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IMPROVED ANTIFOG PROPERTIES FOR POLYETHYLENE SEALABLE LIDS

Master of Science Thesis

Examiner: Prof. Jyrki Vuorinen
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ABSTRACT

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Humidity tends to condense as water droplets and fog on the inner surfaces of food packaging films. This phenomenon is common especially when product with high moisture content is packed in plastic package and stored in cold conditions. A great amount of water droplets makes visual appearance of package unattractive and unhygienic, and additionally, fog prevents consumer from seeing the packed food supply. The surface of polymer film is hydrophobic by its nature, in which case condensation of water droplets on the surface of film can be prevented by changing the surface to hydrophilic. In this case, condensed water droplets spread as uniform water layer on the surface of film, and transparency of film is improved. This phenomenon is called antifog effect. Hydrophilicity of surfaces of films can be improved with different antifog additives and coatings. Additionally, surfaces of films can be treated with several physical methods.

Good antifog properties are difficult to achieve and maintain for the resealable polyethylene structure. This is because antifog masterbatches utilizing polyethylene carrier are not well applicable, and on the other hand, antifog lacquers do not anchor well on polyethylene surface. Antifog property should maintain at acceptable level for six months, which is the demanded shelf-life of the product. However, recent tests have shown that antifog performance significantly reduces as a function of time.

Goal of this research was to find out, how functionality of antifog lacquer could be improved on the surface of polyethylene film. The dilemma was approached by studying functionality of antifog lacquers of two different suppliers on resealable polyethylene structure. Antifog properties, sealability and static contact angle were studied from film samples coated with studied antifog lacquers during test period of six months.

During this research, differences were detected between durability of antifog performances of studied antifog lacquers. One of studied antifog lacquers maintained its antifog properties for desired six months. Sealability properties of all antifog lacquer coated film samples were at acceptable level. It was detected that dilution ratio of antifog lacquers affected the studied properties.

TIIVISTELMÄ

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Kosteudella on taipumus tiivistyä pisaroiksi ja sumuksi pakkauskalvon sisäpinnalle, etenkin tilanteissa, joissa suuren kosteuspitoisuuden sisältämä elintarvike pakataan muoviin ja säilytetään viileissä olosuhteissa. Suuri määrä pisaroita kalvon pinnalla tekee pakkauksesta epämiellyttävän näköisen ja epähygieenisen, sekä estää kuluttajaa näkemästä pakatun tuotteen. Polymeerikalvojen pinta on luonteeltaan hydrofobinen, jolloin veden kondensoitumista pisaroiksi kalvon pinnalle voidaan ehkäistä muuttamalla kalvon pinta hydrofiiliseksi. Tällöin kondensoituneet vesipisarat leviävät kalvon pinnalle yhtenäiseksi vesikerrokseksi, ja kalvon läpinäkyvyys paranee. Tätä ilmiötä kutsutaan antifog-efektiksi. Kalvojen pinnan hydrofiilisyyttä voidaan parantaa erilaisten antifog-lisäaineiden ja -pinnoitteiden avulla. Näiden lisäksi kalvon pinta voidaan käsitellä erilaisten fysikaalisten menetelmien avulla.

Hyvät antifog-ominaisuudet on haasteellista saavuttaa uudelleensaumautuvassa polyeteenirakenteessa. Tämä johtuu siitä, että polyeteenikantajapolymeerin sisältämän antifog-masterbatsin käyttö ei ole mahdollista. Toisaalta myöskään antifog-pinnoitteet eivät kiinnity tehokkaasti polyeteenin pinnalle. Tuotteille määritetty hyllyikä on kuusi kuukautta, jonka aikana antifog-ominaisuuden tulee pysyä hyväksyttävällä tasolla. Aikaisemmat tutkimukset kuitenkin osoittavat, että antifog-ominaisuus heikkenee huomattavasti ajan funktiona.

Työn tavoitteena oli selvittää, miten antifog-pinnoitteiden toimintaa voisi parantaa polyeteenikalvon pinnalla. Tutkimuksessa vertailtiin kahden eri toimittajan antifog-lakkoja uudelleensaumautuvassa polyeteenirakenteessa. Pinnoitetuista kalvoista tutkittiin antifog-ominaisuutta, saumautuvuutta ja staattista kontaktikulmaa kuuden kuukauden testijakson ajan.

Tutkittujen antifog-lakkojen välillä huomattiin eroja antifog-ominaisuuden kestossa. Toinen tutkittavista antifog-lakoista säilytti erinomaisesti antifog-ominaisuutensa kuuden kuukauden ajan. Saumautuvuusominaisuudet säilyivät hyväksyttävällä tasolla kaikilla pinnoitetuilla näytteillä. Antifog-lakkojen laimennussuhteella oli vaikutusta tutkittaviin ominaisuuksiin.

PREFACE

This Master of Science thesis was made in alliance with Bemis Europe that commissioned the thesis. Working on this thesis has been a very eye-opening experience, which allowed me to get to know research and development circumstances and its challenges. I am delighted about the fact that I was given a chance to work with this both challenging and inspiring subject and moreover, to get to know a lot of new interesting people.

I would like to thank and show my appreciation to the instructor of my thesis, Ilari Jönkkäri, and the examiner of my thesis, Professor Jyrki Vuorinen, for the possibility to complete this thesis under their supervision. Special thanks I want to show to Principal Development Engineer Kimmo Lahtinen and Product Development Manager Kalle Nättinen, who believed in my abilities, and supported and helped me throughout my thesis working process. I am grateful for having such great instructors, who helped me through challenges whenever I needed. I would also like to thank the whole personnel of research and development department and laboratory of the company for creating a pleasant atmosphere in which working was delightful and inspiring.

Finally, I want to show my gratefulness to my family and friends for their understanding and patience towards my time-consuming studies. They supported me all the way and believed in me even in the times I forgot to do so. Now I have reached a significant milestone in my life and I am looking forward to what future lies ahead.

Tampere, 5th of May 2017

Neea Juvonen

CONTENTS

APPENDIX A: THE SEALABILITY AND RE-TACK TEST RESULTS OBTAINED FOR THE SAMPLES ACROSS THE 6-MONTH AGEING PERIOD

LIST OF SYMBOLS AND ABBREVIATIONS

Chemicals and Materials

BON	Biaxially oriented nylon
C_3H_8O	Isopropanol
CO_2	Carbon dioxide
EVA	Ethylene vinyl acetate
EVOH	Ethylene vinyl alcohol
GMO	Glycerol mono-oleate
GMS	Glycerol monostearate
H_2O	Water
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
OPP	Oriented polypropylene
PA	Polyamide
PC	Polycarbonate
PE	Polyethylene
PET	Polyethylene terephthalate
PGE	Polyglycerol ester
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
SMO	Sorbitan mono-oleate

Greek and Latin symbols

ΔG_{SL}	Free energy of hydration
γ_L	Liquid surface tension
γ_S	Solid surface free energy
γ_{SL}	Solid-liquid interfacial free energy
φ	Fraction of the liquid base
θ	Contact angle
D	Diluent portion
L	Lacquer portion
r	Roughness factor
TV	Theoretical volume
W_S	Spreading coefficient

Other abbreviations

AF	Antifog
DoC	Declaration of Compliance
EASI	Enhanced Atmospheric Surface Improvement
GU	Gloss unit
LV	Liquid-vapor

MD	Machine direction
OML	Overall migration limit
PSA	Pressure sensitive adhesive
SIT	Seal initiation temperature
SL	Solid-liquid
SML	Specific migration limit
TD	Transverse direction

1. INTRODUCTION

1.1 Context

This research was carried out in alliance with the research and development department of Bemis Europe. Bemis manufactures plastic films for food packaging industry and the customers of it are typically food supply companies. Consumers mostly determine the properties required for food packages. One of the most important properties is the possibility to see the product. Visibility of the product is made possible by the antifog (AF) property of plastic films. Functionality of AF property is important especially when the packed food supply has high moisture content and is stored in cold climates. In this kind of circumstances, it is possible that moist condenses as water droplets on the surface of film and visual appearance of the product degrades. The goal of research and development department is to find ways to meet up demands of the consumers.

The fog, that is formed in the food casing, consists of tiny droplets of water on the surface of polymer. Formation of the fog can be prevented by using AF agents. The functionality of AF agents is based on balancing the surface tensions and formation of a continuous, invisible thin layer of water on the polymer surface. AF property can be created for plastic films in various ways depending on structure and properties of the film. AF agents can be applied on the surface of polymer films either as a masterbatch incorporated in the sealing layer of the film or as a separate liquid coating. AF property can also be created without using additives or chemicals by using alternative techniques. Masterbatches are typically used in the case of polyethylene carrier layers but sometimes the constitution and low thickness of the sealing layer does not allow the use of the masterbatch. In such cases the option that remains is to apply an AF lacquer coating on the surface of the film. Challenges are faced especially in reclosable polyethylene structures. Competitor analyses have also shown very poor AF performances for reclosable polyethylene structures revealing that the technical problem is common. [1] Because of these findings, an investigation over the different AF lacquers on polyethylene surface was started.

In this research functionality of AF lacquers of two different suppliers were studied on polyethylene surface. One of studied AF lacquers has been tested in the company, but AF property attained with it has not been completely satisfactory. AF property should maintain at acceptable level for six months, which is the demanded shelf-life of the product. With the AF lacquer that has been tested the AF property is lost after about three months. In preliminary tests, another AF lacquer has been providing better AF properties. This research focuses on comparing functionality and properties of these two AF lacquers through laboratory tests.

1.2 Subject, objectives and research problem

The purpose for this research is to improve functional properties of polyethylene sealable lids in food packaging. The focus is in improving AF properties and in achieving an acceptable AF performance for polyethylene surface across the six months' shelf life of the product without compromising other properties of the film. The objectives of this research are to understand the AF phenomenon and the theory behind it, and to improve the functionality of AF lacquers on the surface of polyethylene through theoretical and experimental research.

The research tries to solve the following problem:

- There is insufficient information about understanding thoroughly the antifog phenomenon related to antifog lacquers. This affects the development of food packaging films with antifog lacquers functioning on the surface of polyethylene.

The research question is following:

- How can the functioning of antifog lacquer on the surface of polyethylene be improved?

To answer the main research question, the sub-questions are following:

- Why it is not possible to reach wanted results/set goals with the antifog lacquer coating that has been tested?
- In which way, should the antifog properties be improved?
- What could be the new methods or alternatives to improve the antifog properties?
- How would it be possible to maintain the antifog and sealability properties over the six-month ageing period?
- Why another AF lacquer obtains better results? Do the differences originate from the raw material or coating method?
- What is the best working method to get the antifog lacquer anchored onto surface of polyethylene? How is it done in the most efficient way?
- How does printing affect to the obtained antifog properties?
- Does antifog lacquer compromise the quality of printing?

Objectives set to this research are aimed to be accomplished by finding solutions to research questions presented above. To accomplish objectives various research methods that help to understand and interpret subject more precisely, are used. In this way, the presented research problem is aimed to be solved and explain the phenomenon behind this problem. Theoretical part of this research is executed as literature research, with interviews and by experimental observing. Necessary material is collected by experimental part of this research and this material is analyzed. Interpretations and conclusions based on experimental part are finally connected with the theoretical part. Results found by this research are also evaluated and considered by paying attention to their reliability and validity.

This thesis has two main restrictions. First, thesis is related to company’s schedule which may change because of factors that cannot be predicted. This sets the research to fit company’s time manners, which have an impact on the time-sequence. Second, thesis covers short time-sequence, which sets restriction to research to cover long-lasting evaluation. The AF behavior changes over time and a rigorous analysis is covering months to years.

2. THEORETICAL PART

2.1 Food packaging

Production of plastics has been stable in Europe since 2011. In 2015, 58 million tons of plastic was produced in Europe. Approximately 40% of it was used in packaging and slightly over 20% specifically in food packaging. [2] This fact proves the significance of packaging industry and, especially, food packaging industry as a consumer of plastic films. This chapter concentrates on food packaging, what kind of demands are set for it and what efforts have been made to meet these demands.

Nowadays the package itself has become increasingly more remarkable part of food production. A food package works as a kind of barrier between the content of packaging and the surrounding atmosphere. The main purpose of package film is to keep among other things, dirt, bacteria, liquids and gas only on one side of the film, in other words, to protect the food. However, from food package is demanded more than just protection and hence the active and intelligent packaging will play an increasingly important role in the future. Active package can interact with food and the environment by the additives incorporated into packaging film. The aim can be, for example, maintaining and extending shelf life of product. Period between packaging of the product and its use is called shelf life. During this period the product properties must remain acceptable to the product user. Intelligent package, instead, can sense some properties of the content or the environment and can inform these properties. Intelligent packaging includes sensors and indicators which can be used in information gathering and product traceability. [3] [4, p. 1] [5, s. 7-10] [6]

In addition to mechanical and technical demands, food packages have also some other demanded properties. Authorities and consumers demand acceptable and sufficient level of information, retailers and transportation demand suitability for logistics chain and owner of brand demands sufficient marketing communication. Apart from things mentioned above, significant demands are set by needs of customers and the obtaining of affordable price in relation to quality. Among others, consumers may demand that the food package should be easy to open and reclosable. Technically, is challenging to meet these demands, because the seams of the package must resist the penetration of oxygen and water vapor at the same time. [7, p. 368] [8, s. 136-137]

The challenge set for food package is significant, because all food supplies spoil sooner or later while they age. Still, a proper and suitable package can delay the spoiling critically. Some products are heat-treated to kill the bacteria before packaging and products that are not fully sterilized with heat, are usually stored in cold surroundings so that the growth of bacteria can be slowed down. Exposure to air of some food supplies remarkably accelerates the growth of bacteria and development of mold, but also even without exposure to air some food supplies forward the development of bacteria, that possibly cause food poisoning (Clostridia). To maximize the storage time of food supplies it is also important that food packaging maintains a specific and suitable water content in product. If dry food supplies are saturated, they are vulnerable to increased biochemical decomposition. Respectively, if moist food supplies dry out, their physical properties change, which may lead to increased formation of microbes. If packaging film allows water vapor and other environmental gases to go through the film from outside to inside of the package, or the other way around, the taste, color or nutritional content of product may also be changed. Therefore, it is important, that food supplies can be protected from harmful environmental factors with a functional packaging. [8, p. 184] [4, p. 1]

Some food supplies are vulnerable to microbiological and physical changes already in few days. To lengthen the service time of these products, advanced and relatively expensive packaging alternatives are required. To measure up the demands that food packaging industry has appointed, plastic films have become the dominant packaging material to almost all food supplies and products. In the last decade development and improvement of food packaging has increased significantly. Nowadays more than 30 different group of polymers are used as packaging materials. That is to say, plastics are often able to solve packaging challenges and guarantee the best combination of protection, appearance and affordable price. [8, p. 184] [9, p.256]

Plain polymers are only rarely used as such in food packaging films. In addition to copolymers and different plastic mixtures, also additives have a great importance in the qualities of packaging materials. A great deal of additives, for example antioxidants, stabilizers, lubricants, antistatic agents and antiblocking agents, are available in order to improve performance and properties of packaging materials. Additives are used to improve appearance, mechanical properties and workability, and hence different plastic types can be differentiated better to obtain the demands of final usage. Extended storage times of processed food, even stricter rules with additive usage and consumers’ demand for minimalized usage of preservatives in food production have led to innovative development of active packaging. [7, p. 368] [9, p.256]

As the usage of additives has become common in packaging industry, a lot more attention has been paid to migration of chemical compounds from packages to food supplies. The biggest concern falls upon food additives: both additives that are added into food supplies on purpose, and additives that end up into food supplies from packaging materials or processing machines. Migration may cause off-odors and off-flavors for the food or safe migration levels of some chemicals may be surpassed. Consequently, control authorities around the world have concluded that it is important to superintend contamination. Even strict laws have been enacted by some authorities to make supervision more effective. Increased usage of additives in development and manufacturing of food packaging films has also added up consumers’ safety concerns towards food supply applications. [7, s. 368-369] [9, p.256]

2.2 Safety regulations

One of the most important tasks of food packages is to protect the product from harmful environmental effects. Increased usage of additives in manufacturing of polymeric packaging materials has however caused that the package itself may act as the source of contamination. Migration of additives from the packages to food supplies has been increasingly under consideration. In addition to statutes that authorities have enacted, plenty of different analytical methods and theoretical predictions have been developed to find out the amount of migrates in food supplies. [9, p. 256] Food legislations differ significantly between Europe and USA. In this chapter EU legislation is dealt with, because the studied operating area of the case company is Europe. Regulations treated in this chapter are based on interviews of Maria Töyrylä [10] and concern plastic packaging materials which are in contact with food supplies.

EU legislation has been developed to remove barriers to trade within the EU. Legislation aims to protect the health of consumers from the harmful compounds that may migrate from package into food. Specific laws and regulations in different EU Member States caused problems in developing the EU legislation. Council of Europe and the European Commission strived to harmonize these laws and regulations to ease control and trade inside EU. [11] In 2004 The European Parliament and the Council of the European Union adjusted regulation No 1935/2004 [12] in which common principle of removal of differences in laws of member states was enacted.

Regulation No 1935/2004 defines general codes in relation to packaging materials and articles, which will or may come directly or indirectly in touch with food supplies. In the legislation, different material groups and possible measures that fall upon for example standards and list of used substances related to these materials are defined. Also, needed measures for implementation of new substance are identified. When a new substance is being enabled, an application must be delivered to national authority, who forwards it to European Food Safety Authority for expert opinion. Materials used in food packaging must also be identified as compatible for food supply usage for example with image or logo that signals about the application. In this legislation, it is also defined that it is possible to dismiss some substances if they are found harmful for humans’ health. This legislation replaces Council Directive 89/109/ETY, which was also meant to bring regulations of different member states closer together, but turned out to be hard to comply with. [12]

Regulation No 1935/2004 includes a lot of defined measures related to materials which come in contact with food supplies. For example, traceability (Regulation No 178/2002 [13]) of used substances must be possible, and if needed, harmful materials and products should be recalled. Measures and decisions regarding active and intelligent packaging are presented in the statute and, considering them, the Regulation No 450/2009 [14] by The Commission of the European Communities has been created. The European Commission Regulation No 10/2011 [15] is a statute which has been enacted to complete the Regulation No 1935/2004. In this statute, specific measures related to different materials and substances are defined.

In regulation No 10/2011 [15], also migration limits are regulated. Migration limits mean the maximum amount of substances that materials and articles may transfer to food. Migration limits have been regulated, because poisonous and harmful substances can transfer from plastic materials to food supplies that will be sold to consumers. In this statute two types of migration limits are defined to plastic materials: overall migration limit (OML) and specific migration limit (SML). OML involves the sum of all substances that can migrate from material that is in contact with food supply. Substances from plastic materials must not migrate to food so that the overall amount of migrated substances is over 10 milligrams towards one square decimeter of surface area of food packaging. The overall migration limit 10 mg/dm^2 of plastic leads to the fact that from cubic package, which contains one kilogram of food supply, migrates 60 milligrams of substances towards one food supply kilogram. In that case OML is 60 mg/kg. As for SML, it describes the allowed maximum amount of specific substance in food supply (mg/kg). If SML value is not notified related to some substance, the OML value is considered as general limit. Migration limits therefore ensure that the final product is safe and healthy to consume. In case of dual use additives, it must be confirmed, that when substance is released from package, it does not change the composition of food supply in unacceptable way.

The regulation No 10/2011 presents separate codes related to test circumstances, in which OML and SML tests must be performed. To get comparable results about limiting values, the tests must be done in standard test conditions. Tests are performed with specific test time and temperature, and by using food simulants. The used test conditions represent the most unfavorable predictable operating conditions of plastic materials. Many EN standards present analytical and technical descriptions about the performance of migration tests, but it must be considered that codes defined in regulation No 10/2011 are the main codes. [15] [16]

Regulation No 10/2011 also defines operating conditions for certain packages to guarantee safety, and demands for manufacturing and trade of plastic materials that are in contact with food supplies. In this statute substances, which can be used particularly in manufacturing of plastic materials and products are defined. New substances are added to the list of this statute by European Food Safety Authority, if it has given a positive response to application. [15] A statute, that is complementary to regulation No 10/2011, is European Commission Regulation No 2023/2006 [17]. In this regulation, good manufacturing practices are defined. According to good manufacturing practices, it is possible to manufacture plastic materials so that from them will not be released more than 10 mg of substances towards 1 dm^2 surface area of plastic material.

In addition to above mentioned, regulation No 10/2011 presents demands related to the declaration of compliance (DoC) to bring plastic materials and products to EU market. DoC encompasses all information about intermediate steps of manufacturing of materials and products, and used substances. DoC must be updated always when used substances or methods are changed. Supplier takes care of existence of DoC and forwards it if needed. [15]

All materials, substances and products presented in experimental part of this research are in accordance with regulations mentioned above, unless mentioned to the contrary.

2.3 Plastic films used as sealable lids in food packaging

Nowadays many food packaging applications include heat sealable films or are completely comprised of these structures. The term heat sealable, refers to ability of two plastic surfaces, for example lid and tray, to form a bond between each other. The bond is formed when heat and pressure are locally applied to articles for a certain time. The formed bond has sufficient strength to resist opening of the seal, and it may also be hermetic. For this reason, by using heat sealable films food supplies can be packed safely and hermetically. Sealing process must be performed so that possible leak-paths are not formed in critical sealing areas. In sealing process, attention must also be paid on the fact that heat sealable packaging must be able to withstand possible malpractice during operating, delivery and storage. With careful sealing a safe, durable and leak-proof structure can be attained. [18] [19, p. 2] [20]

Certain applications demand higher level of sealability than others. The level of sealability can be determined by the seal strength or resistance to leakage of package. The force that is needed to pull sealed surfaces apart from joint, is called seal strength or heat seal strength. The required seal strength depends on the application. For example, it is important to attain high seal strength when the purpose is to retain freshness of packed food supplies. In general, flexible packaging applications have slightly lower seal strengths compared to rigid packages. [20] [19, p. 2]

The following sections will narrowly deal with the plastic materials used in food packaging films and the fabrication of them. Additionally, structure of multilayer films and sealable lids which are used in food packaging are focused.

2.3.1 Raw materials and fabrication

European Commission Regulation 10/2011 [15] that considers plastic materials in contact with food supplies, determines following: Plastics are made of monomers and other raw materials by chemical reaction also known as polymerization process. The formed macromolecular structure otherwise polymer is the main structural component of plastics. Several different additives are added to polymers to attain certain technical properties.

Almost all plastic can be engineered into a form of a film and be used in food packaging. Many properties of plastic such as low density, resistance to breaking, no sharp edges, ready sealability, fabrication flexibility, environmental durability, barrier and permeability properties, print and metal coating receptivity, resistance to tear and puncture, and flexibility at low temperatures make them very compatible for food packaging. Considering the food packaging applications, the most important properties of plastics are for example glass transition temperature, crystalline melting point, flexural modulus, tensile strength, tear strength, impact strength, flex life, water vapor transmission rate, oxygen permeability, optical properties, heat sealing properties, and bonding strength. Nowadays plastic film manufacturers are combining many different plastic types to make the most of functional and esthetic benefits of different plastic types. In this chapter the focus is on commercial plastic films which are used in food packaging. [6] [21, p. 40]

The following polymers are commonly used as main raw materials in flexible packaging films [22, p. 177] [4] [23, s. 1-15]:

- polyethylene (PE)
- polypropylene (PP)
- polyesters (e.g. PET, PC)
- ethylene vinyl acetate (EVA)
- polyamides (PA)
- polyvinyl chloride (PVC)
- polyvinylidene chloride (PVDC)
- ethylene vinyl alcohol (EVOH)
- polystyrene (PS)
- biodegradable polymers (e.g. cellulose-based materials).

