [18, p. 70])*

Different peeling angles lead to different peel values [2, p. 10:33]. In addition, the adhesive bond strength depends on the peel rate, because of the viscoelastic properties of PSAs and the mechanical properties of the face material. This has to be taken into account when practical application conditions differ from test conditions. Peel is also affected by the contact time between the adhesive and the substrate (= dwell time) as well as modulus and thickness of the adhesive layer. When the peel rate is low, the peel adhesion depends mainly on the work of adhesion, but at higher peel rates it is affected more by the deformation energy. In addition, substrate, adhesive composition, interface, response to stress, stress distribution and mode of failure are factors that affect the peel adhesion [38].

Shear

The third important property of PSAs is its shear strength or cohesion [59, p. 57]. When the PSA is subjected to increasing shear force, distortion of the adhesion begins, and proceeds until a point of product failure. The type of failure depends on how quickly the liquid component of the viscoelastic adhesive can respond to the applied shear force. If the stress is increasing rapidly, the PSA behavior is elastic and the adhesive separates at the interface, or the backing substrate is broken. If the stress is increasing slowly, the liquid component has time to respond fully, allowing molecular disentanglement, and the result is cohesive failure of the adhesive. Shear strength of PSA can be modified with tackifiers and cross-linking.

Adhesion–cohesion balance

The balance between adhesion (which is required for binding and debonding) and cohesion (required for debonding) is important for the performance of PSAs [59, p. 57]. Adhesion is characterized by tack and peel and cohesion by shear resistance and also somewhat by peel. The bonding efficiency is related to the adhesive’s ability to exhibit viscous flow.

3.3.6 Effect of rheology on the performance of PSAs

Prerequisite for good tack for an adhesive is low glass transition temperature (between -70°C – -25 °C or below use temperature) and completely amorphous structure [2, p. 10:11] [58, p. 466]. Modulus of the PSA has an important role in the performance of PSAs. Tack, peel, and shear, all have a certain characteristic time scale, and requirements of the rheological properties (e.g. G′, G″) at those time scales [25, p. 505]. Cases for tack and peel are described here mainly according to Yarusso [25].

So-called *Dahlquist’s criterion for tack* is that adhesive should have G’ $< 10^5$ Pa, since this is the highest modulus that allows the adhesive to wet out the surface and form dispersive bonds (1 s chosen as time scale for tack) (originally presented by Dahlquist, cited in e.g. [25, p. 505][38, p. 172][65, p. 25]). Dahlquist’s criterion ensures that the adhesive deforms sufficiently to wet the surface and form the bond but it does not ensure resistance to debonding, so it is not sufficient criterion for tack alone.

Dwell time in *a peel* test is much longer than in a tack test, due to slow wetting and bonding processes [25, p. 506]. The tendency of adhesion to increase with dwell time depends on the ability of the adhesive to undergo viscous flow, especially with rough surfaces (in addition to interfacial chemistry mechanisms). Time scale characteristic to PSA adhesive deformation in peeling depends on peeling rate and adhesive thickness. Peel front for a PSA tape is presented in Figure 32. λ is length of stress wave, and it is approximately the length over which the PSA is significantly deformed (in the direction of peel) and it is always of the order of the adhesive thickness. Characteristic time scale

(t) of PSA deformation for typical adhesive thickness h (30 μm) and moderate/slow peel rate v (30 cm/min = 5 mm /s) is as follows:

$$t = \frac{h}{v} = \frac{30x10^{6}m}{30x10^{-2}m/min} * \frac{60s}{min} = 6x10^{-3}s \qquad (5)$$

Value 0.01 s often used as a representative value for time scale of peel [25, p. 507].

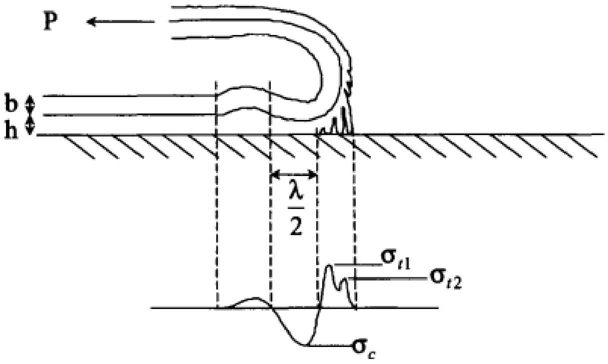


Figure 32. *Typical PSA peel front which shows local tensile and compressive stresses which the adhesive has caused to the substrate [25, p. 507].*

In the bonding time scale (1 s) low modulus of the adhesive is needed for wetting [25, p. 507–508]. In the debonding time scale (0.01 s), the adhesive should be stiff (high modulus) according to a common qualitative rule but Yarusso [25] states that it is probably more important that the adhesive has high energy loss characteristics (high G'') at the relevant frequency. Linear viscoelastic properties (G(t), G*, G', G'') as a function of frequency and time scale for a typical PSA is presented in Figure 33 [25, p. 508].

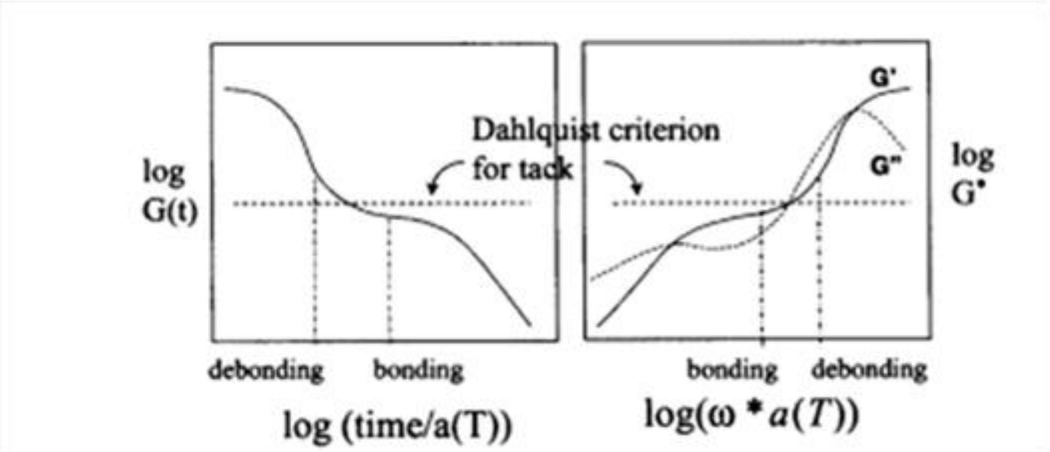


Figure 33. *Linear viscoelastic master curves of PSA and Dahlquist criterion for tack as presented by Yarusso [25, p. 508].*

In the Figure 33, the moduli (G(t), G*, G’, G’’) are shown in relation to Dahlquist criterion for tack and typical time scales for bonding and debonding in tack and peel tests. In the lower frequency (bonding time scale), G’ of PSA is typically higher than G’’, although best wetting would be achieved if the viscous component (G’’) would dominate [25, p. 508]. However, this would make removing of the PSA difficult. According to Yarusso, it is sufficient that the G’ is low enough to allow deformation for wetting. At the higher frequency (debonding time scale), PSA is stiffer (higher G’) and has also higher energy dissipation (higher G’’) than in the bonding time scale.

Relationship of G’, G’’, tan δ and peel force in literature

In the present study, we are most interested in understanding the PSA behavior in peel, and influence of PSA properties on it. In the literature of PSAs and rheology, different authors present different connections between viscoelastic parameters (G*, G’ and G’’, tan δ) and peel force.

Several authors suggest as Yarusso [25] above, that high G’’ at higher (debonding) frequency is of importance: According to e.g. Mazzeo [68] and Brase et. al [69] the higher the G’’ (at debonding frequencies), the higher the peel strength. Brase, Walter and Bhongir from Henkel Corp. investigated how hot-melt PSA formulae affect the release performance with siliconized systems in labels [69]. They used a series of commercially available hot-melt pressure-sensitive adhesives (HMPSA) together with a single, UV-cured silicone release formulation. Effects of rheology, tackifier chemistry as well as elastomer chemistry on the release performance were estimated by determining the release force under both ramped and constant velocity. They found that there was a strong inverse correlation between loss modulus value (G’’) and the release-force value (lower release force for higher G’’ (stiffer) adhesives and vice versa). Correlation between the tackifier or elastomer chemistry and the release force was not found [69]. Smith and Walter (Henkel Adhesive Technologies) continued the study by investigating release liners of increasing additive amount and thus decreasing surface energy [70]. They conclude that the loss modulus of the HMPSA is a critical parameter, which has strong influence on the high-speed release performance and that this effect is higher in softer (lower G’’) adhesives. For higher G’’ adhesives, greater liner surface energy is needed if release performance is desired to be changed. The “softer” (lower G’’) adhesive were found to be more sensitive to the variation of the surface energy and also the coating weight [70]. However, these two studies dealt with labels, which have higher peel speed than in the applications in the present study.

Chang [71, p. 15–16] states (in accordance with Yaurusso [25]) that the lower the G’ at low frequency, the more favorable is bonding. Debonding strength comes from two contributing terms, the cohesive strength, indicated by G’ and the energy dissipation term, G’’ and the higher are the debonding G’ *and* G’’ values, the higher is the debonding strength according to Chang (somewhat different to correlation between only G’’ and peel force presented above). According to Benedek [2, p. 10:33] instead, the peel strength is proportional to tan delta (= G’’/G’) at the respective debonding and bonding frequencies. Gordon et.al [13][14] found that release profile of PSA–silicone system is dictated by the relative ability of PSA to dissipate and store energy (i.e. tan δ), and specifically the frequency dependence of tan δ (position of tan δ maxima) correlated with release profiles. Figure 34 presents a rheological data for a rubber-based adhesive form the work of Gordon et. al. [13][14] and Figure 35 shows a satisfactory linear correlation between logarithmic of release force and logarithmic of adhesive tan δ(ω, h) (h = adhesive thickness). Gordon and Schmidt [14] present an empirical model based on the viscoelastic properties of the adhesive and release coating, which describe release force profiles of acrylic and rubber based PSAs.

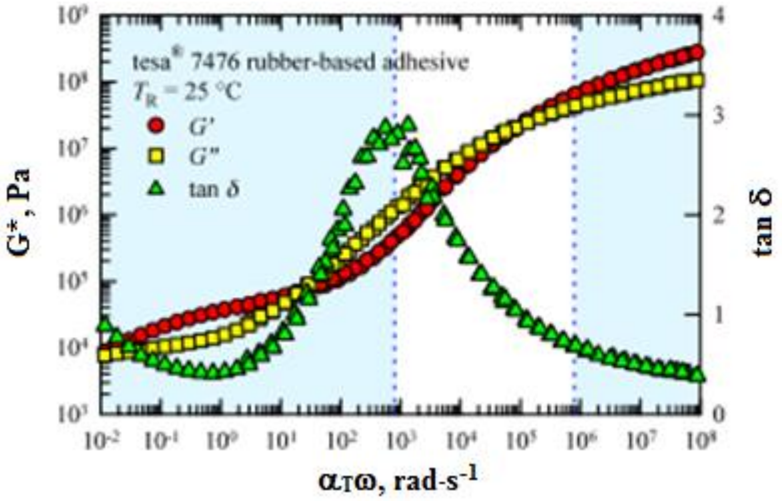


Figure 34. *Rheological master curves for tesa® 7476 rubber-based adhesives (T = 25 °C). The white area is the frequency windows corresponding to the used peel rates and the thickness of the adhesive as measured from scanning electron microscopy image. TTS was used to enlarge the frequency range. [13, p. 9]*

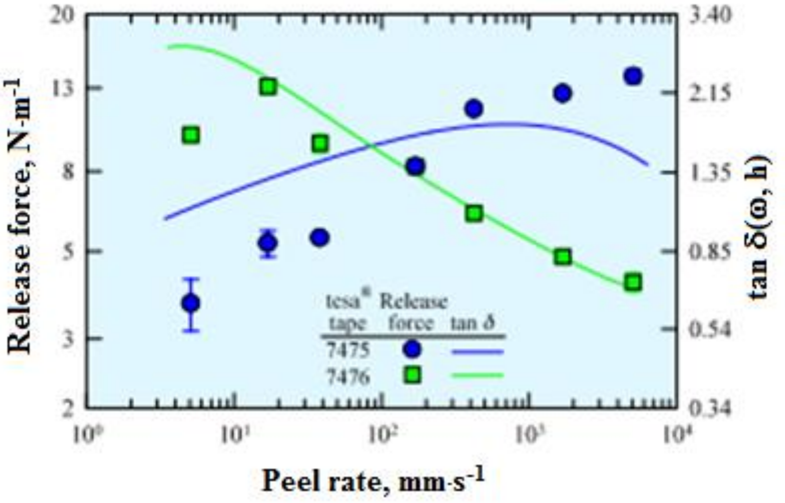


Figure 35. *Release force and tan δ as a function of peel rate for siliconized liners and acrylic (tesa 7475) and rubber (tesa 7476) based adhesives. Tan δ(ω, h) (h = adhesive thickness), can be related to peel rate (v) with empirical equation $\omega = 2\pi v/h$.[13, p. 10]*

Benedek [2, p. 2:11] states that peel force is related to the storage modulus (G') of the PSA as follows: High tack, removable adhesives should have low G' (apparently Benedek means low G' at low frequency). For maximum peel force, highest possible G' is required at higher frequency. This means that for high peel force, the slope of G' is high. Benedek [2, p. 2:23] states that removability can also be achieved another way, by low tack of PSA with high elasticity, poor contact with surface and thus poor wetting.

Description of Ulman [72] (referring to text of Chu [38]) is similar to Benedek of high slope of G' correlating with high peel force: bonding correlates with G' at low frequency (0.1 rad/s) and debonding with a ratio of the elastic moduli at high and low frequency: G'(100 rad/s)/G'(0.1 rad/s). Chu criterion for optimal combination of peel, tack and shear is [38] (original reference), cited in e.g. [34][65][72]:

(i) $G'\ (\omega = 0.1\ \text{rad/s}) \sim 2\text{–}4 \times 10^4$ Pa, and

(ii) $5 < [G'\ (\omega = 100)/G'\ (\omega = 0.1)] < 300$.

Since the energy-absorbing capability of the adhesive layer is the greater the greater is the thickness of the layer, the release force is also higher for higher adhesive thickness (as also for silicone layer, Chapter 3.2.3). Influence of adhesive thickness on release force for water-based and hot-melt adhesives according to DowCorning [11], is presented in Figure 36. The influence of layer thickness for stiff, fairly inelastic materials, may be very small. It can be seen from the figure, that that layer thickness has less influence on hot-melt than water-based adhesives.

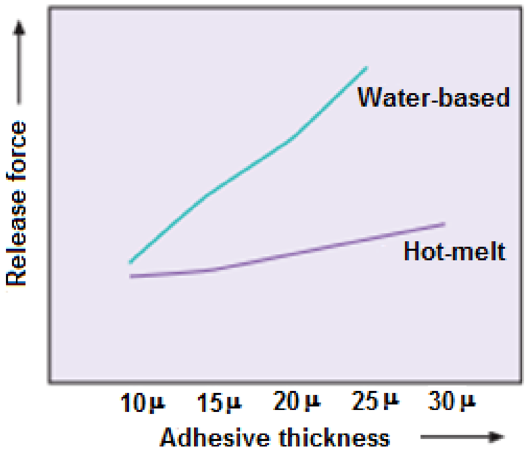


Figure 36. *Effect of adhesive thickness on release force for water-based and hot-melt adhesives. Figure adapted from [11, p. 1].*

As a summary, the following rheological parameters have been presented to correlate with peel force: G'' at debonding frequency, tan δ, position of tan δ peak (correlation with release force as a function of peel rate), magnitude of G' and G'' at binding and debonding frequencies, low G' at bonding frequency (correlates with bonding, meaning high tack), and a ratio of the G' at high and low frequency (slope of G').

4. RELEASE PERFORMANCE SUMMARY

Release of a pressure sensitive adhesive from a release coating is a complex phenomenon with several factors affecting it. Both interfacial and rheological properties interact in bonding and debonding processes of PSAs [25, p. 500]. Interface-related factors are the interfacial energies, the wetting behavior and the strength of intermolecular forces which act across the interface discussed in Chapter 2.1. Surface and interfacial properties and work of adhesion are important but not alone responsible for adhesion control and the actual work of separation is higher that would be predicted from the surface energies of the adhesive and adhered, because of the energy dissipation occurring in the separation [13]. Rheology of the PSA, as well as the rheology of the release system also affects the release of PSA from the release liner. Flexibility of the PDMS molecule makes silicone a good release material mainly due to interfacial slippage, which decreases the effect of the energy dissipation [4, p. 542] Requirements of the PSA rheological properties are different in the bonding (high time-scale, low frequency) and the debonding (low time-scale, high frequency) steps.

Factors affecting the release liner performance are base the material variations (porosity, roughness), the silicone coating, the nature of the adhesive, the laminate/PSA product characteristics and the peeling (liner stripping) process [2, p. 7:38][5]. Factors due to the release liner and silicone coating have also been discussed in Chapter 3.2, as well as the role of the PSAs in Chapter 3.3., and all the factors are summarized below.

Variables in the release liner: Base paper properties, mainly roughness, porosity and possible surface treatments have influence on the final performance of the release liner [5][10, p. 604]. Factors affecting the release performance in silicone coating are chemical composition, coating weight, film continuity and coverage, degree of cure and cross-link density and modulus [5][10, p. 604][56]. Way of applying silicone coating (solventless, solvent based, emulsion) also affects the release performance [5]. There are two main approaches to control the release forces with silicone coating: controlling cross-link density and addition of high release additives [8]. The cross-linking density depends on the molecular weight of the PDMS and the amount of active cross linker sites. HRA increases the energy-dissipating ability of the silicone network (change of G’, G’’, tan δ) [5].

Also the silicone coat weight has influence on the release performance [10], p. 604]. In addition, the thickness/ amount of precoating, as well as the porosity of the base paper, has importance on the release performance of the release liner [1, 02][6]. In this study, three values of base paper porosity, and two levels of precoating and 3 levels of silicone coating were considered with silicone emulsion cured by heat (and no HRAs used).

Variables related to the PSA: Mechanical and rheological properties of the PSAs are important for the adhesion / performance of adhesives [25, p. 500]. Factors affecting the release performance that are related to adhesives are chemical type, thickness, modulus, and diluents [10, p. 604]. Sun [34] mentions also compatibility of components in PSA. According to rheological theory discussed by Feldstein and Siegel [39], important factors in determining the strength of the adhesive joint are high cohesive strength, high diffusion coefficient and long relaxation time of the PSA material. At the molecular level, the high strength of the adhesive joint is a compromise between two generally conflicting factors (and thus difficult to combine in a single polymer material), high energy of intermolecular cohesion and large free volume. The ratio between these two can be expressed with parameters such as glass transition temperature, diffusion coefficient, relaxation time, elastic modulus and tangent δ.

Variables in the lamination and stripping process: Laminate or PSA product characteristics also affect the release performance. Both paper age and laminate age may have influence, as well as the thickness and the modulus of the product and the mode of the lamination process including adhesive coater design, temperature and speed [5][10, p. 604]. Regarding hygiene products, important variables are also the face stock material of the product as well as the way of application of the adhesive (spray/ strip) [6]. In addition, stripping operation variables are dwell time, peel speed, peel angle, temperature, and physical dimensions of the product components [2, p. 2:16][10, p. 604].

5. MATERIALS AND RESEARCH METHODS

The purpose of the experimental part of the work was to examine the effect of porosity of the base paper as well as coat weights of precoating and silicone coating on the release performance of the release liner. In addition, several different commercial adhesives were examined. In this chapter, release liner samples and adhesives are first shortly presented, and then all equipment and test methods used. These methods are those used for fabrication and characterization of the release liner samples (base paper and coated paper) including e.g. air permeance, contact angle and profilometer measurements, rotation rheometer measurements for characterizing the adhesives, hot-melt application for applying the adhesives and finally release force measurements.

5.1 Release liner samples and adhesives

Release liner samples with three different base paper porosity levels, two different precoating coat weight levels and three different silicone coat weight levels (18 samples) are presented in Table 3 with increasing coating mixture solids content / coat weight (Pre1, Pre2 and Si1, Si2, Si3) and decreasing porosity (increasing air permeance in Gurley units; Po1, Po2, Po3).

***Table 3**. The 18 release liner samples with 2 levels of precoating, 3 levels of silicone coating and 3 levels of base paper porosity*

Sample name	Precoating (increasing SC% and coat weight)	Silicone (increasing SC% and coat weight)	Air permeance/ Porosity (increasing Gurley value / decreasing porosity)
Pre1/Si1/Po1	Pre1	Si1	Po1
Pre1/Si1/Po2			Po2
Pre1/Si1/Po3			Po3
Pre1/Si2/Po1		Si2	Po1
Pre1/Si2/Po2			Po2
Pre1/Si2/Po3			Po3
Pre1/Si3/Po1		Si3	Po1
Pre1/Si3/Po2			Po2
Pre1/Si3/Po3			Po3
Pre2/Si1/Po1	Pre2	Si1	Po1
Pre2/Si1/Po2			Po2
Pre2/Si1/Po3			Po3
Pre2/Si2/Po1		Si2	Po1
Pre2/Si2/Po2			Po2
Pre2/Si2/Po3			Po3
Pre2/Si3/Po1		Si3	Po1
Pre2/Si3/Po2			Po2
Pre2/Si3/Po3			Po3

For each base paper porosity level (presented in Table 3), air permeance range of ca. 10-25 ml/min was selected (see Chapter 6.1). Base paper porosity variations had been carried out by changing the degree of refining in the papermaking process. During this work, the ready-made base paper was hand coated first with precoating and then with silicone coating. Original plan was to prepare samples with three different base paper porosity levels, three different precoating coat weight levels as well as three different silicone coat weight levels (3*3*3 = 27 samples). However, it turned out to be difficult to get clear differences between the three precoating coat weights, and only two levels were thus used (3*2*3 = 18 samples).

Six commercial adhesives were used in the study (presented in Table 4). These adhesives are hot-melt styrenic-based block copolymer (SBC) adhesives with SIS or SBS as base polymer. Four of the adhesives (A1, A2, A5, and A6) are for feminine hygiene products and two (A3 and A4) for envelope applications. A4 is also used to fasten medical drapes to skin.

Table 4. *Adhesives used in the study. All the adhesives are synthetic rubber based.*

Name	Application	Working T [°C]
A1	Feminine hygiene products	125–165
A2	Feminine hygiene products	150–165
A3	Envelope / security bags (tapes, labels, coatings)	160–190
A4	Envelope / security bags, also to fasten medical drapes to skin (tapes, labels, coatings); high tack	150–180
A5	Feminine hygiene products	130–175
A6	Feminine hygiene products	130–175

5.2 Equipment and test methods

5.2.1 Methods for release liner samples

Air permeance (porosity). Air permeance, which is closely related to the porosity of paper [50, p. 274], can be measured with different air leakage instruments, which measure the flow of air through a defined area of the paper caused by a defined pressure difference between the sides of the paper [48, p. 155]. The most common air permeance testers are Bendsten and Sheffield testers which measure air flow in milliliters per minute (ml/min) and Gurley tester, which measure the time required for 100 ml of air to flow through paper (unit Gurley). In this work, target porosities/ air permeance values of the three different base papers (Po1, Po2, and Po3) were expressed in Gurley units, and re-measured using ml/min units with L&W air permeance tester and a defined range of variation of the air permeance values was selected for the experiment (according to Table 5 in Chapter 6.1), in order to get clear differences between the three different porosity levels. Air permeance values were also measured for precoated and silicone coated papers.

Cobb60 water absorption. Cobb water absorption tests were performed for base paper samples, in order to see if there would be differences in absorption of coating colour between the base papers of different porosities. Cobb value gives the penetration speed of water to the substrate [73, p. 100]. Cobb value can be defined for different measuring times. Cobb value of 60 seconds, Cobb60, was used in this exercise. In this test, a 13x13 cm piece of the paper is attached to the Cobb water absorption apparatus (test area 100 cm^2) and 100 ml water is put on it for 45 seconds, after which water is thrown away and paper is pressed dry between two absorbent papers moving a metal roller back and forth. Sample is exposed to water for 45 seconds + 15 seconds (time for throwing the water away and drying) = 60 seconds. Mass of the samples were taken dry and wet, and the absorbed water mass is obtained by subtracting these values.

Coating mixture measurements. Viscosity, pH, and solids contents were determined for each batch of precoating and silicone coating mixtures. Viscosity was measured using Brookfield viscometer (model RVDV-I PRIME, spindle S02-04, 100 rpm), pH with Mettler Toledo SevenCompact pH/Ion meter, and solid content with some of the three following moisture analyzers: Sartorius MA100, Mettler Toledo HB-43-S or Mettler Toledo HG53.

Hand coating. Coating of precoating and silicone coating were performed using a hand coater K202 Control Coater by RK Print Coat Instruments Ltd. In hand coating, the paper is fastened on the base of the coating device, and a coating rod is placed on top of the paper. Coating mixture is applied on/besides the rod, and the rod then moves over the paper. An even rod was used for coatings. Grooved rods are also available, which can be used to control the amount of coating, but it leads to uneven coating thickness. The speed of the coater can be adjusted with a scale 1–10. Speed 10 was used in all coatings. The coated paper was then dried in oven at 120° C (precoated papers for 1 min 40 s and silicone coated for 1 min) to remove the water involved with the coating mixture.

Coat weight determination. Coat weight of precoating was determined by weighing so that only a half paper sheet was coated, and 10 * 10 cm^2 pieces of coated and uncoated half of the paper were weighed and values subtracted from each other. In addition, ash contents of the precoated samples were determined for recalculating coat weights according to standard ISO 1762 (3–5 g sample in a crucible at least 5 hours at 525 °C in the oven) [74]. Silicone coat weight were measured using Lab-X3500 LZ3108N X-ray fluorescence (XRF) analyzer by Oxford Instruments. Since precoating also contains some silicone (in clay), the silicone amount of precoated paper had to be first determined for each precoating levels, and this value was subtracted from the value of siliconized paper.

In addition, *optical microscope* images were taken for precoated samples. Contact angle and profilometer measurements with are presented in more detail below.

Contact angle measurements

Contact angle measurements are the easiest way to estimate the surface energy of solids (see Chapter 2) In this work, contact angles of water were determined for the release liner samples, but surface energies were not calculated since the same information about the differences between the samples can be obtained from the contact angles. Calculation of adhesion work is in any case not possible in this work since the surface energy of the adhesive can't be measured with the device available. Therefore, only contact angles of the different samples are presented in this work. In a contact angle measurement, a liquid drop is placed on the solid surface, and the angle of contact is measured at the point between solid, liquid, and vapour (as was presented in Figure 7) [18, p. 94–95]. The solid surface is assumed to be perfectly rigid and smooth, and the liquid is chosen so that it does not interact chemically with the surface. These assumptions are difficult to achieve in reality, but contact angle methods can still provide useful data.

In a contact angle measurement, the liquid drop is laid carefully by the contact angle instrument to the surface [18, p. 94–95]. The measurements depend on the direction in which the measurements are made: when the droplet spreads, it *advances* over the surface (*advancing contact angle*), and if liquid is withdrawn from a drop it is called *receding contact angle.* This difference between advancing and receding contact angles is called *contact angle hysteresis.*

Contact angle measurements were performed using KSV CAM200 equipment (Figure 37) at ambient conditions (23 °C and 50% relative humidity). Distilled water was used as liquid.

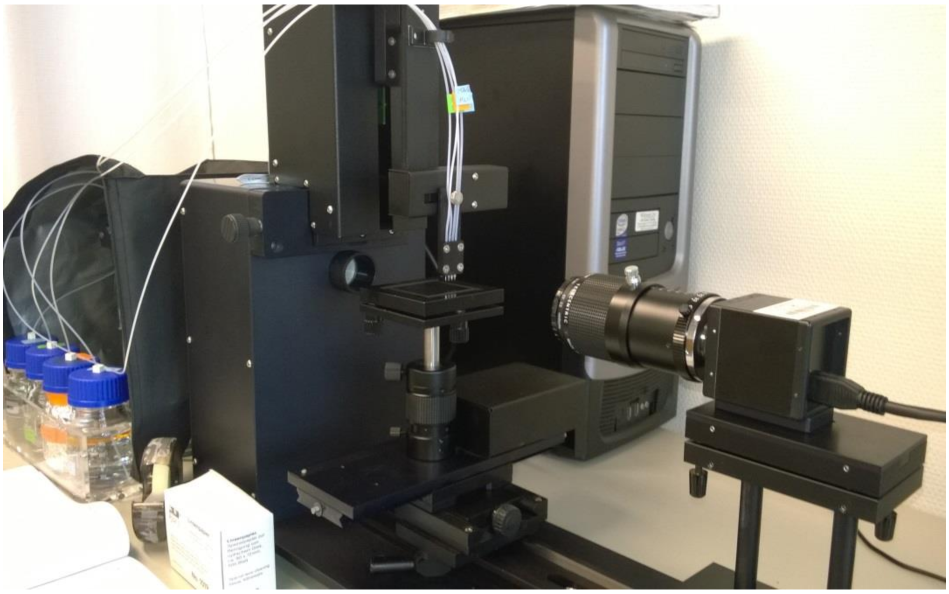


Figure 37. *KSV CAM200 contact angle measurement equipment.*

For static contact angles, three parallel sample papers were used, and 5–10 droplets (2 μl) were used for each sample. Since differences in static contact angles between the samples were small (negligible), also dynamic contact angles (advancing and receding angles) were measured, since they can provide better information for small differences of surfaces. For dynamic angles, three droplets for one sample were used. Advancing and receding angles were measured by increasing and decreasing the droplet volume (up to 30 μl). An image was taken from the droplet with 1 s interval to determine the contact angles. An average value was calculated from the points were the advancing/receding droplets were constantly changing.

Profilometer measurements

Surface roughness measurements were performed for the siliconized papers using Alicona InfiniteFocus G5 optical 3D measuring system based on focus-variation technology (Figure 38). Objective magnification 10x was used with LED ring light, and size of the area scanned was 2 x 2 mm (total measurement area 4.5 x 4.5 mm). Measurements were performed by Jarmo Laakso from TUT. Surface roughness measurements provide profile roughness data (e.g. R_a, R_q, R_z values) or surface texture (e.g. S_a, S_q, S_z), which means area based roughness.

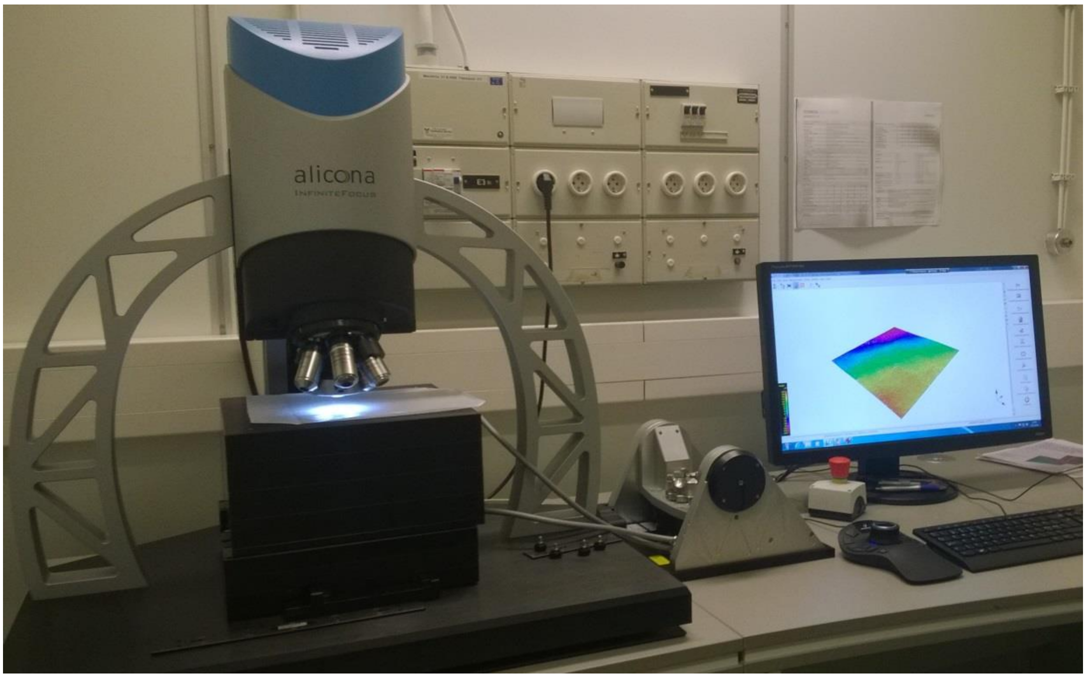


Figure 38. *Alicona InfiniteFocus G5 optical 3D measuring system.*

5.2.2 Rotation rheometer measurements for adhesives

Rheology is a useful and fast way to examine properties of pressure sensitive adhesives [34, p. 98]. Rotation rheometer measurement provides information such as evolution of the complex shear modulus G* (and its real and imaginary parts, G' and G'') as a function of angular frequency (ω), which describes rheological properties of the PSA through its various relaxation processes [75, p. 4–17]. Rotation rheometer measurements were performed for adhesives in order to characterize their viscoelastic parameters, storage modulus (G'), loss modulus (G''), and loss factor (tan δ), and to examine if these parameters have correlation with the release performance of the adhesive (see Chapter 3.3.6).

Measurements were made by Pekka Laurikainen with Rotational Rheometer Anton Paar MCR301 at Tampere University of Technology using plate–plate geometry. Temperature was kept constant (room temperature) and measurements were made as a frequency sweep, as a function of the angular frequency. Amplitude (strain) was ca. 1 %. Maximum angular frequency available with the rheometer used was 1000 1/s, and minimum angular frequency in the measurements was 0.1 rad/s. In the peel test, the angular frequency (debonding frequency) depends on the thickness of the adhesive and the rate of speed. In the peel test used, the speed is "low", v = 5 mm/s, and ordinary thickness of the adhesive h ≈ 25 µm (e.g. reference [13]). Corresponding angular frequency is $\omega = 2*\pi*v / h = 1300$ rad/s (equation from e.g. from Gordon et. al [13][14]). Bonding frequency often used is 0.1 rad/s (e.g. Ulman [72]). The desired angular frequency level could thus approximately be reached. (Frequency range could be enlarged using time-temperature-superposition (TTS) principle [76], but it was not needed here.)

5.2.3 Hot-melt application

Adhesives were applied to the release liner samples using AltaBlue 4 TT melter and TrueCoat Slot Applicator by Nordson (Figure 39). MG kraft paper of 60 g/m^2 was used as a model face stock (rough, unglazed side against the adhesive). Temperature of the adhesive tank, hose and nozzle were adjusted according to use temperature instructions of the adhesive manufacturers. If temperature was too high, the adhesive flowed too much. Therefore, the lower limit of the use temperature given by the manufacturer (Table 4) was used. Speed of hot-melt application machine affects the thickness of the adhesive layer, which has some influence on the release force. The adhesive amount (mass of adhesive strip) was tried to keep constant for each adhesive (about the same level as is usually used in the quality control 0.6–0.8 g), and it was controlled by weighing the adhesive layer and fixing temperature and speed. Unfortunately, the thickness of the adhesive layer obtained with the hot-melt device used is not even, but thicker from the other end and thinner at the other (all release tests were performed starting from the same end). In addition, it appeared difficult to find right temperatures for controlling the adhesive amount, and adjustment of the speed was limited.

Therefore, the amount of adhesive was somewhat higher than in quality control, between 0.8–1.0 g. The effect of adhesive amount on the release force was also examined, but no clear trends could be seen at the mass range used (0.8–1.0 g).

Figure 39. *Hot melt adhesive melter (right) and slot applicator (left).*

After applying the adhesive to the release liner, the face stock was attached gently to the release liner with adhesive, and a gum roll was moved back and forth 3 times over the samples. After that, a weight (load 70 g/m^2) was put for 5 minutes above the sample. The release test was performed immediately after the 5 minutes under press.

5.2.4 Release tests

In this work, 180° peel test was used. Tests were performed with peel test device by TestPoint presented in Figure 40. Calibration papers (both side silicone coated paper of 100 g/m^2) were first used to check that the adhesive had been stabilized and the results remain at a similar level. Example of a release test curve is presented in Figure 41. The final result of release test is the average value of the peel force in unit N/m at x-axis range 40–120 mm. The curve is somewhat irregular. Some of the irregularity can be due to unevenness of the adhesive layer, since there were lines or steps in the transverse direction of the adhesive strip.

Sample preparation for peel tests was described above together with hot-melt application. In the peel test machine, the release liner was attached to the bottom, and model face stock (in which the adhesive was fastened) was peeled off.

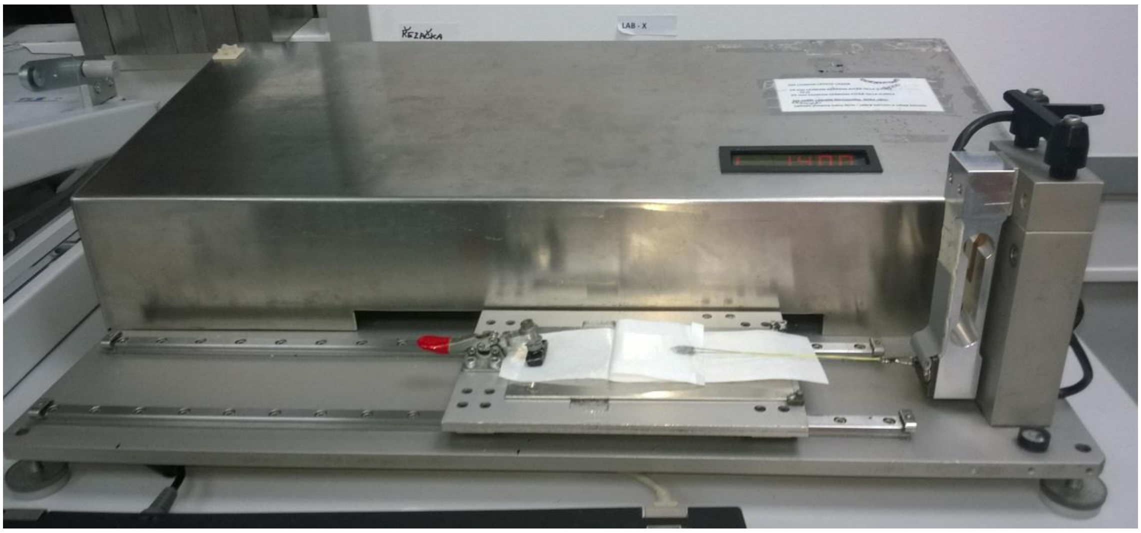


Figure 40. *180° peel test device by TestPoint.*

Nolla_Count 12399
Voima/g 0
Kerroin 0.3924
Pituus 200
3kg_Count
Count/10g 51.269
Leveys 25
TILA 16:59 19/04/16
Paluu Seis
Rulla

VetoArvot

	A
0	0
1	-0.06888
2	0.007653
3	0.926097
4	7.661351
5	5.594853
6	12.71279
7	11.02897
8	15.31504
9	14.54968
10	19.67765
11	18.60614
12	20.97878
13	19.90726
14	16.53964
15	17.22847
16	17.45808
17	17.99384
18	18.22345
19	17.99384
20	17.68769

Keskiarvo 14.785
K/A Alku 40
K/A Lop. 120
Vetojen K/A 15.342
Vedot 4
Vedot1-10 61.37
Paluunopeus -5000

	Veto1	Veto2	Veto3	Veto4	Veto5	Veto6	Veto7	Veto8	Veto9	Veto10
0	" 14.79"	" 17.78"	" 13.54"	" 15.26"	""	""	""	""	""	""

Figure 41. *Example of a peel test curve. The final result is average value of the peel force at x-axis range 40–120 mm. Width of the sample is 25 mm and the result is given in units N/m.*

TESA 7476 tape peel tests were performed for 6 of the 18 different release liner samples, in order to compare the results with the ordinary release liner, since there are less variables in the TESA tape test than in hot-melt adhesive test. TESA 7476 tape is for rubber-based adhesive. TESA test sample was prepared so that a piece of TESA tape was put on the release liner sample, and a gum roll was moved back and forth 3 times over the samples. After that, a weight (load 70 g/m^2) was put for 20 hours above the sample, after which one hour was waited before the measurements. Peel tests of TESA 7576 were performed with Zwick Roell peel test device (Figure 42) by a laboratorian.

Figure 42. *Zwick Roell 180° peel test device, which was used for TESA tape tests.*

6. RESULTS AND ANALYSIS

In this chapter, the results of the experimental part of the work are presented and analyzed. Air permeance values were measured for both base paper, precoated, and silicone coated papers (results for precoated papers are presented in Chapter 6.4 together with those of siliconized papers). In addition, grammage values (mass per unit area, g/m^2) and Cobb60 water absorption were determined for base paper. Viscosity, solids content, and pH were determined for the coating mixtures. Coat weights of precoating and silicone coating were determined and contact angle and roughness measurements were carried out for the release liner samples. Adhesives were characterized by their viscoelastic properties using rotation rheometer. Finally release tests were performed for the release liner samples first with TESA 7476 tape and then with the different adhesives (hot-melt tests).

6.1 Base paper

Base paper of the release liner was characterized by its air permeance, grammage, and Cobb water absorption. Air permeance values for base paper porosity levels of Po1, Po2, and Po3 were measured using ml/min units, and a defined permeance range was selected for the experiment according to Table 5, in order to get clear differences between the three different porosity levels. Porosity variation of papers of porosity level Po2 was narrow, and it was easy to select paper sheets with narrow (10 ml/min) range, but the other two porosity levels had more variation and the range became 20–25 ml/min.

Table 5. *Base paper air permeance range in ml/min selected for the experiment for porosity levels of Po1, Po2, and Po3.*

Porosity level	Min [ml/min]	Max [ml/min]	Range [ml/min]
Po1	Po1, min	Po1, max	25
Po2	Po2, min	Po2, max	10
Po3	Po3, min	Po3, max	20

Grammage values of the papers were measured by weighing 100 cm^2 samples of 10 sheets and calculating g/m^2 (Table 6). Average grammage value was 34 g/m^2 for paper of porosity Po1 and 35 g/m^2 for papers of porosities Po2 and Po3. Standard deviations for grammage values were small, between 0.2–0.4 g/m^2, which is around 0.5–1 %.

Cobb water absorption test was performed for base paper, in order to see if there would be differences in absorption of coating between the base papers of different porosities. Five parallel samples were used. Cobb60 results are presented in Table 7. Cobb60 values for base papers of different porosities are very similar, between 19–22 g/m^2 with standard deviations of 1–2 g/m^2 (5–9 %), so there are not significant differences in absorption of coating colour between these porosity levels.

Table 6. Base paper grammage (g/m^2) for 10 samples of Po1, Po2, and Po3 porosities.

	Po1	**Po2**	**Po3**
1	33.90	34.95	34.06
2	33.55	35.42	34.83
3	34.59	34.95	34.80
4	33.69	35.11	34.89
5	34.36	35.06	34.77
6	33.42	35.21	34.81
7	33.76	35.21	34.96
8	33.55	35.04	34.78
9	33.68	35.04	34.90
10	33.81	34.92	35.06
Average	**33.8**	**35.1**	**34.8**
Standard dev	0.37	0.15	0.27
Min	33.4	34.9	34.1
Max	34.6	35.4	35.1

Table 7. *Cobb60 water absorption (g/m^2) for base paper of Po1, Po2, and Po3 porosities.*

	Po1	**Po2**	**Po3**
1	20.1	21.7	18.8
2	19.5	20.5	17.4
3	19.5	19.3	17.9
4	18.5	21.6	20.1
5	21.3	24.7	21.8
Average	**20**	**22**	**19**
Standard dev.	**1**	**2**	**2**

6.2 Precoating and coat weight

6.2.1 Coating colour preparation

A typical coating color (pigment coating) formulation is presented in Table 8 [7, p. 17]. The formulation gives the dry amounts of the coating components relative to the dry amount of pigment (100). In addition to pigment, various binders and additives are used.

Table 8. *Typical coating colour (pigment coating) recipe* [7, *p. 17*].

		Relative amount (of dry weights)
Pigment	Clay, $CaCO_3$	100
Binder	SB latex, starch, CMC	12–14
Additives		1–2
Solids content		60

In this study, the coating included clay, latex (SBA copolymer + water), starch, CMC, and additives (defoamer). Three levels of solids contents were tested with goal of obtaining three coat weight levels with ca. 1 g/m^2 differences. Since it appeared that there can be relatively large variation in the coat weights between parallel samples of the same coating colour mixture, only two coat weight levels (Pre1 and Pre2) were finally made, with ca. 10 % unit difference in the solids content.

Starch, CMC, and latex were taken from tanks as water dispersion, and clay was either taken from the tank, or mixed as powder with water (and dispersing agent) in order to get higher solids content. Coating colour was then prepared by mixing starch, CMC, clay, and possible additive water and stirring first these ingredients for 10 minutes, and then adding latex and defoamer and stirring for additional 10 minutes. PH, (static) viscosity, and solids content were determined for the coating colour. Usually pH of the coating colour is adjusted with NaOH. In this work, pH adjustment of the precoating was not considered important and it was not performed. The temperature of the coating in the tanks and coating process is usually ca. 35° C for optimal runnability. However, the hand coating was made in room temperature. Dispersions taken from the batch were ca. 35° C when the coating was mixed, but the small amount of coating mixture (½–1 l) cools down quickly, and when the coating was ready and viscosity and pH measurements of the coating were performed, temperature was already close to the room temperature (24–27° C). Viscosities, pH, temperature, and solids contents of coatings are presented in Table 9.

Table 9. *Viscosity, pH, and solids content (SC) measurements for the precoating mixtures Pre1 and Pre2. Two batches were used for Pre2 coating colour. Po1-Po3 refer to the base paper porosity levels.*

	Pre2 batch 1	**Pre2 batch 2**	**Pre1**	**Ordinary coating**
Papers coated with this batch	**Po1 and Po2**	**Po3**	**Po1, Po2, and Po3**	
Viscosity* [mPas]	1058 (S04 52.9%)	380 (S04 18.9%)	245 (SO3 24.4 %)	1300 (S04)
pH	6.92	6.62	6.74	8
T [°C]	27.4	25.9	23.8	
SC%	Pre2, 1	Pre2, 2	Pre1	-

*S0X below viscosity value refers to spindle size used in the viscometer, and % value to load level in the measurement

Since the coating colour can be stored only a couple of days, two batches of Pre2 coating were made. Solids content of the second batch was very close to that of the first batch, but as it can be seen from the Table 9, there was a significant difference in viscosities of the two batches (first batch 1058 mPas, second batch 380 mPas). Only one viscosity measurement was performed, and it is possible that there is error in the viscosity measurement, since both SC%, temperature, and pH of the two coating mixtures are so similar, and in the coat weights (see below) of the precoated papers difference corresponding to this viscosity dissimilarity cannot be observed. Several viscosity measurements should have been performed in order to get more reliable viscosity data. In addition, viscosity values of both Pre2 batches are below the viscosity value (1300 mPas) of the ordinary coating mixture, but this is mainly due to the pH, since pH affects the viscosity, and pH adjustment was not performed. For precoating level of Pre1, all samples were coated with the same batch. Viscosity of the Pre1 coating mixture (lower SC%) is smaller than that of Pre2 (higher SC%) as it should be.

6.2.2 Coat weight

First, it was tested if different coat weight levels could be carried out by changing the speed (scale 1–10) of the hand coating, but no clear difference in coat weights with different speeds were achieved. Different coat weight levels were then carried out by changing the solid content of the coating color (using speed 10). Coat weight determined by weighing (10 * 10 cm^2 pieces of coated half and uncoated half and subtracting these form each other, measured from three paper sheets) are presented in Figure 43. Obtained coat weights of papers with precoating level of Pre2 and porosity of Po2 was used for estimating the right SC% of the coating, and five parallel results are available for this sample. Coat weights were also determined with ash contents, and these results are presented in Figure 44 together with weighing results. Only one parallel sample was available for ash content determination.