The polymers mostly used in food packaging are polyolefins and polyesters. Polymers are not very often the only raw material in manufacturing of plastic films. Importance of blending of polymers has increased amongst food packaging applications. By combining different polymer types and adding additives to blend, properties and processability can be greatly improved while decreasing the costs. By blending, for example surface properties of film can be adjusted, adhesion properties improved, output can be increased and easy-opening features can be created. Most blends are immiscible and consist of minor and major components. The major component forms a continuous phase in matrix. Within the major component a separate dispersed phase or domain is formed by the minor component. The resin manufacturers often add additives and processing aids to polymers. Film manufacturers can also add additives such as slip, antiblock, AF and antistatic agents or processing aids. Some blends are however challenging to put into action in in-line mixing, and in that case, it is sensible to let the manufacturing to resin manufacturers or compounders. In final polymer blend is often less than 1 % of additives which are usually in powdered or liquid form. Typically, additives are at first made as masterbatches because they have low concentrations. Highly concentrated blend of the additive with a carrier resin is called masterbatch. Masterbatches are blended into the resin by the film manufacturer. [21, p. 42] [23, s. 311-312]

In film manufacturing, also different polymer types are blended together. For example, low density polyethylene (LPDE) can be blended with linear low density polyethylene (LLPDE) to decrease extruder pressure and increase output. Often also soft polymers are blended with stiffer ones, to improve the toughness. As an example of this blending EVA into LLDPE can be mentioned. Costs can also be decreased by blending polymers with each other. For example, polyethylene terephthalate (PET) is more affordable than polycarbonate (PC) and for this reason PET is usually blended into PC. Properties of plastic films, such as barrier performance and adhesion, can also be affected by blending. By using polymer blends adhesion between different polymers in coextrusion or between film and certain inks can be improved. By blending certain additives into polymers adhesion for example between LDPE and aluminum foil can be improved or adhesion during the heat seal process controlled. [21, p. 42] [23, s. 311-312]

In some cases, the desired film properties cannot be attained with one polymer or not even with polymer blend. In that case, properties of plastic films can be controlled by using multilayer film structures. Plastic layers can be joined together by lamination and coextrusion technologies. In lamination two or more film layers are joined together with some other material, for example adhesive. In coextrusion two or more plastic layers are joined in molten form when manufacturing the film. Compared to lamination, coextrusion is faster process because it has only one process step whereas lamination has multiple steps. However, the number of materials suitable for coextrusion is limited comparing to lamination. By using multilayer structures, the properties of all separate materials can be utilized. In addition, the amount of packaging material, thickness of film and the costs needed can be decreased. In multilayer structures a lot of different materials are typically combined, which unfortunately leads to the fact that recycling becomes more difficult. [23, p. 21] [21, p. 43]

Manufacturing of polymer films can be performed either by blown film or cast film extrusion. A typical blown film process is shown in Figure 1. In blown film technology, molten polymer mass is extruded through an annular die to form a tube. After that, molten polymer mass is lead to go around the mandrel and exit through a ring-shaped die opening. With the help of air pressure the tube is expanded into a vertical bubble with a certain demanded diameter. The bubble cools down when air from an air ring placed around the die is blown at it. Air pressure must remain constant inside the bubble to attain uniform thickness and width of film. At the top of line, the bubble is flattened and, eventually, two separate sheets are wound-up as reels after the line has passed through guide rolls and edge cutting. In some equipment there can be a pre-treatment unit such as corona before the winder. [8, s. 44-54] [24, s. 75-79]

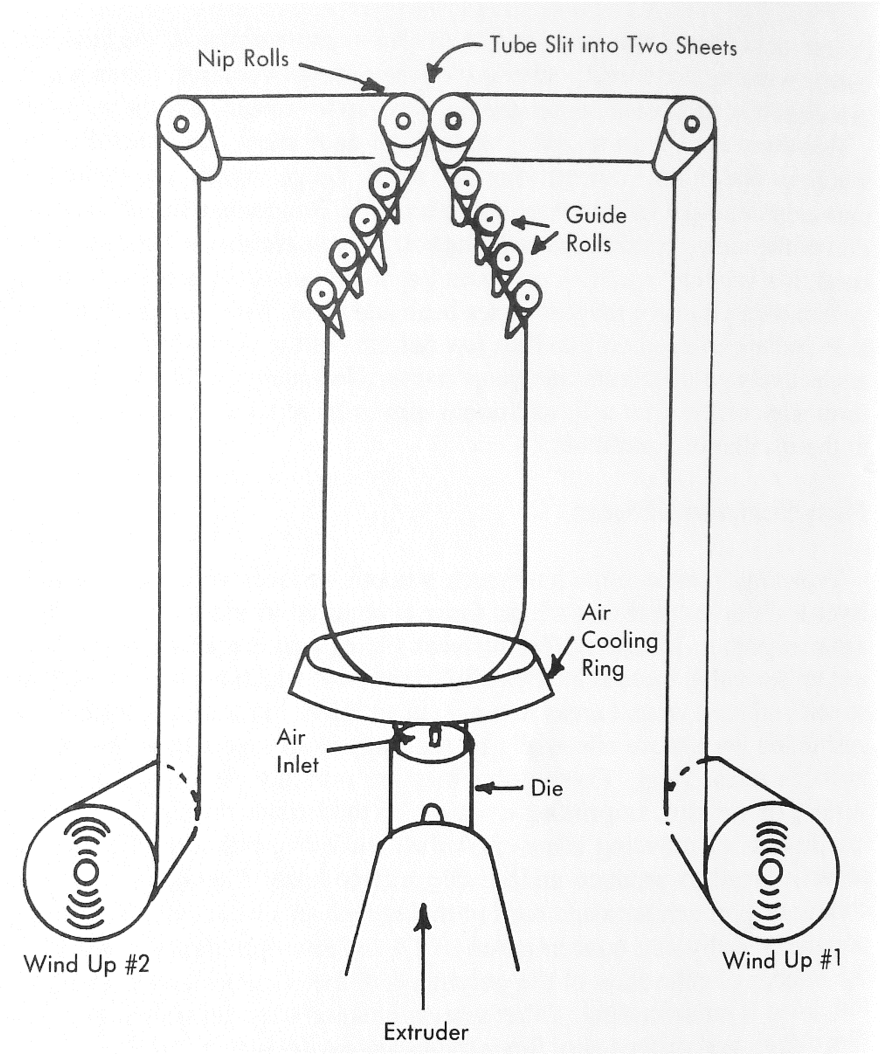

Figure 1. *Blown film extrusion [8].*

In cast film technology (shown in Figure 2), molten polymer mass is extruded through a flat die to form a wide film. After the melt leaves the die, it must be quenched quickly either with water bath or a chilled roller to avoid thickness variation and excessive haze. Typically, chill-roll assembly is used, in which case film is guided against a rotating roll or drum having cold metal surface. In chill roll system, the cooling is executed by circulating cold water or antifreeze solutions through the hollow drum. During cooling the film is cooled down only on one side. Through cooled rolls the film goes to so called pre-treatment unit, which includes rolls and nips of different sizes. These rolls can have specific additional functions such as changing the gloss and texture of the film surface. By varying the roll speeds, the degree of stretching and film thickness can be controlled. After passing through a system of rollers the finished film is wound-up as a reel. [8, s. 44-54] [24, s. 75-79] In both blown and cast film processes the film can be orientated and the polymer molecules realigned to improve the mechanical and barrier properties of the film. Orientation can be executed in both machine (MD) and transverse direction (TD). Film orientation only in one direction is called monoaxial orientation and in both directions it is called biaxial orientation. [22, p. 181]

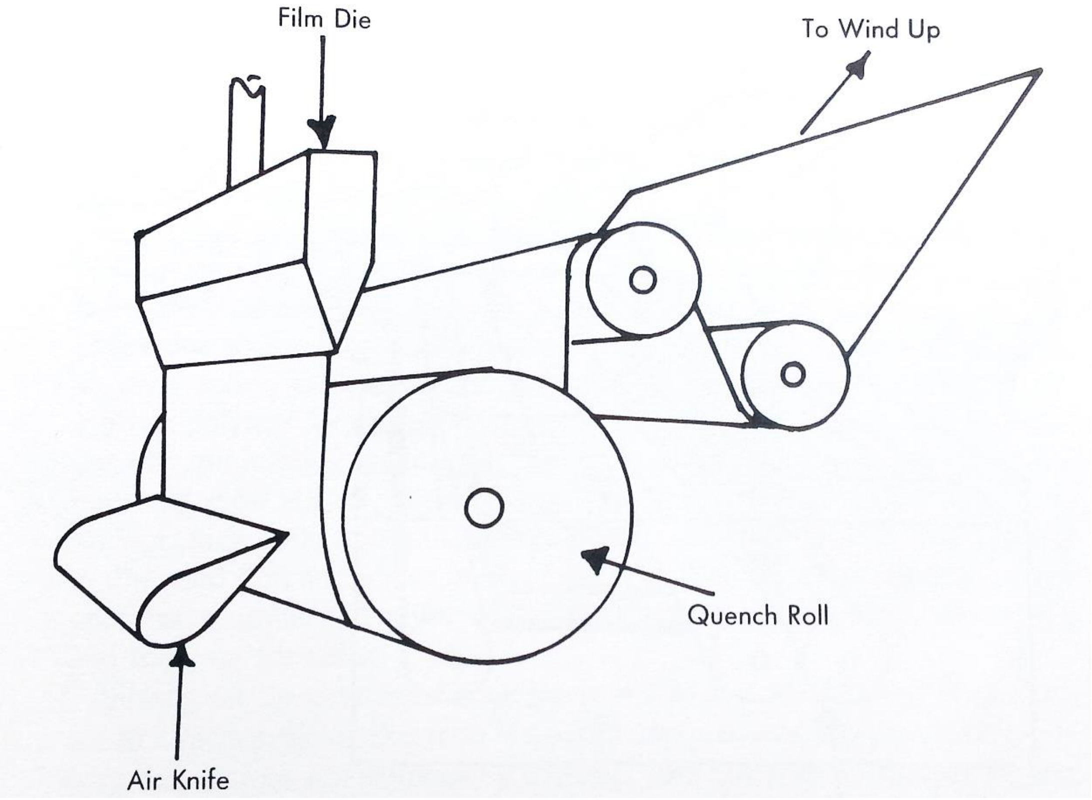

Figure 2. *Cast film extrusion [8].*

Cast film technology is a functional choice for larger volume production, because the process generally operates at much higher output rate than blown film extrusion. Even though blown film extrusion runs at a lower rate, its advantage is that films with different widths can be manufactured with the same device. This results from the fact that bubble-size adjustment, and hence changing width of the film is relatively easy to do.

Films manufactured with blown film extrusion has generally better mechanical properties and manufacturing costs are much lower comparing to cast film extrusion. In addition to that, blown film process is easier and more flexible to operate. Variation of thickness is usually lower with slit-die extruded films. Also, cast films are less crystalline and have a lower haze level than blown films. [23, p. 22] [24, s. 79-80] [8, s. 54-55]

Both blown and cast films can be coextruded. Coextrusion process is cost-effective, because properties of several different polymers can be combined into one film. An example of this is the coextrusion of a barrier polymer such as EVOH with a sealant resin such as LLDPE or EVA. In coextrusion process two or more streams of polymer melts from separate extruders are merged into one stream in the melt film formation step. Merging is done so that formed layers remain separate in the final film. Coextrusion is widely used to produce high-performance packaging films for food packaging industry. The number of layers has increased over the past years as the coextrusion technology has developed. Nowadays it is common to use seven, nine or even more layers in lines instead of only three or five. As the number of layers' increases, also the controlling of process becomes easier. For example, with five-layer line it can be challenging to produce a structure which has five layers with different thicknesses, because controlling of layer thicknesses is difficult. Manufacturing of same structure on a seven- or nine-layer line is easier. In this case, the thicker layers can be divided into more than one layer and fed by multiple extruders. Like this greater output and control over the process is attained. By laminating it is possible to combine materials, which cannot be combined in coextrusion. Lamination can be done either by adhesive lamination or by extrusion lamination. In adhesive laminations, the layers are combined using an adhesive which can be water-, solvent-, or solid-based. Adhesive lamination process can be divided into wet bonding and dry bonding, of which latter is more suitable for the lamination of plastic films. In this process laminating adhesive is applied on one web by direct gravure or reverse kiss coater. After that the coated web goes through oven so that all water or solvent is removed. Then the web is combined with the other layer in a pressurized nip. In extrusion laminating substrates are fixed to each other by using molten polymer. Most processed meat and cheese products are packed in packages that are laminates. [23, s. 22-24] [24, s. 327-329, 331-333] [8, p. 105, 119] [21, p. 43]

Films manufactured by the ways mentioned above can also be coated. Typically, film is coated with polymer or additive layer to improve the properties of film such as heat sealability, gas barrier and AF performance. Coated materials must be in liquid form and the liquid must wet the film completely. The coating material can be dispersed in water or dissolved in a solvent. It is evenly applied on the substrate surface with desired thickness and dried so that water or solvent evaporates from the system. After dryers the film is wound up again as a reel. [8, s. 87-89, 94-96]

The simplest way to manufacture heat sealable film is to manufacture a coextruded structure having a surface layer for heat sealing. Usually LDPE, LLDPE or copolymers of ethylene and propylene are used for the sealing layer. Alternatively, also EVA copolymers, ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers or ionomers can be used. These copolymers provide broader seal range and increasing ability to seal through contamination. Film manufactured by blown film or cast film extrusion can also be coated or laminated to attain heat seal properties. [24, p. 336] [8, s. 122-124]

Every packaging material has its advantages and disadvantages that must be taken into account when planning its use in packaging application. Raw materials must be chosen so that required properties are attained, consumer and marketing issues solved and environmental considerations and cost-effectiveness considered. By reasonable choices of raw materials and manufacturing technologies, the quality and freshness of food products are maintained across the shelf life of them. [6] [21, p. 40]

2.3.2 Structure

Food packaging industry is the most important user group of multilayer films. Common practice in identification of the multilayer films is to recognize the outermost layer first, and after that recognize the next layer and so on, until the innermost layer has been recognized.

Example for lidding film structure: OPP/tie layer/PE/PE/EVOH/PE/PE

In this structure, oriented polypropylene (OPP) forms the outermost layer and PE the innermost one. The outermost layer is in contact with surroundings and the innermost layer with the packed food supply. In the middle, there are several layers including tie and EVOH layer as barrier layer. [8, p. 179]

The barrier feature of packaging films prevents water loss, protects the food supply from organisms that eddy along air and slows down spoilage caused by oxidation. In some cases, penetration of ultraviolet light is prevented by the film. If the barrier character is more important than the visibility of the product, it can be achieved by using metalized polyethylene terephthalate or aluminum foil. Aluminum foil is relatively expensive. Less expensive alternative is metallized film in which plastic film is thin film deposited with a layer of aluminum. In most cases, consumers want to see the products they are about to buy. Then, the barrier properties are typically created by using a transparent PVDC or EVOH layer in the structure. [8, p. 190] [21, p. 41]

Some food products generate carbon dioxide (CO_2) as they age and, thus, the gas formed inside the package must be removed. This problem can be solved by using biaxially orientated nylon (BON). BON allows CO_2 to exit the package by diffusion, but prevents additional oxygen from entering the package. [8, p.191]

In addition, many different film structures including special characteristics have been developed to meet the requirements of advanced and changed markets. Nowadays consumer demands have created a trend towards heat sealable, peelable and reclosable lid structures. Those kinds of structures have combination of properties such as standard peel strength over a large scale of heat seal temperatures, cohesive failure upon peeling and great burst strength in the lid. [18]

Heat sealable and peelable lids are typically multilayer polymer structures having a mechanically strong bulk structure and a specific heat sealable layer on the top of it. Thermoplastic polymers such as polyesters (e.g. PET, PC), polyolefins (PE or PP) and PA can be used in the bulk structure to obtain tear strength, tensile strength, elongation and relatively high melting point for the material. Other materials such as PVC, PVDC, aluminum or other metal foil and cellulosic material can be incorporated in the structure to provide additional properties such as better barrier properties or opaqueness. In the heat sealable layer, polymers with low softening point are used. Mostly used coating material is LDPE yet copolymers of ethylene with propylene, isobutylene, 1-olefins, vinyl acetate and ethyl acrylate are also usable. As regards to copolymers, the softening point of them should be in the same range as for LDPE. The heat sealable layer can also contain inorganic fillers such as talc, silica and alumina trihydrate. The fillers may improve the peelability of the lid by changing the seal failure system from adhesive to cohesive failure. [18] [25] [26]

As mentioned previously the bonding or sealing material must have lower melting point than bulk material has. It must also have the lowest tensile and tear strength of the structure. Thus, the weakest point of the structure will be the bond formed during the heat sealing and that bond will fail when the cover is peeled away. Also, the thickness of the heat sealable layer should be adjusted to achieve a continuous peeling of seam. [25]

If the layers to be sealed with each other are compatible, the seams of the package can be accomplished by heat sealing. If they are not compatible a thin layer of adhesive is utilized to bond the parts together. The adhesive must be compatible with both of the used materials. The suitable adhesive can be heat sensitive or pressure sensitive (PSA) depending on the used materials. Also by using PSA reclosable lid structures can be produced. PSA layer on the surface of lid has so called quick-grab properties that can be reactivated by hand pressure. Reactivation takes place when reclosing the package again after the first opening has already taken place. [27] [25] [28]

In heat sealing, the top web can be sealed against the base web by jaws which can apply heat, or pressure, or both. Usually the sealing temperature ranges from about 149°C to 182°C. This temperature range is used because these temperatures are suitable to obtain the peelable seal for packaging. However, heat sealing is always accomplished in a temperature suitable for the combination of materials and their physical properties. [25]

2.4 Fogging phenomenon

Fogging is a phenomenon which can be observed from plastic films typically used in the field of food packaging, agricultural, automotive and indoor appliances. Fog appears on a film when water vapor condenses on the surface of it. This happens when enclosed air mass cools down to temperature, which is under the dew point of water. At this temperature, the air cannot contain all the water vapor anymore and condensed water vapor starts forming small discrete water drops onto the surface of the plastic film. The extent of phenomenon depends on relative humidity and temperature of enclosed air mass and temperature of the plastic film. [29] [30]

Condensation includes phase transition from vapor to liquid. Condensation is also associated with transition of air mass during time, when vapor migrates towards liquid-vapor interface and passes into liquid. The transition of air is caused by pressure drop, which occurs on the interfaces of phases. Condensation process is activated by temperature difference, which is called subcooling, between bulk vapor and solid surface. The energy resulting from the condensation is removed from the area of interfaces with either conduction or convection. [31, p. 1]

Condensation process can be divided into homogeneous and heterogeneous condensation. Homogeneous condensation occurs in free space and in the absence of any foreign material. It occurs stochastically because of the sway of vapor molecules and is only occasionally detectable. Heterogeneous condensation occurs when water vapor condenses onto or under the surface of some other material (liquid or solid) or on spatially distributed nuclei. Heterogeneous condensation can be further divided in volume condensation and surface condensation depending on the type of the surface to be condensed. Formation of, for example, clouds, fog and mist is volume condensation. Surface condensation occurs under or on the subcooled surface when the surface is exposed to vapor. [31, p. 1]

Process which is founded on phase transition may result in either formation of continuous film or drop complex onto the surface of the substrate. These processes are called filmwise and dropwise condensations, respectively. Illustration of these two condensation types are presented in Figure 3. In addition to these two condensation models, also a so called mixed model can occur. It owes characteristics specific to the both filmwise and dropwise condensations. [31, p. 3]

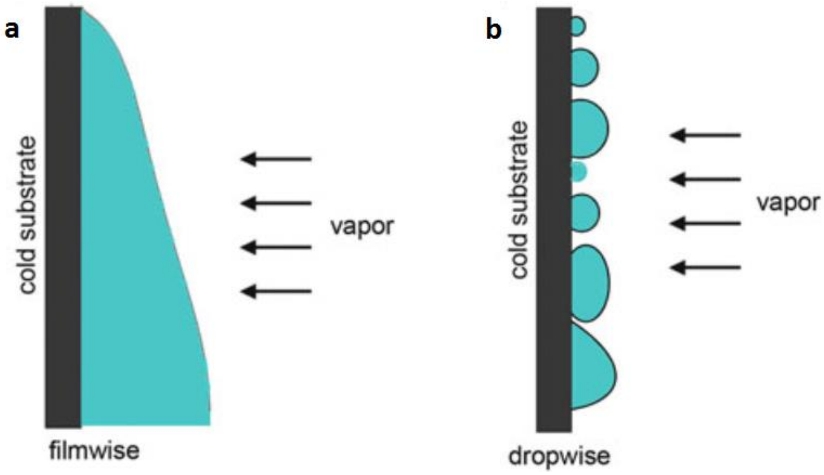

Figure 3. *Filmwise condensation (a) and dropwise condensation (b) on a vertical cold substrate, adapted from [31].*

The type of condensation detected depends on the surface wettability, which relates to surface tension of condensate and free energy of condensing wall. Filmwise condensation is detected when a liquid film completely covers the substrate surface and dropwise condensation when the liquid has not clear affinity with the substrate. [31, p. 3]

In dropwise condensation the condensate wets the substrate only at locations where well-wetted contaminant nuclei exist and forms discrete drops on or underneath a cold substrate. Drop formation starts at preferred nucleation sites in atomic scale. These nucleation sites attract the vapor atoms and these atoms will eventually form stable clusters leading to microscopic droplets. The size of the drops grows because of the direct condensation between neighboring drops, which is determined by the distance between neighboring nucleation sites. The drops grow until the specific size has been reached and coalescence of neighboring drops starts to occur. Altogether, the growth of drops occurs as a combination of direct condensation and coalescence of drops. When a single drop reaches a size in which its body forces exceed over surface tension the drop departs from the substrate surface and wipes the surface clear. In consequence, new nucleation sites become available. Coalescence and sliding of the drops makes the substrate area to constantly offer new nucleation sites for drops. Due to this reason, dropwise condensation is a cyclic process and complicated phenomenon influenced by many factors. [31, s. 3-6]

Condensation process depends on several different factors, such as substrate orientation, hydrophilicity, hydrophobicity, nucleation site density, thickness of promoter layer and degree of subcooling. Also, environmental conditions add their own challenges to modeling and analyzing of the process. Understanding of the condensation process is also complicated because of the phenomena such as drop formation at the atomic scale, contact angle hysteresis, growth and coalescence mechanisms, instability of drops, dynamics of the three-phase contact line, hierarchical phenomena and leaching. Ideal substrate for dropwise condensation has characteristics such as low surface energy, high durability and low thermal resistance. In the case of filmwise condensation process, the characteristics are the opposite. Nowadays the condensation process can be affected by several different ways. These include, for example the use of nanotechnology, physical and chemical texturing, thin film coating and experimental techniques. [31, s. 4-5]

In the beginning of condensation, a stable cluster is formed on the substrate surface. After that physicochemical properties of substrate and bulk-thermophysical properties of the liquid become important. These characteristics affect the growth of the drops and if the condensate does not wet the entire surface, the phenomenon at stake is dropwise condensation. The wetting properties of substrate can be studied by measuring contact angles (θ). The angle between the tangents drawn at the liquid-vapor interface (LV) and the solid-liquid interface (SL) is called contact angle (Figure 4b). Liquid influences the surface wettability which is a consequence of combination of different complex processes. Some of the processes are active in microscale and can be understood with help of surface chemistry. Some factors can vary between different samples and be completely statistical. As examples of these factors the pinning of the contact line and wetting transitions can be mentioned. The shape of drop is also affected by the principles of fluid dynamics. [31, p. 6]

With contact angle measurements can be characterized the solid-liquid interaction in a drop when the drop achieves its mechanical equilibrium. The phenomenon in which liquid spreads over and completely wets the solid surface is called complete wetting. In such case the contact angle value equals to 0°. On the other hand, the system is said to be fully non-wetting if the contact angle equals to 180° and liquid retains its full spherical form of a drop. The situation is called partial wetting when the contact angle is between 0° and 180°. In partial wetting, the droplet has a finite liquid-solid separating surface. Different kinds of surface-drop interactions on a planar surface are represented in Figure 4. [31, s. 6-7] [32, s. 1802-1803]

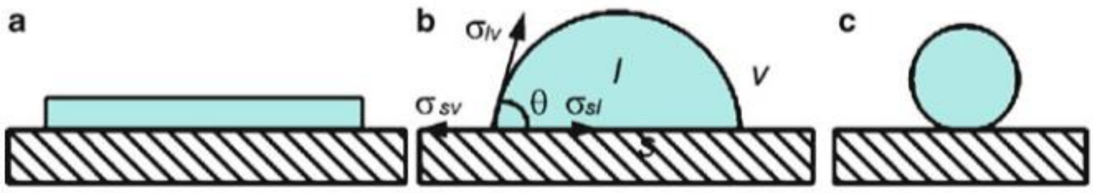

Figure 4. *a) Complete wetting (θ = 0), b) Partial wetting (0 < θ < 180°), c) non-wetting (θ = 180°) [31].*

Majority of the systems including solids and liquids show surface-drop interactions between the wetting and the non-wetting limits. The interactions at various interfaces such as solid-gas, liquid-gas, solid-liquid and solid-liquid-gas can be characterized by contact angles. Knowing the contact angle provides information about the behavior of a liquid drop under or on a solid surface and helps understand it from the perspective of mechanics. Many important phenomenon, which occur during condensation, depend on partial wetting of the solid substrate that is caused by the condensing liquid. The heterogeneity of the surface of condensing substrate has an influence on the apparent contact angle and causes hysteresis in the contact angle and local pinning of the three-phase contact line. Contact angles also provide a way to define surface tensions of liquids and surface energies of solid substrates. [31, p. 7]

Several different substrates, both natural and engineered, and liquids are being used to generate different contact angles. Contact angles can be classified as hydrophilic ($0° < \theta < 90°$), hydrophobic ($90° < \theta \leq 140°$) and superhydrophobic ($140° < \theta \leq 180°$) contact angles [31]. Classification of contact angles differs a bit between different publications even though the gist of different classifications is approximately the same. For example to classify smooth solid surfaces Chibowski et al. proposed [33] hydrophilic ($\theta \cong 0°$), weakly hydrophilic ($0° < \theta < (56\text{-}65°)$), weakly hydrophobic ($(56\text{-}65°) < \theta < 90°$) and hydrophobic ($90° \leq \theta \leq 120°$).

2.5 Hydrophilic surfaces

In recent years, many research groups [34] [35] [36] [37] [38] have tried to create hydrophilic surfaces and substrates by techniques such as advanced machining, nanotechnology, photopolymerization, plasma and various thin film coating methods. Interest to process hydrophobicity and hydrophilicity of solid surfaces and produce coatings, which create either strong or weak affinity to water, has increased. However, there are only little knowledge about hydrophilic and superhydrophilic surfaces. In their review [33], Chibowski and his co-workers dealt with major definitions of hydrophilic surfaces and the physics behind superhydrophilic phenomenon.