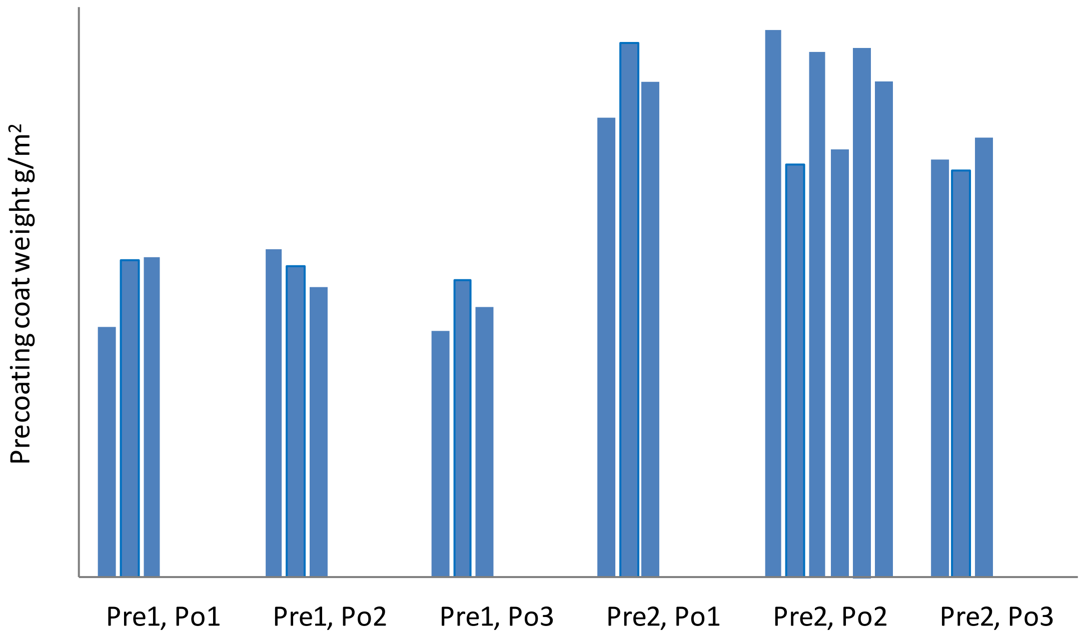


Figure 43. *Weighing results for precoating coat weight determination for precoating levels Pre1 and Pre2 and base paper porosities Po1, Po2, and Po3. Five parallel samples were measured for Pre2/Po2 sample, and 3 parallel samples for other samples.*

Figure 43. show that variation in coat weight between parallel samples is quite high, especially for the five samples of Pre2/Po2 sample (standard deviation was 14.4 %). This may be due to several factors, including variation of the tightness (pressure) of the coating rod in hand coating, insufficient mixing (although coating colour was always mixed after standing) changes in viscosity of the coating colour due to e.g. temperature. In addition, possible but improbable factors are influence of pH on the viscosity as well as conditions of drying. However, difference between precoating levels Pre1 and Pre2 is large enough to get differences between two different precoating levels.

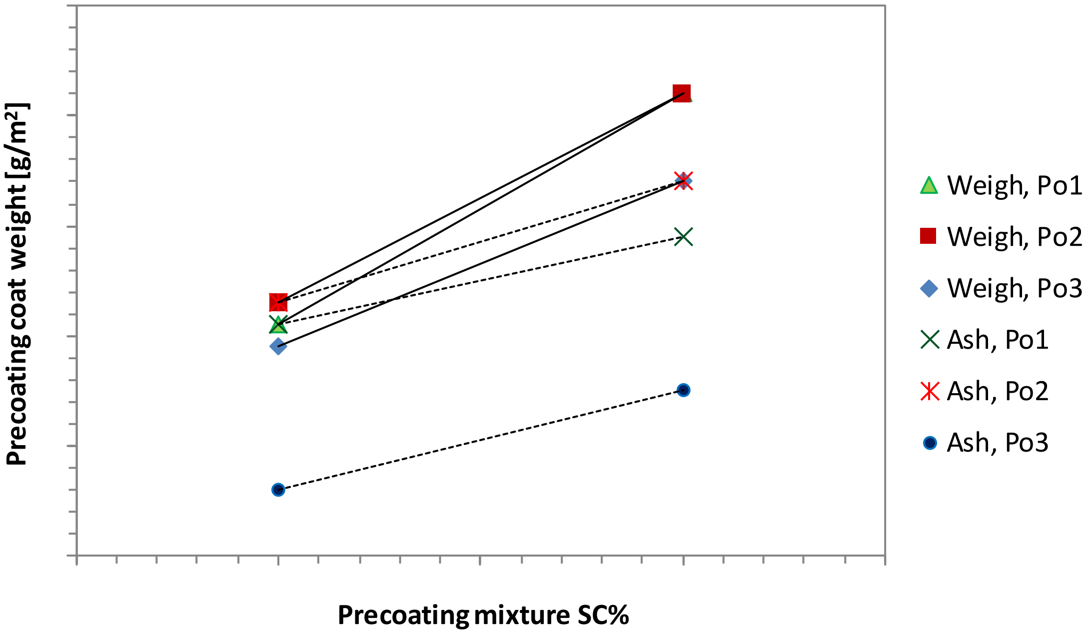


Figure 44. *Precoating coat weight as a function of solids content of the precoating mixture determined by weighing (solid lines) and by ash content (dashed line) for precoating levels Pre1 and Pre2 and base paper porosities Po1, Po2, and Po3.*

Coat weights of Pre1/Po1 and Pre1/Po2 samples are similar with both methods of coat weight determination (Figure 44). With Pre2/Po1 and Pre2/Po2 the variation of coat weight determined by weighing was larger, so somewhat lower coat weight determined with ash contents is understandable result. However, Po3 coat weight values determined using ash contents is significantly lower both for Pre1 and Pre2 samples. Pre2/Po3 samples were coated using a different batch of precoating mixture than Pre2/Po1 and Pre2/Po2 samples, but all Pre1 samples were coated with same precoating mixture batch, so difference is not due to different batches. In addition, variation of coat weight (determined by weighing) between parallel samples of Pre1 precoating level was small, and coat weight for sample Pre1/Po3 obtained from ash contents is clearly below this. More parallel samples would have been needed for ash content determination, but since these measurements were made at the end of the project, more samples were not left anymore.

Both methods of coat weight determination indicate that there is less precoating at the paper of porosity Po3 than papers of porosities Po1 and Po2. However, the large difference in ash content results for Po3 paper does not seem reliable, and therefore coat weight values used later in this work are those obtained by weighing (Figure 43).

6.2.3 Microscope cross-cut images

Microscope images of cross-cut of precoated samples Pre1/Po2 and Pre2/Po2 were taken with optical microscope (original image 400 x magnification). These images are presented in Figures 45 and 46. The cross-cut images indicate similarly to the coat weight determinations (weighing and ash content) that the coat weight is higher for precoating level of Pre2 than for Pre1. It can be seen from the figures that the MG side of the paper is more even and dense than the UG side, and that the surface of the paper is uneven, and the precoating equalizes somewhat this unevenness, but not all of it. Better coverage of the base paper for precoating level of Pre2 compared to Pre1 can be seen in the figures.

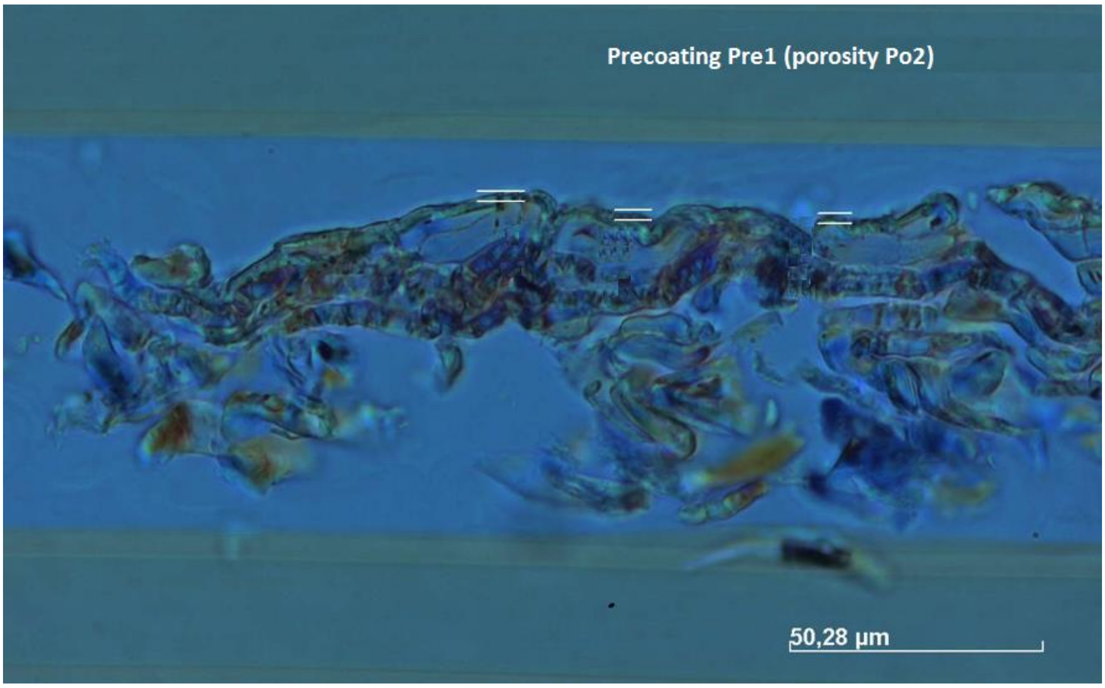


Figure 45. *Optical microscope crosscut image of precoated paper with precoating level of Pre1 (porosity Po2).*

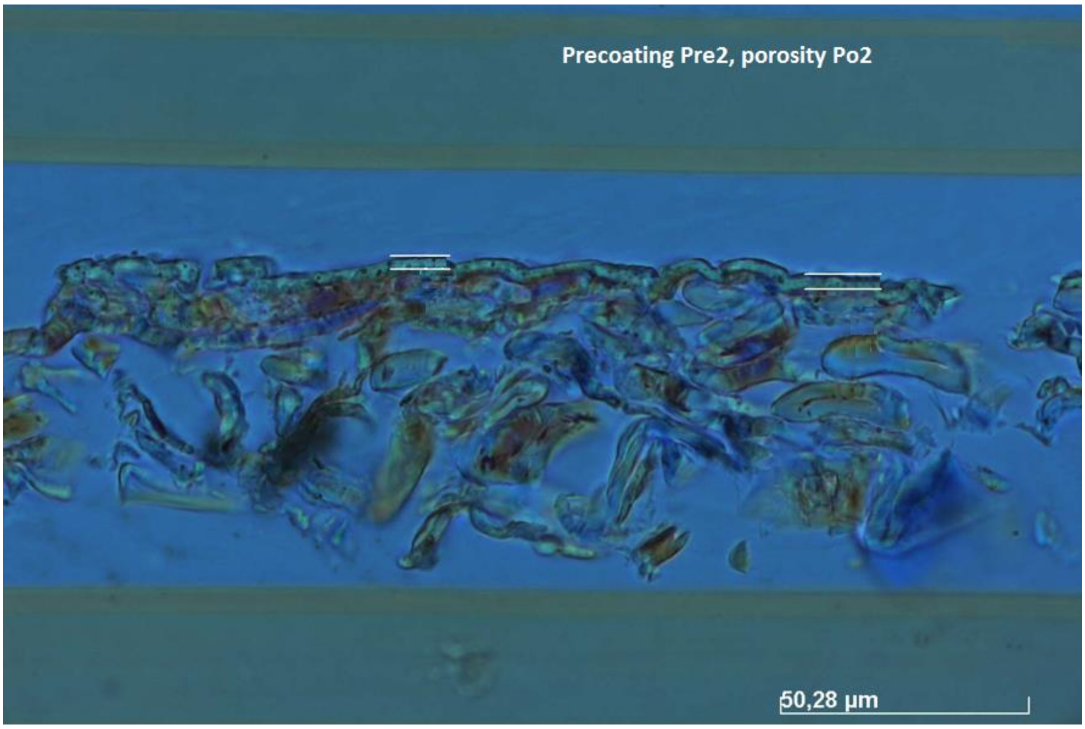


Figure 46. *Optical microscope crosscut image of precoated paper with precoating level of Pre2 (porosity Po2).*

6.3 Silicone coating and coat weight

Precoated papers were hand coated with silicone mixture and dried in oven at 120° C for one minute. Heat activates the catalyst and silicone cross-linking process initiates and completes. The silicone mixture contained HEC (thickener), silicone in emulsion and Pt catalyst. Silicone coat weight variations were also carried out by changing the solids content of the coating mixture. The first silicone coating mixture (Si2) was made with the ordinary recipe, and the other two silicone levels were ca. 4-5 % units lower (Si1) and higher (Si3) the than Si2 level. Viscosities and pH of the silicone mixtures are presented in Table 10.

Table 10. *Viscosity, pH, and SC% measurements for silicone mixture. Two batches were made for Si1 and Si2 silicone mixtures. Pre1 and Pre2 refer to two precoating levels, Si1-Si3 to silicone levels and Po1-Po3 to base paper porosity levels.*

Silicone SC%	**Si1, 1**	**Si1 , 2**	**Si2 , 1**	**Si2, 2**	**Si3**	**Ordinary coating**
Papers coated with this batch	**Pre1**	**Pre2**	**Pre2: Po1 and Po2 G**	**Pre2: Po3 Pre1: All**	**All**	
Viscosity [mPAs]	107.6 S02 27.3%	118.8 S02 30.0%	280 S02 57.8%	222 S02 55.0%	357 S03 35.7%	400 ± 100
pH	7.76	7.70	7.67	7.68	7.56	7.5 ± 0.2
T [°C]	24.1	24.5	25.2	23.9	23.1	
SC%	Si1, 1	Si1, 2	Si2, 1	Si2, 2	Si3	-

*S0X below viscosity value refers to spindle size used in the viscometer, and % value to load level in the measurement

The silicone mixture was made by first preparing HEC by mixing HEC powder with appropriate amount of water (for target solids content) and stirring for 5 minutes, adjusting pH with 10% NaOH to 9–10, stirring for at least 90 minutes and adjusting pH with 10% acetic acid to 7.3–7.7. The HEC and silicone emulsion were then mixed for 5 minutes and catalyst was added and mixture stirred for 10 minutes. Viscosity and solids contents were then determined (see Table 10). Viscosity for the ordinary silicone mixture is 400 ± 100 mPas. Viscosity of the Si2 mixtures prepared (two batches) were under this range. pH of all batches were well in the given range 7.5 ± 0.2. Temperatures of the coating mixtures were between 23–25°C at the time of viscosity and pH measurements.

Silicone coat weight was determined with XRF, using a calibration method intended for measuring silicone coat weight at “ordinary” level of clay precoating and silicone coating for quality control purposes. It is possible that this calibration method does not work in an optimal way at other coat weight levels. In addition, variations in precoating coat weight between parallel samples affect also results of silicone coat weights. First, three samples of three precoated papers (9 measurements) were measured for each porosity level in order to get the silicone amount due to clay in precoating, and then the same was performed for the 18 silicone coated samples. The results (XRF result of precoated paper subtracted from that of silicone coated paper) for silicone coat weights are presented in Figure 47.

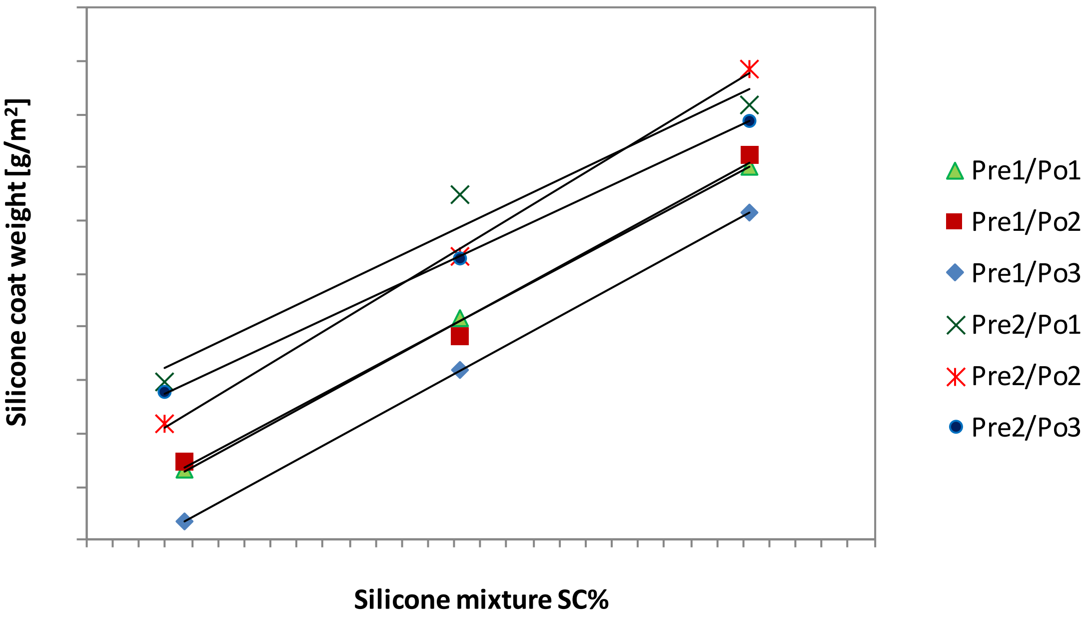


Figure 47. *Silicone coat weight as a function of solids content of silicone mixture for base paper porosities Po1, Po2, and Po3.*

From Figure 47 it can be seen that silicone coat weight is roughly same for the papers of porosities Po1 and Po2, but somewhat lower for the Po3 paper at least with lower level of precoating. However, there is more variation in trends with precoating level of Pre2 than with Pre1 (lines are not straight with Pre2), which can be due to larger variation in precoating level of parallel samples of Pre2. Standard deviations for XRF measurements for siliconized samples varied between 2–10% (mainly between 4–6 %), except one sample (Pre2/Po2), which had standard deviation of 14%.

It is difficult to say if the result of lower silicone coat weight of the Po3 paper is real, or due to precoating amount variations and/or unsuitable XRF calibration method. Since accuracy of the XRF coat weight determination may not be optimal, the release force data in Chapter 6.8 is presented both as silicone SC% and coat weight in x-axis.

6.4 Air permeance of coated samples

Air permeances of papers were measured also after coatings. Ten samples were measured, and the results (average values) are presented in Figures 48 and 49. In the beginning of the work, the air permeance values of all base paper sheets used were measured and marked in the paper sheets, and only papers with porosity values of selected range (Table 5) were chosen for the experiment. After coatings, air permeance values of 10 coated papers were measured, and the data presented in Figure 48 contains air permeance values of the base paper of the same paper sheet than precoated or silicone coated samples. Air permeance values after precoating were not marked in the paper sheets, and therefore, Figure 49 does not present air permeance of the same sheets of precoated and siliconized samples, but occasional 10 samples. For some siliconized samples, there were not more than 5 sheets left when the measurements were made.

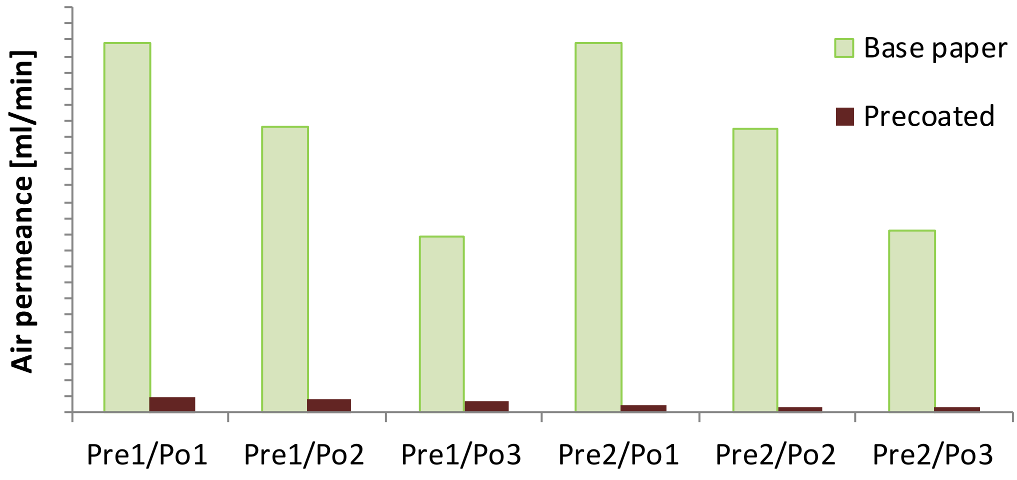


Figure 48. *Air permeance for base paper and precoated paper.*

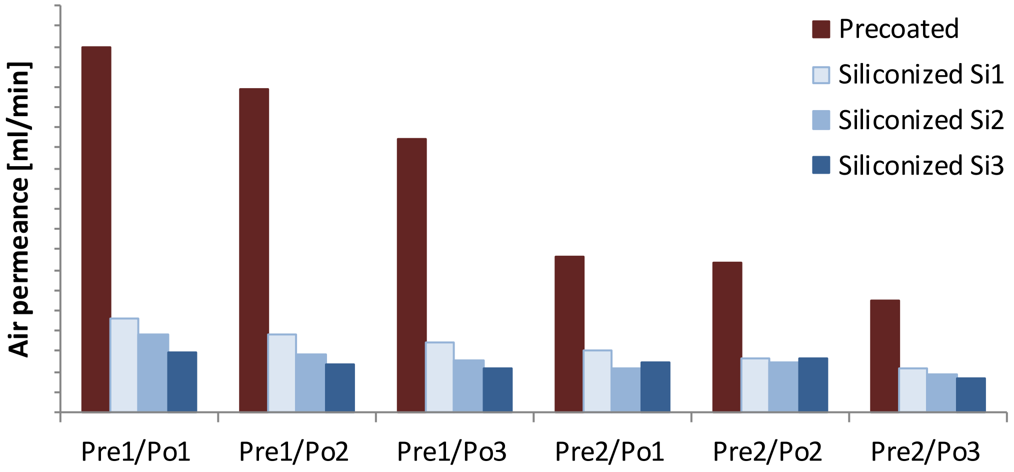


Figure 49. *Air permeance for precoated and silicone coated papers.*

Air permeance of Pre1 precoated paper is only ca. 5% of the air permeance of the original base paper. Air permeance of Pre2 precoated paper is ca. 2 % of that of the base paper. Precoating decreases thus significantly the porosity of the base paper and differences between the base papers (Po1, Po2, and Po3) are attenuated especially with Pre2 precoating. Silicone coating further decreases the air permeance, thicker coating somewhat more than thinner coating. In the final, siliconized samples, differences in Po1, Po2, and Po3 papers are small, but especially with the smaller precoating level (Pre1), differences between base paper and silicone amounts can still be noticed (in Figure 49). In this experiment, the air permeance of siliconized papers was well at the target level of final porosity / air permeance of precoated and silicone coated MG kraft release liner [6].

Standard deviations of air permeance measurements of base papers were small, between 2–5 %. However, standard deviations were larger for coated samples (between 4–13% for precoated and 7–17 % for silicone coated samples), which may be due to variations in coat weights. Air permeance results correlate well with SC% of both precoating and silicone coating. With Pre1 precoating, the air permeance values are roughly double of the values of Pre2 precoating at all porosity levels. Similarly, air permeance values of silicone coated samples decreases with increasing silicone mixture SC% (with exception of samples Pre2/Si2/Po1 and Pre2/Si3/Po1). However, it is not possible to say anything about the coat weight differences between different porosity levels (observed in coat weight determination of precoating both by weighing and ash content, Figure 43 and 44, or coat weight determination of silicone in Figure 47) on the basis of air permeance results.

6.5 Contact angle measurements

Results of contact angle measurements of release liner samples are presented in Figures 50–52. In general, static contact angles should be between the values of advancing and receding angles, as was in all the measurements. In Figure 50, static and dynamic (advancing and receding) contact angles as a function of air permeance are presented for two different precoating levels (Pre2 and Pre1; silicone level Si2).