To simplify, hydrophilic surface corresponds to a surface, which has a strong affinity to water. Typically, different wetting characteristics are studied in three-phase systems. Wetting phenomenon takes place in three different interfacial boundary surfaces which are solid-air, liquid-air and solid-liquid. Hydrophilic substances are easily soluble in water compared to hydrophobic substances which are poorly soluble. Hydrophilic solids are also often hygroscopic meaning that those materials pick up water from air. Some polymers are soluble in water by their nature, when individual molecules and ions from a solid matrix are released. Then, the released molecules become surrounded by water molecules. These polymers are hydrophilic by their nature and have hydrophilic surfaces. However, dissolution test can be misleading in some cases, when solids having hydrophilic surfaces are identified. The balance of intermolecular forces between solid and liquid controls the solubility process with an entropy change that accompanies the dissolution and solvation. For example, surfactants, which are amphipathic substances, are soluble to water. Dissolution of surfactants in aqueous phase is controlled by their hydrophilic-hydrophobic balance. Hydrophobic portion of the surfactant molecules prevents the complete spreading of water droplets. Therefore, orientation of surfactant molecules can produce either hydrophilic or hydrophobic groups. Arrangement and orientation of surface atoms and functional groups have an influence on wettability of surfaces exposed to wetting liquid. [33] [39]

The most common approach in anticipation of solubility of materials is based on a thought that any solid with a similar chemical structure to water will dissolve in it. In other words, polar solids will well dissolve in polar water. The same mindset is used with surfaces. Forces between molecules can be divided into two groups. Lifshitz-van der Waals -forces occur between all molecules and surfaces. Lifshitz-van der Waals -forces result from electric fields that are induced by dipole moments of molecules. The other group of forces, acid-base interactions, are interactions between alkaline and acid groups of molecules. Nonpolar surfaces do not have acid nor alkaline groups, but surfaces interact with other substances only by Lifshitz-van der Waals -forces. Polar water therefore does not moist nonpolar hydrocarbon surface, because adhesion between these two is quite small and the contact angle is big. For this reason, in case of hydrophobic surfaces, it is desirable that the adhesion between liquid and solid surface is increased and cohesive forces of liquid are decreased, to allow the liquid to wet the surface. [33] [40]

As mentioned above, the wetting properties of substrate can be studied by measuring contact angles. When water contact angles are larger than 90° and surface has a low surface free energy the surface is called hydrophobic. Hydrophilic surfaces, on the other hand, produce water contact angles smaller than 90° and have a high surface free energy. Figure 5 presents different wetting states and how they are placed in comparison with 90° of water contact angle. Most of natural and man-produced materials can be sited to the latter category. In fact, it is easier to identify hydrophobic materials and surfaces because a lot of hydrophilic ones appear in nature. Only saturated hydrocarbon-based products such as wax, polyethylene, polypropylene, self-assembled monolayers with hydrocarbon functional group and fluorine-based polymers are hydrophobic. Polarity of polymers and molecules can be increased by inclusion of heteroatoms, particularly oxygen, into the structure of hydrocarbons. Even presence of double or triple bonding reduces hydrophobicity of polymers and molecules, and enhances hydrophilicity of the surface. [33] [41]

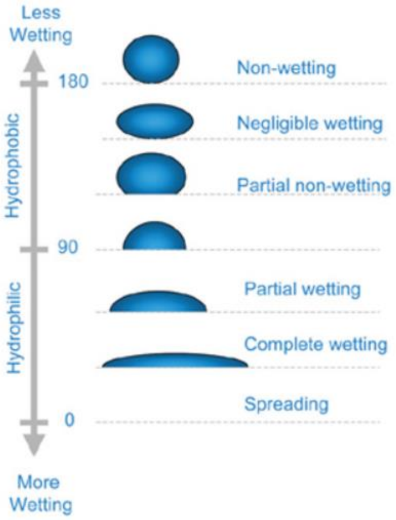

Figure 5. *Water contact angles of hydrophilic and hydrophobic surfaces [42].*

One way to measure hydrophilicity is to use the contact angle value. Because hydrophilic surface is a surface that attracts water, the water contact angle should be smaller than 90°. In order to completely spread on a hydrophilic surface, the water contact angle must be zero.

The energy balance is greatly influenced by true zero contact angle. This can be expressed by the Young’s equation which is formed in Equation 1. Since 1805, when Young published the equation, it has been the mostly used equation in wettability studies of solids. A correlation between contact angle and surface tension on an ideal surface was reported by Young. [43] [33] [44]

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\theta \tag{1}$$

where γ_S is the solid surface free energy, γ_L is the liquid surface free energy (the liquid surface tension), γ_{SL} is the solid-liquid interfacial free energy and θ is the equilibrium contact angle.

If contact angle is zero ($\theta = 0$), Equation 1 reduces to Equation 2. [33]

$$\gamma_S - \gamma_{SL} = \gamma_L \tag{2}$$

The limit of applicability with Young's equation is the contact angle value zero. However, in practice, complete spreading appears only rarely. Even though it visually seems that the contact angle is zero, it does not necessarily mean that Equation 2 will be accurate. Chibowski et al. stated that these kinds of systems are more appropriate to be examined by the work of liquid spreading W_S (spreading coefficient). Spreading coefficient illustrates the work performed to spread a liquid over a unit surface area of a clean and non-reactive solid or liquid at constant temperature and pressure and in equilibrium with liquid vapor. Equation to calculate this is presented in Equation 3. [33] [40]

$$W_S = \gamma_S - (\gamma_L + \gamma_{SL}) \tag{3}$$

All components of Equation 3 are either liquid surface tensions or liquid-liquid interfacial tensions, if two liquids are in question but in the case of solids, surface free energy or interfacial free energy are not that easily measured. Definite contact angle is formed if the liquid does not spread completely, and in that case the Young's equation can be applied. Spreading coefficient can be calculated with Equation 4, by using measured contact angles and surface tension of liquid if contact angle is more than zero ($\theta > 0$). [33]

$$W_S = \gamma_L(\cos\theta - 1) \tag{4}$$

When contact angle is zero, defining W_S is challenging, because zero contact angle would imply zero work of spreading as well ($W_S = 0$). Actually, $W_S > 0$ for a complete spreading and contact angle cannot be measured. For liquids that retreats into droplets with finite contact angle $W_S < 0$. Consequently, spreading coefficient can be used to determine solid surface hydrophilicity. [33] [40]

One way to determine hydrophilicity and hydrophobicity of both molecules and condensed phases is to use the free energy of hydration (ΔG_{SL}). The free energy of hydration can be determined with the Dupre equation (Equation 5). [33] [45]

$$\Delta G_{SL} = \gamma_{SL} - \gamma_S - \gamma_L \tag{5}$$

Equation 5 can be modified with the help of Young's equation resulting in Equation 6.

$$\Delta G_{SL} = -\gamma_L(\cos\theta + 1) \tag{6}$$

Van Oss, who proposed the usage of the free energy of hydration, also researched this subject. It was discovered, that hydrophobic molecules which attract each other in water have $\Delta G_{SL} > -113$ mJ/m^2. For hydrophilic molecules $\Delta G_{SL} < -113$ mJ/m^2. Van Oss used this value as a divider between hydrophilic and hydrophobic material. With this value and by using Equation 6 the value of the equilibrium contact angle can be calculated. The value is $\theta \approx 56°$ for ΔG_{SL} = -113 mJ/m^2. This result proves that the water contact angle does not have to be zero to call a solid surface hydrophilic. [33] [45]

Referring to Young's equation, it could be thought that zero contact angles are common. However, it must be perceived that the Young's equation is not accurate in the situations where zero apparent contact angle appears, as mentioned previously. If water-solid interfacial free energy, γ_{SL}, has zero value, like for example in cases of solid substances interacting with water molecules through hydrogen bonding, it is ended up in a situation where $\gamma_S \geq \gamma_L$. If the surface tension value of water measured in temperature of 22°C is used, all solids with $\gamma_S \geq 72.8$ mJ/m^2 at ~22°C should satisfy the conditions of complete water spreading. γ_L –value can differ along the temperatures. In practice, for example metals, alloys and ceramics have surface free energy higher than 72.8 mJ/m^2. In case of organic polymers surface free energy value is less than that. [33] [40] To get condensed water spread on the surface of polymer films, such as PE film, as uniform layer and to get the contact angle value of zero, the surface energy of film must be increased to be near the water surface tension.

Zero contact angle is challenging to detect on hydrophilic materials in the case of smooth surfaces, because autophobic properties of thin film usually prevents formation of thick water films. This can also be explained with the fact that water film causes changes in surface free energy of solid surface and properties of water film differ from the bulk water. Diffusion, orientation and rotation of water molecules, that are located near hydrophilic solid surfaces, are changed. Thus, the interfacial water molecules are more organized than in the bulk. It can also be assumed that between reorganized thin film of water and amorphous bulk water there is an interface and, therefore, tension. The measured tension at the surface of a reorganized water layer must be smaller than the surface tension of water. This difference between tensions explains why the experimentally determined contact angles can be relatively large. [33]

By manipulating roughness of the surface of hydrophilic materials, superhydrophilic surfaces can be attained. Even though water seems to spread completely over hydrophilic surfaces, they may still not be superhydrophilic ones. Superhydrophilic surfaces are surfaces, in which water apparent contact angle is less than 5° and roughness factor (r) defined by Wenzel equation is larger than 1, and on which water spreads completely. For a surface having apparent zero contact angle, a minimum roughness can be predicted through the Wenzel Equation 7. [33] [39]

$$r \geq \frac{1}{cos\theta} \tag{7}$$

Chibowski et al. stated that superhydrophilicity is possible for all materials having intrinsic contact angle less than 60° (r = 1.2-2). However, for the materials having θ > 65-70°, the high values are needed for r and the roughening might not be a practical approach. Theoretically, it can be thought that in the case of any rough material water should spread with zero or nearly zero apparent contact angle. [33] [39] In practice, however, this is not the case as has been proved by Onda et al [46].

Surface topography has a significant role considering the spreading of liquid on a solid surface. Surface topography, the contours and size of the protrusions, may either improve or reduce wetting. Wenzel and Cassie-Baxter have presented two possible cases, which can occur related to surface wetting. If liquid fills the valleys in the rough surface, the apparent contact angle θ_{rough} can be determined by Wenzel Equation 8. [33] [39] [47]

$$cos\theta_{rough} = rcos\theta \tag{8}$$

where θ_{rough} is the Wenzel contact angle on a rough surface, θ is the ideal Young contact angle on a smooth surface and r is the average roughness ratio ($r > 1$).

In the case liquid does not fill the pores of the surface, but remains on the tops of the protrusions, air is trapped beneath the liquid. In this case the contact area between liquid and solid surface is reduced. This situation can be illustrated by Cassie-Baxter equation (Equation 9). [47] [33]

$$cos\theta_{C-B} = \varphi_S cos\theta - (1 - \varphi_S) \tag{9}$$

where φ_S is the fraction of the liquid base in contact with solid surface ($\varphi_S < 1$), and $1-\varphi_S$ is the fraction of the liquid base in contact with air pockets. Because water does not wet air, the contact angle of water on air is 180° (cos180° = -1) and the air under the droplet significantly increases the surface hydrophobicity. For this reason, Cassie-Baxter equation (9) predicts, that superhydrophobic surface can be obtained by roughening of solid surface and by manipulating its texture.

Wenzel state behavior is typical to liquid droplets on minor roughness hydrophobic surfaces and Cassie-Baxter behavior is typical to droplets on greater roughness surfaces. Relations in homogeneous solid-liquid interphase can be illustrated by Wenzel’s equation whereas Cassie-Baxter equation can be applied for heterogeneous surfaces. It must also be understood that both Wenzel and Cassie-Baxter interactions can coexist in droplets at the same time. [48] Because many superhydrophobic and superhydrophilic surfaces consist of multiscale protrusions and valleys, the usage of Wenzel or Cassie-Baxter equations is not completely straightforward. For nonuniformly rough surfaces generalized Wenzel and Cassie-Baxter equations have been developed. [49]

2.6 Purpose of antifog effect

Typically, lidding films in food packaging are multilayer films. Achieving the AF effect for sealing layer is nearly impossible without separate actions because polyolefins are typically hydrophobic. Situation, in which water does not condense in the shape of water droplets on the surface of film but is spread as uniform and transparent layer, is called the antifogging effect. AF effect can be achieved by creating hydrophilic surface on the polymer film either by using different AF additives, liquid coatings or by taking advantage of physical methods. AF additives are chemicals that prevent water from condensing as drops. Hydrophilic surface created on the film attracts water vapor that condenses on the surface of the film forming continuous and transparent water layer instead of separate water drops. Fog can be formed because of climate change or radical temperature conditions. Amount of fog formed depends on for example predominant temperature, relative humidity and temperature of the plastic film. [29] [50] [7]

In food packaging fogging (the condensation of water droplets) is a common problem and occurs especially in packages stored in chiller cabinets. Formation of water droplets hinders light transmission and hence reduces the amount of light penetrating the film. Water formed on the surface of film changes the light refraction index of the film. It can be considered that in such case light must travel through two material layers instead of one. This compromises the visibility of packed food supply. Furthermore this directly affects to the product’s visual appearance from the consumer’s point of view. [29] [30] [51] Reflecting and refracting of light caused by dropwise and filmwise condensation are demonstrated in Figure 6.

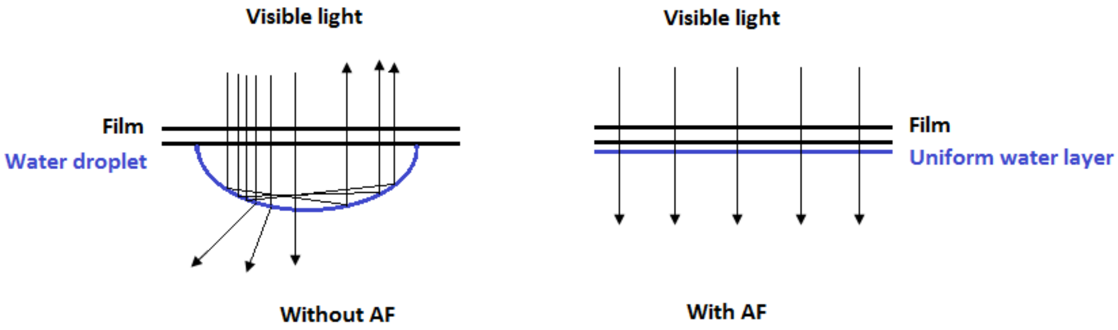

Figure 6. *Effect of AF performance on the light transmission through film [51].*

AF effect is typically utilized in plastic films, which are in direct contact with fresh food supplies. Typical food products causing fog are meat, cheese and convenience food. These kind of food supplies have high moisture content. When they are stored in cold surroundings, moisture starts to condense and fog is inevitably formed on a packaging film. [52] The purpose of AF effect is to prevent the formation of droplets onto the surface of plastic films. The formation of fog affects the package by reducing the transparency of the film and hence dimming visibility of the product, which prevents consumers to see and evaluate the product properly. AF effect is therefore important factor to attain appearance of the product that better pleases the eye of consumers. In Figure 7 is presented an example of film with AF property and without AF property. When moisture is not condensing as water droplets onto the surface of film, attractiveness of the packed food product can be maintained. In that case, the consumer can see the food product more clearly and the product itself appears more fresh and hygienic. [53] [7] [29] [51] For this reason AF effect has a great esthetic influence on food packages, but in addition to that, AF effect has been found to help in extending the shelf life of packed food supplies. Markarian reports [54] about Cryovac's Microwaveable Vegetable Bag which according to the company has an AF coating that extends the shelf life of the product. Synergistic effect of the AF coating reduces moisture, which may promote the formation of bacteria that is causing food spoilage.

Figure 7. *a) Plastic film with AF property, b) Plastic film without AF property.*

AF additives include surfactants, meant to decrease the surface tension of water. The difference between wetting tension of plastic film and surface tension of water is therefore the most significant reason for formation of fog. The AF surfactants applicable are, for example, detergents, hydrophilic coatings, hydrogels, hydrophilic colloids and nanoparticles, such as titanium dioxide. Polyolefins are strongly hydrophobic and they have substantially lower surface energy than water has. Surface energy of polyolefins is around 30 mJ/m^2 and the surface tension of water 72 mJ/m^2. Because of this water condenses on the surface of plastic film as water droplets having high contact angles. Consequently, the surface tension of water is aimed to be decreased and the surface energy of plastic film to be increased with the help of AF surfactants. In conclusion, the contact angle of water droplets decreases and they spread over the surface of film forming one uniform layer of water. [50] [29]

2.7 Methods to produce antifogging surfaces

In packaging industry, a lot of different methods are used to create AF effect on the surface of plastic film and this way minimized formation of fog. Methods can be divided in internal additives, external coatings and physical methods. Plenty of characteristics should be dealt with when considering which method applies best to which product.

Choice of a proper AF effect depends on at least following criteria [55] [52]:

- use of the product
- polymer type
- thickness of the film
- processing circumstances
- effect on other characteristics of the product
- temperature, in which plastic film is used
- further processing that affects AF performance
- food supply contact.

Same AF agents do not necessarily work with different polymers. When choosing AF additive, possible effects on mechanical properties and appearance of the product must be taken into account. Some polymers have higher surface energy than others, which may ensue compatibility problems between them and additives. For example, surface energy properties and polarity of PET differ from polyolefins resulting in a different selection of suitable AF agents. The more polar nature of polyesters make them compatible with internal AF additives and due to that less migration appears towards the surface of film. [52] [7]

Thickness of the film is one factor that has an influence on the chosen method. Polymer layer that is thick enough enables the use of internal AF additives. The most efficient AF agent dosing, balance of compatibility and migration properties must be found out through experimental study. Masterbatches are generally used in PE carrier layers, but in some cases the thickness of sealing layer and constitution does not allow the use of masterbatches. In some cases the sealing layer for which the AF property is wanted, is so thin that masterbatches cannot be used. In that case it is not profitable or effective to use migrating AF additives. Options in these cases are to add external AF coating or use physical methods further discussed in chapter 2.7.3. [52] [56]

Processing conditions and operating temperature also influence the choice of AF additive and the method for implementing the AF effect. For example, processing temperature of PET is high, usually between 280 and 285 °C [57, p. 1], which can degrade the incompatible internal AF additive during melt extrusion. In the same way, high operating temperatures can degrade AF coatings faster than wanted. In AF coating process, it must be ensured that the coating evenly spreads across the whole area to be coated. Otherwise the wanted AF effect will not be attained consistently. The spreading of AF coating can be improved by corona pretreatment, which increases the surface energy of substrate. In addition, the corona treatment improves the adhesion of the AF coating on the substrate surface. [7] [52]

Further processing of the films with AF effect may affect the AF performance of them. For example in thermoforming temperature can rise so high that the AF effect is wiped out. However, it has been found out that the AF property is recovered in thermoformed films after 24 hours in storage. [52] Studies have also shown that printing affects the AF performance. When a food packaging film is surface printed, the printing color has been found to absorb AF additive when the film is stored as reel. [1]

2.7.1 Internal additives

Internal AF additives are generally speaking tensoactive materials, mainly nonionic surfactants such as glycerol esters, polyglycerol esters, polyoxyethylene esters, sorbitan esters and alcohol ethoxylates. These additives are added to plastic film during compounding or manufacturing and they are mostly in the form of masterbatches. Internal AF additives form a hydrophilic layer on the surface of the plastic film when they are migrating towards the surface. Migration from bulk layer towards the surface of the plastic film results from the fact that these additives and polymer matrix are incompatible with each other. AF additives are constantly migrated towards the surface of plastic film over time. If AF additive is available in the polymer there will be migration and the wetting properties will improve. [52] [58, p. 2023] [59, p. 1484] [55, p. 31]

Internal AF additives reduce the surface tension of water droplet that has condensed on the surface of the plastic film, and at the same time increase the surface energy of the plastic film. When the surface energies of water drops and plastic film reach the same value, the water drops spread and form continuous water layer on the surface of plastic film. Performance of AF additive is based on its migration from bulk layer towards the surface of plastic film. At the same time, when additive is migrating towards the surface, some of AF molecules are absorbed in water droplets. Surface concentration of AF molecules decreases when water layer slides away from the surface of plastic film. This results in concentration gradient between the surface of plastic film and bulk layer. Furthermore, AF molecules continue migrating from bulk layer towards the surface of film.

The decreasing in concentration of AF agent leads to the weakening of AF effect. [58, p. 2023]

The AF agent is a surfactant which consist of a hydrophilic head and a hydrophobic tail also known as lipophilic tail. Hydrophilic head contains polar hydroxyl groups (OH) and hydrophobic tail is comprised by non-functionalized hydrocarbon chain. The surfactant acts as wetting agent and helps the material to wet out. Figure 8 illustrates the operational principle of an antifogging additive. In step 1 the AF additive is incorporated in a polymer and is equally distributed in the polymer matrix. In step 2 the AF additive migrates from the bulk to the surface of the film. AF molecules are oriented so that the hydrophilic head is pointing towards the film-air interface. The surface of the film becomes more hydrophilic and compatibility between water droplets and the polymer surface is improved. In step 3 part of the AF molecules absorb in water. Hydrogen bonds are formed between the water molecules (H_2O) and AF molecules, and thus, the droplets coalescence and spread to form a continuous transparent water layer (step 4). In Figure 9, step 4 is described in more detail. AF molecules penetrate in between water molecules and hydrogen bonds are formed (dotted line) between AF molecule’s oxygen atom and water molecule’s hydrogen atom. Surface tension of water decreases when the number of AF molecules on the water exceeds over a certain limit. Eventually, the water washes the AF molecules from the surface and, over time, the number of AF molecules decreases. [55, s. 30-31] [51] [60, p. 224] [61, s. 264-265]

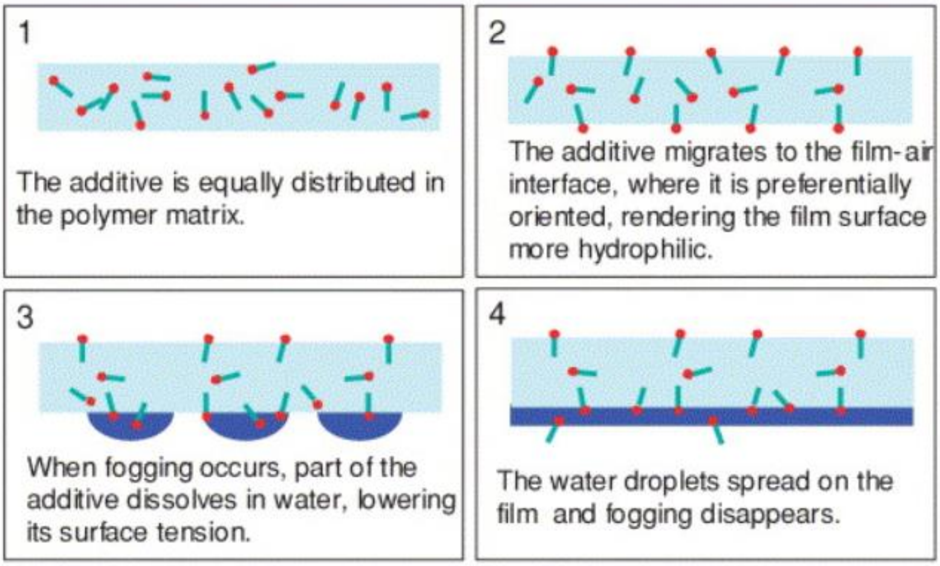

Figure 8. *Operational principle of an antifogging additive [55, p. 30].*

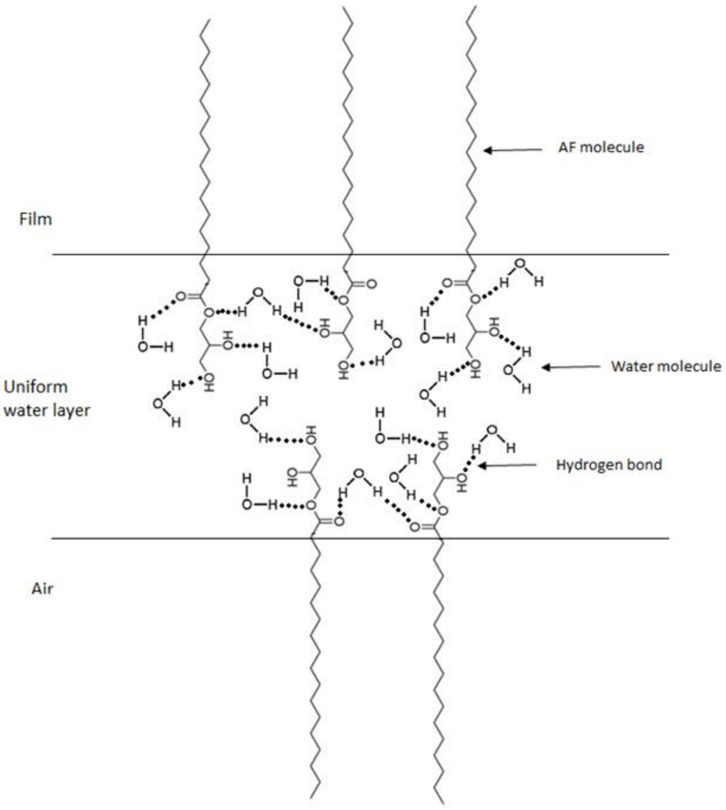

Figure 9. *Schematic description of the interaction between AF molecules and water molecules, adapted from [61] [51] [55].*

There are different ways to create AF additives that can be incorporated into polymer system. Mainly the process consists of two phases. First, the AF particles (non-ionic surfactants) are prepared by esterification. Depending on the used raw-materials there are many alternative processes to utilize. [62, p. 141] [63] [64] Also modified AF particles are presented where esters are mixed with nano-particles or compatibilizers to get improved properties. The second step is to mix those AF molecules with polymer pellets such as PE pellets to get polymer/AF system. In recent years, producers have focused on methods like grafting in which the AF molecules are grafted to polymer chains. Grafted molecule structure between backbone species, polymer, and a covalently bonded side-chain species, AF molecule, is created by graft polymerization. [65] [58] [59] [66, p. 51] Higher concentration of AF additives can also be incorporated into one or more polymers by using a melt compounding technique which takes place in a high shear mixer cell equipped with a batch plastograph at certain conditions which depend on the properties of desired end product. After a good mixing process the AF compounded polymer is ready for further processing. So called AF masterbatches can be combined with other polymers in film extrusion. Another way to mix AF particles with polymers is just to put AF additive and polymer pellets directly to the extruder without prefabrication of masterbatches. In this case, the manufacture takes place via a conventional extrusion compounding system. The mixture of resins is fed into a single or twin screw extruder where the resins start to melt. The different additives are then added into the extruder with relevant controlled system and by this way the additives are incorporated into the final composition. The well mixed melt is then guided to the extrusion die. After passing through die the melt is cooled by air or water. The melt is molded as strands, cooled down and cut into pellets to achieve the final product. [65] [58] [59] [19, p. 5]

As mentioned previously internal AF additives are typically nonionic surfactants such as esters which are derived from the esterification reaction between carboxylic acid and alcohol. The composition of esters may differ extensively due to the used raw materials and manufacturing process. Examples of internal AF agents include polyoxyethylene esters such as polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan tristearate, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan mono-oleate and polyoxyethylene sorbitan trioleate; sorbitan esters such as sorbitan monolaureate and sorbitan monostearate; alcohol ethoxylates such as polyethoxylated fatty alcohols; glycerol derivatives such as polyglycerol fatty acid esters, monoglycerides, diglycerides and glyceryl stearate; and others such as polyhydric alcohol, propylene triol, propylene glycol, ethylene diol and all of their mixtures. [19, p. 5] Due to the wide range of AF agents, this chapter will only be examine few different AF additives having nonionic surfactants as active material. Thus, this thesis focuses on the investigation of the nonionic surfactants such as glycerol esters, sorbitan esters, polysorbates and polyglycerol esters.