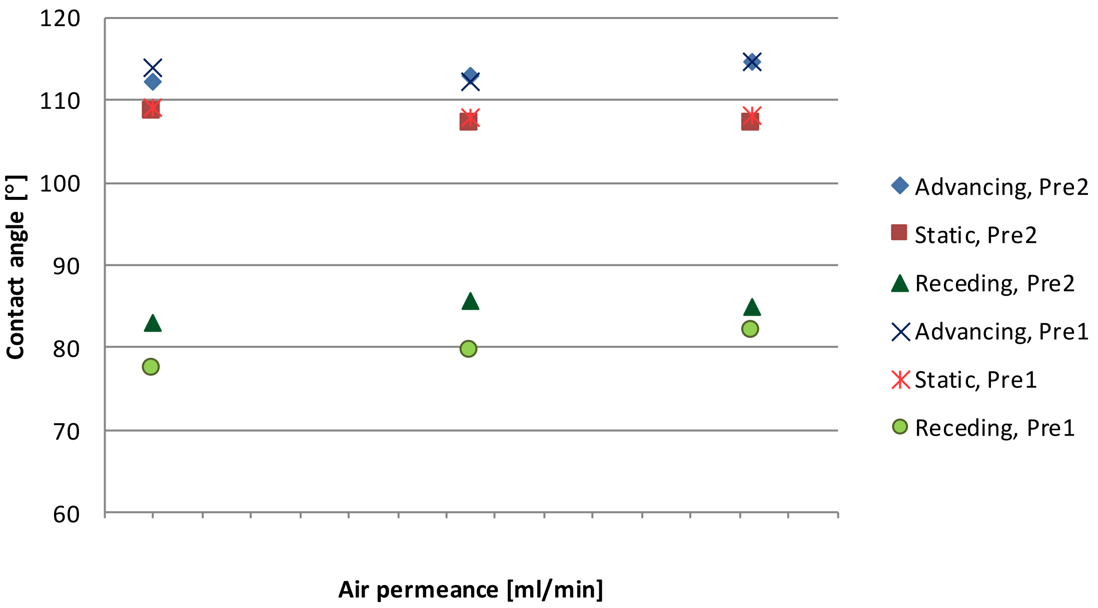


Figure 50. *Static and dynamic (advancing and receding) contact angles as a function of porosity/air permeance (ml/min) of the base paper for precoating levels Pre1 and Pre 2 (silicone level Si2).*

Differences in contact angles with different coat weight levels are negligible. Static contact angles (red markers) may show slightly decreasing trend with increasing porosity. Receding contact angles increase (green markers) somewhat with increasing porosity. Advancing contact angles (blue markers) with Pre2 precoating level also increase somewhat with increasing porosity, but with Pre1 level the trend is unclear. Effect of porosity at these porosity values (Po3-Po1) is thus small or negligible on the contact angles (and thus also on the surface energies).

In Figure 51, static and dynamic (advancing and receding) contact angles as a function of silicone coat weight are presented for the two different precoating levels (Pre1 and Pre2; porosity Po2), and in Figure 52 as a function of precoating levels. These results do not show any clear trend.

Variations between parallel samples in contact angle measurements were relatively small. For static contact angles, three parallel sample papers were used, and 5–10 droplets of 2 μl. Standard deviations in static contact angle measurements of three parallel samples were between 0.5 – 2 %, for example for the sample Pre2/Si2/Po1 the static contact angle was 107.2° with standard deviation of 1.8° (1.7 %). Also advancing contact angles (3 droplets on one paper sample) had small standard deviation (0.5–2%), but receding contact angle determination was not that straightforward and standard deviations were between 1–8 %

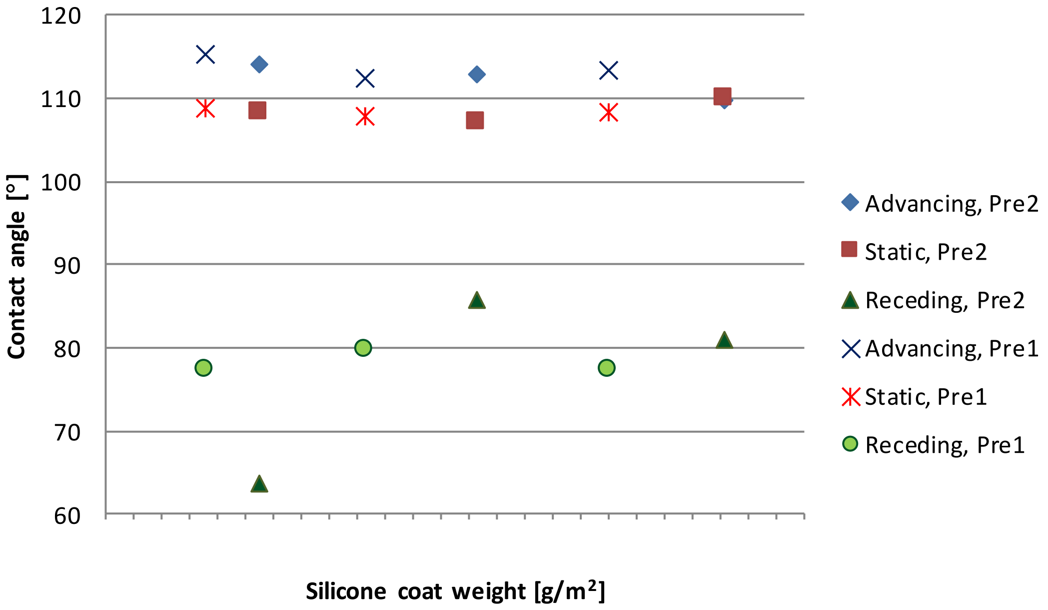


Figure 51. *Static and dynamic (advancing and receding) contact angles as a function of silicone coat weight for precoating levels Pre1 and Pre2 (porosity level Po2).*

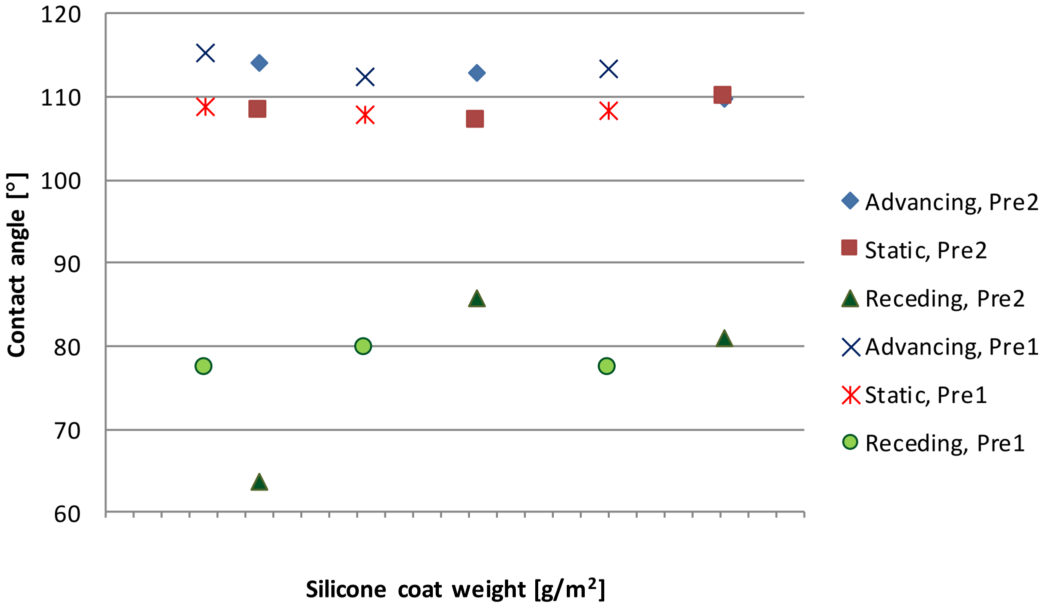


Figure 52. *Static and dynamic (advancing and receding) contact angles as a function of precoating coat weight (porosity Po2, silicone level Si2).*

These results suggest that even the lowest level of silicone coat weight (Si1) used is enough to provide the low surface energy for the release liner, and the influence of the silicone coat weight to the release force is due to other factors than the surface energy. Larger contact angle (not good wetting) means lower surface energy. Higher porosity could mean higher roughness and thus higher surface energy and lower contact angle. On the other hand, surfaces are expected to be perfectly smooth in contact angle measurements. These measurements were performed using only water as liquid and the result might be different if PSA could be used as liquid, but this was not possible with the equipment available.

6.6 Profilometer results

Surface roughness measurement results for all measured samples are presented in Table 11 and Figures 53–57. Texture and topographic images are presented for samples Pre1/Si1/Po2 and Pre2/Si3/Po2 (Figures 55–56). Pre1/Si1/Po2 sample has lowest precoating and silicone coating coat weights, and Pre2/Si3/Po2 sample has highest coat weights. Other images are not presented since there seemed not to be clear differences between the samples. Some of the Pre2 precoated samples were not measured due to time limitations, and since enough information was obtained even without them. Presented values are Ra, Rq, Rz, Sa, Sq and Sz. Ra is average roughness profile (arithmetic mean roughness), Rq is root mean square roughness profile, Rz is mean peak to valley height of roughness profile, Sa is average height of selected area, Sq is root mean square height of selected area and Sz is maximum height of selected area. Higher values of each of these parameters means higher roughness. Two 2 mm x 2 mm areas of each sample were scanned (total measured area 4.5 x 4.5 mm), and the values presented are average values of these two measurements. With some samples, the profilometer had difficulties to measure some points/areas, and these points are seen as white dots in the texture images (see Figure 55). If there were large areas of non-measured data, a third measurement was performed, and the measurement with most non-measured areas was abandoned.

As can be seen from Table 11 and Figures 53 and 54, any clear trends cannot be seen in profile roughness or surface texture parameters. If we look at the R values (Figure 53) of nine different samples of precoating level of Pre1, it can be seen that with the exception of Pre1/Si2/Po1, the porosity difference of the original base paper can be observed, although it is small. R values of Pre2/Si2 sample also show higher roughness for porosity Po1, but roughness of Po2 sample is lower than that of Po3 sample. If we compare precoating levels of Pre1 and Pre2, difference is difficult to observe. Also silicone amount seems not to have influence (with Pre1 precoating higher silicone amount seems to give slightly higher roughness). Area based roughness (S values, Figure 54) do not give clear trend. In some cases, roughness seems to increase with increasing porosity, in other just the opposite. Also the difference between coating amounts is not clear. Pre2 precoating might have lower porosity in general.

Table 11. *Profile roughness (Ra, Rq, Rz) and surface texture (Sa, Sq, Sz) data from surface roughness measurement.*

	Ra(μm)	Rq(μm)	Rz(μm)	Sa(μm)	Sq(μm)	Sz(μm)
Pre1/Si1/Po1	2.19	2.82	16.58	28.52	34.72	206.7
Pre1/Si1/Po2	2.12	2.72	16.48	35.93	43.37	252.2
Pre1/Si1/Po3	2.07	2.62	15.19	18.63	23.18	136.0
Pre1/Si2/Po1	2.06	2.65	14.39	14.59	18.98	137.4
Pre1/Si2/Po2	2.16	2.78	15.18	19.18	23.48	156.4
Pre1/Si2/Po3	2.13	2.73	16.15	30.93	36.21	183.1
Pre1/Si3/Po1	2.30	3.08	18.73	22.21	28.70	191.4
Pre1/Si3/Po2	2.27	2.98	16.68	22.16	27.56	179.9
Pre1/Si3/Po3	2.18	2.85	16.77	21.03	25.48	184.6
Pre2/Si1/Po1	2.13	2.71	15.64	18.36	19.26	143.9
Pre2/Si1/Po2						
Pre2/Si1/Po3						
Pre2/Si2/Po1	2.46	3.27	17.53	13.14	20.37	130.6
Pre2/Si2/Po2	2.01	2.54	14.23	16.31	26.59	187.8
Pre2/Si2/Po3	2.10	2.71	15.47	26.64	31.90	219.7
Pre2/Si3/Po1	2.16	2.74	15.93	23.69	29.14	203.0
Pre2/Si3/Po2						
Pre2/Si3/Po3						

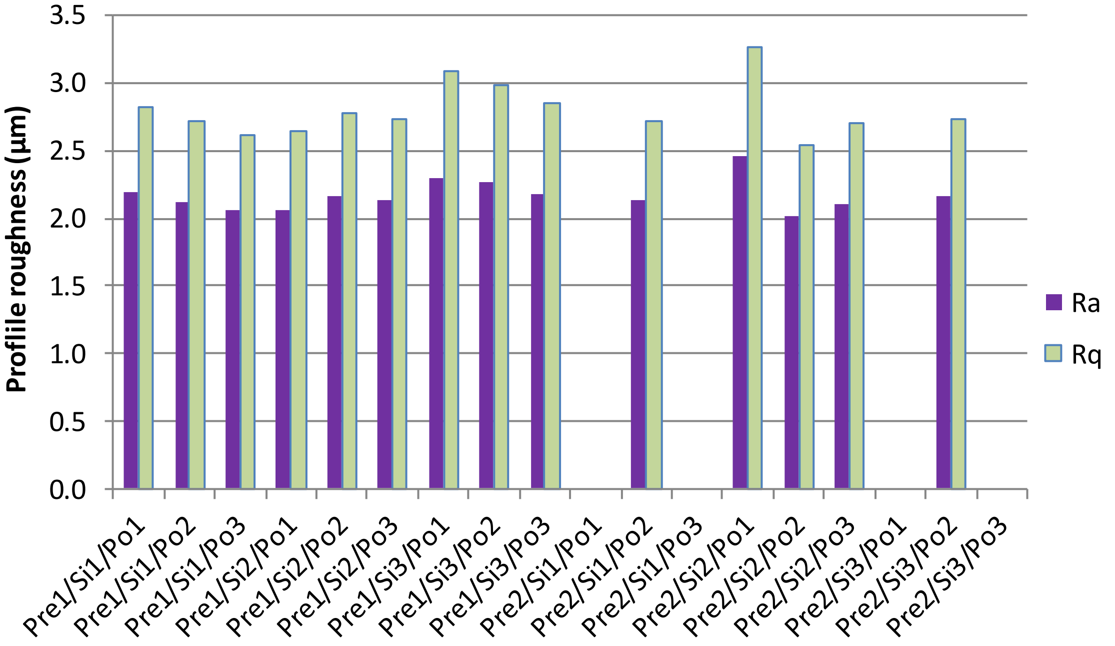


Figure 53. *Profile roughness (Ra, Rq) data from surface roughness measurements.*

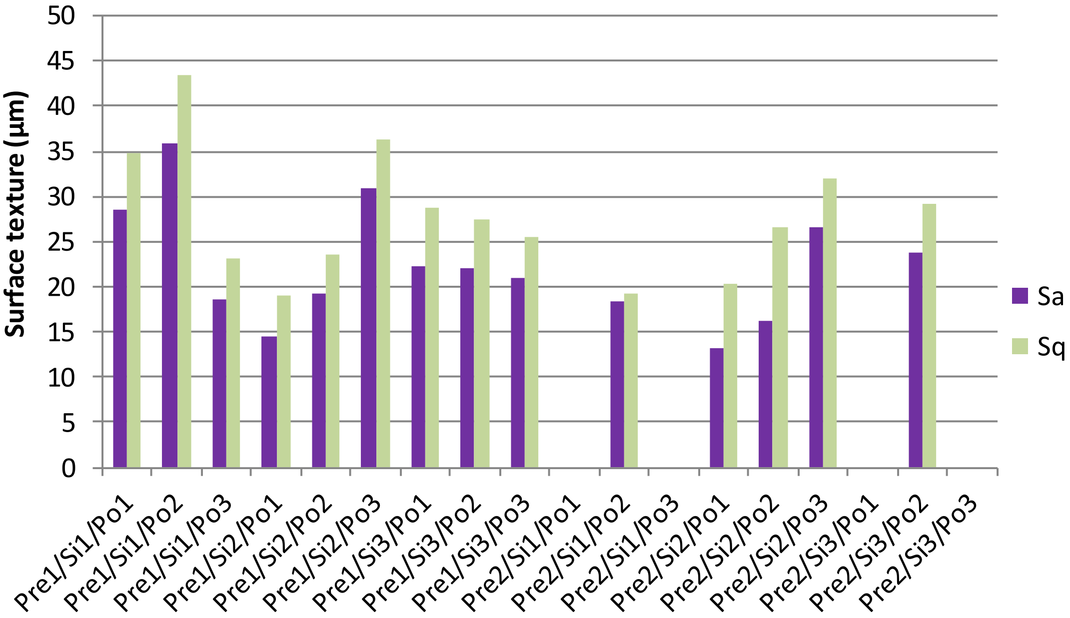
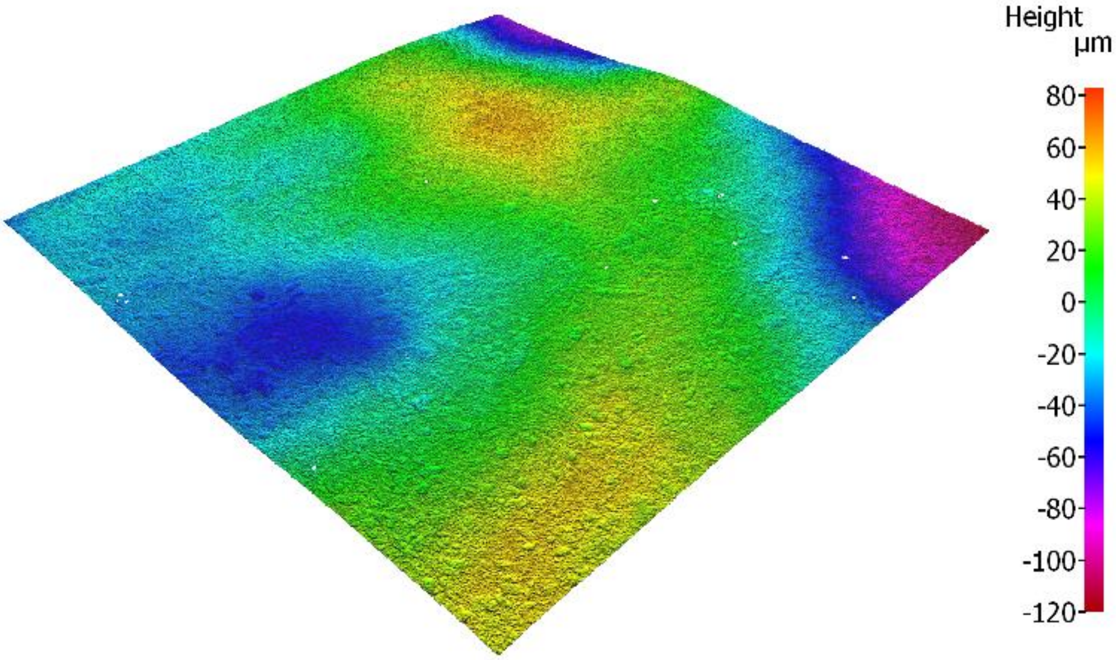


Figure 54.*Surface texture (Sa, Sq) data from surface roughness measurements.*

Also topographic and texture images (Figure 55 and 56) of highest and lowest coat weights are very similar. This may be due to wrinkles in the paper due to getting wet in the coating process, which affect the profilometer result, and real roughness of the surface is not reached. It can also mean that already the lower amount of precoating (together with silicone coating) is enough to equalize the roughness of the base paper, and the reason why precoating and silicone coating coat weights affect the release force (see Chapter 5.2.4) is not due to differences in roughness between the samples, but other factors. Also silicone layer itself may possess some roughness.

Figure 55. *Profilometer texture images for samples with lowest coat weights Pre1/Si1/Po2 (left) and highest coat weights Pre2/Si3/Po2 (right). Measured area is 4.5*4.5 mm. White spots in images are areas that profilometer could not measure.*



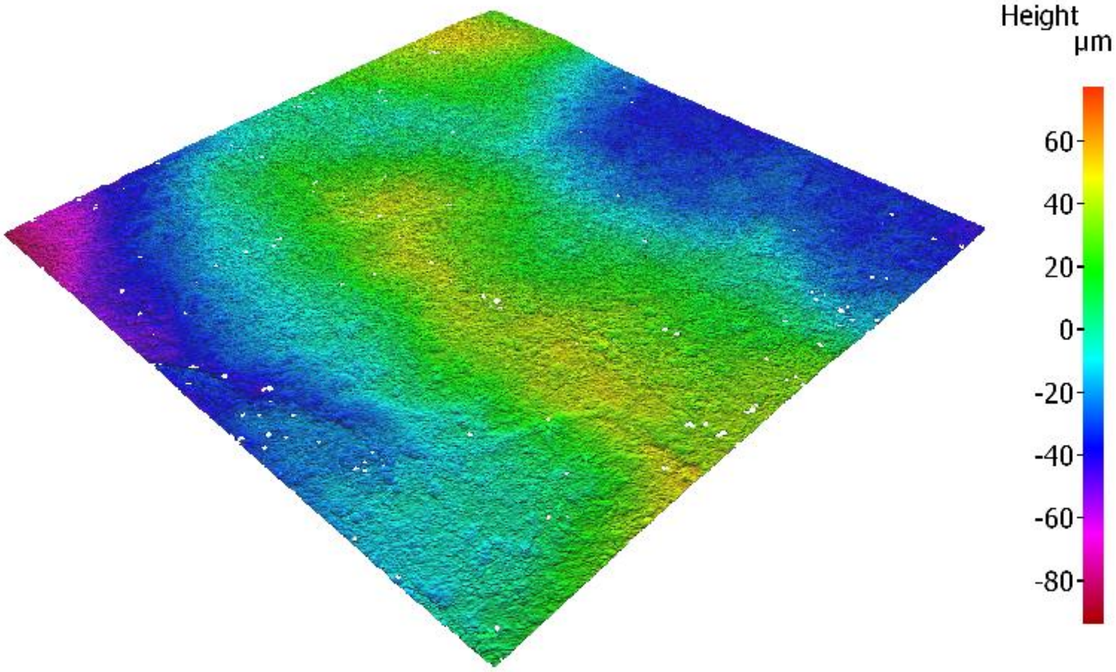
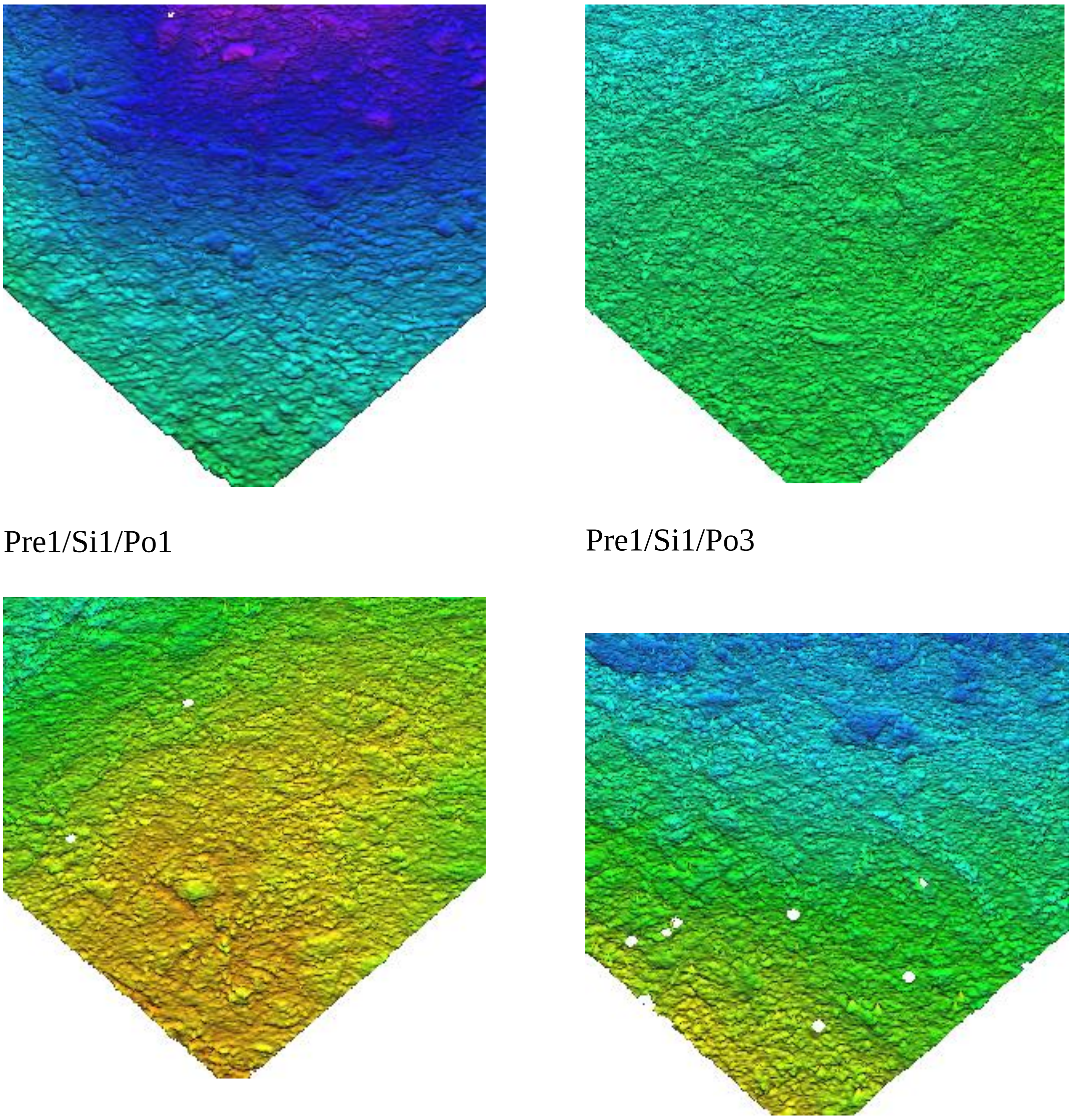


Figure 56. *Profilometer topographic images for samples with lowest coat weights Pre1/Si1/Po2 (above) and highest coat weights Pre2/Si3/Po2 (below.)*

If we have a closer look at the profilometer topographic images (Figure 57), without considering colours, which may have been affected by the paper wrinkles, but looking at the pore size and overall appearance of the surface, it seems that Po3 sample have smaller pores than Po1 and Po2 samples even with coatings. Pre1/Si1/Po3 (less precoating, lower porosity) seems smoother than Pre2/Si1/Po1 (more precoating, higher porosity), which means that even the higher amount of precoating does not totally fill all the pores of the base paper.