The most commonly used AF agents are glycerol esters such as glycerol monostearate (GMS) and glycerol mono-oleate (GMO), and sorbitan derivatives such as sorbitan monostearate and sorbitan mono-oleate (SMO). These surfactants have been used in various applications for a long time to achieve antifog effect. These polar additive molecules are relatively small and may migrate fast to the polymer film surface as regards to polyolefin. Due to this those agents are not very durable in providing the AF effect and their presence on the film surface can increase the stickiness of the film leading to the increased dirt and dust pick-up. [67, s. 228-229] [59] [68] [69, s. 178-179] In Figures 10 and 11 the structure of relatively small AF molecules glycerol monostearate and sorbitan monostearate are presented. Both molecules consist of one alcohol or alcohol derivative unit and one acid unit. In Figure 10 the structure has been divided in hydrophilic and hydrophobic parts with a dash line. Same principle applies to all nonionic surfactants. With relatively small AF agents the use of longer chain AF molecules has become more common. AF molecule chains can be lengthened by combining more alcohol groups together with one acid group or combining more acid groups to the one alcohol group or doing both at the same time. More commonly used way to affect the activity of AF additives is to increase the number of hydrophobic group (acid group). However, new esters have been lately developed consisting of more than one alcohol groups. [68] [70] Examples of longer chain AF molecules are polysorbates, polyglycerol esters (PGE), diglycerides and triglycerides. In Figure 12, PGE having multiple glycerol units esterified with one stearic acid unit is presented. It is also known as polyglycerol monostearate.

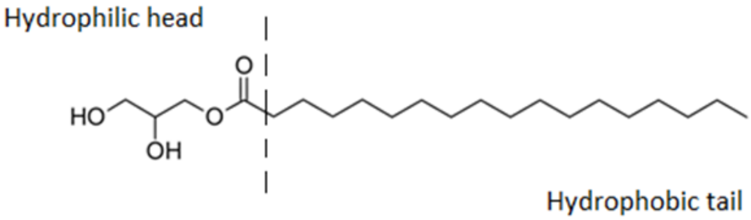

Figure 10. *Structural formula of glycerol monostearate. Structure has been divided to hydrophilic head and hydrophobic tail with dash line. Same principle applies to all surfactants, adapted from [71].*

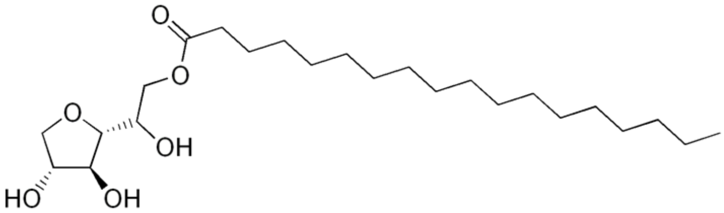

Figure 11. *Structural formula of sorbitan monostearate, adapted from [72].*

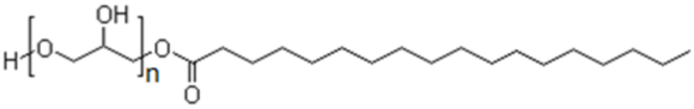

Figure 12. *Structural formula of polyglycerol monostearate, adapted from [71].*

Polyglycerol esters have improved thermal stability compared to glycerol esters, sorbitan esters and polysorbates. Due to better thermal stability polyglycerols are less volatile than glycerol esters which can be seen as reduced evaporation of the additive during processing. Possible discoloration during film processing can be prevented with higher thermal stability of esters since the formed esters may be slightly yellowish depending on the purity of the used polyglycerol. Boulos et al. [55] compared the discoloration of different esters between each other and found that esters derived from sorbitan are more yellowish than those derived from glycerol. In the same study the antifogging properties of different esters in food packaging films were investigated. The results showed excellent antifogging properties of polyglycerol esters versus the monoglycerides which was confirmed by a visual evaluation and contact angle measurements. Also, polyglycerol esters had good compatibility with other additives and various polymers.

Danisco Emulsifiers of Denmark reported [68] the development of an AF additive for packaging films based on polyglycerol esters. Glycerol molecule is a trifunctional molecule thus it may condense with itself by polymerization of glycerol to form polyglycerols. Depending on which of the hydroxyl groups take part in the reaction both linear and branched polymer chains can be formed. Hence the degree of polymerization defines the number of possible isomers which increases exponentially when the polymerization proceeds to higher glycerols. [73, s. 423-424] The AF additive developed by Danisco is created by varying the degree of polymerization of glycerin. In this way, different fractions can be separated from each other to produce restricted distribution of polymerized glycerin without compromising the polarity of molecules. By this process it is possible to design smaller and slimmer AF molecules migrating faster in a crystalline polymer such as PP.

Same AF additives cannot be used in all polymers as those additives behave differently in each structure due to various reasons. Migration of internal additives to the polymer surface is the main limiting factor. Since internal AF additives function by migration from bulk to the surface of the film, their concentration will be decreased over time due to migration. By influencing the properties of additives and polymers which affect to the migration behavior it is possible to reach longer-lasting AF effect. For example, coextruded film which comprising AF additive only in inner layer, which is exposed to condensation, may rapidly lose the AF effect. When adding AF additive to the other layers as well so called reservoir effect can be provided to replenish the inner layer. [69, s. 177-178] Crystallinity of polymers affect to the migration of AF additive and therefore for example antifogs suitable for PE cannot be used with PP. PE has low crystallinity which allows the faster migration of additives whereas migration is slower in PP system because of the higher crystallinity which does not allow the AF agents migrate fast enough to the polymer surface. [68]

One way to control the migration of AF additives is to modify the AF molecules. In markets, there are AF agents that work well in polyolefin systems yet the difference in crystallinity of polyolefin may cause problems related to additive migration. Thus, AF molecules need to be redesigned to migrate slower in a low crystalline polymer and faster in a high crystalline polymer to ensure the desired level and duration of AF performance. [68] Small AF molecules have low solubility and high diffusion rate thus those molecules migrate faster to the polymer surface. By changing the solubility and the diffusion coefficients of small AF molecules it is possible to control the migration rate in a polymer matrix. The size and shape of the migrating additive, and the magnitude and distribution of the free-volume in the polymer are the things of which the migration rate depends on. Thus, it can be concluded that the migration process includes both the motion of AF molecules and the motion of polymer segments. [65] [60, p. 220]

Földes et al. [60] investigated different sorbitol esters. The study indicated that the migration of AF agents depends on the length of the hydrocarbon chain and the effectiveness of AF agents is influenced by the ratio between hydrophilic and hydrophobic groups. The shorter the aliphatic chain length is the faster is the migration speed and thus the time to achieve the complete effectiveness of the AF performance decreases. The studies show that not only the effectiveness correlate with the relative number of OH groups but also the solubility of the additives. The additives with high OH group concentration migrate fast to the surface and are the most soluble in water. In other words, the increase of hydrophilicity, with increasing number of the OH groups, increases the effectiveness but the duration time of effectiveness, so called service life, decreases. In the same study, they also indicated the effect of temperature to the migration of AF additive. The diffusion rate and the migration rate depends on the temperature so that the mobility of the additives increases as a function of increased temperature.

In other studies and publications [68] [55] [70] PGEs having slow migration speed are presented. Examples of antifogging agents which are slow migrating and, still, show good antifogging properties are diglycerol and triglycerol monostearates. As indicated previously, the additives with high OH group concentration migrate fast to the surface but in the case of PGEs, polysorbates or other same kind of structures the situation is slightly different despite of OH group concentration. Alcohols or alcohol derivatives can link together with an ether linkage by polymerization. The formed molecule is said to be nonpolar and thus decrease the polarity of the AF molecule. The size of the ether molecule is meaningful since the small molecules are still able to dissolve in water and when the size increases the water solubility is lost. By varying the degree of polymerization it is possible to control the size and shape of formed molecule. However, it needs to be considered that the polarity of the AF molecules should not be too much reduced to maintain the AF functionality of the molecule. [61, s. 155-156] By affecting the shape and size of the AF molecules it is possible to create additives that migrate fast enough in highly crystalline polymers and slowly enough in more amorphous ones.

Albizu et al. [74] studied the effect of temperature on the migration rate of additives. In addition to that they showed correlation between the duration of the AF effect and the concentration of AF additive on the film surface. The loss of the AF effect was found to be related to the additive surface concentration. Therefore, the AF property of the film is not connected to the total concentration of the AF additive even if the total concentration decreases along with exposure time. The water dissolution rate and the additive migration rate must be in balance to obtain long lasting AF effect. This process is diffusion controlled if the water solution rate of the additive is higher than the migration rate. This results in the higher reduction of the additive surface concentration compared to the total additive concentration and, thus, there is still additive left in the bulk of the plastic film while the AF effect of the film is lost. After a time of storage the film may show its AF property again since during storage the migration continues but there is no contact with water vapor that removes the AF agent from the surface. Same kind of results were also indicated by Hirt et al. in [75].

In addition to the above mentioned, many other methods have been presented to control the migration of additives and extend the effect of additives in polymers. One way is to control the AF additive migration from bulk to the surface of the film by modifying the AF particles. Narkis et al. presented [58] [65] a method for controlled migration of AF additives by grafting AF molecules (GMO molecules) onto the surface of silica particles via a radical reaction. Methacrylic silica nano-particles were used as physical migration inhibitors. After grafting the AF particles were mixed with the polymer matrix. By using silica particles it is possible to create good optical clarity for films since silica particles do not scatter light due to their small size. Moreover, large interfacial area for grafting is a result of the small particle size of silica. During the grafting reaction free and grafted GMO fractions are formed. It should be noticed that only the unattached fraction can migrate. As a result of the study modified GMOs migrating slower than the clear GMO were obtained. In another article Narkis and co-workers studied migration of SMO from linear low density polyethylene films also containing a compatibilizer. [59] The compatibilizer used was a maleic anhydride modified. It was used to increase the compatibility between the polar AF additives and polyolefin. In general, the interfacial adhesion between the AF additives and non-polar LLDPE was modified with the compatibilizer. [32, p. 1802] The study showed that addition of an optimal amount of AF additive and compatibilizer significantly decrease the AF additive migration rate and the contact angle.

Most commercially available internal AF additives are suitable for polyolefin systems, but in case of polyester system, there are only few additives available. Polyolefins are more hydrophobic than polyesters, which can be observed from the surface energies: polyolefins have a surface energy of approximately 30 mJ/m^2 whereas the surface energy of polyesters is about 40-44 mJ/m^2. The hydrophobic nature of polyolefins enables a wide supply of possible AF agents. A great deal of these agents are incompatible with polyolefins and hence these agents migrate easily through the film towards the surface. Migration may, however, be too fast in some systems and, thus, the required shelf life of the AF performance may not be achieved. For this reason, a slow migration rate should be targeted in some systems. One way to slow down migration is to increase the polarity of the polymers used. For example, by modifying PE with EVA the resulting polymer blend is more polar due to the increased proportion of vinyl acetate. Polyesters are more polar polymers in nature and, thus, they are more compatible with internal AF additives. [52] [55, p. 31] [59, p. 1484] [76, s. 31-32] [74, p. 2307]

2.7.2 External coatings

AF performance can also be achieved by adding an external AF coating that includes the AF property, on the surface of film. External coatings function just like internal additives. Their objective is to help wetting out the surface of substrates. External coatings are developed to decrease contact angles of water droplets that have condensed on the surface of plastic film, and hence to improve transparency of film. [52] [7]

External coatings are generally viscose liquids that are diluted with either water or alcohol, or they are used as undiluted. AF coating is spread consistently on the surface of plastic film with a dip or spray coater. After the external coating has been added, film usually goes through dryers where the solvent evaporates and the coating cures on the surface of film. AF coatings are typically applied off-line, but in-line application is more desirable because of cost savings. With external coatings, it is important to perceive two things. The coating must spread as a uniform and consistent layer on the surface of plastic film and, similarly, condensing water must spread on the surface of the coating to attain the AF effect. AF agents included in AF coating migrate to water droplets formed on the film surface. Thus, surface tension of water droplets decreases and they lose their spherical form. Even with small amounts of surfactants on a hydrophobic surface or in the liquid, the wettability of it can be significantly improved in practical applications. [52] [7] [77] [78]

As mentioned before, internal AF additives are used generally with polyolefins, but their suitability with esters is worse. The compatibility of PET with internal agents is in most cases too good and, thus, migration towards the surface of film turns out to be very slow. In such case, it is common to use external AF coatings. As also presented before, processing temperatures of PET are considerably higher than those of polyolefins, and hence internal additives may degrade during melt extrusion. [52] [7] The use of AF coating is also common when the thickness of the polymer layer is very thin. Thin polymer layer includes smaller amount of AF additive than thicker layer which causes the rapid decrease of AF effect. [56]

AF coatings include surfactants in the similar manner as internal AF additives. In the case of liquid coatings, the used surfactants are generally anionic or nonionic surfactants. Nonionic surfactants are discussed in chapter 2.7.1. In anionic surfactants, the polar group can be carboxylate, sulfate, sulfonate or phosphate. The polar head group has negative charge and, therefore, in case of ionic surfactants the choice of counter-ion plays an important role in determining the physicochemical properties. Anionic surfactants, which are used in AF lacquers, have potassium or sodium as the counter-ion. Potassium or sodium are used, because they enable higher solubility in organic solvents. The hydrophobic tail is typically a hydrocarbon chain. In Figure 13 the structure of a common anionic AF agent sodium bis(2-ethylhexyl)sulfosuccinate is presented. [78] [79, s. 10-11, 385-386]

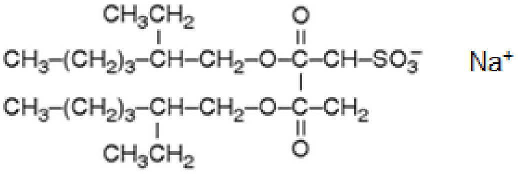

__Figure 13.__ Structural formula of sodium bis(2-ethylhexyl)sulfosuccinate, adapted from [79, p. 386].

The AF coating can also include surface active silicone polymers that are polymeric surfactants. They consist of a hydrophobic backbone and hydrophilic side chains that alternate in hydrophilic and hydrophobic segments. Surface active silicone polymers are graft copolymers which have polar side chains. There are a lot of different types available, but they all include polydimethylsiloxane as backbone (Figure 14). The backbone polymer is strongly hydrophobic and completely insoluble in water. This type of polymers can be made to adsorb as a monolayer on hydrophobic surfaces. Interaction between the hydrophobic backbone and the solid surface inflicts that the adsorption occurs and the hydrophilic chains orientate towards the aqueous phase. The surface active silicone polymers are special products that are used in applications where they show better functionality compared to conventional surfactants. One common application for them is to work as wetting agents on polyolefins and other hard-to-wet type materials. [79 s. 197-206] [80] [81]

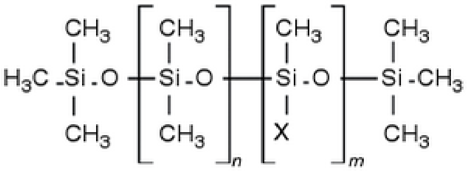

__Figure 14.__ Surface active silicone polymer (Polydimethylsiloxane is obtained when m is 0) [79, p. 205].

Fluorosurfactants can also be used in AF coatings. They have many different structures and their properties are directly dependent on the structure. For example, in Figure 14 substituent X can be replaced with some fluorosurfactant. Fluorosurfactants are chemical compounds which consist of polar hydrophilic head and hydrophobic fluorocarbon tail. Fluorocarbons have excellent physicochemical properties originating from the very special properties of fluorine. Fluorine is bigger by size and more electronegative compared to hydrogen. However, it has smaller polarizability compared to hydrogen. Fluorocarbon chains are therefore more bulky than those of hydrocarbons. The carbon-fluorine bond is really strong and chemically stable and consequently forms the most stable single bond in organic chemistry. For this reason, fluorocarbons have high chemical and thermal stability. Because of the low polarizability of fluorine, weak van der Waals interactions affect between fluorinated chains. As a result, the cohesive energy of fluorocarbons is low. This further gives low dielectric constant, high vapor pressure, high compressibility, high gas solubility, low surface tension, high surface activity in aqueous solutions and low critical micelle concentration. Fluorocarbons are extremely hydrophobic and therefore they can be both hydrophobic and oleophobic. Thus, they are surface active in aqueous solutions and organic solutions. [82] [78]

Fluorocarbon surfactants are rarely used alone in AF lacquers. To attain complete spreading, hydrocarbon and fluorocarbon surfactants are used together. Hydrocarbon surfactants decrease the interfacial tension between hydrocarbon solid and water while fluorocarbon surfactants decrease the water-air surface tension. Hydrocarbon surfactants decrease the water-air surface tension as well but not as effectively as fluorocarbon surfactants. This way positive spreading coefficient and good wetting properties are attained, which is very important in coating applications. Researches have, however, proven that wetting properties of fluorosurfactants on low energy hydrocarbon solids are poorer than those of hydrocarbon surfactants. Aqueous solutions including fluorosurfactants do not spread as well on the hydrophobic surface such as polyethylene or polypropylene. Solutions of fluorocarbon surfactants have greater contact angles on hydrocarbon solids than solutions of hydrocarbon surfactants, even though surface tension of them is lower. Ivanova and her co-workers studied this inconsistency in their research [82]. They discovered that fluorosurfactant has lower free energy of adsorption on hydrocarbon solid-water interface than hydrocarbon surfactant has.

Adhesion of AF coating onto the surface of substrate is enabled with binders. Binder included in AF coating is used to anchor the AF coating to the surface of polymer film. The most effective binders are polymeric binders. Binders can be water soluble and water dispersible. The use of these kind of binders is preferred, because water sensitivity results positive AF performance. Functionality of water soluble binders is excellent especially in combination with anionic surfactants. Surfactants contribute spreading of water droplets on the surface of film and the water sensitive binder absorbs the water. In this way, the water is conducting away from the surface. One example of water soluble binders is copolyesters. All water soluble copolyester binding the coating to the surface of the base polymer can be used. In films that are coated with an AF coating, improved adhesion to inks and metals have been detected when these kinds of binders are present. Water-based binders can also be used. Those are safe alternatives due to the elimination or reduction of potentially hazardous solvents. One example of water-based hydrophobic binders is an ethylene acrylic acid copolymer emulsion. Hydrophobic binders are mixed with nonionic surfactants in aqueous media to form an emulsion. Because the coating remains as an emulsion until it dries, other substances can be added and mixed to it. Also, it has been detected that high pH environment assists maintaining of the coating composition as an aqueous homogenous emulsion. This can be attained by adding sodium, potassium, ammonium hydroxide or ammonium chloride to the mixture. In this case, the binder becomes crosslinked and hydrophobic when the coating is dried. The adhesion between water-based AF coatings and the film surfaces must be enhanced with corona treatment or some alternative method. The treatment oxidizes surface of film so that its surface energy increases and adhesion is improved. The composition of AF coatings can also include other additives such as fillers, stabilizers, plasticizers, colorants, pigments, slip agents, antiblocking agents, antistatic agents and adhesion promoters. Adding slip agents to AF coating improves the ability of coated film to wind smoothly during the manufacturing process. [78] [83]

In AF coating method, hydrophilic components are combined into the coating formula. After this, coating is cured onto surface of film and hydrophilic substances are chemically crosslinked to the base polymer. However, the interface between coating layer and base polymer is sensitive to water invasion due to absorption by hydrophilic groups. Thus, in the high humidity conditions the AF coating can swell and detach from the substrate. The creating of a durable AF coating onto surface of polymer substrate is still under development. One problem is also that several AF coatings are water soluble materials washing away when water condenses on the coated film. It has also been detected that other properties of the film, such as gloss or heat sealability, can reduce because of water soluble coatings. In recent years, a lot of new innovative ways have been presented to create durable AF coatings on plastic substrate. [84]

Bianchi et al. have presented a new AF coating made of pullulan for packaging applications. The study pointed out that polysaccharide functions as an effective wetting enhancer. Also, the pullulan coating had better overall performance than other commercial AF films. Additionally, pullulan coating is an environmentally friendly alternative in comparison with conventional AF additives. [85] Muhammad et al. developed a coating that is made of UV cured quaternary ammonium salt. This coating appeared to have durable AF property and antibacterial properties were also found for the coated films. [38] Furthermore, Chang et al. presented a coating that has an excellent AF performance and, additionally, it resists water penetration effectively. This coating has hydrophilic/hydrophobic bilayer design, which consists of photosensitive modified surfactant and multifunctional crosslinking agent. [84]

2.7.3 Physical methods

Generally, the way to reduce formation of fog on the surface of film is to increase the surface energy of it. In addition to methods mentioned previously, there are other methods to increase surface energy. In this chapter the methods that do not demand the use of special chemicals or additives are considered. Hence, they are cost effective alternatives for creating AF property to plastic films.

A lot of surface treatment methods are available to process polymer surface properties. The chemistry of polymer surfaces can be changed for example by using plasma, corona, flame, photon, electron, ion, X-ray, gamma-ray and ozone treatments. Plasma treatment takes place in air or oxygen environment and it is the most designated technique when oxidizing surfaces of polymers. Equally used techniques are corona and flame treatments. In plasma and corona treatments, the accelerated electrons bombard the surface of polymer film with energies two to three times. During bombardment, molecular bonds break and free radicals are formed that react with surrounding oxygen. The polar groups forming on the surface of polymer film are typically hydroxyl, peroxy, carbonyl, carbonate, ether, ester and carboxylic acid groups. In flame treatment, surface combustion of polymers occurs, where hydroperoxide and hydroxyl radicals are formed on the film surface. The depth of oxidation in flame treatment is from five to ten nanometers. In air plasma treatment, the depth can be over ten nanometers. All plasma, corona and flame treatments effectively process polymer surface resulting in improved wettability properties. However, the efficiency of treatment depends on the polymer that is being treated. Even if the surface of polymer can be processed to be hydrophilic it does not necessarily correspond to excellent AF performance. Polar groups that are formed during surface oxidation do not remain on the surface of polymer film, but they tend to penetrate in the polymer bulk when the film is in contact with air for a long time. The polar groups remain better on the surface if the surface is in contact with polar environment. [33]

In recent years, the use of plasma in processing polymer films has increased significantly. For example, polyethylene is affordable and easily processed raw material that has excellent mechanical properties but it is quite inert and has low surface energy. To enhance printability and bondability of products made of polyethylene plasma treatment is frequently employed. Plasma can broadly be defined as a gas that consists of charged and neutral species. Plasma treatments do not affect the bulk properties, especially mechanical properties, of the base polymer. With gas plasma properties of all polymer surfaces can be processed regardless of their structure and chemical reactivity. Additionally, the type of chemical modification can also be affected by the selection of used gas. Plasma treatment is a considerable alternative also because the effects of it evenly spread over the whole surface area of the film. [86]

The number of functional groups created by plasma treatment on the surface of polymer can change in time due to the environment and temperature. In different conditions the surface of polymer can reorientate, because polymer chains have much higher mobility there than in the bulk. Surface orientation can occur due to diffusion of oxidized materials with low molecular weight into the bulk. Also, the migration of polar functional groups away from the surface can cause surface reorientation. Ageing of plasma treated polymer surfaces can be prevented by increasing crystallinity and orientation of the polymer surface. This increases the degree of order and thus reduces mobility of polymer chains. Mobility of polymer chains can also be avoided by crosslinked surface. [86]

Vetaphone has presented an advanced plasma technology called Enhanced Atmospheric Surface Improvement (EASI-Plasma) in a Dielectric Barrier Discharge Plasma. This method enables different functionalization of surface. According to Vetaphone, this method is more homogeneous and gentler than corona treatment. Plasma with low heat impact to the surface makes diverse surface chemistry modification possible. Method functions as gas primer that replaces both the use of corona treatment and liquid primer. With the EASI-Plasma Nano Coating Technology durable AF performance can be created for polymer films. In the process nitrogen based atmosphere is balanced with vaporised monomers. Film is coated with extremely thin silica layer which has a thickness of only from 5 to 50 nanometers. When the surface of film is coated with a layer of such low thickness a lot of material can be saved and the need for drying is eliminated. According to Vetaphone, AF coating created with plasma treatment does not wear out in the same way as traditional coatings. It is also stated that the EASI-Plasma solution is environmentally friendly and, therefore, safer to use in food packaging applications. [87]

Suitability of plasma treatment for creating durable AF performance on the surface of polymer film has also been reported in scientific studies. In the research of d’Agostino et al. [36] transparent plastic was coated with silica nano layer that has a thickness of 50 nanometers resulting in increased surface energy. The silica coating was easily processed by varying plasma parameters. However, this method was not stable in time due to the decrease of surface energy. It was found out that when the plastic substrate is nanotextured with plasma etching before the silica coating process a permanent AF modification can be obtained.

Currently, corona treatment is the mostly used pretreatment technique in plastic film industry. In corona treatment (dielectric barrier discharge) the electric discharge is controlled by a dielectric barrier. Electrons are accelerated onto the surface of plastic film causing the long molecule chains to break and producing a multiplicity of open ends. Due to the impact of oxygenation new carbonyl groups with a higher surface energy are formed resulting in enhanced hydrophilicity. The efficiency of corona treatment depends on used material and additives it consists of. The disadvantage of corona treatment is that its effect decreases over time. Some additives such as slip cause weakening of corona effect even faster. Also, storage conditions can affect the durability of corona treatment. Typically, corona treatment is not enough to create a proper AF performance as such and, thus, additional treatments are used with it. [87]

Ahn et al. reported [88] about the manufacturing of antifogging low density polyethylene film by using gamma-irradiation. In this research trifluoroacetic acid allyl ester was grafted onto LDPE by gamma-ray irradiation. The polarity of polyethylene was enhanced through the grafting of functional monomers. The use of gamma-ray irradiation has many advantages, such as a high rate of free radical generation without the need of initiator agents.

2.8 Antifog performance in plastic films

AF property on the surface of polymer film is affected by several different factors. The main factors, such as temperature and relative humidity, have been studied by many researchers [60] [74] [75]. However, there is hardly any information about the effects of other factors, such as inks and additives of film. It must also be considered that even though other properties and factors affect AF property, correlation functions also the other way around: AF property affects other properties of polymers.

The hydrophilic surface that has been created with AF coating, must be kept free of contaminants to preserve its wetting properties. When freshly prepared hydrophilic surface is exposed to dominant environmental conditions, instant changes occurs. Hydrophilic surface tends to achieve its most stable state, in other words lowest surface energy. Changes in hydrophilicity of surface have been detected with contact angle measurements. It has been detected that when materials were exposed to laboratory air, contact angle values increase fast in the first 20 hours, after which changes in contact angles were only some degrees. Additionally, it has been detected that OH groups have an influence on hydrophilic surfaces. OH groups that are on the surface of material attract organic contaminants and the greater the amount of OH groups is, the more intense weakening of hydrophilicity is. In other words, the amount of OH groups correlates with the adsorption of organics from the atmosphere. [33]

Dominant humidity and temperature of environment decrease hydrophilicity of the surface of film. The weakening is based on the degradation of molecules. Temperature is a critical factor in degradation because it significantly speeds up some chemical reactions. High temperature can degrade the structure of AF coating, and additionally degradation of other substances in structure of film can affect the AF performance. Therefore, the effect of structure of film is a remarkable parameter in weakening of AF performance. Relative humidity and water condensation effect also on the degradation of AF coating. When water condenses on the surface of film, it results in wash-out of AF additives and, thus, loss of the AF properties. Composition and pH of condensed liquid have an influence on weakening of AF performance. [89] In addition, other additives of polymer film can also affect the AF performance. Fillers may absorb part of the AF agents and other migrating agents may cause blooming. [51]

Studies regarding testing and development of AF properties show that AF properties have not significant effects on mechanical properties of plastic films. In some cases, mechanical properties have even slightly improved. However, it has been detected that heat seal initiation temperature of polymer films increases when the surface of film is coated with AF lacquer. Also, weakening of re-tack property in time has been detected in case of some AF lacquers. Depending on composition of AF coating, tests have shown weakening of hardness of the coated surface. Therefore, AF coating can decrease the scratch resistance and pencil hardness of film. Some AF additives can also affect the visual appearance of film and for example cause yellowing of the film. Discoloration of film results from low thermal stability of AF additives. [65] [55] [1] [38]

3. EXPERIMENTAL PART

3.1 Aim of the study

AF property is required in all lid structures of thermoplastic packages when food supplies with high moisture content are packed. It is generally achieved for PE sealable lids by using AF lacquers. However, difficulties have been faced with some products to achieve and maintain the wanted AF performance during the whole six-month shelf life. It has been detected that the AF performance dramatically weakens already after three months in storage.

To solve the problem, a series of AF lacquer test runs were performed. In these test runs the PE surface (sealing layer) of studied film was coated with AF lacquer. The purpose was to study and find out the performance of AF lacquers from two different manufacturers. The AF performance and other important properties of the AF lacquered films were tested across the whole six-month shelf life.

3.2 Materials and methods

Materials and test methods used in the experimental part of this thesis are presented in chapters from 3.2.1 to 3.2.6. Before performing any tests, the films to be tested were manufactured. After this, the samples were carefully prepared for the laboratory tests.

At first, the appearance of film sample was inspected visually, to confirm that appearance meets up with the set demands. In addition to visual inspection, the laboratory measurements included AF coldpool test, sealing curve between 100 °C and 200 °C sealing temperature, peel strength test and 10 x re-tack force test from the samples sealed in 150 °C and 160 °C temperatures. Also, contact angles and surface energies of the AF lacquer coated film samples were tested. Other laboratory tests were also performed and those are presented in chapter 3.2.6.

3.2.1 Plastic materials

Figure 15 presents a simplified structure of the tested plastic film. This film in question was selected as a studied object because AF performance on the structure had been found to be compromised. The film consists of a PE film, which is adhesive laminated with PET film. Possible printing is made against PET surface and AF lacquer is made on the surface of PE.

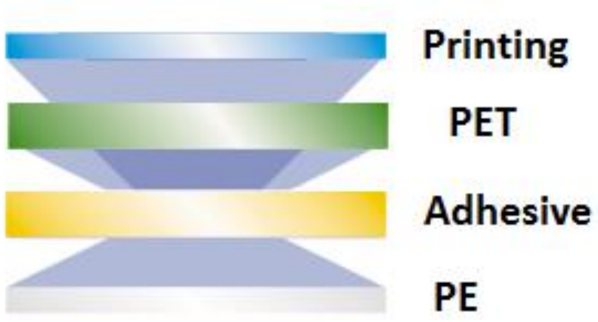

Figure 15. *Simplified illustration of structure of test film [90].*

3.2.2 Antifog coatings

The AF lacquers used in experimental part were AF lacquer no. 1 and AF lacquer no. 2. Typical product data from both lacquers is presented in Table 1.

Table 1. *Product data of antifog lacquers used [91] [92].*

Product	Dry content	Density 25 C° (g/cm^3)	Viscosity (AFNOR)	Appearance
AF lacquer no. 1	2 ± 0,2 %	0,768-0,808	12-14 SEC	Clear
AF lacquer no. 2	1,10 %	0,78	10-15 SEC	Clear

AF lacquer no. 1 has already been tested in the factory of Bemis Europe, but the AF performance related to it has not fulfilled the requirements. The AF performance does not last in the film across the wanted six months' time. For this reason, this research aimed at clarifying how the AF performance of lacquer no. 1 can be improved and made to last for a longer period of time. Based on preliminary observations the AF lacquer no. 2 was selected as the second AF lacquer to be tested in this research. The target was to clarify if this alternative lacquer could improve the AF performance of the film without compromising the other properties of it at the same time.

According to supplier information, AF lacquer no. 1 is applicable with polyethylene films and it can be diluted by using ethanol or isopropanol. However, the supplier does not promise long-term AF properties for the product. Instead, it offers very good immediate and short term AF properties, typically for 14 days. [91]

AF lacquer no. 2 is also applicable with polyethylene films. With this lacquer, AF performance can effectively be maintained on the surface of LDPE film even for six months after lacquering. In the information offered by the supplier it is urged that AF solution must be used as undiluted and on unprocessed film. In addition, the supplier promises that the use of this AF solution will not affect the mechanical properties of the film. [92]

3.2.3 Antifog level evaluation

The AF level evaluation test of this research was based on working instruction of laboratory [93]. The course of the AF test in question was following: At first, 200 milliliters of hot water was measured into AF cup with a capacity of 500 milliliters. The tested AF film was set on the surface of cup as a lid the AF treated side down, and closed tightly by using a cover ring. The sample container was held in cold pool in temperature of about +4 °C. In Figure 16 shows AF cups in coldpool environment. Appearance of plastic film was inspected and evaluated after the sample had been stored in the cold pool for 1 hour, 4 hours, 24 hours, 3 days and 7 days. Results of performed AF evaluation were finally entered in spreadsheet and graphs for AF performance evaluations were drawn.

Evaluation of AF performance was conducted by following the criteria presented below:

- 0 = Excellent
- 1 = Good
- 2 = Bad
- 3 = Very bad
- E = No AF effect

Figure 16. Test arrangements for antifog level evaluation.

3.2.4 Sealing curve, peel strength and re-tack test

Sealability and sealing ranges of plastic films were studied and evaluated by using sealing curve, peel strength and re-tack tests. All of these tests were performed according to the working instructions of laboratory [94] [95]. The sealing curve tests were started by cutting one sealing strip per sealing temperature in machine direction from sample films. Sealed sample was about 25 millimeters wide and the seal area was about on the middle of sample strip. In Figure 17 examples of sealing strips are presented. The temperature range was set between 100 °C and 200 °C and samples were tested in this range at intervals of 10 °C. In the tests, all the seals were performed with 1 second pressure time and 900 N pressure. Sealing machine, in Figure 18, had heated upper jaw and cold lower jaw.

Figure 17. *Sealing strips for seal strength measurements.*

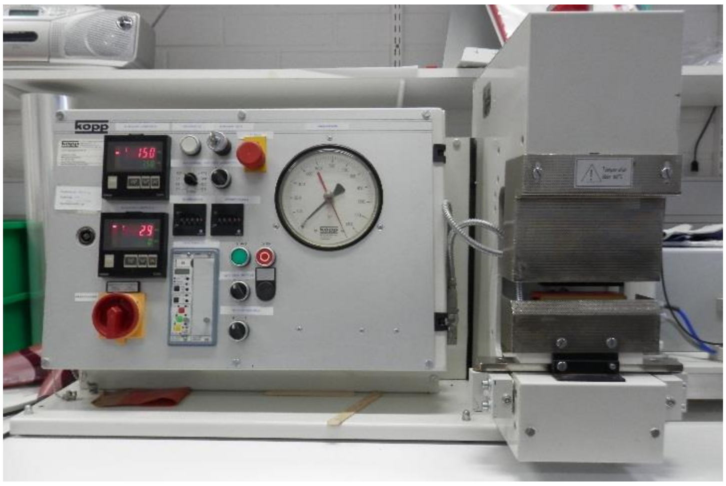

Figure 18. *Sealing machine.*

After sealing the seams were opened with tensile testing machine Lloyd LF-Plus (Figure 19). The starting peaks and average values of strengths were reported and sealing curves drawn.

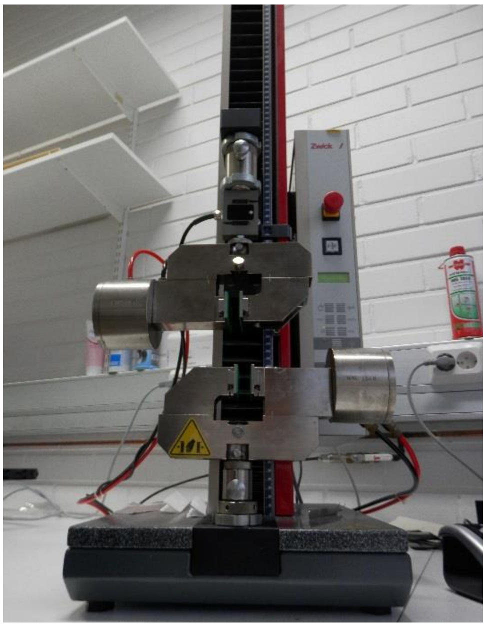

Figure 19. *Tensile testing machine.*

From the sealing curves the optimal temperature range for sealing was discovered. This temperature range was used in peel strength and re-tack tests. The aim of the peel strength test was to measure the maximum strength of seams of peelable films when opened for the first time. Opening of the seam was also analyzed visually. After the first opening, the seam was closed and opened repeatedly for 10 times. The aim of this test was to evaluate the re-tack performance of seams. The peel strength and re-tack tests were performed in the sealing temperatures of 150 °C and 160 °C. All the peel strength and re-tack tests were performed for the same-size samples and with the similar sealing parameters as the sealing curve tests.

3.2.5 Contact angle and surface energy measurement

Water contact angles and surface energies were measured with PGX+ Pocket Geniometer equipment following User's Manual (Program version 4.0) [96]. The used method was based on standard ASTM D5946 - Standard Test Method for Corona-Treated Polymer Films using Water Contact Angle Measurements. In this calculation model the water contact angle is converted into a dyne value.

The measuring device dropped 4 µl of water on the film sample and the camera took a picture of the droplet on the surface of film. An example of a picture taken by the software is shown in Figure 20. In measurements, distilled water was used. From each film sample water contact angle and surface energy was measured from five different points.

As a result, the average value of these five measuring points was reported. In this study, only static contact angle with water was observed.

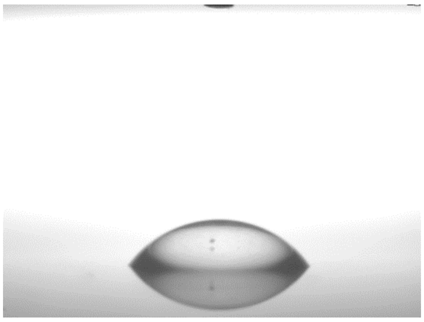

Figure 20. *Picture of droplet from static water contact angle measurement.*

3.2.6 Other tests

In addition to tests mentioned before, some other tests, such as residual solvent tests and friction tests, were performed to film samples. Optical properties, such as haze and gloss, were also observed.

When surface of plastic film is lacquered with a solvent-based lacquer, extra solvent must be evaporated away during drying. In the AF lacquer coating processes of the study the film went through two ovens set to optimal temperatures based on the used substrate and machine speed. Incompatible drying conditions may leave extra solvent in the film. The purpose of residual solvent test is to find out the amount of extra solvent left on the film after drying. In AF lacquered films the overall amount of residual solvent must not be over 10 mg/m^2, if clear laminates are in question. In the case of printed laminate the maximum value is 20 mg/m^2. [97] The residual solvent test is performed by using Agilent 650 gas chromatograph and the amount of solvents as milligrams towards one laminate square meter is informed as a result.

Friction test was performed with Testometric pulling device. In this test the film sample was adjusted on itself with a weight and pulled. The measuring program drew a graph regarding the needed force and calculated the static and dynamic friction value for the material. [98] With the friction tests it was studied how AF lacquer affects properties of the surface of plastic film. High friction of the surface is related to stickiness of the film. Sticky film collects dirt and dust from the packaging machine and causes blocking of the film reel.

Gloss was measured from the surface of film with micro-TRI-gloss 4520 gloss meter. Gloss of the film is measured across the whole width of the film from five different spots. An average value of these five measurements was reported as a result. Glossy surface is much smoother than mat surface. When a beam of light hits on the glossy surface, it reflects evenly. In gloss test, a beam of light is directed on the surface of sample film and its reflection is measured. Completely glossy surface has a gloss value of 100 and completely mat surface has a gloss value of 0 gloss units (GU). [99] Measurements in this study were performed with the angle of 60°.

Haze of the sample films was measured by using Haze-Gard plus haze meter. In this device there is a halogen lamp in which beam of light is directed through the sample to integrating ball (Ulbricht's ball) and detector attached to it. When measuring haze the shutter of the ball is opened and only diffused light goes into detector. The measured value of haze reports share of diffused light going through the sample as percentages. [100]

3.3 Fabrication of samples

In experimental part of this research AF lacquered samples were fabricated for laboratory tests. AF lacquer coatings were applied on the sealable side (PE) of peelable and reclosable lid film. The PET side of the film was either clear or printed. The PE film was fabricated with blown film coextrusion line, which is presented in Figure 21.

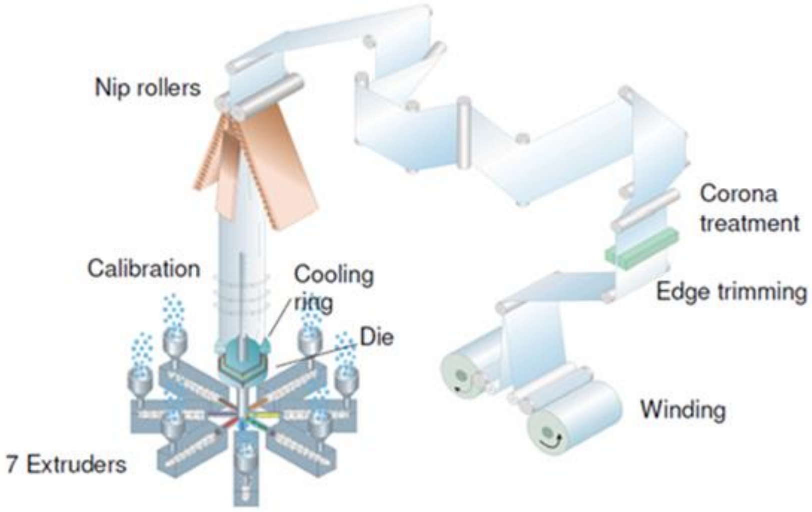

Figure 21. *7-layer blown film line [101].*

After fabrication of the PE film a lamination run followed. The PE film was adhesive laminated against PET film. After lamination, the film was further printed with a matte surface print. Approximately half of the film was surface printed with a window-type material and half of it remained clear as shown in Figure 22. With this the purpose was to obtain both clear and printed test point for laboratory tests.

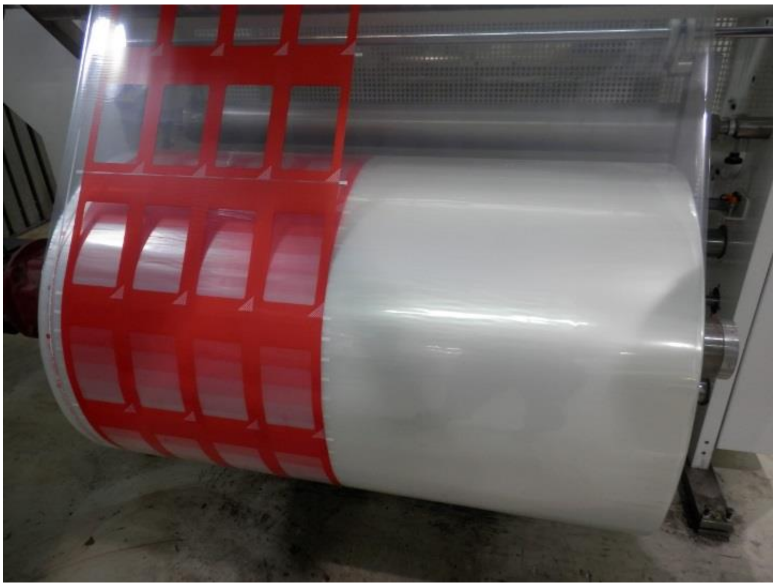

Figure 22. *Surface printed AF film after AF lacquer coating process.*

From printing, the film roll was directed to AF lacquer coating process. Lacquers of two different suppliers were used and the dry contents of lacquers were set as variables. Corona pretreatment was used before the AF coating. Lacquer was added on the surface of film in rotogravure unit of lamination machinery. First, lacquer was spread on rotogravure roller, after which half of the lacquer was transferred directly on the surface of film. Before rewinding the lacquered film went through two ovens to evaporate the solvent. Temperatures of the ovens were 55° C and 65° C.

3.4 Test runs execution

Two lacquer test run cycles were performed in experimental part of this research. Both test run cycles consisted of four AF lacquer test runs. As a result of those test runs AF performance on the surface of PE film was inspected. In all AF lacquer test runs corona treatment was used as a pretreatment before lacquering. The purpose of corona treatment was to improve adhesion between AF lacquer and lacquered film. The corona power used was 26 Wmin/m^2. This corona power was selected based on previous tests and permanent instructions. Objective of these test runs was to study the AF lacquers of two different manufacturers with different solvent dilutions.

The AF lacquers were used with different dilutions so that the dry coating weights of the final coatings varied. The lacquers were diluted with isopropanol (C_3H_8O) [102] [103]. They were applied on the sealing side of the film. The AF lacquers used in test runs were AF lacquer no. 1 and AF lacquer no. 2. In addition to these two, untreated (no AF treatment) film worked as reference sample in the tests.

Performed test points of the first test run cycle are presented in Table 2. In the first test run cycle the performance of two lacquers were inspected during the ageing period of six months. In the first test run cycle, also printed films were tested.

Table 2. *Trial runs to study the functionality of AF lacquers on PE surface (1st test run cycle).*

Test point	Run number	Trial number	AF lacquer	AF dry coating weight (g/m^2)	Dilution ratio (lacquer:diluent)
1	567464	K3451	AF lacquer no. 1	0,028	1:1
2	567465	K3452	AF lacquer no. 1	0,037	2:1
3	567466	K3453	AF lacquer no. 2	0,021	2:1
4	567467	K3454	AF lacquer no. 2	0,031	1:0 (undiluted)
REF	566304	K3437	No AF treatment		

In the second test run cycle, the sample films were fabricated for the contact angle and surface energy tests. These test points are presented in Table 3. In the second test run cycle only clear film samples were fabricated.

Table 3. *Trial runs for the contact angle and surface energy tests (2nd test run cycle).*

Test point	Run number	Trial number	AF lacquer	AF dry coating weight (g/m^2)	Dilution ratio (lacquer:diluent)
1	571938	K3497	AF lacquer no. 1	0,019	1:2
2	571939	K3498	AF lacquer no. 1	0,028	1:1
3	571940	K3499	AF lacquer no. 2	0,021	2:1
4	571942	K3500	AF lacquer no. 2	0,031	1:0 (undiluted)

The AF dry coating weight can be calculated from the dilution ratio when theoretical volume of rotogravure roller and dry content of used lacquer are known. If theoretical volume is 5.6 g/m^2, then real wet coated volume after split is 2.8 g/m^2. Dry coating weight of AF agent can be determined with Equation 10.

$$L * \frac{\frac{TV}{2} * \%}{L+D} \tag{10}$$

where L is lacquer portion, D is diluent portion, TV is theoretical volume and % is percentage value of AF dry content as decimal.

3.5 Laboratory tests execution

All laboratory tests were performed in the R&D laboratory of factory of Bemis Europe. For all samples the tests were performed throughout six-month ageing period. The test period length of six months is based on the fact that all products should have a six-month shelf-life. In other words, AF performance must be maintained at acceptable level at least across this period.

Tests that were performed to film samples of the first test run cycle were AF coldpool test, sealability tests and other tests mentioned in chapter 3.2.6. Tests that were performed to film samples of the second test run cycle were AF coldpool test, and contact angle and surface energy measurements. The measurements were repeated four times throughout the six months of ageing. As an exception, the tests presented in chapter 3.2.6 were performed only once. Measurements were repeated: 1) instantly, 2) after one month of ageing, 3) after three months of ageing and 4) after six months of ageing. The samples were stored in storage conditions of 23 °C temperature and 50 % relative humidity.

4. RESULTS AND DISCUSSION

4.1 Visual observation

After AF lacquer coating process the visual appearance of all film samples appeared to be fine. However, differences were detected in the surface properties of the samples. The film samples coated with AF lacquer no. 2 felt sticky compared to the film samples coated with AF lacquer no. 1. In addition, blocking of reels was detected with AF lacquer no. 2. The reels with AF lacquer no. 1 did not block as much. When the reels with AF lacquer no. 2 were rewound significant amount of static electricity was also observed. Presumably, this was caused by the stickiness of the film. It can be assumed that films coated with AF lacquer no. 2 have a greater amount of AF agent on their surfaces, which concludes stickiness and electricity of the surface. Electric charge is discharged when water is condensed on the surface of film, because water functions as a path for electric charge.

When studying blocking of reels it was detected that printed films blocked more than clear films. Especially in case of white printing ink the sticking was significantly strong. The visual appearance of the films that were aged for three months was changed as the films coated with AF lacquer no. 2 had turned blotchy and, especially, in printed films there were a lot of blotches. In Figure 23, the blotches are presented on the printed film after three months of ageing. Same kind of blotches were detected from the films that had been aged for six months.

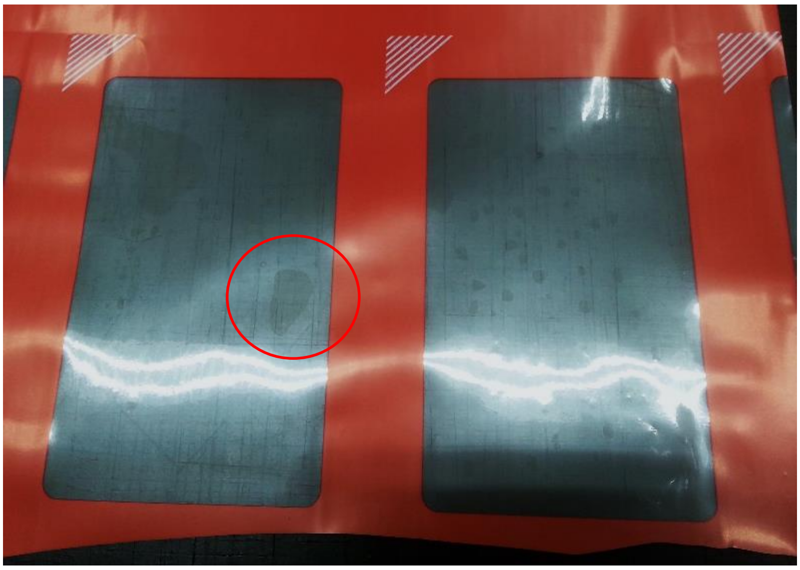

***Figure 23.** Blotches on the printed film after three months of ageing. The film is coated with AF lacquer no. 2.*

4.2 Antifog properties

The results of the AF coldpool tests are presented in this chapter. More detailed information about the trials K3451, K3452, K3453 and K3454 are presented in Table 2. Evaluation of AF performance is following: 0 = Excellent, 1 = Good, 2 = Bad, 3 = Very bad, E = No AF effect.