Pre1/Si1/Po1

Pre1/Si1/Po3

Pre1/Si3/Po1

Pre2/Si1/Po2

Figure 57. *Profilometer topographic images for samples with lowest coat weights and two different base paper porosity levels, Pre1/Si1/Po1 (upper left) and Pre1/Si1/Po3 (upper right) as well as for lowest precoating level and highest silicone and porosity level Pre1/Si3/Po1 (below left). From Pre2 precoated samples Pre2/Si1/Po2 picture is shown (below right). These images are cropped from topographic images similar to those presented in Figure 56.*

6.7 Rotation rheometer measurements of adhesives

Frequency sweep rotation rheometer measurements were performed for the adhesives in order to characterize the adhesives with their viscoelastic parameters G’, G’’, and tan δ, which may correlate with the release forces (see Chapter 3.3.6). Table 12 presents parameters of Chu criterion for optimal combination of peel, tack and shear for PSAs [34][38][65][72]: (i) G’ (ω = 0.1 rad/s) ~ 2–4 × 10^4 Pa, and (ii) 5 < [G’ (ω = 100)/G’ (ω = 0.1)] < 300.

Strictly speaking only adhesive A2 fulfils the first Chu criterion, but A21, A3, and A6 are also very close to it, and A4 is furthest. A3, A4, and A5 fulfill the criterion 2. However, all the six adhesives fulfill the Dahlquist’s criterion of tack; G’ < 105 Pa (see Chapter 3.3.6). A4 has lowest G’ at low frequency and highest change of storage modulus (G’ (ω = 100)/G’ (ω = 0.1) value), although A5 is close to that.

Table 12. *Parameters of Chu criterion for the six adhesives.*

	G’ (ω = 0.1 rad/s)	**G’ (ω = 100)**	$\frac{G'(\omega = 100)}{G'(\omega = 0.1)}$
A1	1.8 x 10^4	2.7 x 10^4	1.5
A2	2.6 x 10^4	8.3 x 10^4	3.2
A3	1.5 x 10^4	1.4 x 10^5	8.9
A4	2.7 x 10^3	3.5 x 10^4	13.3
A5	8.0 x 10^3	8.5 x 10^4	10.6
A6	1.2 x 10^4	3.6 x 10^4	3.1

Storage modulus G’, loss modulus G’’, and tan δ (also called loss factor) as a function of angular frequency (frequency sweep) at range 0.1 rad/s – 1000 rad/s for the six adhesives are presented in Figure 60. The same data is presented in Appendix 1 with G’ and G’’ in the same graph (two adhesives in the same figure). From these Figures in Appendix 1 it can be seen that frequency range of 0.1 rad/s – 1000 rad/s is the part of G’(ω) and G’’(ω) curves which include the cross-over point of G’ and G’’’ curves (where tan δ = 1) and which is somewhat before (to left side) the tan δ maximum (compare to Figures 33 and 34).

Angular frequency in the peel test (debonding frequency) depends on the thickness of the adhesive layer as well as the peel speed. If we expect the “ordinary” adhesive thickness h = 25 µm (e.g. reference [13]) and speed v = 5 mm/s, the valid debonding angular frequency (ω = 2πv/h; empirical equation presented by Gordon et. al. [13][14]) is about 1300 1/s, thus at the right edge of the figures. The mass of adhesive strip applied was between 0.8–1.0 g. Assuming density of 1–1.5 g/cm^3, the average thickness of the adhesive layer is much higher than 25 µm, around 200 µm. Corresponding angular frequency is ca. 150–200 1/s. Bonding frequency often used is 0.1 1/s (e.g. Ulman [72]), which is at left edge in the figures.

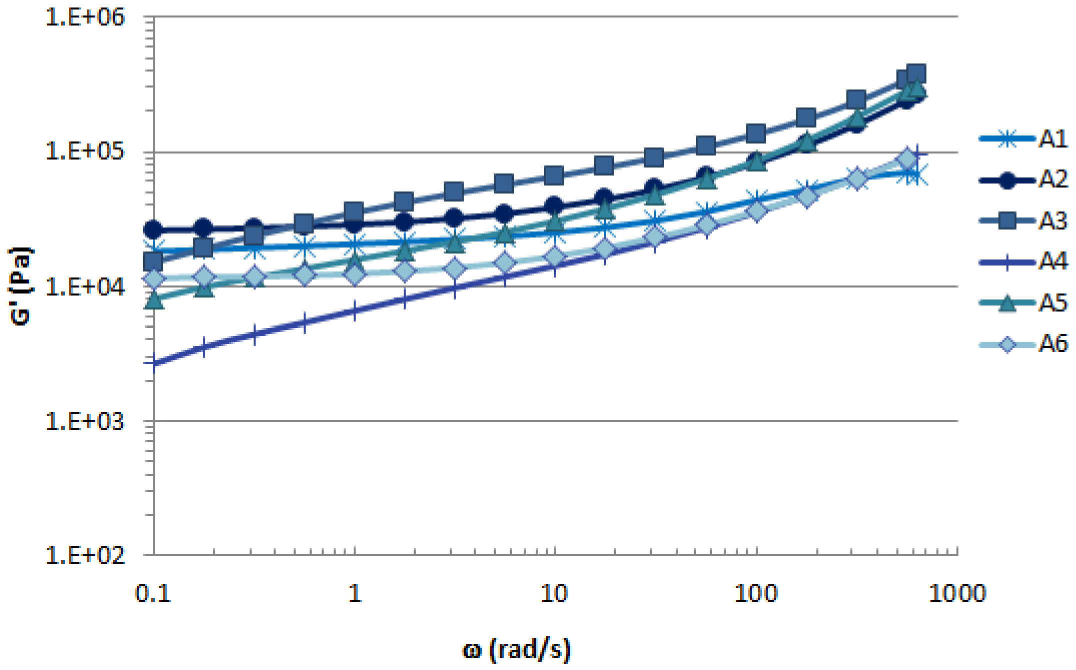


Figure 58. *Storage modulus as a function of angular frequency for the six adhesives A1 –A6.*

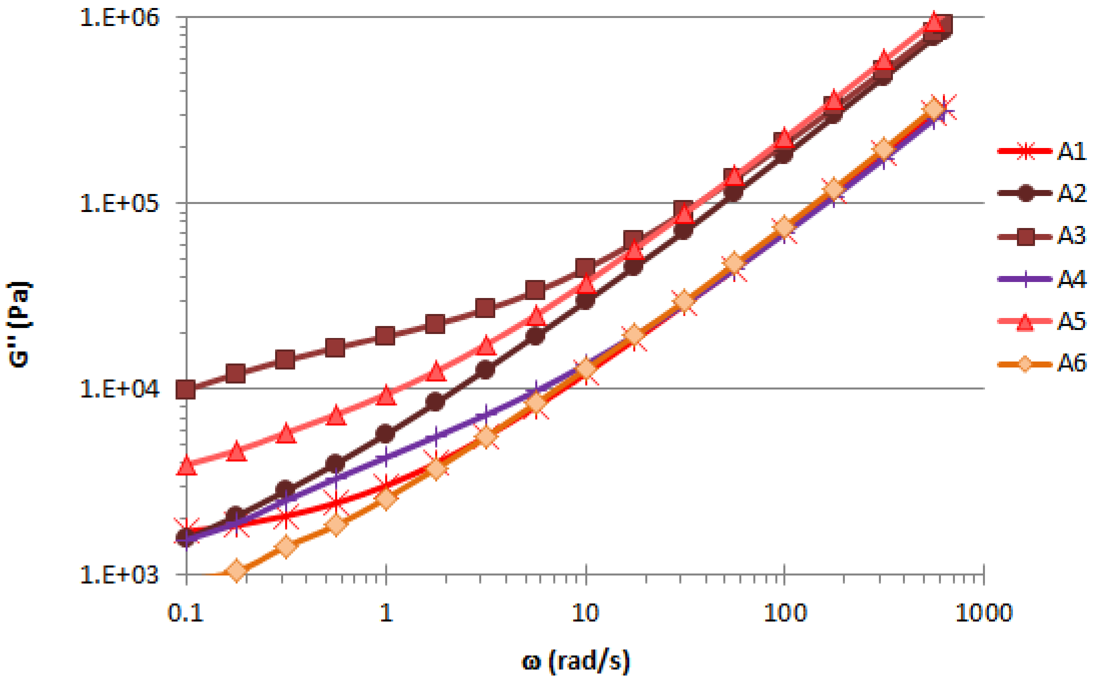


Figure 59. *Loss modulus as a function of angular frequency for the six adhesives A1 – A6.*

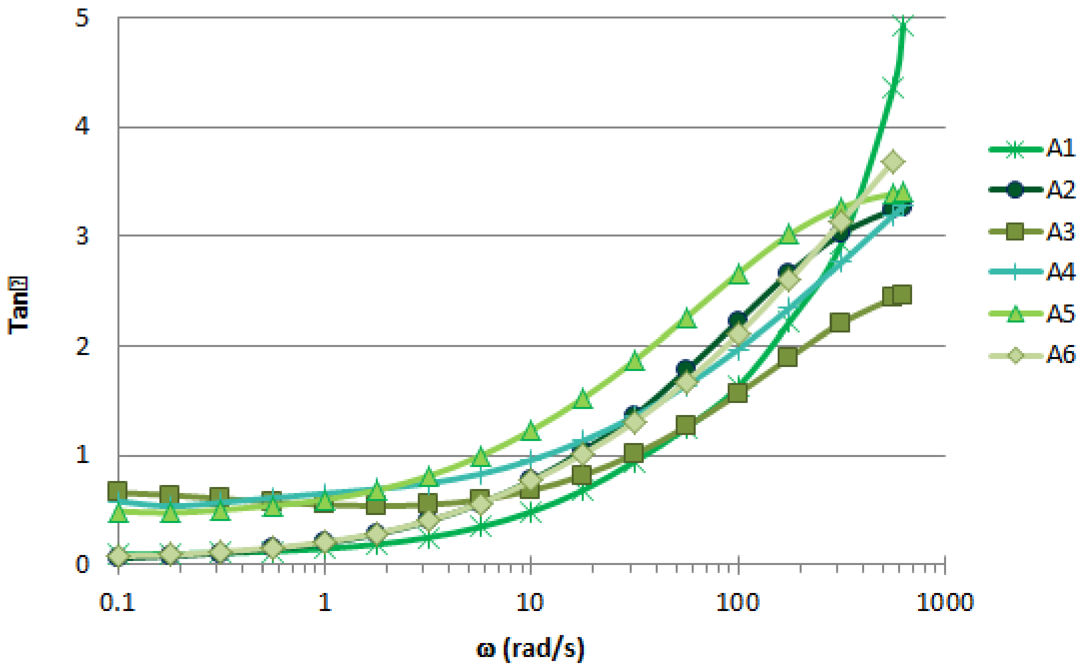


Figure 60. *Tan delta as a function of angular frequency for the six adhesives A1 – A6.*

It can be seen from Figure 58 (as in Table 12), that G’ at low (bonding) frequency is lower for adhesive A4 than for the other adhesives. Adhesives seem to fall under two categories according to their G’ at higher frequency: A2, A3, and A5 somewhat higher, A1, A4, and A6 lower. The same is true with G’’ at higher frequencies, A2, A3, and A5 have similar value, and A1, A4, and A6 lower, similar value. Tan delta values have more variation, A3 lowest tan δ at angular frequency of 100–1000 1/s, A5 one of the highest. A1 has significantly higher tan δ than the other adhesives at highest frequency, but with our thick adhesive layer, the relevant frequency value of debonding is lower. Slope of G’ (also indicated by ω = 100)/G’ (ω = 0.1) value in Table 12) is higher for A4, A5, and A3, and lower for the other three adhesives.

6.8 Release tests

6.8.1 TESA tape tests

Release tests were first performed with TESA tape 7476 for reference information, since there are fewer variables in TESA tape release tests than in hot-melt tests. Only 6 different release liner samples (presented in Table 13) were used for these tests. These samples provide information about the influence of precoating amount (samples 1 and 4 in Table 13), silicone amount (samples 2, 4, and 6) and porosity of the base paper (samples 3–5).

Table 13. *Six release liner samples used for TESA tape 7476 release tests.*

	"Name" (Precoating/ Si coating/ permeance)	**Precoating**	**Silicone coating**	**Porosity**
1	Pre1/Si2/Po2	Pre1	Si2	Po2
2	Pre2/Si1/Po2	Pre2	Si1	Po2
3	Pre2/Si2/Po1		Si2	Po1
4	Pre2/Si2/Po2			Po2
5	Pre2/Si2/Po3			Po3
6	Pre2/Si3/Po2		Si3	Po2

TESA 7476 release test results are presented in Table 14 and figures 61 and 62. Results as a function of air permeance are presented in Figure 61. These release liner samples had precoating level of Pre2 and silicone level of Si2. Influence of base paper porosity on the release force at the used porosity/air permeance range (Po1–Po3) is small. Release liner with lowest base paper porosity (Po3) has slightly smaller release value, but papers with air permeance values of Po1 and Po2 have nearly identical release force value (and actually Po2 negligibly larger).

Table 14. *TESA 7476 release test results (N/m)*.*

	Sample	**1**	**2**	**3**	**Average**	**SD**
1	Pre1/Si2/Po2	34.24	33.30	32.00	33.2	1.13
2	Pre2/Si1/Po2	27.20	27.40	24.08	26.2	1.86
3	Pre2/Si2/Po1	26.64	24.30	23.40	24.8	1.68
4	Pre2/Si2/Po2	27.28	24.36	24.84	25.5	1.67
5	Pre2/Si2/Po3	24.96	23.56	24.04	24.2	0.71
6	Pre2/Si3/Po2	22.76	21.96	21.12	21.9	0.82

*Values were given in N/25 mm, which was then multiplied with 40 to get N/m

TESA 7476 release test results as a function of precoating coat weight and silicone coat weight are presented in Figure 62 (porosity Po2). Influence of precoating coat weight increase level Pre1 to level Pre2 (increase of ca. 10 SC% units of the precoating mixture) is ca. 8 N/m decrease in release force (from 33 N/m to 25 N/m). This 8 N/m is 23 % of the release force (33 N/m) of precoating level of Pre1.

Influence of silicone coating coat weight increase from from Si1 to Si3 (increase of 9 SC% units of the silicone mixture) was 4 N/m decrease in release force (from 26.2 to 21.9 N/m). The first step decrease (from Si1 to Si2) was smaller (0.7 N/m) than the second step, 3.5 N/m (from Si2 to Si3). Change of 4 N/m is 16 % of the release force (26.2 N/m) of the lowest silicone coat weight (Si1).

Standard deviations for the three parallel samples in TESA tape test were at acceptable level, between 3–7%. For example, for sample Pre2/Si2/Po1, the release force was 25.5 N/m with standard deviation of 1.7 (7%).

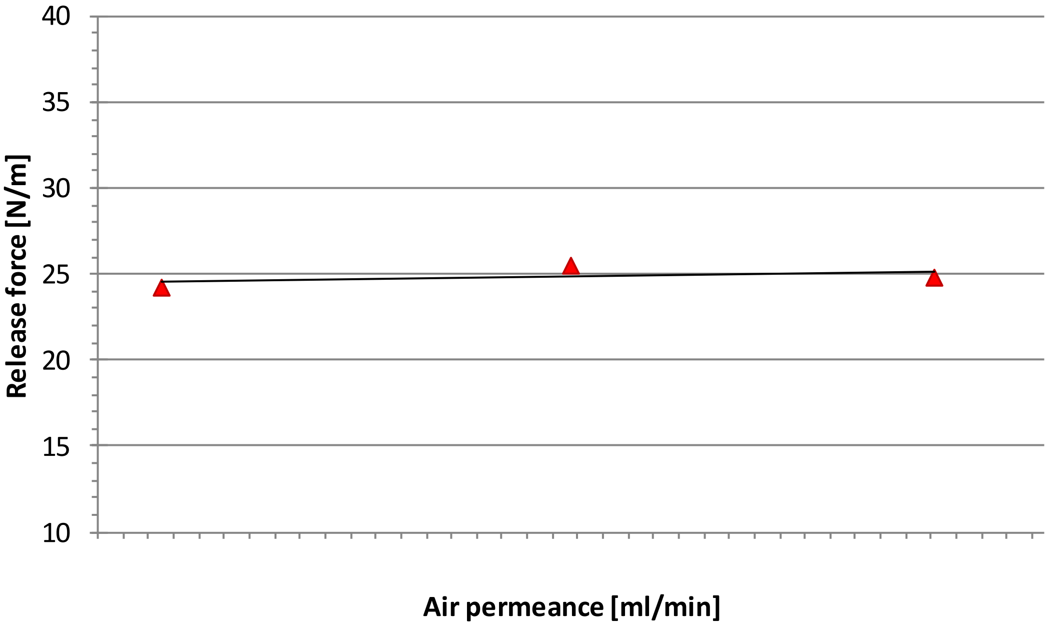


__Figure 61.__ Release force with TESA tape 7476 for different porosity/air permeance values of the base paper (Po3 (lowest porosity/air permeance), Po2, and Po1) for samples of precoating Pre2 and silicone coating Si2 (= samples Pre2/Si2/Po1, Pre2/Si2/Po2, and Pre2/Si2/Po3).

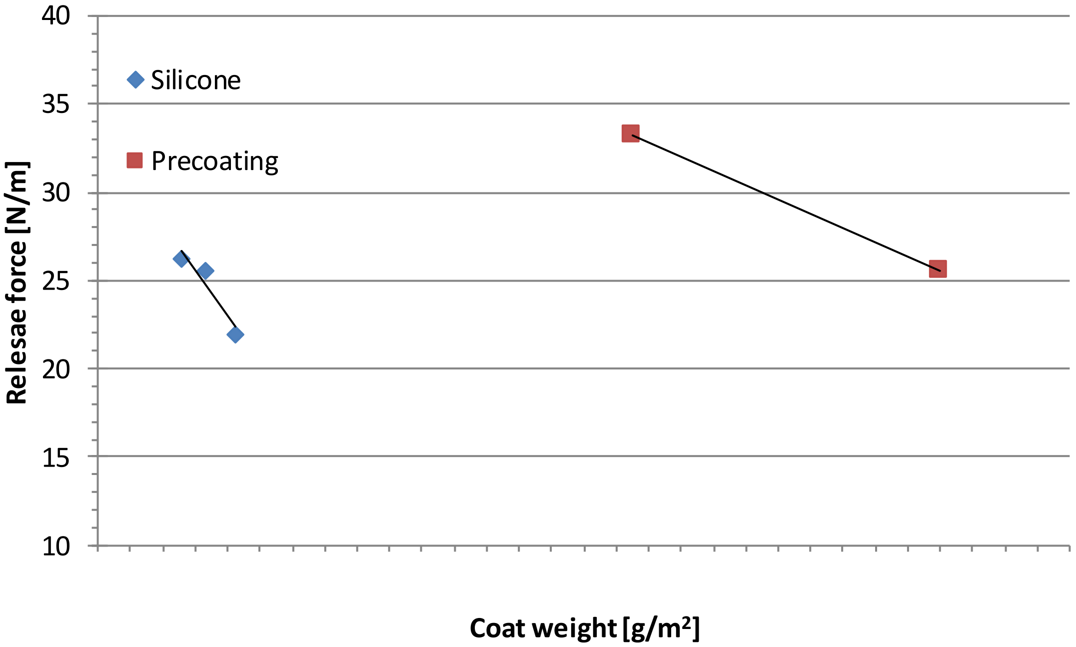


__Figure 62.__ Release force with TESA tape 7476 for different silicone and precoating coat weights (porosity Po2; samples Pre1/Si2/Po2, Pre2/Si1/Po2, Pre2/Si2/Po2, and Pre2/Si3/Po2).

6.8.2 Hot-melt tests: Porosity, precoating and silicone amount

Hot melt release tests were performed for all 18 release liner samples (presented in Table 3). Release force results for one of the adhesives, adhesive A6, are presented in this chapter as a function of the base paper porosity, the level of precoating and the level of silicone coating. Differences between the adhesives are considered in Chapter 6.8.3. All measured data is found in Appendix 2–7.

Release tests for adhesive A6 as a function of air permeance are presented in Figure 63. Compared to TESA tape tests, results are similar, but the trend of slightly increasing release force with increasing porosity is more clear, although results with porosities Po1 and Po2 are close to each other, and sometimes porosity Po1 has higher, sometimes lower value than porosity Po2. Paper of lowest porosity (Po3), has lowest release force in all cases.

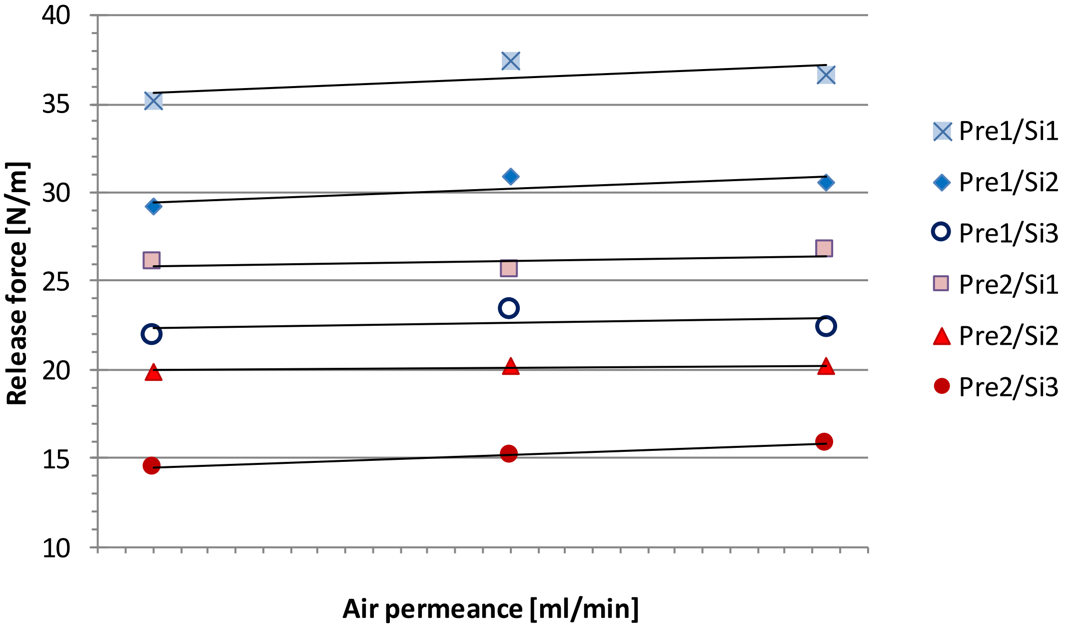


Figure 63. *Release force for different porosity/air permeance values of the base paper (Po3 lowest porosity/air permeance, Po2, and Po1), for precoating levels of Pre1 (blue markers) and Pre2 (red markers), and silicone coating levels of Si1, Si2, and Si3.*

Release tests for adhesive A6 as a function of precoating amount are presented in Figure 64, and as a function of silicone amount in Figure 65. Results are presented both as coating mixture solids content % and coat weight (determined by weighing) in x-axis. Figures with coat weight in x-axis looks more disordered due to variation in coat weights between samples. When the release force is presented as a function of precoating coat weight, Pre1/Po3 line seems to be clearly lower than Pre1/Po1 and Pre1/Po2. If the release force is presented as a function of silicone mixture SC% (only position at the x-axis of the test points change), the difference is not that clear (Pre1/Po3 is still lowest, but difference does not look as large).

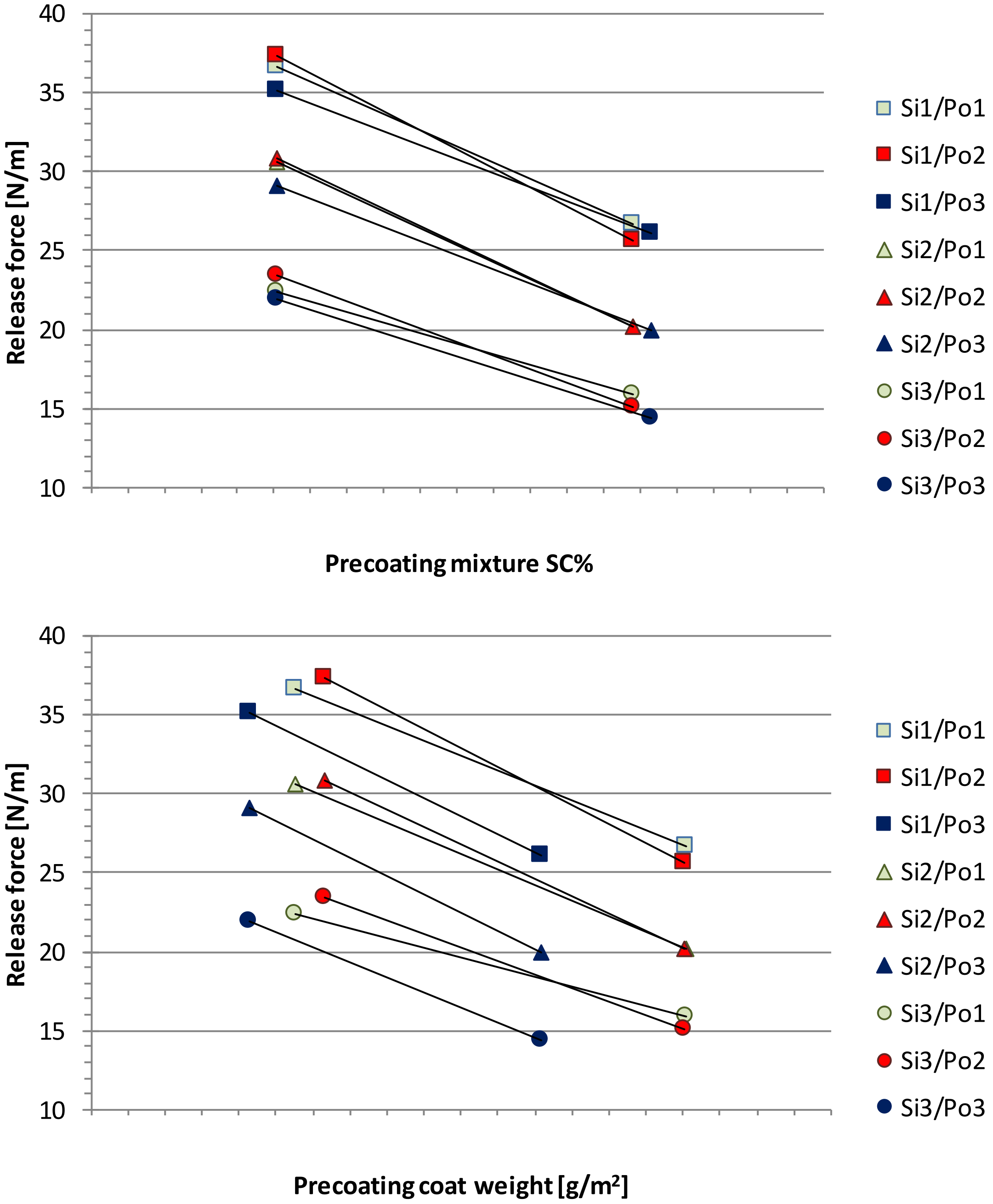


Figure 64. *Release force as a function of precoating mixture SC% and precoating coat weight for silicone coating levels of Si1, Si2, and Si3 and porosities Po1, Po2, and Po3.*

The difference between the different porosity levels is thus small, but at lower precoating level porosity Po3 (lowest porosity) gives slightly lower release. Lower coat weight level of Po3 paper, which was observed both in coat weight determination by weighing and ash contents, together with similar or slightly lower release force levels means that less precoating sticks to paper surface with lower porosity paper (Po3), but it stays better on the surface (better holdout). In other words, the coating colour does not penetrate that much inside the pores in the paper. This is especially the case with lower precoating level (Pre1) and lower viscosity of the coating colour. It seems thus that with lower base paper porosity level, lower precoating coat weight might be sufficient to provide similar level of release force than with higher porosity and higher precoating coat weight. On the basis of release force results, the very low level of coat weight of Po3 papers according to ash content determination does not seem reliable, and the coat weights determined by weighing are thus used.

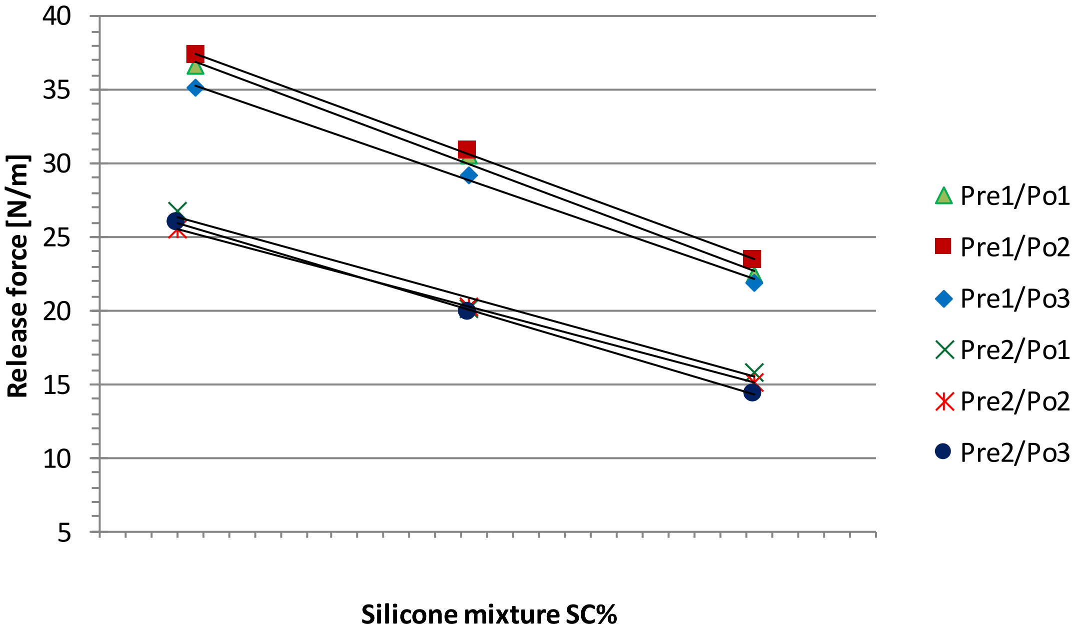
As can be seen from Figure 64, precoating coat weight change from Pre1 to Pre2 decreases release force ca. 10 N/m with Si1 and Si2 silicone levels, and ca. 8 N/m for Si3 silicone level (see also Table 15). In percentages of the release value (30 N/m) of the lower precoating coat weight (Pre1) and silicone level of Si2, the change of 10 N/m is 33%. The same values in TESA tests was 8 N/m change, which is 23 % of the release force of 33 N/m. Influence if precoating coat weight was thus slightly stronger in hot-melt test than in TESA tape test. Reason for influence of precoating coat weight on release force was expected to be due to increasing surface smoothness, change in surface energy and especially silicone holdout. We did not get evidence of influence of precoating level on surface energy or roughness of the siliconized paper. However, the main function of precoating in release liner is improving silicone holdout.

Table 15. *Influnce of procoating amount on release force level. These values are average values for the three porosity levels.*

SC	**ΔSC**	**CW**	**ΔCW**	RF Si1	ΔRF	RF Si2	ΔRF	RF Si3	ΔRF
%	**% unit**	**[g/m^2]**	**[g/m^2]**	[N/m]	[N/m]	[N/m]	[N/m]	[N/m]	[N/m]
Pre1		**Pre1**		36.4		30.2		22.6	
	10		**1.9**		10.3		10.1		7.5
Pre2		**Pre2**		26.1		20.1		15.1	

SC=solids content, CW= coat weight, RF = release force, Δ = change in value

The influence of porosity levels on the release force can also be examined with Figure 65 with release force as a function of silicone amount. In XRF coat weight results it seemed that paper of porosity Po3 has lower silicone amount than Po1 and Po2 papers. Po3 paper gives lower release force at least with lower precoating level, which means that if there really is less silicone, it must have better holdout and coating coverage. Profilometer topographic figure (Figure 57) suggested that the coatings do not totally fill the pores of base paper, and that e.g. Po3 paper with Pre1 precoating seems smoother than Po2 paper with Pre2 coating (although numerical values of the roughness data of different samples were very similar probably due to wrinkles in the paper). This could mean that smoother Po3 paper provides better silicone holdout. It is also possible that XRF results are not right, and silicone coat weights are more similar. In this case the reason for lower release force in Po3 paper is only due to better holdout of precoating with lower porosity paper.



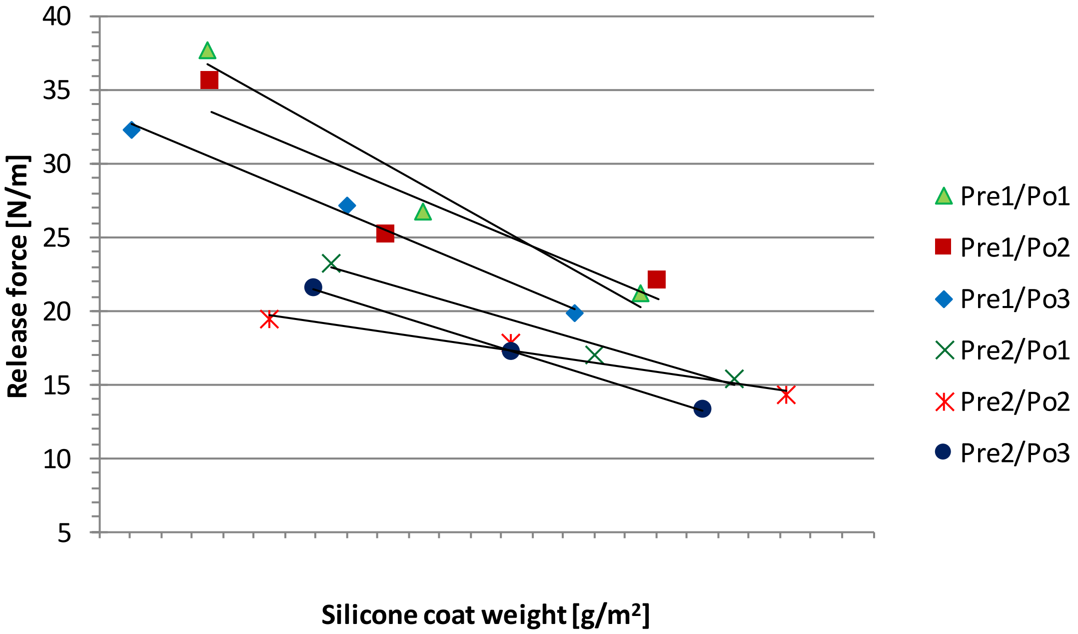


Figure 65. *Release force as a function of silicone mixture SC% and silicone coat weight for precoating amount Pre1 and Pre2 and porosities Po1, Po2, and Po3 (adhesive A6; feminine hygiene adhesive). Mass of the adhesive 0.86g.*

Figure 65 and Table 16 shows that silicone coating SC% change of ~4.5 percentage points (from Si1 to Si2 or from Si2 to Si3) resulted in ca. 5.5 N/m change in release force with precoating level of Pre2, and ca. 7 N/m change with precoating level of Pre1 (see also Table 16). Change of release value for silicone coating SC% change of 9 percentage points (from Si1 to Si3) with Pre2 precoating was 11 N/m, which is significantly more than with TESA test (4 N/m). Change of 11 N/m is 42% of the release force (26.1 N/m in average for all porosities) of the lowest silicone coat weight (Si1), when the same percentage value was 16 % in TESA tape test. Influence of silicone coat weight was thus stronger in hot-melt test than in TESA tape test.

Table 16. *Influnce of silicone amount on release force level. These values are average values for the three porosity levels. Pre1 and Pre2 refer to precoating solids content.*

SC	**ΔSC**	**CW**	**ΔCW**	RF Pre1	ΔRF	RF Pre2	ΔRF
%	**% unit**	**[g/m^2]**	**[g/m^2]**	[N/m]	[N/m]	[N/m]	[N/m]
Si1		**Si1**		36.4		26.1	
	4.4		**0.14**		6.2		6.0
Si2		**Si2**		30.2		20.1	
	4.4		**0.14**		7.6		5.0
Si3		**Si3**		22.6		15.1	

SC=solids content, CW= coat weight, RF = release force, Δ = change in value

SC% of both precoating mixture and silicone mixture correlates well with the release forces so that higher SC% of the coatings gives lower release force, which is due to better coating holdout and coating coverage according to general understanding. We did not get evidence of influence of the base paper porosity, or precoating and silicone coat weight levels on the surface energy or roughness of the release liner. Low surface energy is a prerequisite for release performance, but even the lowest level of silicone coating used may be enough with regard to surface energy properties. Increasing release force with increasing precoating and silicone coat weight is thus due to other factors than the surface energy. We have not examined the rheological properties including interfacial slippage of the silicone coating, which is the other important property in addition to low surface energy of silicone. We did not either get clear difference between the samples with roughness data of profilometer measurements. Roughness data could have provided information of possible mechanical interlocking mechanism in adhesion, or influence of roughness due to influence on the surface energy, but in this study this was not found. However, profilometer topographic figure (Figure 57) showed that paper with lowest porosity (Po3) seems smoother than papers of porosities Po1 and Po2, and that the coatings do not totally fill the pores of base paper, which could support the thought of better coating holdout of less porous paper.

Standard deviations in hot-melt test were larger than in TESA tape test, due to many factors affecting the process. Standard deviations were usually between 2–15 %, but in some cases as high as 25%. For example, sample Pre1/Si3/Po1 with adhesive A2 (see

Appendix 3), the release force results for three parallel samples were 15.59, 14.02 and 21.10 N/m. Fourth measurement gave 21.78 N/m. Average of these values is 18.1 N/m with standard deviation of 3.9 N/m (25.5%). In these four measurements, it seems that there are two release force levels for this sample, and several more measurements would have been needed to resolve the right level. Due to time limitations, it was not possible to perform several more measurements for several test points, and therefore the solution is just to take the average value. The two levels in the results could be due to precoating coat weight variation or variations in the behavior of the adhesive due to variations in the application preparations, such as viscosity changes caused by long storing time at high temperature.

6.8.3 Effect of adhesive

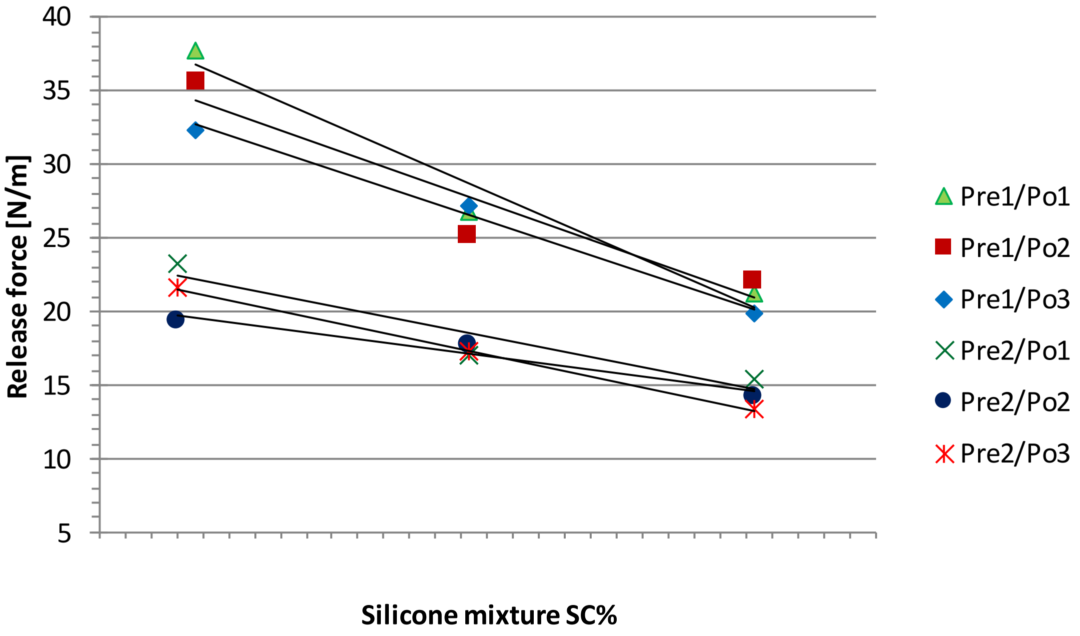
Release forces for adhesives A1–A5 are presented in Figures 66–70 as a function of silicone coat weight and silicone mixture SC% (results for A6 were presented earlier). All measured values are found in Appendix 2–7. The adhesive amount was tried to keep constant for each adhesive, but it appeared to be difficult. Therefore, masses of the adhesives are reported for each case (average value of several weighing). Rheological parameters of the adhesives were already considered in Chapter 6.7. Some parameters are re-presented in Table 17 together with selected release force data, average release force of the three porosities for lowest coat weight sample (Pre1/Si1) and highest coat weight (Pre2/Si3).

Table 17. *Rheological parameters and release force levels (average for the three porosities) for adhesives A1–A6.*

	G' (0.1)	$\frac{G'(100)}{G'(0.1)}$	**G'' (100)**	**Tan δ (100)**	**Release F Pre1/Si1**	**Release F Pre2/Si3**
A1	1.8×10^4	1.5	7.1×10^4	1.6	35	14
A2	2.6×10^4	3.2	1.8×10^5	2.2	31	10
A3	1.5×10^4	8.9	2.1×10^5	1.6	23	11
A4	2.7×10^3	13.3	6.9×10^4	2.0	140	57
A5	8.0×10^3	10.6	2.3×10^5	2.7	30	12
A6	1.2×10^4	3.1	7.5×10^4	2.1	36	15

No clear correlation between the rheological parameters and release forces could be found. Two categories of the adhesives with regard to G''(100) seen in Figure 59 (A2, A3, and A5 higher G'', A1, A4, and A6 lower) does not correlate with release forces, where A4 has significantly higher release force (Pre1/Si1: 140 N/m) , and A3 lowest release (Pre1/Si1: 23 N/m). A4 has highest G'(100)/G'(0.1) value, and lowest G'(0.1) value, but otherwise these parameters do not correlate with release forces levels. Low G' at low frequency correlates with high tack, and "subjective tack test" (= how much adhesive sticks to fingers) also proved this to be true, but peel tests should correlate more with G'' according to discussions in Chapter 3.3.6

Although there appeared to be variation both in the precoating amounts and the silicone amounts between parallel samples, as well as the adhesive amount between the different adhesives and also between the parallel samples, which all give some uncertainly to the results, there are some clear trends which are repeated in all the figures of different adhesives (as already mentioned together with the adhesive A6 above). Influence of the porosity on the release force at air permeance/porosity range of Po1–Po3 seems to be small, or negligible at least for the higher precoating level (Pre2) with all adhesives. All hygiene product adhesives give release force of level 30–35 N/m for Pre1/Si1 samples (lowest precoating and silicone coat weights). At this release force level, the influence of precoating amount is significant, ca. 10 N/m, and the effect is somewhat large at lower silicone coat weight (Si1) than at higher one. In the case of silicone coating, the change in release force is ca. 5 N/m for 4% change in silicone coating SC% at precoating level of Pre1, and smaller at precoating level of Pre2. As mentioned, all the adhesives for hygiene products were quite similar, but there was still some variation: release force levels can differ at least 5 N/m between two hygiene product adhesives. However, there was some differences in the amount of adhesive between the different adhesives, and this may have some influence on the release force. Envelope adhesives differed from hygiene product adhesives: adhesive A4 gave significantly higher release values than the other adhesives. A4 is also used to fasten medical drapes to skin, and it needs thus high tack. A3 gave somewhat lower values than the hygiene product adhesives. It has to be noted that the face stock material is different for hygiene product and envelope products. Testing different face stock materials (e.g. nonwovens) could also be beneficial.



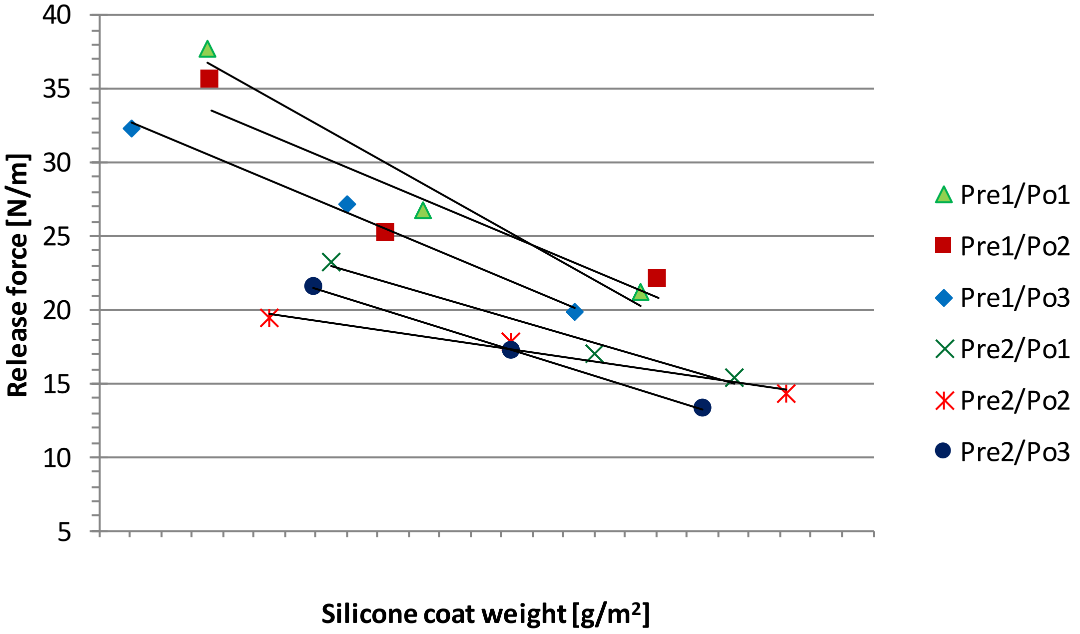
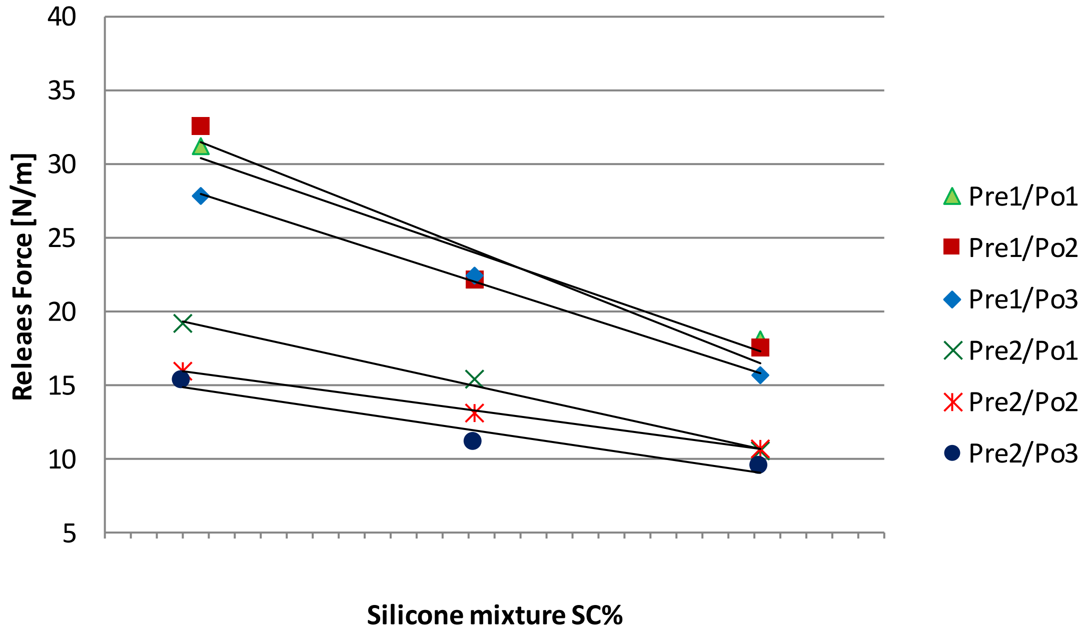