Table 4 presents results from the AF coldpool test, which was performed for studied films instantly after the AF coating process. These results are further illustrated in Figures 24 and 25. Figure 24 presents the results of clear film samples and Figure 25 the results of printed film samples. It can be seen from the results that AF lacquer no. 2 (Trial numbers K3453 and K3454) provides excellent AF performance after initial tests. Differences between clear and printed films were not detected. In general, AF lacquer no. 1 (Trial numbers K3451 and K3452) showed poorer results than AF lacquer no. 2. However, it can be noticed with AF lacquer no. 1 that the AF dry coating weight has a great effect on the results. In sample K3451 the AF dry coating weight is 0,028 g/m^2 and in sample K3452 it is 0,037 g/m^2. In the initial situation the both samples give same results, but already after four hours in coldpool storage sample K3451 shows better results. The same difference can also be detected for printed film samples.

Table 4. *AF coldpool test results from instant test.*

AF Coldpool test	K3451		K3452		K3453		K3454	
	Clear	**Printed**	**Clear**	**Printed**	**Clear**	**Printed**	**Clear**	**Printed**
1 hour	2	2	2	3	0	0	0	0
4 hours	2	1	2	3	0	1	0	0
1 day	1	0	2	2	0	0	0	0
3 days	1	0	2	2	0	0	0	0
1 week	0	0	2	2	0	0	0	0

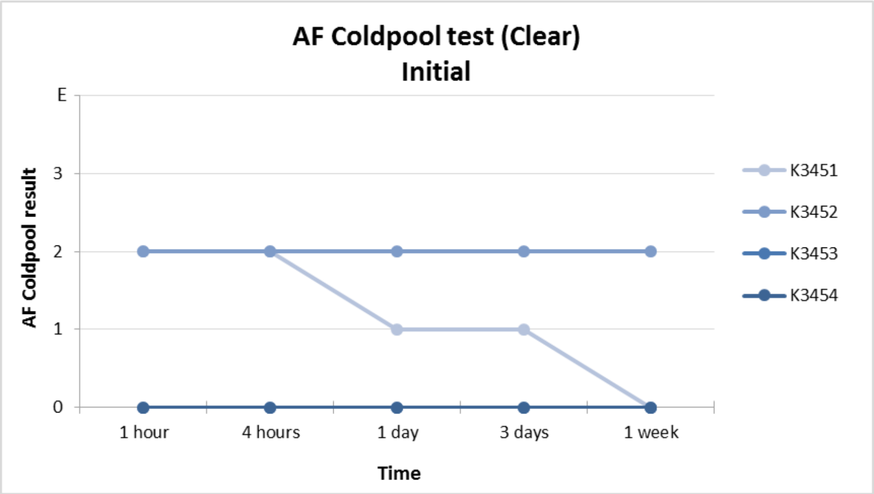

Figure 24. *AF level evaluation from clear film samples instantly after the coating process.*

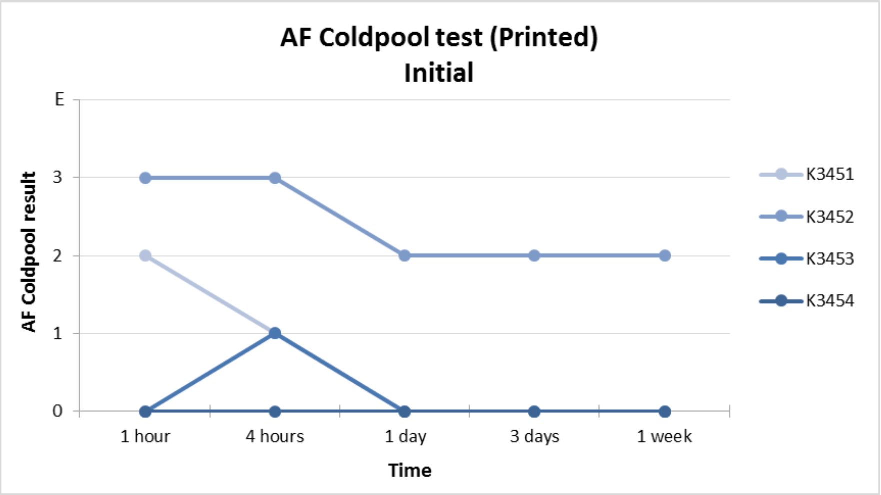

Figure 25. *AF level evaluation from printed film samples instantly after the coating process.*

Results from AF coldpool test performed to film samples that had been aged for one month are presented in Table 5 and in Figures 26 and 27. Again, it can be seen from the results that AF lacquer no. 2 (samples K3453 and K3454) has better AF performance than AF lacquer no. 1 (samples K3451 and K3452). The results of samples K3453 and K3454 are still zero in the case of clear film samples. As for printed film samples, weakening can be detected in the AF performance of samples coated with lacquer no. 2 after one month of ageing. In the case of samples coated with AF lacquer no. 1, K3451 and K3452, AF performances had been weakened significantly from the beginning in both clear and printed film samples. The reduction is probably caused by the transfer of AF agents to the PET side of structure when the film is on reel. The transfer of AF agents was verified with surface energy and contact angle measurements in chapter 4.5. It was found to be the most intense during the first month of ageing.

It was also detected that the tightness of reel affects the transfer of AF agents. The tighter the sample reel was wound the more intense the transfer of AF agents was. In the AF coldpool test, the AF results measured from tightly wound reel were considerably poor than those of measured from looser reel. The AF performances of samples K3453 and K3454 from tighter reel were at the level of one or two in the case of clear films and at the level of zero for loose reel. The results for the films from looser-wound reel are presented in Table 5. Results for printed film samples from looser-wound reel after the ageing of one month were not available in this research. Therefore, all printed film samples were taken from tighter reel and the AF results of them were relatively poor, which needs to be taken into account in considerations.

Table 5. *AF coldpool test results after one month of ageing. *Results are from tight reel.*

AF Coldpool test	K3451		K3452		K3453		K3454	
	Clear	**Printed***	**Clear**	**Printed***	**Clear**	**Printed***	**Clear**	**Printed***
1 hour	3	3	3	3	0	1	0	2
4 hours	3	3	3	3	0	1	0	2
1 day	3	3	3	3	0	1	0	2
3 days	2	2	2	3	0	1	0	2
1 week	2	2	2	2	0	1	0	1

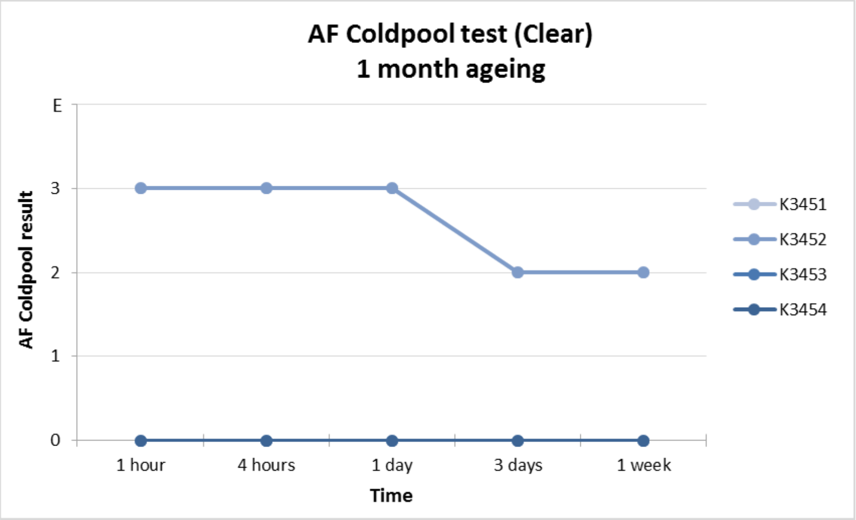

Figure 26. *AF level evaluation from clear film samples after one month of ageing.*

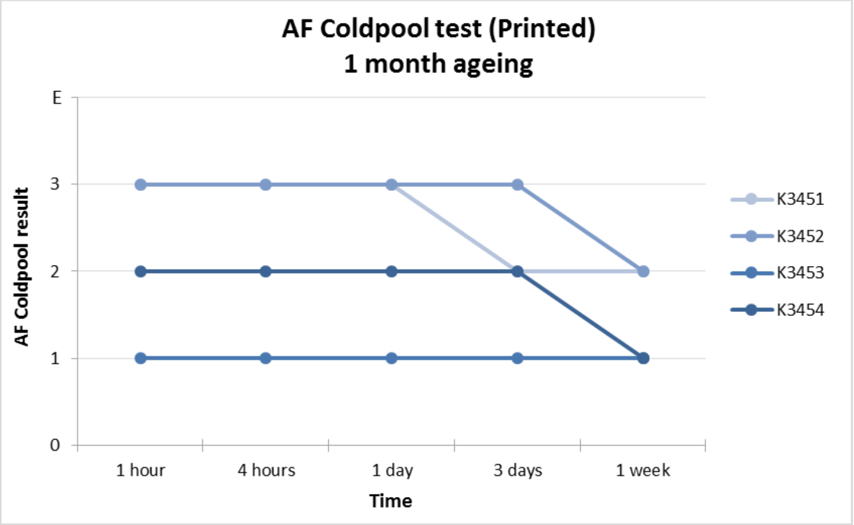

Figure 27. *AF level evaluation from printed film samples after one month of ageing.*

AF test results after three months of ageing are presented in Table 6 and after six months in Table 7. Figures 28 and 29 present the development of AF performance for clear and printed sample films after three months of ageing. In the similar manner, Figures 30 and 31 present the development of AF performance after six months of ageing. When comparing these results with the results after one month of ageing (Table 5), there has not been detectable change in AF performances. Still, AF lacquer no. 1 (samples K3451 and K3452) shows poorer AF performance than AF lacquer no. 2 (samples K3453 and K3454). The only detectable difference is for the printed film samples K3453 and K3454. It can be seen from the results that the AF performance is restored at the same level as in the starting situation when the samples have been aged for three months. The AF performance is also at excellent level still after six months of ageing. The reduced AF performance of the samples aged for one month can be explained by the transfer of AF agents as mentioned before. The tests of film samples aged for three and six months were possible to do with looser-wound reels and, thus, the effect of reel tightness on AF performance was detected. It can be assumed, that if the tests after one month of ageing would have been performed with samples from looser-wound reel, the AF performance of those samples would have been better.

Table 6. *AF coldpool test results after three months of ageing.*

AF Coldpool test	**K3451**		**K3452**		**K3453**		**K3454**	
	Clear	**Printed**	**Clear**	**Printed**	**Clear**	**Printed**	**Clear**	**Printed**
1 hour	3	3	3	3	0	0	0	1
4 hours	3	3	3	3	0	0	0	1
1 day	3	3	3	3	0	0	0	1
3 days	2	3	2	2	0	0	0	0
1 week	2	2	2	2	0	0	0	0

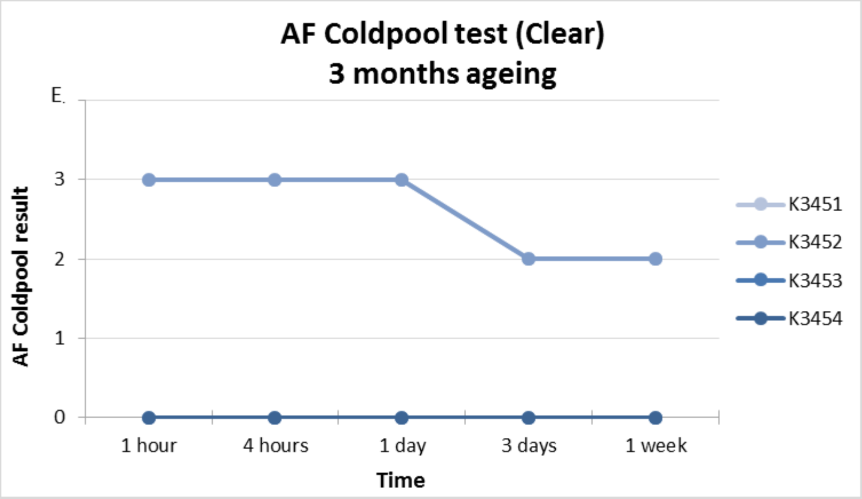

Figure 28. *AF level evaluation from clear film samples after three months of ageing.*

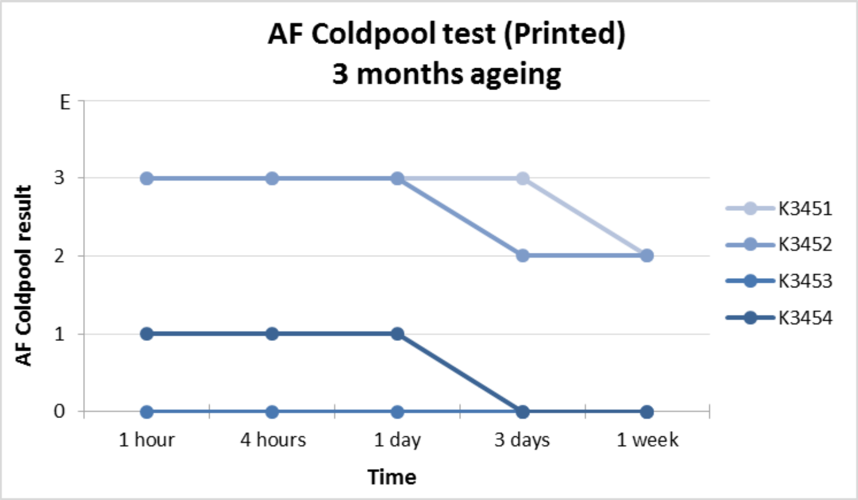

Figure 29. *AF level evaluation from printed film samples after three months of ageing.*

Table 7. *AF coldpool test results after six months of ageing.*

AF	**K3451**		**K3452**		**K3453**		**K3454**	
Coldpool test	**Clear**	**Printed**	**Clear**	**Printed**	**Clear**	**Printed**	**Clear**	**Printed**
1 hour	3	3	3	3	1	0	1	0
4 hours	2	3	3	3	0	0	0	0
1 day	2	3	3	3	0	0	0	0
3 days	2	3	2	3	0	0	0	0
1 week	2	2	2	2	0	0	0	0

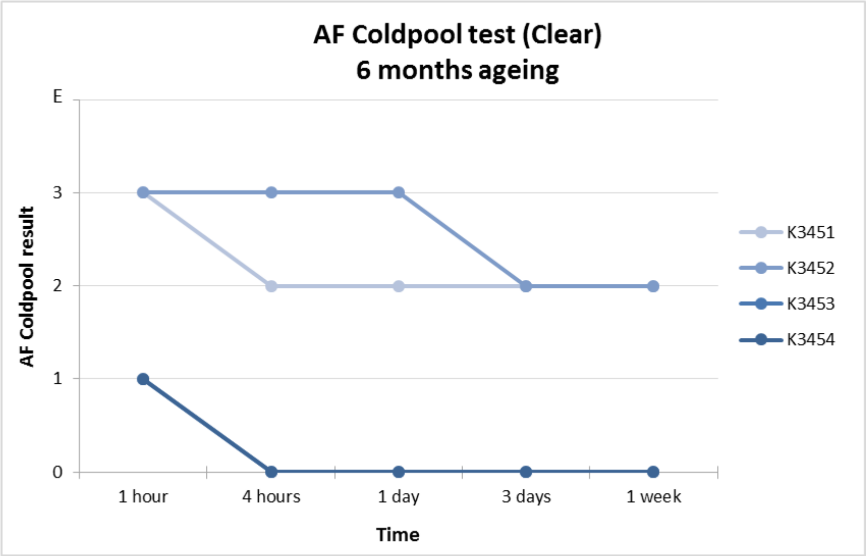

Figure 30. *AF level evaluation from clear film samples after six months of ageing.*

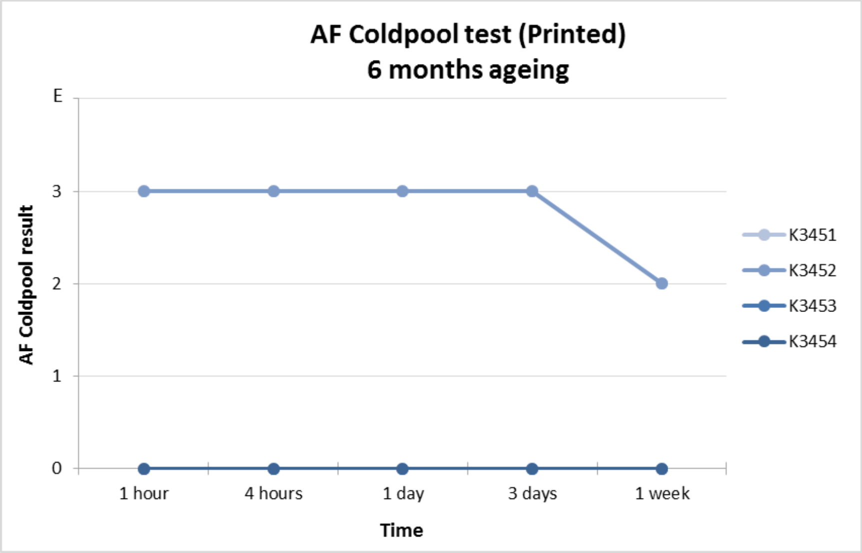

Figure 31. *AF level evaluation from printed film samples after six months of ageing.*

Graphs illustrating the results of AF coldpool tests are presented in Figures 32 and 33. They show the AF performances of lacquer no. 1 and lacquer no. 2 after one hour in +4 °C coldpool storage / six months of ageing. The optimal goal is that the AF performance activates on the surface of film as soon as possible after water has condensed as water droplets on the surface of film. For this reason, the first hour is an important benchmark in AF coldpool test. The dotted line presented in Figures 32 and 33 illustrates acceptance criteria. The AF results 0-2 are considered as acceptable AF performance, whereas the results 3 and E typically lead to further actions due to the poor AF performance. The upper curve presented in Figure 32 represents both clear film samples coated with AF lacquer no. 1 (K3451 and K3452), whereas the lower curve represents the film samples coated with AF lacquer no. 2. The graph shows that there is a great difference between these two lacquers. AF lacquer no. 2 (K3453 and K3454) achieves the required AF performance across the whole six-month shelf life of the product. All the AF measurements with this lacquer gave the result 0 or 1 in coldpool environment. For the film samples coated with AF lacquer no. 1 (K3451 and K3452), the results were a lot poorer. After one hour in coldpool, the results of AF test were at the level of 2 or 3.

When comparing the results presented in Figures 32 and 33 with the acceptance level, it seems that the results of samples K3451 and K3452 lead to further actions due to poor AF performance. However, when inspecting the results in Table 7, it can be stated that the AF performance is significantly improved after one week in coldpool. In one week, the value of AF test has decreased from 3 to 2 in the case of both clear and printed film samples. Therefore, also AF lacquer no. 1 can retain the AF performance at acceptable level. It can be stated that the AF performance of AF lacquer no. 1 activates remarkably slower than that of the AF lacquer no. 2.

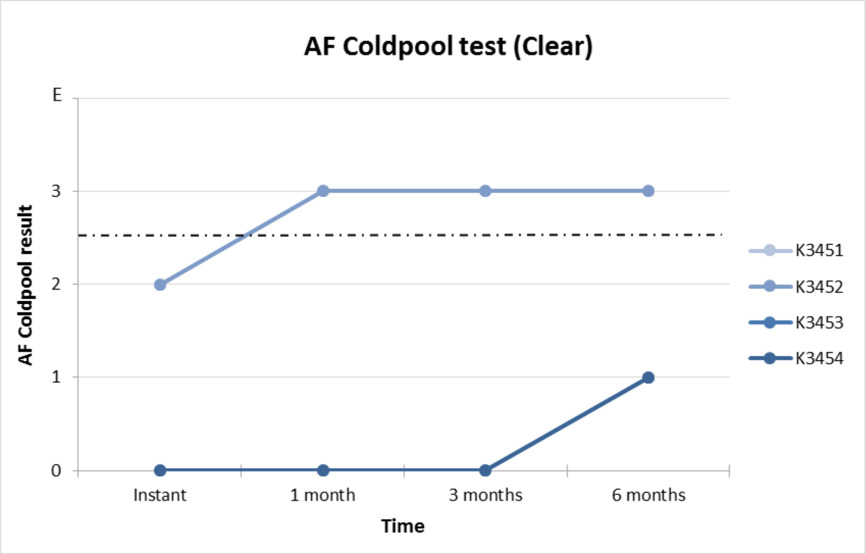

Figure 32. *AF coldpool test results after one hour in coldpool storage / six months ageing period. Results are for clear film samples.*

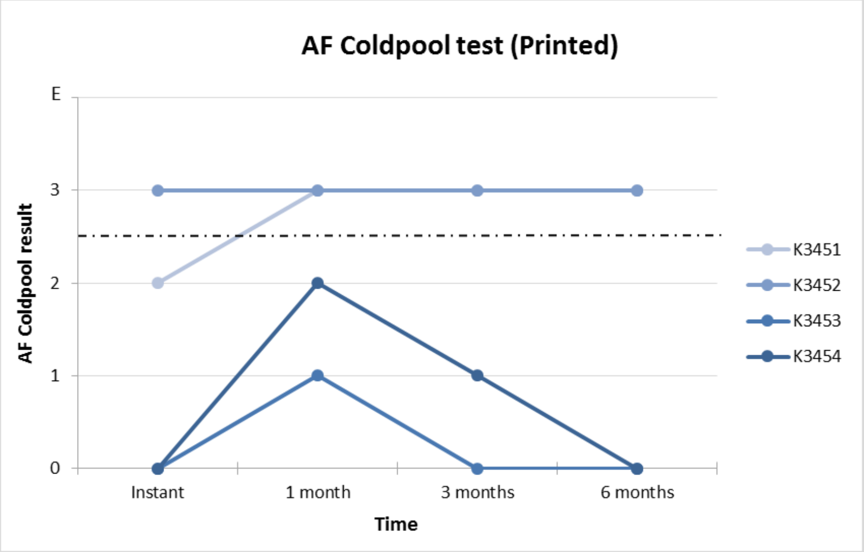

Figure 33. *AF coldpool test results after one hour in coldpool storage / six months ageing period. Results are for printed film samples.*

As was noticed in instant tests (Table 4), dilution ratio and consequently AF dry coating weight have an influence on AF performance. This influence can be detected especially in film samples coated with AF lacquer no. 1. Still, after six months of ageing sample K3451 has a bit better AF coldpool test result comparing to sample K3452. In sample K3451, AF dry coating weight is 0,028 g/m^2 and in sample K3452 it is 0,037 g/m^2.

In summary, it can be stated that changes in the AF performance of AF lacquer no. 1 are the most intense during the first month of ageing when it reduces significantly. After this the AF performance maintains almost unchangeable until the end of the ageing period of six months. AF lacquer no. 2 maintains excellent AF performance for PE surfaces throughout the whole six-month shelf life of the product. With it there are no detectable differences between the behavior of clear and printed films.

4.3 Sealability and re-tack properties

In this chapter, sealability and re-tack properties of the AF lacquer coated film samples are discussed. Sealability properties of the samples were studied across the six-month ageing period with sealing curve, peel strength and re-tack tests. The results of all performed tests are presented in Tables 16-43 of Appendix A: The sealability and re-tack test results obtained for the samples across the six-month ageing period. Figures 34-57 present the graphs drawn based on the results of Tables 16-43. More detailed information about the film samples being studied is presented in Table 2.

When observing Figures 34-41, it can be detected that there is no significant difference in the seal strengths of the samples utilizing the studied lacquers. However, when observing Figures 34-37, it can be noticed that there is a detectable difference between lacquered film samples and unlacquered reference film. The sealing curve of reference film rises higher than the sealing curves of lacquered films. In the temperature range from 110 to 200 °C, the seal strength of unlacquered reference film is just above 500 N/m whereas the seal strength of lacquered films vary between 300 N/m and 500 N/m. Differences between clear and printed film samples utilizing AF lacquer could not be detected.

After three months of ageing, the differences in seal strengths between lacquered and unlacquered films decreased. When observing Figures 38-41, it can be seen that the sealing curve of unlacquered reference film is still a bit above the level of 500 N/m in temperature range from 110 to 200 °C. However, now the sealing curves of AF lacquer coated film samples were almost at the same level. It seems that the rise of seal strength correlates with the weakening of the AF performance.

In sealing curve test, the seal areas of film samples were clean-cut and seals opened correctly throughout the whole six-month ageing period. After one month of ageing, in the case of some occasional AF lacquer coated film samples, wrinkles were detected in seals in the temperature range of 180-200 °C. It seemed like the seal area would have been shrunk in TD direction by the influence of temperature.