Figure 66. *Release force as a function of silicone mixture SC% (above) and silicone coat weight (below) for adhesive A1 (feminine hygiene adhesive). Mass of the adhesive 1.1 g.*



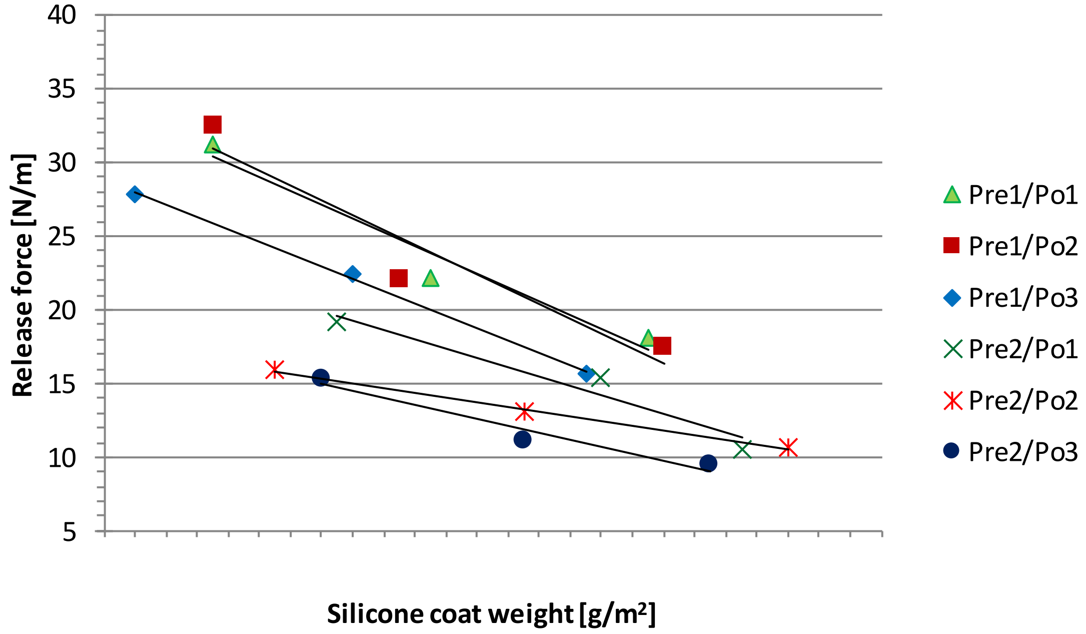
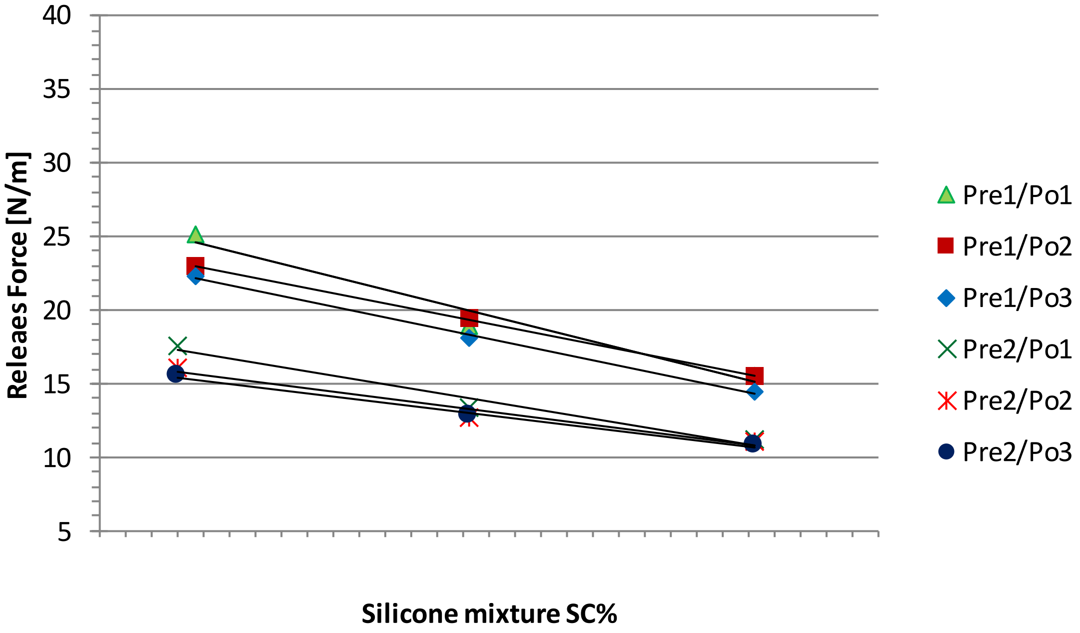


Figure 67. *Release force as a function of silicone mixture SC% (above) and silicone coat weight (below) for adhesive A2 (feminine care adhesive). Mass of the adhesive 1.0 g.*



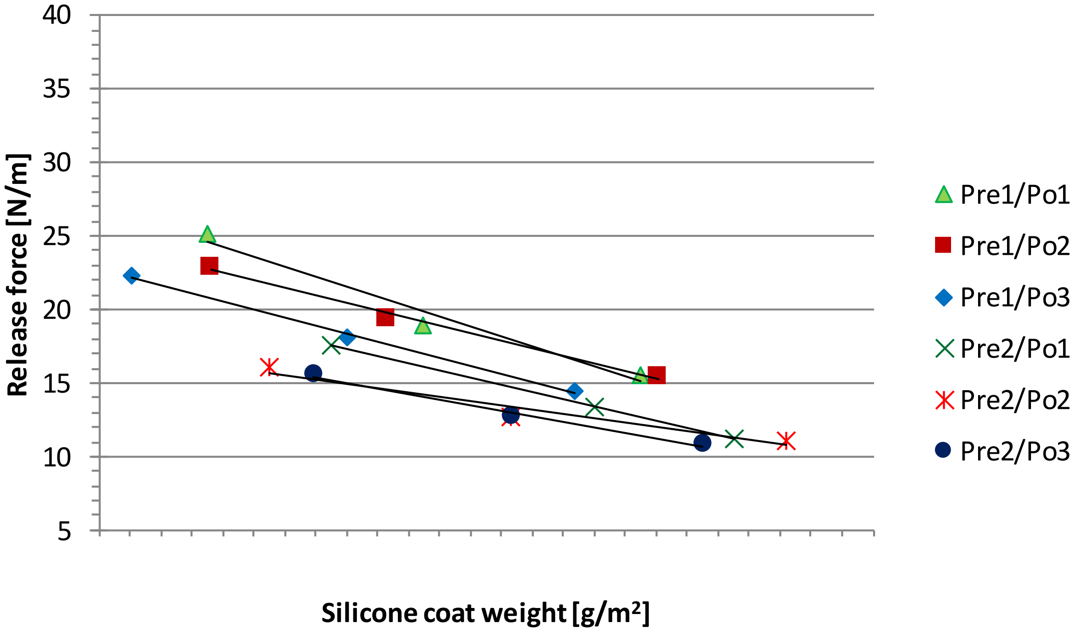


Figure 68. *Release force as a function of silicone mixture SC% (above) and silicone coat weight (below) for adhesive A3 (adhesive for envelopes and security bags). Mass of the adhesive 0.84 g.*

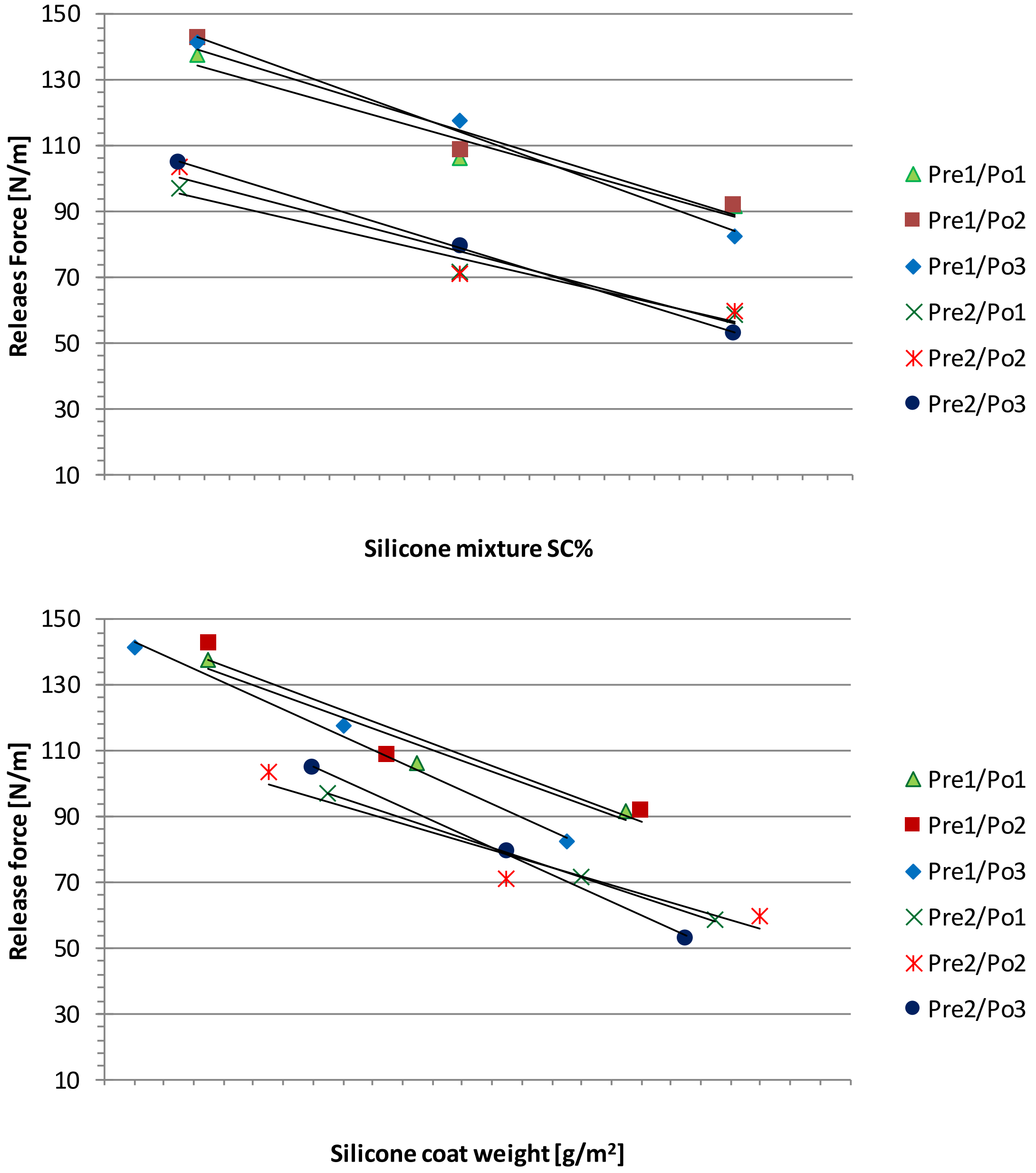


Figure 69. *Release force as a function of silicone mixture SC% (above) and silicone coat weight (below) for adhesive A4 (adhesive for envelopes and security bags and also to fasten medical drapes to skin, high tack). Mass of the adhesive 0.88 g.*

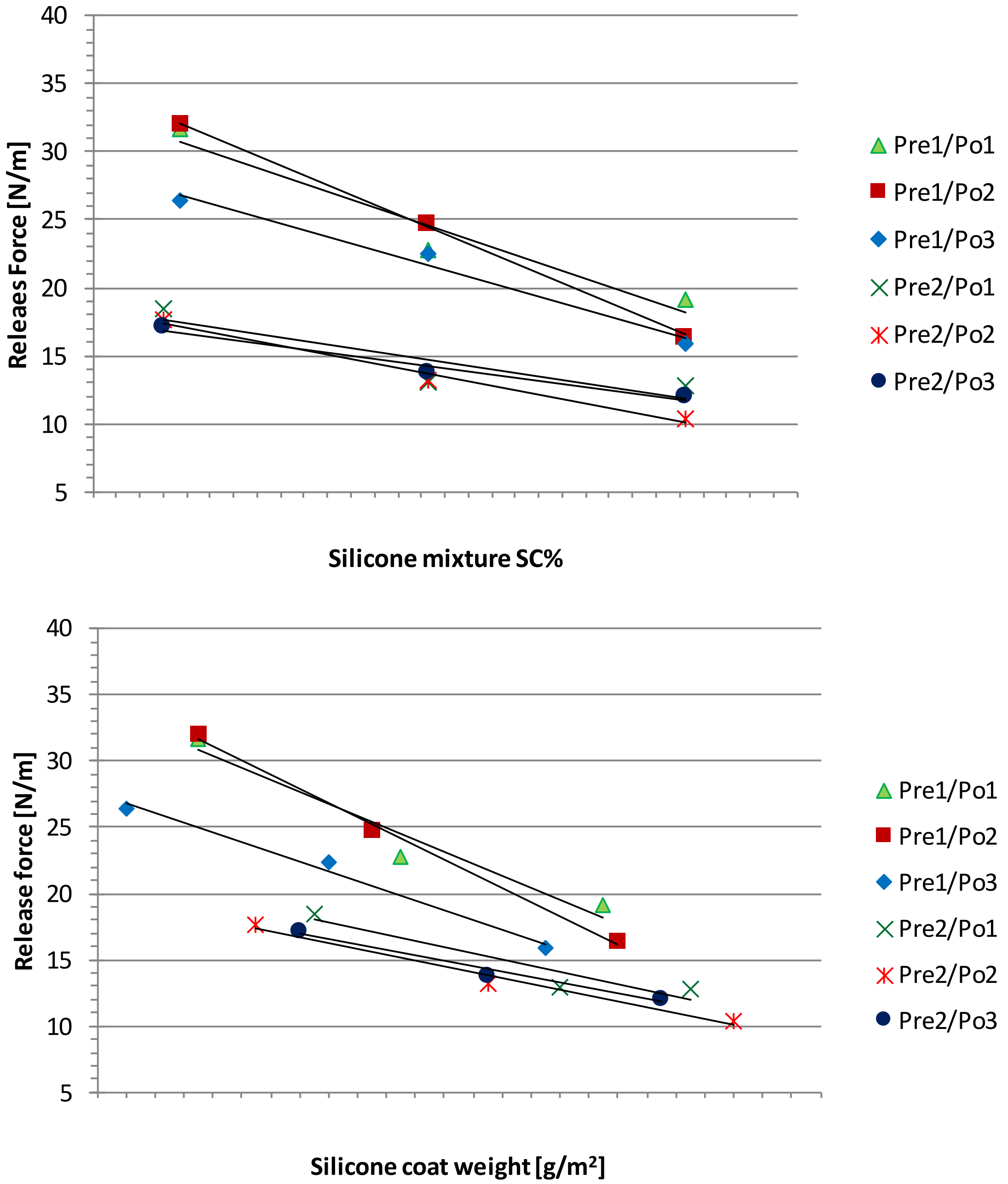


Figure 70. *Release force as a function of silicone mixture SC% (above) and silicone coat weight (below) for adhesive A5 (feminine care adhesive). Mass of the adhesive 0.91 g.*

6.9 Reliability of the results

Coat weight. Accurate determination of the coat weights was problematic and specifically variation of coat weights of Pre2 precoating samples was large. Factors that can have caused the coat weight variation of precoating are pressure variation of the rod in the hand coating device as well as viscosity of the coating colour, which is affected by pH and temperature. Coat weight determination by weighing is affected by the water content in the paper. Coat weights were determined using paper sheets, which were coated only halfway. In the oven, water from the precoating evaporates, but some of the natural moisture of especially the non-coated half may also evaporate resulting into variations in moisture content between different sections. This alternative was not verified due to time constraints. Results of coat weight determination by ash content seemed not reliable, and more parallel samples might have helped this. Coat weight determination of silicone coating by XRF might not have been accurate due to the calibration method and also coat weight variation of clay precoating. However, problems in coat weight determination do not have to affect the reliability of the results, since release force data can be presented as a function of SC%, although accurate knowledge of the coat weight level would be beneficial. Large variation of the precoating level between parallel samples anyway affects all the results. Variation was smaller with Pre1 precoating (probably due to lower viscosity) and also release force results of this precoating level are more even.

Air permeance. Standard deviations of air permeance measurements of base papers were small (2–5 %) but larger for coated samples (4–13% for precoated and 7–17 % for silicone coated samples). Variations in coat weights can affect this variation in air permeance values. Air permeance results correlated well with coating solids contents and can be regarded reliable.

Contact angles. For static contact angles, 3 parallel sample papers were used, and 5–10 droplets were used for each sample. Standard deviations of the parallel samples were small, between 0.5 – 2 %. Also advancing contact angles (3 parallel samples) had small standard deviation (0.5–2%), but receding contact angle determination was not that straightforward and standard deviations were between 1–8 %. The result that there were no differences in water contact angles with different release liner samples can be considered reliable.

Profilometer. Only two parallel samples were used in profilometer measurements, but the scanned area was relatively large, 2 x 2 mm, and total measured area 4.5 x 4.5 mm. Surface roughness and surface texture data was very similar for all release liner samples, but it is possible that wrinkles in the paper have affected the results. More careful sample preparation for roughness measurements would give more reliable roughness data.

Adhesives. Rheometer measurements were performed by an experienced person, but on the other hand, pressure-sensitive adhesives were a new type of materials. It was unexpected that correlation between rheological properties of the adhesives (especially loss modulus G’’ or tan δ) with release forces was not found. More learning about the PSA properties and behavior would be needed. Adhesive layer thickness might also need more learning as well as influence of time the adhesive is stored hot, since these factors may have some influence on the release test results.

Release tests. Many factors affect the release test results. In addition to those related to release liner samples (mainly coat weight variation), also thickness of the adhesive layer, possible changes in adhesive during storage at high temperature, and the whole adhesive application and release test process has influence on the results. Three parallel samples were used in the release test. In cases were some measurement gave very different value than the others, 1–2 more tests were performed and possibly a value significantly different to all others was abandoned (this was not done more than 1–2 times, and in other cases the final average value contained all these 3 + 1 or 3 + 3 measurements). Standard deviation for TESA tape tests were at range 3–7 %, but larger for hot-melt test: usually below Si1, but in some cases as high as 25 %.

When hot-melt release tests were performed with calibration paper for dozens of parallel samples, and it was found that there were usually ca. 5 N/m variations in the release force, and in addition some single samples might differ significantly from the other results. Therefore, differences of the order of 5 N/m may not be significant in release tests results (unless a difference or trend is repeated in several cases). Due to the large variations and many factors affecting the release force, more parallel samples would have increased the reliability of the release force results. 5–10 parallel samples might be sufficient. However, since same trends in release force data were repeated with several adhesives, qualitative data about the influence of release liner properties could be obtained, as well as some information about the influence of different adhesives.

7. CONCLUSIONS

In the theoretical part of the work, common adhesion theories were introduced, and continued with considerations of practical strength of adhesive bond and energy dissipation in the peeling process. Then components of the release liner, base paper, precoating and silicone coating were discussed, as well as nature and performance of pressure-sensitive adhesives. Release mechanism of PSA–silicone system includes interfacial interactions (mainly dispersion interaction) and energy dissipation in the peel process mainly due to adhesive deformation, with impact of interfacial slippage of the silicone surface reducing the effect of the energy dissipation. The factors affecting the release performance include the properties of the base paper, factors related to silicone coating (mainly layer thickness, holdout and coating coverage), the rheological properties of the adhesive as well as different face stock material and factors related to the stripping operation (peel angle, peel speed). Understanding all the factors affecting release performance is important for release liner manufacturer in order to provide suitable release liners for their customers.

In the experimental part of the work, influence of porosity of the base paper, precoating amount, silicone amount as well as different commercial adhesives were considered. Base papers of three different porosities [Po1 (highest porosity), Po2, and Po3 (lowest porosity)] were first precoated and then silicone coated with coating mixtures of different solids contents, so that samples had two different precoating levels [Pre1 (lower) and Pre2 (higher)] and three different silicone levels [Si1 (lowest), Si2, and Si3 (highest)]. Coat weights, air permeance values, contact angles and roughness data were determined for the release liner samples. Six different commercial adhesives were considered, and their rheological properties determined (G’, G’’, and tan δ) with rotation rheometer. Adhesives were applied to the release liner samples with hot-melt applicator and release tests were performed for the samples.

Coat weights of precoated samples were determined both by weighing and by ash content determination (only one parallel sample). Both methods showed that paper with lowest porosity (Po3) had lower coat weight than papers of higher porosities (Po1 and Po2) papers, but difference given by ash content was so large that results by weighing were considered more reliable. There seemed to be quite large variation in precoating coat weights between parallel samples (standard deviation 14%). Coat weights of silicone coating were determined by XRF, but variation of precoating level (which contains clay and thus silicone) and possibly unsuitable calibration method of the XRF made the coat weight data of silicone unreliable. However, release force results can also be presented as a function of silicone mixture solids content.

Air permeance results of coated samples correlated well with SC% of both precoating and silicone coating. With precoating level of Pre1, the air permeance values were roughly double of the values of Pre2 precoating at all porosity levels. Similarly, air permeance values of silicone coated samples decreased with increasing silicone mixture SC%. All values of silicone coated samples were well below the target maximum level.

In the contact angle measurements of the release liner samples, no difference in water contact angles could be found between the different base paper porosity levels or precoating and silicone coating amounts. Thus surface energies, directly related to the contact angles, cannot explain the differences in release forces for different coating amounts. This is, however, in accordance with the understanding that low surface energy is necessary, but not enough for the low release values, and indicates that even the lowest level of silicone used is sufficient to achieve a coating coverage good enough so that the contact angles (and the surface energies) are the same for all samples. Other factors considered important in silicone properties than the low surface energy is the rheological behavior of silicone, and the interfacial slippage property which decreases the impact of energy dissipation processes in peeling. This phenomenon was not considered in this study.

Roughness of the samples was investigated with profilometer roughness and texture measurements, but clear differences between the samples were not found and thus evidence of differences in roughness on the release force was not found in this study. Wrinkles in the paper due to getting wet in the coating process may have been affected to the profilometer results. However, it seemed that paper with lowest porosity (Po3) has smoother visual appearance in topographic images than the papers of higher porosities (Po1 and Po2), although numerical roughness values were very similar.

Porosity of the base paper had only little influence on the release force. Lower porosity (or air permeance) level gave slightly lower release force, and this impact was smaller with higher precoating level. Difference between porosities Po1 and Po2 was insignificant, but the lowest porosity (Po3) had more clear difference, especially with the lower precoating level (Pre1). Profilometer data suggests that the coatings do not completely fill the pores of base paper, and that Po3 paper seems smoother than Po2 or Po1 papers. Po3 base paper may be better alternative to more porous base papers. SC% of both precoating mixture and silicone mixture correlated well with the release forces, so that higher SC% of the coating gives lower release force due to better coating coverage. For precoating, it seems that with lower porosity level (Po3) less coating colour sticks to the paper (lower coat weight for Po3 determined both by weighing and ash content), but it stays better on the surface (better holdout, does not absorb deeper inside the paper), since release force is at the same level or lower than with Po1 and Po2 porosities. The main role of the precoating is to provide good silicone holdout. It can be concluded that base paper with porosity of Po3 can function better as a release liner substrate than papers of higher porosities (Po1 and Po2), and allow lower level of precoating amount for the same performance. Similarly, higher level of precoating offers better silicone holdout and allows lower level of silicone coat weight. We did not find clear correlation between any of the adhesive rheological parameters considered and the release force. Adhesive A4 (envelope adhesive, which is also used to fasten medical drapes to skin) gave significantly higher release force than the other adhesives. This adhesive had the lowest storage modulus (G') at low frequencies, which correlates with high tack due to good wetting. According to literature, peel test should correlate more with loss modulus (G''), but this correlation was not found in this study.

Different commercial adhesives for hygiene applications performed in a very similar manner in the release tests: All the adhesives for hygiene products gave release force of magnitude of 30–35 N/m for release liner samples of lowest coat weights. The envelope adhesive A4 described as high tack adhesive gave significantly higher release force, of the order 140 N/m for samples of lowest coat weights. When the release force level of samples of lowest coat weights was of the magnitude of 30 N/m, precoating coat weight change from Pre1 to Pre2 (SC% change of 10 percentage points) decreased release force ca. 8–10 N/m. Silicone coating SC% change of ~4.5 percentage points (from Si1 to Si2 or from Si2 to Si3) resulted in ca. 6–7 N/m change in release force.