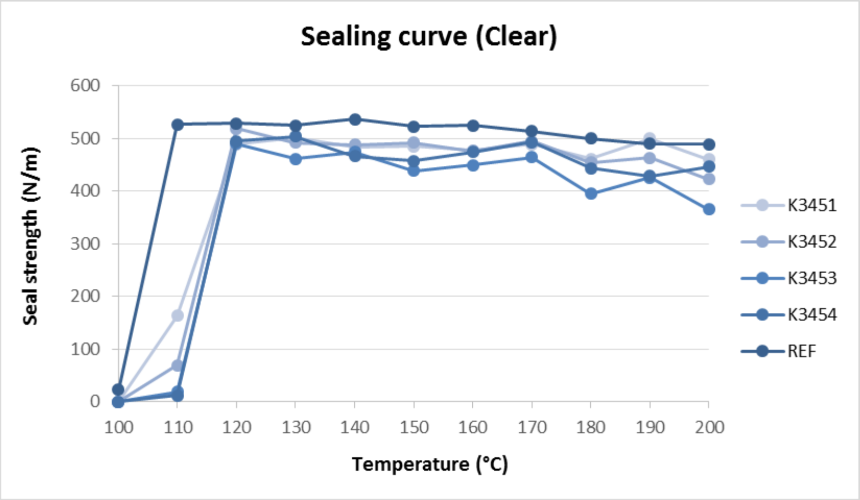

Figure 34. *Sealing curves measured from the clear samples instantly after the coating process.*

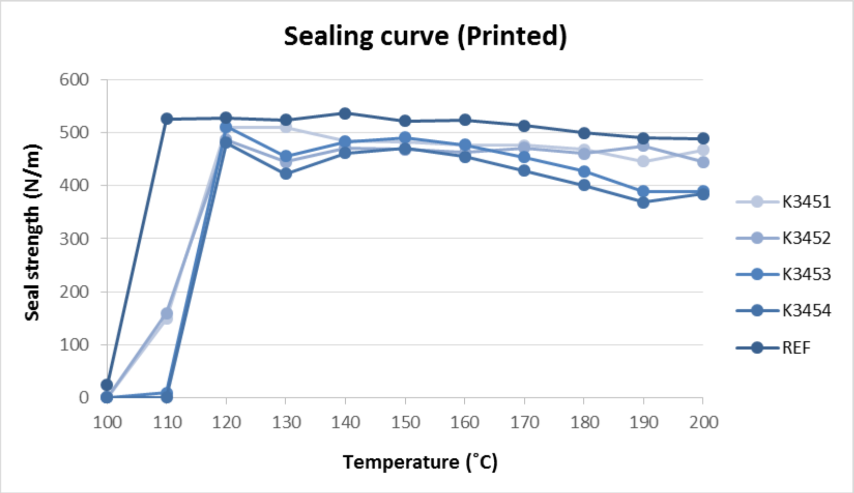

Figure 35. *Sealing curves measured from the printed samples instantly after the coating process.*

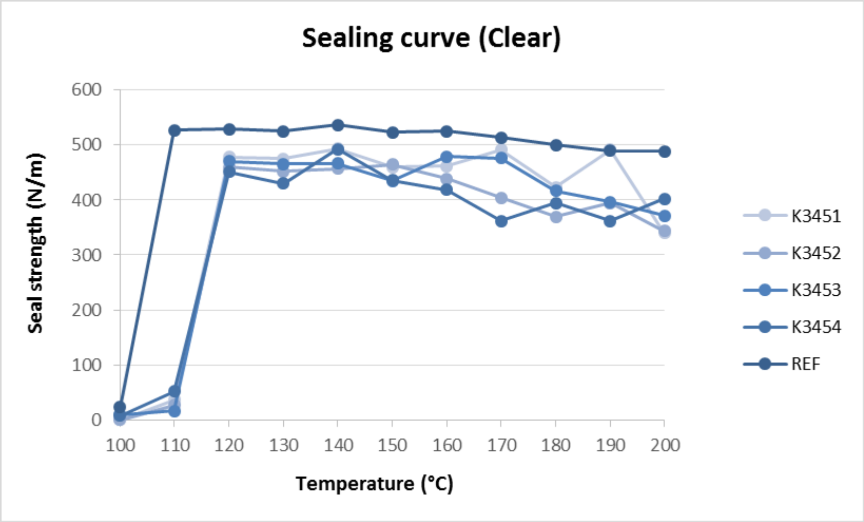

Figure 36. *Sealing curves measured from the clear samples after one month of ageing.*

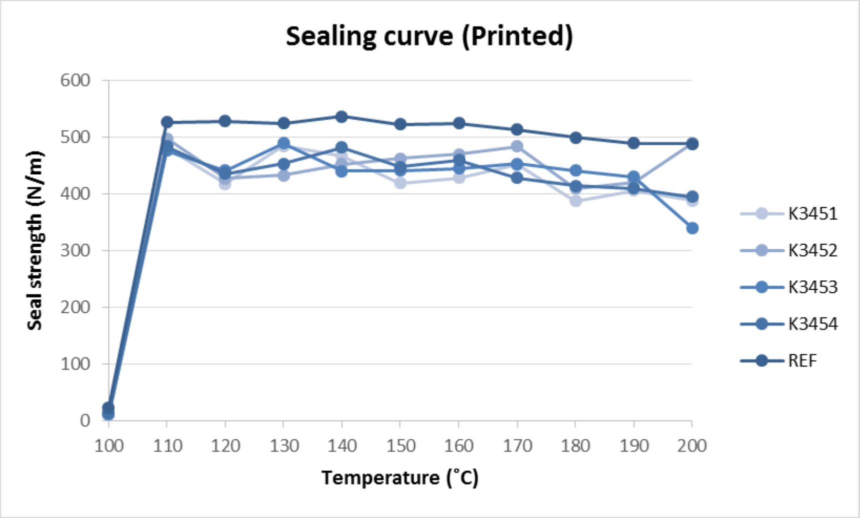

Figure 37. *Sealing curves measured from the printed samples after one month of ageing.*

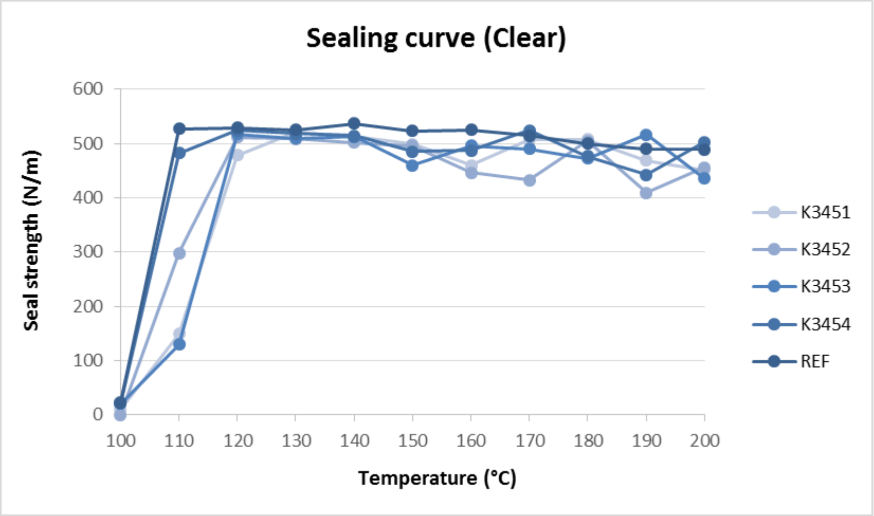

Figure 38. *Sealing curves measured from the clear samples after three months of ageing.*

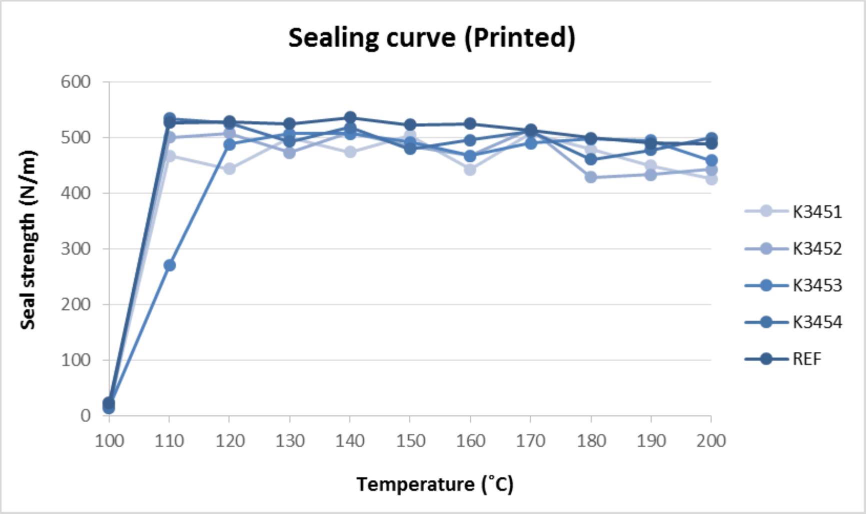

Figure 39. *Sealing curves measured from the printed samples after three months of ageing.*

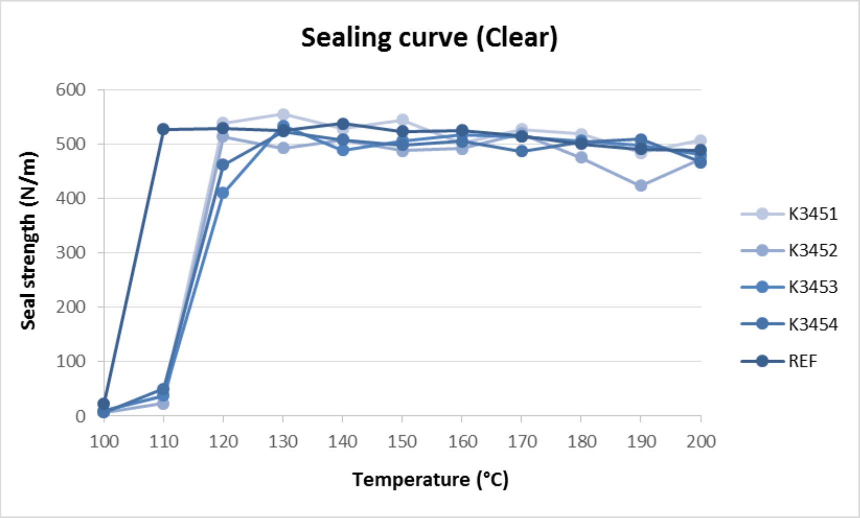

Figure 40. *Sealing curves measured from the clear samples after six months of ageing.*

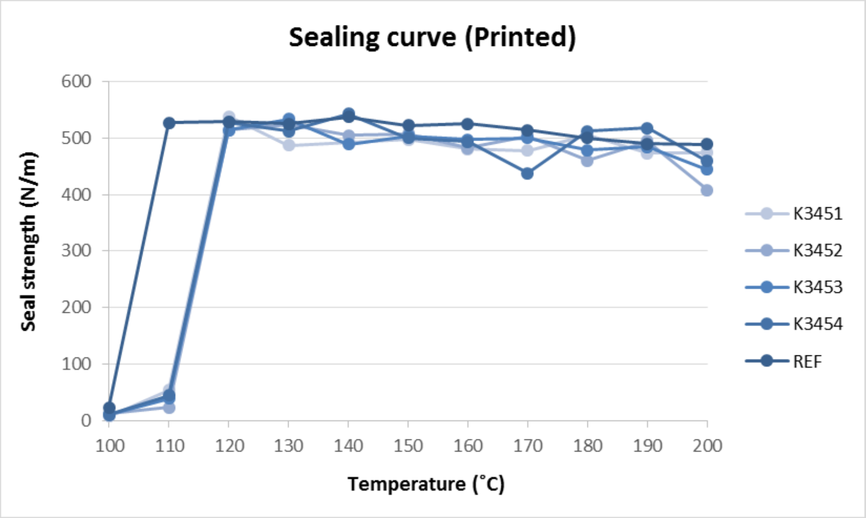

Figure 41. *Sealing curves measured from the printed samples after six months of ageing.*

The results of sealing curve tests also show that lacquering influences sealing temperature. The AF lacquer applied on the sealing surface of the film increases the seal initiation temperature (SIT) of the structure. According to the graphs presented in Figures 34-41, the coated film requires about 20 °C higher sealing temperature than the uncoated film.

RC-peel strengths were determined for each film sample across the six-month ageing period: immediately after AF coating, after one month, after three months and after six months of ageing. Peel strengths were examined from both clear and printed films by using the sealing temperatures of 150 °C and 160 °C. The results from these tests are presented in Tables 24-27 of Appendix A. The results are also shown in the graphs of Figures 34-41. RC-peel strength illustrates the force that is needed to open the seal for the first time in the test cycle of ten openings.

By observing peel strengths, the same result can be detected as in the case of sealing curve test: Unlacquered reference film has greater seal strength than lacquered film in both sealing temperatures. However, the differences are not very big. In addition, differences between the used AF lacquers are not remarkable regarding the seal strength results. During the ageing period of six months, peel strengths did not show any signs of weakening. On the contrary, peel strengths even increased in the case of film samples aged for six months compared to the initial test results. Test results for the film samples coated with AF lacquer no. 1 (K3451 and K3452) are somewhat the same regardless of the sealing temperature. Small differences can be detected between clear and printed film samples. The clear film sample K3451 shows greater average peel strengths than the printed film samples during the six-month ageing period in both sealing temperatures. In the case of film sample K3452, the situation is the opposite. The printed film samples show greater peel strengths than clear films.

In the instant tests, clear film samples coated with AF lacquer no. 2 (K3453 and K3454) showed higher peel strengths with the sealing temperature of 150 °C than with 160 °C. As the clear film samples aged, the situation become the opposite: higher peel strength were observed with the sealing temperature of 160 °C than with 150 °C. In the case of printed film samples, a greater force is needed to open up the seals with the sealing temperature of 160 °C than with 150 °C. On average, when comparing clear and printed film samples, clear films provide greater peel strengths throughout the whole six-month ageing period in both sealing temperatures.

Re-tack properties of the samples were determined from sealed film samples by opening and closing the seals for ten times. Measured re-tack forces during the six-month ageing period are presented in Figures 42-57 and in Tables 28-43 of Appendix A. The tests were performed in parallel with the peel strength tests by using the same sealing temperatures.

From all re-tack test results it can be detected that re-tack properties are slightly better with the sealing temperature of 150 °C than with 160 °C. The re-tack properties of unlacquered reference film were better than the re-tack properties of lacquered film samples in the case of 150 °C sealing temperature. However, in the sealing temperature of 160 °C the re-tack properties of reference film were poorer.

In Figures 42-45, the re-tack test results of clear and printed film samples instantly after the coating process are presented. The results show that re-tack properties of clear film samples are better than the re-tack properties of printed films. There are also some differences between the two studied lacquers. It can be seen from Figure 42 that the samples K3453 and K3454 have better re-tack properties than the samples K3451 and K3452. Regarding Figures 43-45, there are no big differences between the re-tack forces of the samples.

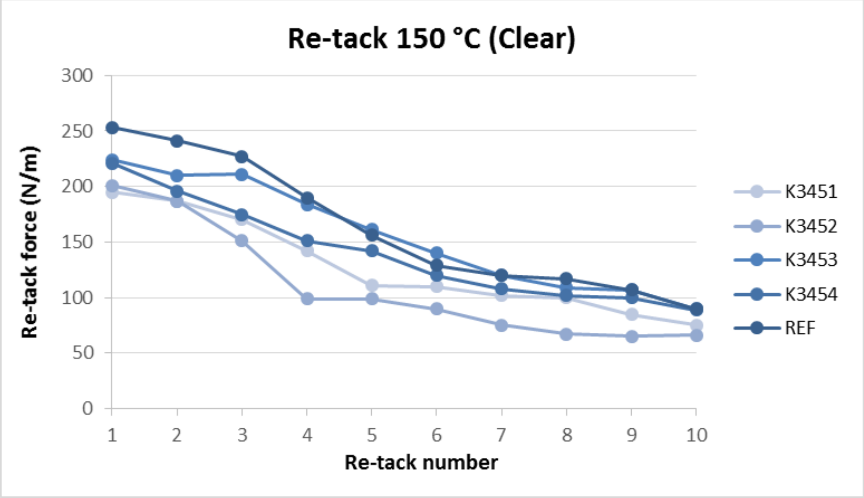

Figure 42. *Re-tack forces x 10 measured from the clear samples instantly after the coating process (sealing temp. 150 °C).*

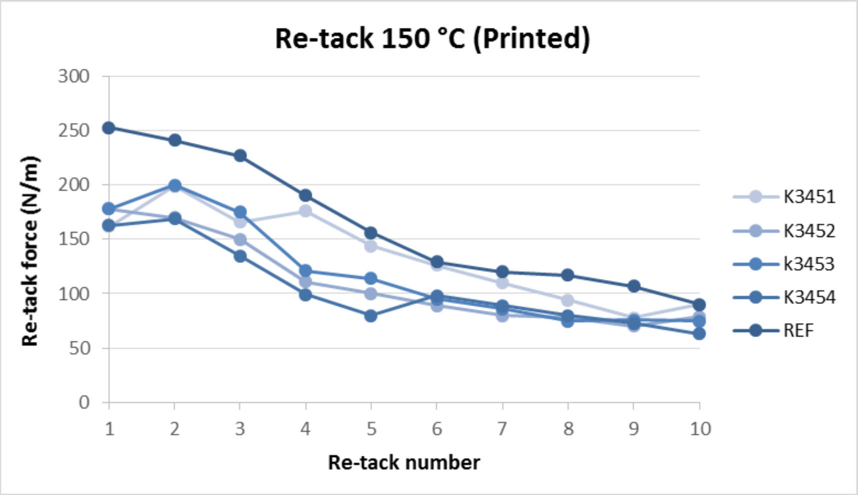

Figure 43. *Re-tack forces x 10 measured from the printed samples instantly after the coating process (sealing temp. 150 °C).*

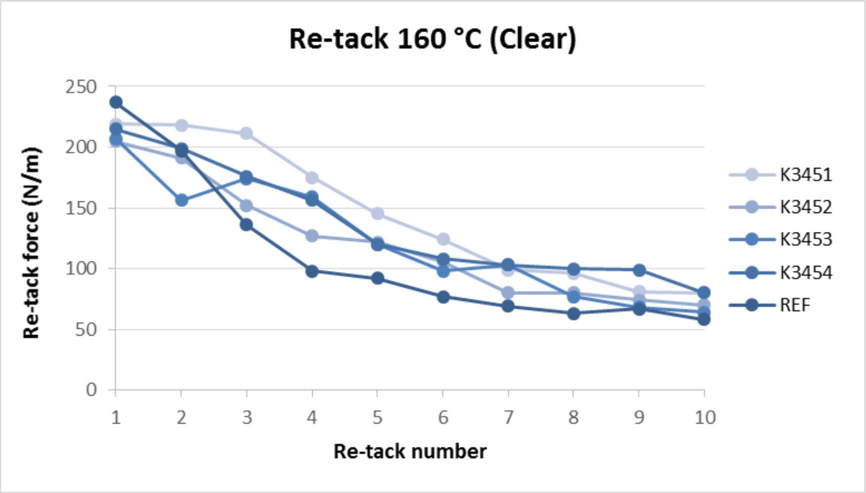

Figure 44. *Re-tack forces x 10 measured from the clear samples instantly after the coating process (sealing temp. 160 °C).*

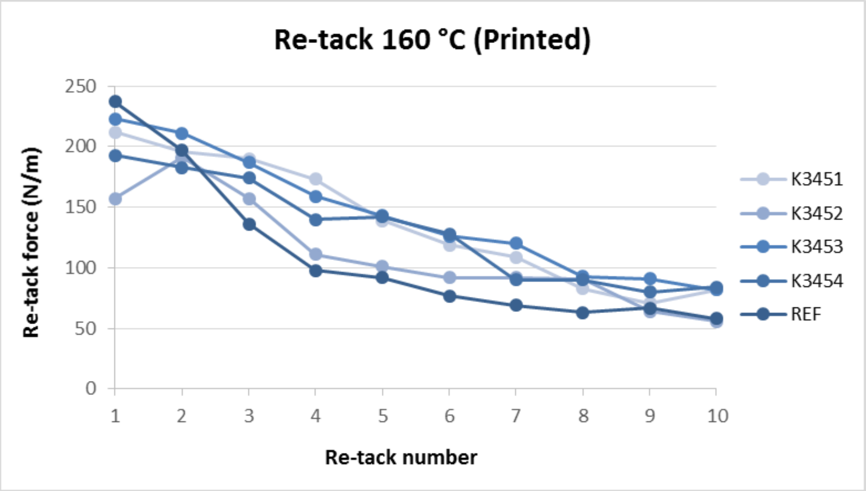

Figure 45. *Re-tack forces x 10 measured from the printed samples instantly after the coating process (sealing temp. 160 °C).*

Results illustrating the re-tack properties of film samples aged for one month are presented in Figures 46-49. There were still some notable differences between the results of clear and printed film samples. The clear film sample coated with AF lacquer no. 2, K3453, still had the best re-tack property. However, sample K3454 coated with the same lacquer had the weakest re-tack results. The clear film samples coated with AF lacquer no. 1, K3451 and K3452, had the same kind of test results as the reference film in the sealing temperature of 150 °C. The printed film samples sealed in the same temperature had poorer re-tack properties. In the sealing temperature of 160 °C (Figures 48 and 49) there were no detectable differences between the studied lacquers.

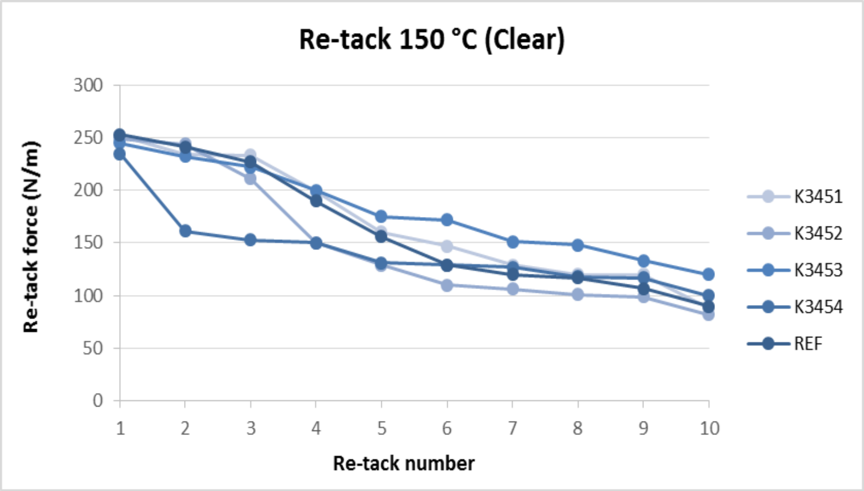

Figure 46. *Re-tack forces x 10 measured from the clear samples after one month of ageing (sealing temp. 150 °C).*

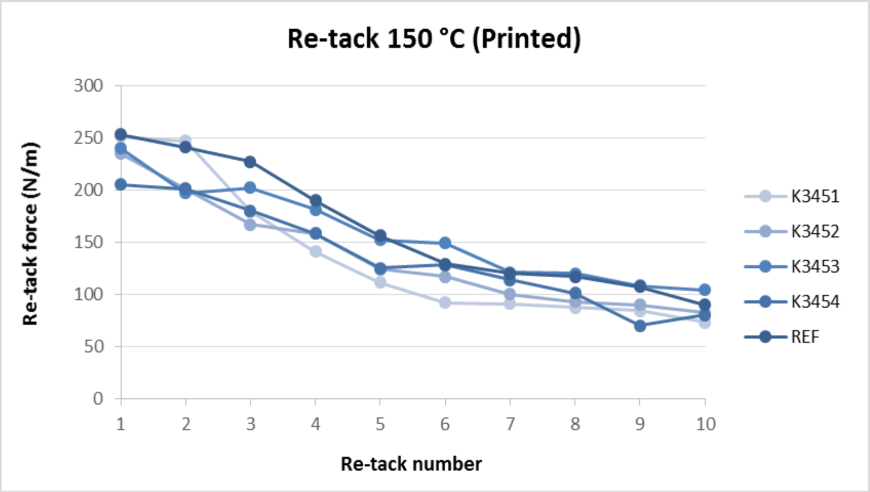

Figure 47. *Re-tack forces x 10 measured from the printed samples after one month of ageing (sealing temp. 150 °C).*

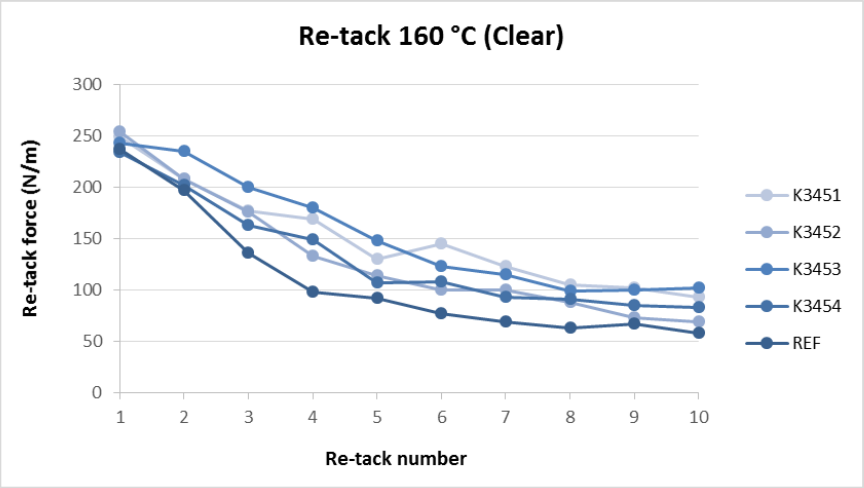

Figure 48. *Re-tack forces x 10 measured from the clear samples after one month of ageing (sealing temp. 160 °C).*

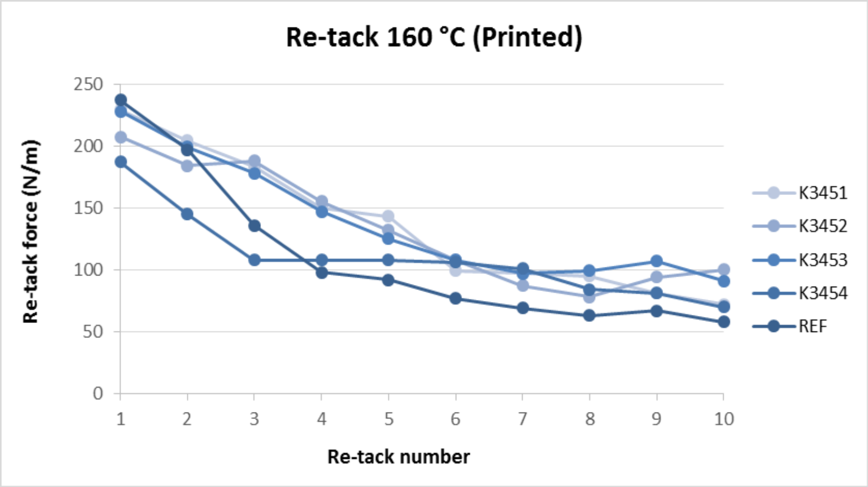

Figure 49. *Re-tack forces x 10 measured from the printed samples after one month of ageing (sealing temp. 160 °C).*

In Figures 50-57, the re-tack results of film samples aged for three and six months are presented. The results of all film samples were somewhat at the same level after three months of ageing. Still, the film sample K3453 showed slightly better test results than the other films. The re-tack properties of clear film samples were better compared to those of printed films.