Influence of the various factors on the release force are summarized in Table 18. This table shows that silicone amount and precoating amount changes have clear impact on the release force, and that the magnitude of the adhesive type influence on the release force is significant.

Table 18. *Summary of influence of various factors on the release force*

Factor	**Influence on release force**	**Magnitude [N/m]**
Silicone amount, **-Increase of 4.5 SC% points**	Decrease (easier release)	6-7
Precoating amount **-Increase of 10 SC% points**	Decrease (easier release)	8-10
Base paper porosity **-Increase of 20 Gurley (= decrease of porosity)**	No direct impact, but indication of lower need for precoating and silicone amount with lower porosity	Some?
Scale of roughness	No clear impact	0
Surface energy/contact angle	No clear impact	0
Adhesive rheology	No impact	0
Adhesive type **-All adhesives in the study** **-Feminine care hygiene adhesives**	 -Adhesive type has a significant impact -Hygiene adhesives are very similar	 ca. 115 ca. 5

8. SUGGESTIONS FOR FUTURE WORK

Important information about the influence of base paper porosity, precoating and silicone coating amounts as well as behaviour of different commercial adhesives was obtained with this work. In further studies, if coating is done with a hand coater, more accurate coat weight determination could be considered for both precoating and silicone coating. More effort could also be made to find the reason for the precoating coat weight variation and to achieve a more constant coat weight. It could be beneficial to examine the coating coverages with e.g. scanning electron microscope (SEM), in order to see the impact of coating coverage with increasing silicone coat weight on the release force. In addition, more studies about the roughness with more careful sample preparation could be performed.

More understanding and ways to study PSA and also silicone rheological properties could be considered. When (hot-melt) release tests are performed, more than 3 parallel samples should be considered (at least 5). Different face stock materials (e.g. nonwoven) could be considered in further studies, as well as different ways to apply the adhesive (spray, or different types of strips). Release tests as a function of adhesives thickness, peel speed and peel angle might also give useful information. In addition, aging tests and studies of possible residues of silicone in the adhesive or residues of the adhesive in the silicone can also be subjects of further studies.

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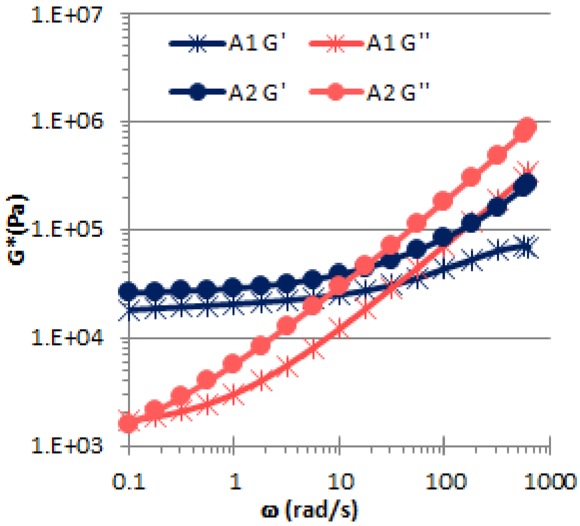
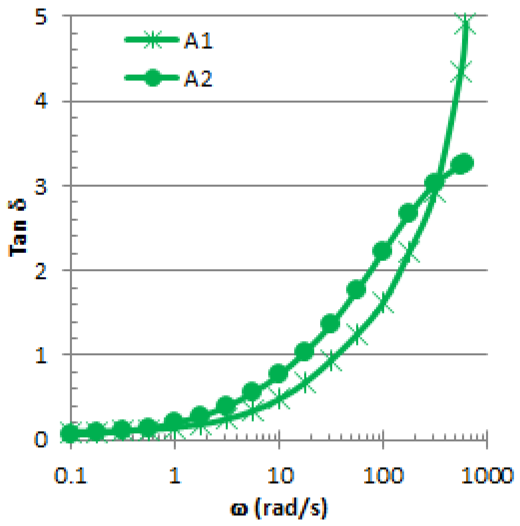
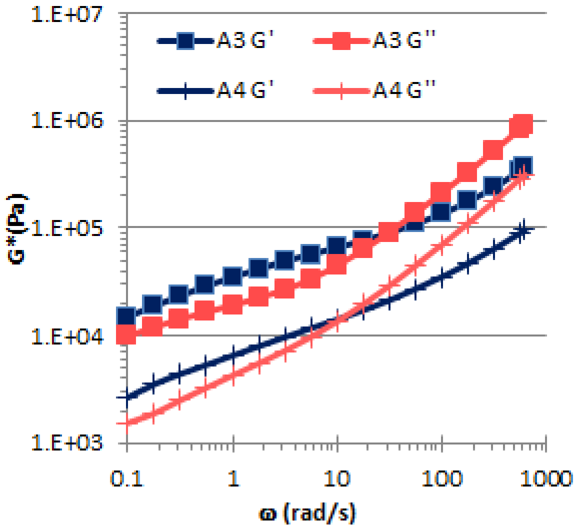
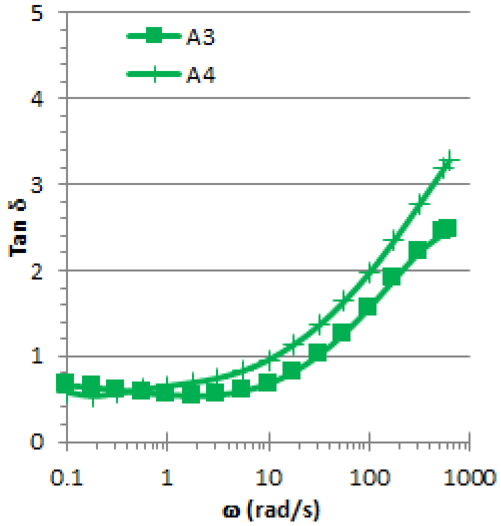
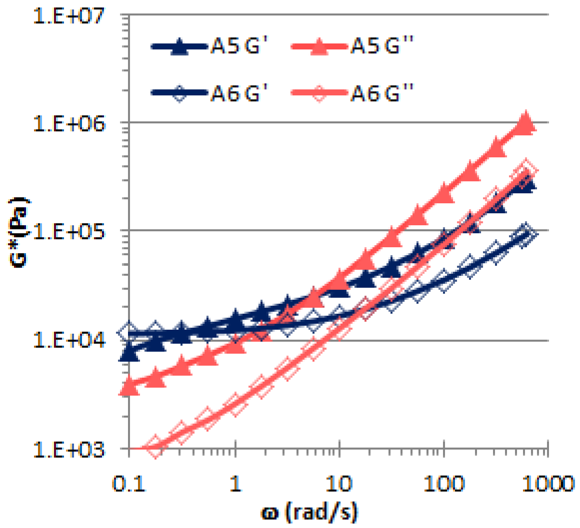
APPENDIX 1: G’, G’’, AND TAN σ FOR ADHESIVES A1-A6

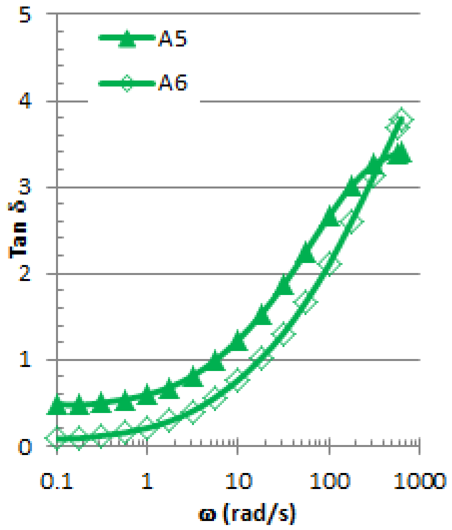












APPENDIX 2: RELEASE FORCE FOR ADHESIVE A1

Release force [N/m] results for adhesive A1 (Mass: 1.1 g)

Date: 28.04.2016		1	2	3	4*	Avg	SD
	Calibration**	7.3	7.8	(8.2)			
1	**Pre1/Si1/Po1**	35.70	40.80	36.24	38.05	**37.7**	**2.3**
2	**Pre1/Si1/Po2**	34.78	35.99	36.12		**35.6**	**0.7**
3	**Pre1/Si1/Po3**	39.17	28.50	27.40	34.35	**32.4**	**5.5**
4	**Pre1/Si2/Po1**	27.03	26.55	26.62		**26.7**	**0.3**
5	**Pre1/Si2/Po2**	27.12	22.29	23.34	28.09	**25.2**	**2.8**
6	**Pre1/Si2/Po3**	25.95	27.79	27.85		**27.2**	**1.1**
7	**Pre1/Si3/Po1**	21.82	21.62	20.06		**21.2**	**1.0**
8	**Pre1/Si3/Po2**	24.86	20.77	19.04	23.83	**22.1**	**2.7**
9	**Pre1/Si3/Po3**	21.70	17.62	20.19	38.05	**19.8**	**2.1**
	Calibration	7.3	8.3	7.9			

		1	2	3	4	Avg	SD
	Calibration*	(7.3)	(8.3)	(7.9)			
1	**Pre2/Si1/Po1**	23.57	20.93	25.13		**23.2**	**2.1**
2	**Pre2/Si1/Po2**	19.46	18.66	20.09		**19.4**	**0.7**
3	**Pre2/Si1/Po3**	22.59	21.42	20.73		**21.6**	**0.9**
4	**Pre2/Si2/Po1**	22.29	17.46	13.61	14.52	**17.0**	**3.9**
5	**Pre2/Si2/Po2**	17.89	15.93	19.55		**17.8**	**1.8**
6	**Pre2/Si2/Po3**	19.40	15.13	19.05	15.33	**17.2**	**2.3**
7	**Pre2/Si3/Po1**	16.40	14.53	15.4		**15.4**	**0.9**
8	**Pre2/Si3/Po2**	14.66	13.89	14.39		**14.3**	**0.4**
9	**Pre2/Si3/Po3**	10.86	14.45	14.72		**13.3**	**2.2**
	Calibration	6.6	8.2	7.2			

T_{use}=125-165°C. T_{Tank}: 135°C; T_{Hose}: 125°C; T_{Die} 130°C; Speed: max; Mass: 1.1 g.

*4:th parallel test was carried out e.g. if standard deviation was higher than with other samples.

**Calibration test was performed before and after every series of 9 different samples. Value in parenthesis means that it is the same calibration result than presented above/earlier. Calibration value presented in the table is average of (at least) 3 calibration tests.

APPENDIX 3: RELEASE FORCE FOR ADHESIVE A2

Release force results [N/m] for adhesive A2 (Mass: 1.0 g)

Date: 19.04.2016		**1**	**2**	**3**	**4**	**5**	**Avg**	**SD**
	Calibration*	4.3	4.3	(4.5)	5.0			
1	**Pre1/Si1/Po1**	28.02	32.30	28.03	36.67		31.3	4.1
2	**Pre1/Si1/Po2**	31.15	34.52	36.52	31.09	29.44	32.5	2.9
3	**Pre1/Si1/Po3**	22.63	25.13	32.00	31.48		27.8	4.7
4	**Pre1/Si2/Po1**	21.81	18.13	20.52	28.26		22.2	4.3
5	**Pre1/Si2/Po2**	19.92	18.81	20.93	27.87	22.93	22.1	3.6
6	**Pre1/Si2/Po3**	21.62	20.83	25.59	21.76		22.5	2.1
7	**Pre1/Si3/Po1**	15.59	14.02	21.10	21.78		18.1	3.9
8	**Pre1/Si3/Po2**	13.39		17.42	19.35	19.75	17.5	2.9
9	**Pre1/Si3/Po3**	13.11	14.53	15.48	19.58		15.7	2.8
	Calibration*	4.3	5.6	5.0				

		1	**2**	**3**	**4**	**5**	**Avg**	**SD**
	Calibration*	4.5		(4.3)	(5.)6			
1	**Pre2/Si1/Po1**	17.78	19.40	20.27			19.2	1.3
2	**Pre2/Si1/Po2**	15.26	14.58	16.04	17.98		16.0	1.5
3	**Pre2/Si1/Po3**	13.54	18.54	14.06	15.15		15.3	2.2
4	**Pre2/Si2/Po1**	14.79	14.69	16.07	15.98		15.4	0.7
5	**Pre2/Si2/Po2**	11.19	14.40	13.59			13.1	1.7
6	**Pre2/Si2/Po3**	8.61	11.87	10.12	13.87		11.1	2.3
7	**Pre2/Si3/Po1**	10.24	10.54	10.79			10.5	0.3
8	**Pre2/Si3/Po2**	10.14	12.70	10.03	9.85		10.7	1.4
9	**Pre2/Si3/Po3**	8.45	13.24	8.20	8.02		9.5	2.5
	Calibration*	4.4	4.4	4.9	4.5			

T_{use}=130-175°C. T_{Tank}: 150°C; T_{Hose}: 148°C; T_{Die} 153°C; Speed: max; Mass: 1.0 g.

*4:th parallel test was carried out e.g. if standard deviation was higher than with other samples. Empty space means that test result was rejected due to some error (e.g. wrinkle in the sample)

**Calibration test was performed before and after every series of 9 different samples. Value in parenthesis means that it is the same calibration result than presented above/earlier. Calibration value presented in the table is average of (at least) 3 calibration tests.

APPENDIX 4: RELEASE FORCE FOR ADHESIVE A3

Release force results [N/m] for adhesive A3 (Mass 0.84g)

Date: 18.04.2016		**1**	**2**	**3**	**4**	**Avg**	**SD**
	Calibration*	7.0					
1	**Pre1/Si1/Po1**	22.50	25.87	27.45	24.52	**25.1**	**2.1**
2	**Pre1/Si1/Po2**	23.30	23.47	21.98		**22.9**	**0.8**
3	**Pre1/Si1/Po3**	23.70	21.66	21.46		**22.3**	**1.2**
4	**Pre1/Si2/Po1**	20.85	18.34	17.61		**18.9**	**1.7**
5	**Pre1/Si2/Po2**	21.69	18.30	18.00		**19.3**	**2.0**
6	**Pre1/Si2/Po3**	20.17	17.08	16.95		**18.1**	**1.8**
7	**Pre1/Si3/Po1**	16.16	16.74	13.81		**15.6**	**1.6**
8	**Pre1/Si3/Po2**	15.49	16.27	14.73		**15.5**	**0.8**
9	**Pre1/Si3/Po3**	15.88	14.00	13.38		**14.4**	**1.3**
	Calibration*	6.6	7.0	6.5			

		1	**2**	**3**	**4**	**Avg**	**SD**
	Calibration*						
1	**Pre2/Si1/Po1**	17.58	18.75	16.48		**17.6**	**1.1**
2	**Pre2/Si1/Po2**	16.05	16.75	15.25		**16.0**	**0.8**
3	**Pre2/Si1/Po3**	17.17	15.56	13.99		**15.6**	**1.6**
4	**Pre2/Si2/Po1**	12.85	13.94	13.44		**13.4**	**0.5**
5	**Pre2/Si2/Po2**	12.78	12.69	12.66		**12.7**	**0.1**
6	**Pre2/Si2/Po3**	12.44		12.44	13.40	**12.8**	**0.6**
7	**Pre2/Si3/Po1**		11.10	11.51	10.87	**11.2**	**0.3**
8	**Pre2/Si3/Po2**	11.68	10.38	11.24		**11.1**	**0.7**
9	**Pre2/Si3/Po3**	10.66	10.96	10.82		**10.8**	**0.2**
	Calibration*	6.8	6.2	7.0			

T_{use}=160-190°C. T_{Tank}: 155°C; T_{Hose}: 160°C; T_{Die} 165°C; Speed: 47.5; Mass: 0.84 g.

*4:th parallel test was carried out e.g. if standard deviation was higher than with other samples. Empty space means that test result was rejected due to some error (wrinkle in the sample, problem with baseline or sample came off from the holder)

*Calibration test was performed before and after every series of 9 different samples. Value in parenthesis means that it is the same calibration result than presented above/earlier. Calibration value presented in the table is average of (at least) 3 calibration tests.

APPENDIX 5: RELEASE FORCE FOR ADHESIVE A4

Release force results [N/m] for adhesive A4 (Mass 0.88g)

Date: 26-27.04.2016		**1**	**2**	**3**	**4**	**5**	**Avg**	**SD**
	Calibration*	16.3	23.9	17.8	12.5			
1	**Pre1/Si1/Po1**	154.64	132.53	147.42	115.43		137.5	17.4
2	**Pre1/Si1/Po2**	139.80	135.50	158.78	136.62		142.7	10.9
3	**Pre1/Si1/Po3**	125.60	163.72	168.73	142.23	106.97	150.1	20.0
4	**Pre1/Si2/Po1**	93.05	121.00	123.68	87.69		106.4	18.6
5	**Pre1/Si2/Po2**	88.89	128.05	90.21	123.91	111.98	108.6	21.1
6	**Pre1/Si2/Po3**	87.04	129.65	129.67	130.92	109.88	117.4	21.5
7	**Pre1/Si3/Po1**	74.12	121.53	81.17	88.79		91.4	21.0
8	**Pre1/Si3/Po2**	67.11	118.04	92.21	90.59		92.0	20.8
9	**Pre1/Si3/Po3**	59.99	95.32	92.41	81.31		82.3	16.0
	Calibration*	14.8	15.6	14.4				
		1	**2**	**3**		**4**	**Avg**	**SD**
	Calibration*	15.6	(14.8)	(15.6)				
1	**Pre2/Si1/Po1**	91.02			88.25	112.48	97.3	13.3
2	**Pre2/Si1/Po2**	99.54	97.30	115.63	102.60		103.8	8.2
3	**Pre2/Si1/Po3**	104.39	107.11	102.96			104.8	2.1
4	**Pre2/Si2/Po1**	67.29	80.20	66.62			71.4	7.7
5	**Pre2/Si2/Po2**	79.08	57.74	76.49			71.1	11.6
6	**Pre2/Si2/Po3**	83.78	79.92	75.07			79.6	4.4
7	**Pre2/Si3/Po1**	65.64	56.46	53.08			58.4	6.5
8	**Pre2/Si3/Po2**	64.18	56.33	57.82			59.4	4.2
9	**Pre2/Si3/Po3**	56.73	55.39	47.18	52.36		52.9	4.2
	Calibration*	24.4	17.2	12.0				

T_{use}=150-180°C. T_{Tank}: 150°C; T_{Hose}: 148°C; T_{Die}: 153°C; Speed: max; Mass: 0.88 g.

*4:th parallel test was carried out e.g. if standard deviation was higher than with other samples. Empty space means that test result was rejected due to some error (wrinkle in the sample)

**Calibration test was performed before and after every series of 9 different samples. Value in parenthesis means that it is the same calibration result than presented above/earlier. Calibration value presented in the table is average of (at least) 3 calibration tests.

APPENDIX 6: RELEASE FORCE FOR ADHESIVE A5

Release force results [N/m] for adhesive A5 (Mass: 0.91g)

Date: 21.04.2016		**1**	**2**	**3**	**4**	**Avg**	**SD**
	Calibration*	5.8	(5.6)	(6.2)			
1	**Pre1/Si1/Po1**	28.87	32.57	33.65		**31.7**	**2.5**
2	**Pre1/Si1/Po2**	30.87	33.28	31.67		**31.9**	**1.2**
3	**Pre1/Si1/Po3**	22.93	28.58	27.72		**26.4**	**3.0**
4	**Pre1/Si2/Po1**	21.08	25.09	24.27	20.67	**22.8**	**2.2**
5	**Pre1/Si2/Po2**	18.46	27.05	22.28	31.16	**24.7**	**5.5**
6	**Pre1/Si2/Po3**	20.52	24.23	22.54		**22.4**	**1.9**
7	**Pre1/Si3/Po1**	19.67	19.09	18.45		**19.1**	**0.6**
8	**Pre1/Si3/Po2**	13.68	17.99	16.67	17.14	**16.4**	**1.9**
9	**Pre1/Si3/Po3**	14.50	16.89	16.24		**15.9**	**1.2**
	Calibration*	5.2	6.1	6.6			

		1	**2**	**3**	**4**	**Avg**	**SD**
	Calibration*	(5.2)	(6.1)	(6.6)			
1	**Pre2/Si1/Po1**	17.89	19.23	18.29		**18.5**	**0.7**
2	**Pre2/Si1/Po2**	15.95	18.25	18.87		**17.7**	**1.5**
3	**Pre2/Si1/Po3**	14.74	16.53	20.14		**17.1**	**2.8**
4	**Pre2/Si2/Po1**	11.46	13.43	14.09		**13.0**	**1.4**
5	**Pre2/Si2/Po2**	14.64	10.45	16.00	11.54	**13.2**	**2.6**
6	**Pre2/Si2/Po3**	14.46	12.62	15.70	12.30	**13.8**	**1.6**
7	**Pre2/Si3/Po1**	14.83	10.65	12.73		**12.7**	**2.1**
8	**Pre2/Si3/Po2**	10.12	9.62	11.37		**10.4**	**0.9**
9	**Pre2/Si3/Po3**	10.93	13.66	11.52		**12.0**	**1.4**
	Calibration*	5.6	6.2	6.6			

T_{use}=130-175°C. T_{Tank}: 145°C; T_{Hose}: 135°C; T_{Die} 140°C; Speed: max; Mass: 0.91 g.

*4:th parallel test was carried out e.g. if standard deviation was higher than with other samples.

*Calibration test was performed before and after every series of 9 different samples. Value in parenthesis means that it is the same calibration result than presented above/earlier. Calibration value presented in the table is average of (at least) 3 calibration tests.

APPENDIX 7: RELEASE FORCE FOR ADHESIVE A6

Release force results [N/m] for adhesive A6 (Mass 0.86g)

Date 03-04.03.2016		**1**	**2**	**3**	**4**	**5**	**Avg**	**SD**
	Calibration*	8.8		(8.5)				
1	**Pre1/Si1/Po1**	37.38	38.42	35.36	35.40		**36.6**	**1.5**
2	**Pre1/Si1/Po2**	37.60	37.29	38.33	36.31		**37.4**	**0.8**
3	**Pre1/Si1/Po3**	33.63	36.62	35.18			**35.1**	**1.5**
4	**Pre1/Si2/Po1**	30.70	32.26	31.28	28.09	29.05	**30.6**	**1.8**
5	**Pre1/Si2/Po2**	26.92	28.93	34.16	31.47		**30.9**	**2.8**
6	**Pre1/Si2/Po3**	29.81	28.15	29.55			**29.2**	**0.9**
7	**Pre1/Si3/Po1**	19.54	20.98	24.89	21.97	24.86	**22.4**	**2.4**
8	**Pre1/Si3/Po2**	23.18	22.52 22.52	24.29	21.88	25.41	**23.5**	**1.4**
9	**Pre1/Si3/Po3**	21.56	23.02	21.92	21.26		**21.9**	**0.8**
	Calibration*		8.5		9.4			
	Name	**1**	**2**	**3**	**4**	**5**	**Avg**	**SD**
	Calibration*	**8.4**		**8.1**				
1	**Pre2/Si1/Po1**	29.30	21.41	26.31	29.91		**26.7**	**3.9**
2	**Pre2/Si1/Po2**	23.54	23.77	29.93	26.09	24.58	**25.6**	**2.6**
3	**Pre2/Si1/Po3**	26.35	24.88	26.95			**26.1**	**1.1**
4	**Pre2/Si2/Po1**	18.85	20.74	22.78	18.31		**20.2**	**2.0**
5	**Pre2/Si2/Po2**	19.64	19.97	21.33	19.95		**20.2**	**0.8**
6	**Pre2/Si2/Po3**	19.98	21.27	19.14	19.35		**19.9**	**1.0**
7	**Pre2/Si3/Po1**	15.52	15.74	18.42	13.71		**15.8**	**1.9**
8	**Pre2/Si3/Po2**	14.58	15.15	15.68			**15.1**	**0.6**
9	**Pre2/Si3/Po3**	15.71	12.68	13.43	15.22	15.19	**14.4**	**1.3**
	Calibration*				8.6			

T_{use}=130-175°C. T_{Tank}: 155°C; T_{Hose}: 130°C; T_{Die} 135°C; Speed: 75; Mass: 0.86 g.

*4:th parallel test was carried out e.g. if standard deviation was higher than with other samples.

*Calibration test was performed before and after every series of 9 different samples. Value in parenthesis means that it is the same calibration result than presented above/earlier. Calibration value presented in the table is average of (at least) 3 calibration tests.