When observing the results of clear film samples aged for six months (Figures 54 and 56), it can be detected that the film samples coated with AF lacquer no. 2 (K3453 and K3454) had better re-tack properties in comparison with the film samples coated with AF lacquer no. 1 (K3451 and K3452). In the case of printed film samples there were no considerable differences. Based on these results, it can be stated that there is no considerable weakening in the re-tack properties of the studied film samples during the ageing period of six months.

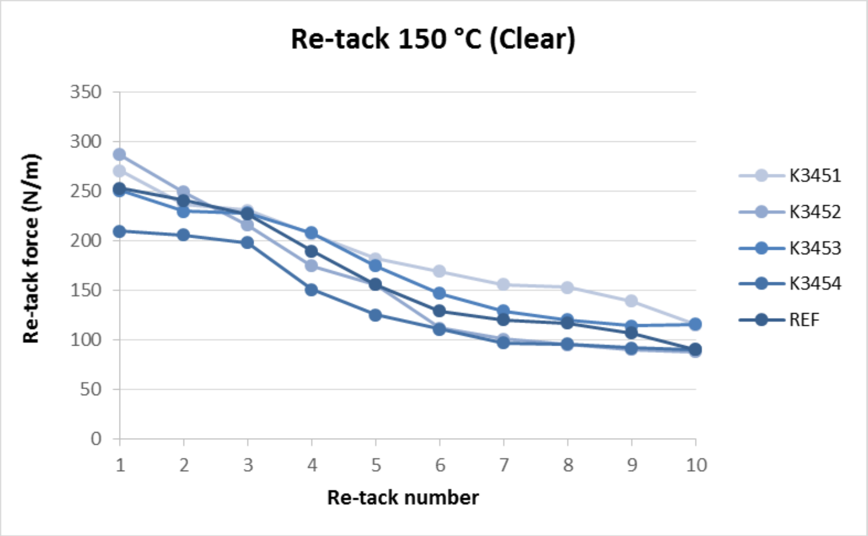

Figure 50. *Re-tack forces x 10 measured from the clear samples after three months of ageing (sealing temp. 150 °C).*

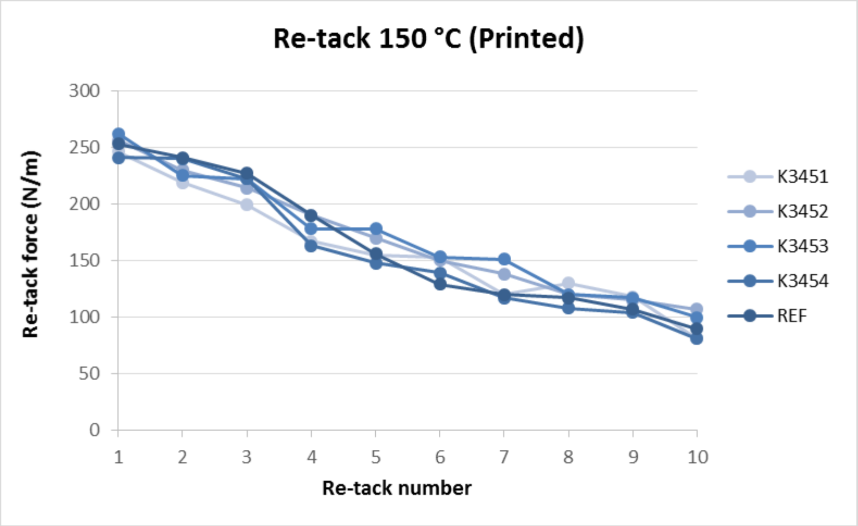

Figure 51. *Re-tack forces x 10 measured from the printed samples after three months of ageing (sealing temp. 150 °C).*

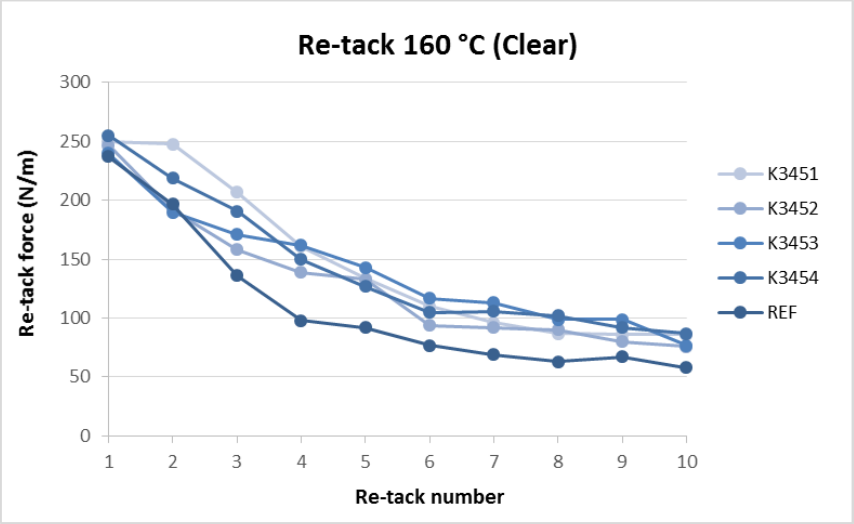

Figure 52. *Re-tack forces x 10 measured from the clear samples after three months of ageing (sealing temp. 160 °C).*

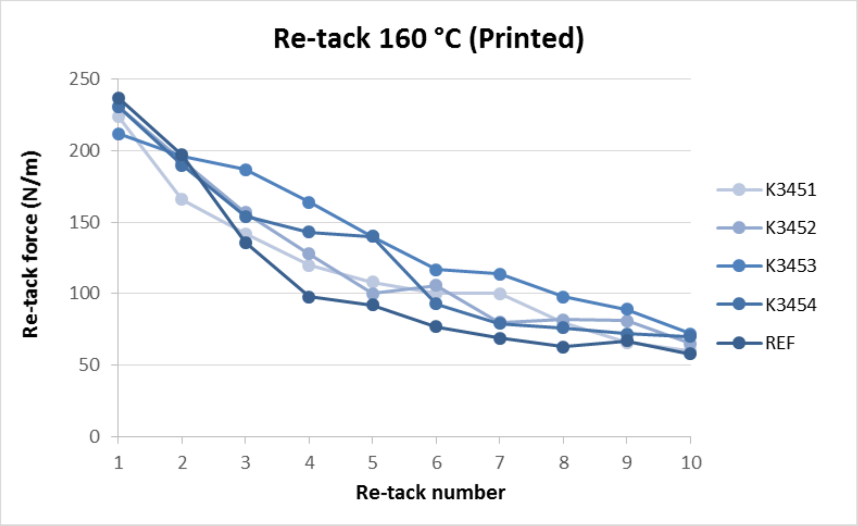

Figure 53. *Re-tack forces x 10 measured from the printed samples after three months of ageing (sealing temp. 160 °C).*

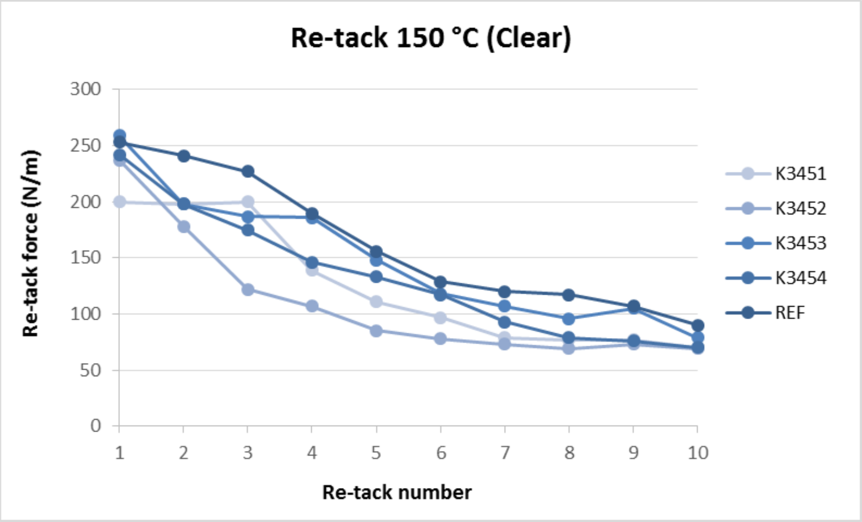

Figure 54. *Re-tack forces x 10 measured from the clear samples after six months of ageing (sealing temp. 150 °C).*

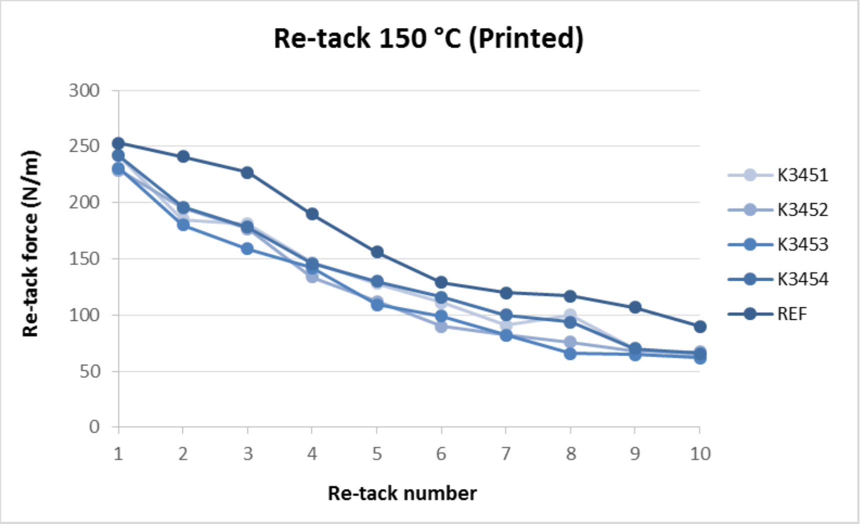

Figure 55. *Re-tack forces x 10 measured from the printed samples after six months of ageing (sealing temp. 150 °C).*

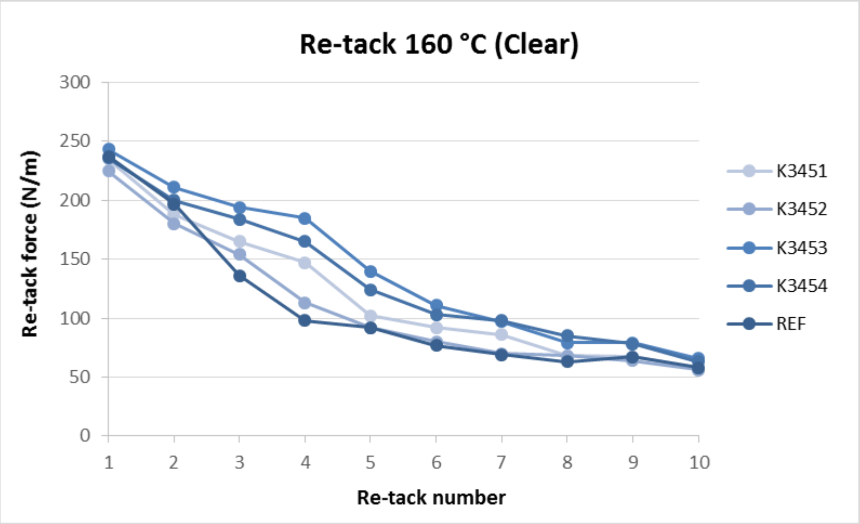

Figure 56. *Re-tack forces x 10 measured from the clear samples after six months of ageing (sealing temp. 160 °C).*

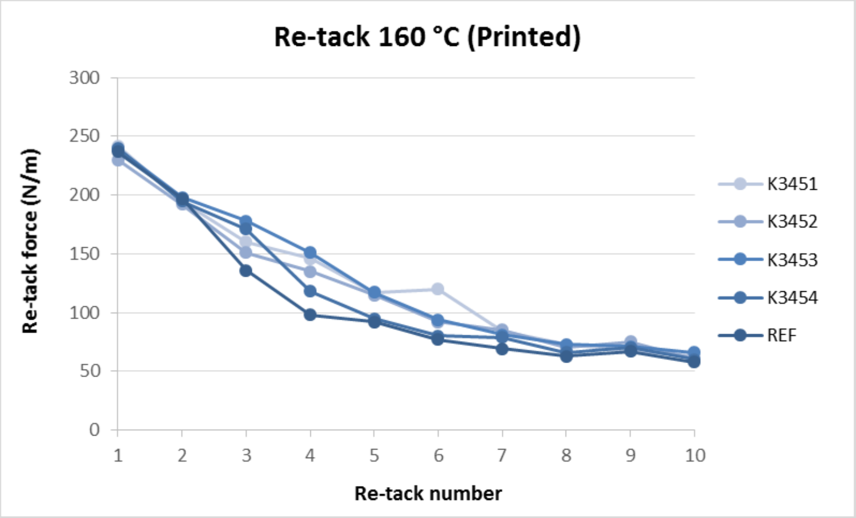

Figure 57. *Re-tack forces x 10 measured from the printed samples after six months of ageing (sealing temp. 160 °C).*

In conclusion, sealability and re-tack properties of all film samples were at acceptable level for the whole research period of six months. Regarding sealability considerable differences between studied lacquers could not be detected. Printing had no significant influence on the test results. However, re-tack test showed that the sealing temperature has pretty much significance. The re-tack properties were better in the film samples sealed in the temperature of 150 °C. It was also detected that dilution ratio of AF lacquer no. 2 influences the re-tack property. The re-tack force is greater in the diluted version than in the undiluted. Still, all the results measured were at acceptable level after the six-month ageing period. Sealing curve tests showed that AF lacquering affects the sealability of films. The AF lacquer applied on the sealing surface of the film increases the seal initiation temperature by approximately 20 °C comparing to uncoated film.

4.4 Other properties

Instantly after the AF lacquer coating process, the film samples were exposed to residual solvent, friction and optical performance tests. The results from these tests are discussed in this chapter.

The results of the residual solvent test are presented in Table 8. “Totals” illustrate the total amount of solvent residues in the film and “Uncalib. totals” illustrate the total amount of unknown compounds in the film. The tests were performed for clear film samples. In the AF lacquered films the total amount of residual solvent must be less than 10 mg/m^2. It can be seen from the results that all the measured values were at acceptable level. It was observed that the film sample coated with AF lacquer no. 2 (K3453) had significantly larger residual solvent amount comparing to the other film samples tested.

Table 8. *The residual solvent test results measured for clear film samples.*

Sample	Totals (mg)	Uncalib. totals (mg)
K3451	0,2	0,2
K3452	0,4	0,2
K3453	0,7	0,2
K3454	0,2	0,2

Table 9 gathers together the friction measurement of all film samples. The “in-in” -columns of Table 9 illustrate the test in which the film sample was set against itself so that its sealable surfaces were against each other. The “in-out” -columns illustrate the test in which the sealable surface was set against the PET surface. In friction measurements, the goal was to study blocking of films. AF lacquer coated films tend to block when the film is wound as reel. As mentioned before, the film samples coated with AF lacquer no. 2 were stickier and blocked more than the film samples coated with AF lacquer no. 1.

As described the “in-out” scenario was considered to illustrate the situation in which films tend to block while being on reel. It can be seen from the results that both static and dynamic friction value were greater in film samples K3453 and K3454 than in film samples K3451 and K3452. The friction values of these samples were greater also in the test where the inner surfaces were set against each other. The “in-in” -test friction values were found to be greater in the printed film samples than in the clear film ones. Regarding the "in-out" -test, the same was observed. When the test results of lacquered film samples are compared with the results of unlacquered reference film, it could be detected that AF lacquer no. 1 decreases both static and dynamic friction value, but AF lacquer no. 2 increases them. Supposedly this results from the different composition of AF lacquers.

Table 9. *The results of friction measurements.*

Sample	**in-in static**		**in-in dynamic**		**in-out static**		**in-out dynamic**	
	Clear	**Printed**	**Clear**	**Printed**	**Clear**	**Printed**	**Clear**	**Printed**
K3451	0,62	0,63	0,35	0,40	0,53	0,59	0,32	0,42
K3452	0,74	0,65	0,45	0,36	0,56	0,67	0,30	0,47
K3453	1,09	0,71	1,11	0,63	0,69	0,70	0,64	0,54
K3454	0,81	0,88	0,75	0,76	0,75	0,69	0,71	0,44
REF	0,87	-	0,64	-	0,69	-	0,60	-

Test results of haze and gloss measurement are presented in Table 10. The tests were performed only for clear film samples. The results show that there are no detectable differences between the haziness of film samples. The weakest transparencies were measured for the film samples in which AF coating contained more isopropanol (K3451 and K3453) in comparison with the less diluted version of same AF lacquer. The transparencies of all lacquered film samples were better than the transparency of unlacquered reference film.

Gloss was measured from both sides of the film samples. A significant increase in gloss was detected on the PE side of the film when compared to reference film. It can also be noted that AF lacquer no. 2 increased the gloss more than AF lacquer no. 1. The effect of dilution on gloss was the same as in the haze tests: the more diluted lacquer the glossier the test film was.

Table 10. *Optical test results of film samples.*

Sample	**Haze (%)**	**Closs 60° (GU)** (PE side)	**Closs 60° (GU)** (PET side)
K3451	21,0	76,9	92,5
K3452	20,3	73,0	92,0
K3453	21,1	88,5	91,0
K3454	20,9	77,6	89,9
REF	23,3	56,7	88,4

4.5 Contact angle and surface energy

In this chapter, contact angle and surface energy test results of the AF lacquer coated film samples are discussed. In these tests the film samples of second test run cycle were used. More detailed information of these samples is presented in Table 3 of Chapter 3.4. In these tests only non-printed film samples were used. AF properties were also determined from these film samples. The results achieved for the samples from contact angle and surface energy measurements were compared to those results got from AF coldpool tests.

Table 11 and Figure 58 present the results of contact angle measurements which were performed on PE side of the films throughout the six-month ageing period. The corresponding surface energies are presented in Table 12 and Figure 59. It can be seen from Figure 58 that the contact angles of film samples K3499 and K3500 were approximately 60° for the whole six months. These film samples were coated with AF lacquer no. 2. In the case of film samples K3497 and K3498 a clear change during the first ageing month could be detected. In the starting situation, the contact angle of these samples was about 20°, but after one month of ageing it was about 60°. The same kind of observations can also be made from the surface energy results of Figure 59. In the starting situation the surface energies of samples K3497 and K3498 were greater, but after one month they decreased at the same level with samples K3499 and K3500. When comparing the contact angle and surface energy results of studied film samples with the results of reference film a clear difference can be detected. It can be stated that the AF coating on the surface of PE clearly increases the surface energy of film and, consequently, the contact angles are significantly decreased.

Table 11. *Contact angle measurements from PE side of the films throughout the six months ageing period.*

	Contact angle (°)				
Time	**K3497**	**K3498**	**K3499**	**K3500**	**REF**
Initial	22,5	21,5	60,2	59,6	133,8
1 month	61,7	64,1	64,9	63,8	133,8
3 months	69,7	69,1	63,8	63,8	133,8
6 months	68,4	68,2	62,6	63,5	133,8

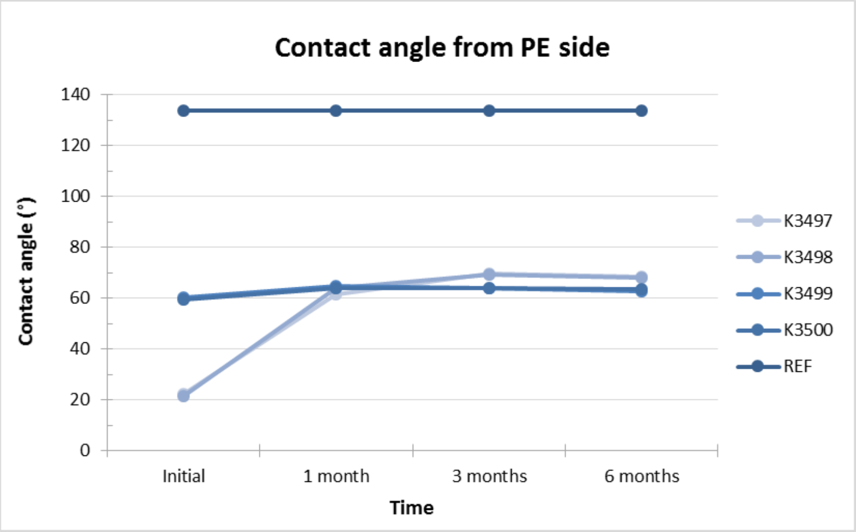

Figure 58. *Contact angles from PE side of the films throughout the six months ageing period.*

Table 12. *Surface energy measurements from PE side of the films throughout the six months ageing period.*

	Surface energy (mJ/m^2)				
Time	**K3497**	**K3498**	**K3499**	**K3500**	**REF**
Initial	56,9	57,3	43,3	43,5	16,6
1 month	42,7	41,9	41,6	42,0	16,6
3 months	39,8	40,1	42,0	42,0	16,6
6 months	40,3	40,4	42,4	42,1	16,6

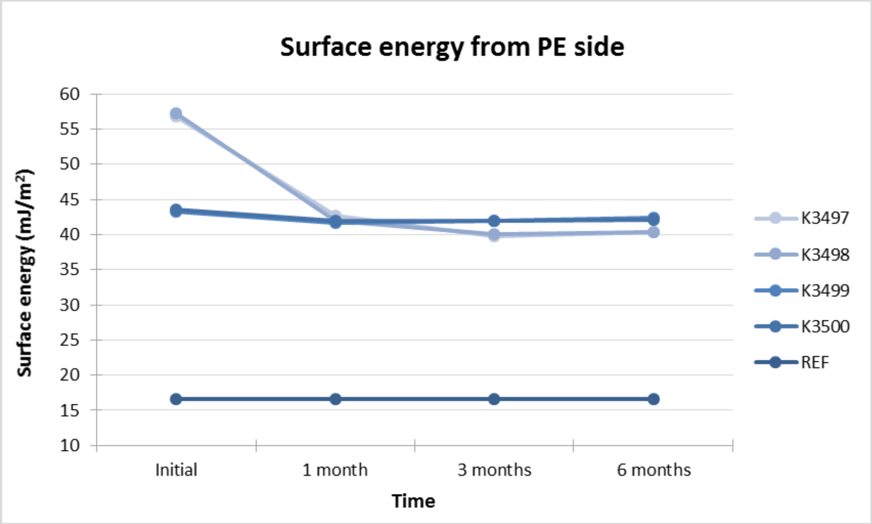

Figure 59. *Surface energy results from PE side of the film throughout the six months ageing period.*

The test results from contact angle measurements performed on PET side of the film samples are presented in Table 13 and Figure 60. The corresponding surface energy results are presented in Table 14 and Figure 61. There are still no considerable changes in the contact angles and surface energies of film samples K3499 and K3500 during six months. The results of these samples were at the same level with the results of reference film. This was also hoped-for, because there was not any processing made to the PET side of the film that should change the properties of PET surface. In the case of samples K3497 and K3498 detectable changes occurred. The contact angles of PET side of these films decreased during the first month after which the results remained almost constant. Correspondingly, the surface energies increased as can be seen from Figure 61.

On the PET side of the film samples K3497 and K3498 the occurring changes were the opposite comparing to the PE side. This can be explained by the transferring of AF lacquer from the PE side to PET side of the film. The transfer process is the most intense during the first month of ageing. As mentioned before, the tightness of film reel affects the intensity of transfer. In addition, PET has naturally higher surface energy than PE, which attracts the AF lacquer. The same kind of transfer could not be detected with the film samples coated with AF lacquer no. 2. Even though AF lacquer no. 2 caused blocking, the transfer with it was not as intense as with AF lacquer no. 1. It is evident that AF lacquer no. 2 better adheres on the film surface than AF lacquer no. 1. The difference in the ability to adhere can be caused by different binders, the amount of binders in AF lacquer mixture and different structures of the AF agents.

In the case of sample K3497, Figures 60 and 61 show that the contact angle and surface energy of the film sample aged for six months returned to the same level as in the starting situation. This change may result from many factors. The most important factor affecting the results is that these measurements were performed already earlier for the film sample aged for six months (run number 559214). This film sample was manufactured with the same recipe as sample K3497 used in this research. This procedure was made because of time limits. The film reel manufactured in run 559214 was wound looser than the later manufactured reel of run K3497. The change in test results could also be affected by different spots of films in which measurements were performed or simply by measuring error.

Table 13. *Contact angle measurements from PET side of the films throughout the six months ageing period.*

	Contact angle (°)				
Time	**K3497**	**K3498**	**K3499**	**K3500**	**REF**
Initial	77,9	75,3	79,5	82,9	74,9
1 month	52,2	45,6	74,1	77,7	74,9
3 months	51,9	43,6	73,3	76,9	74,9
6 months	71,1	40,2	76,7	76,3	74,9

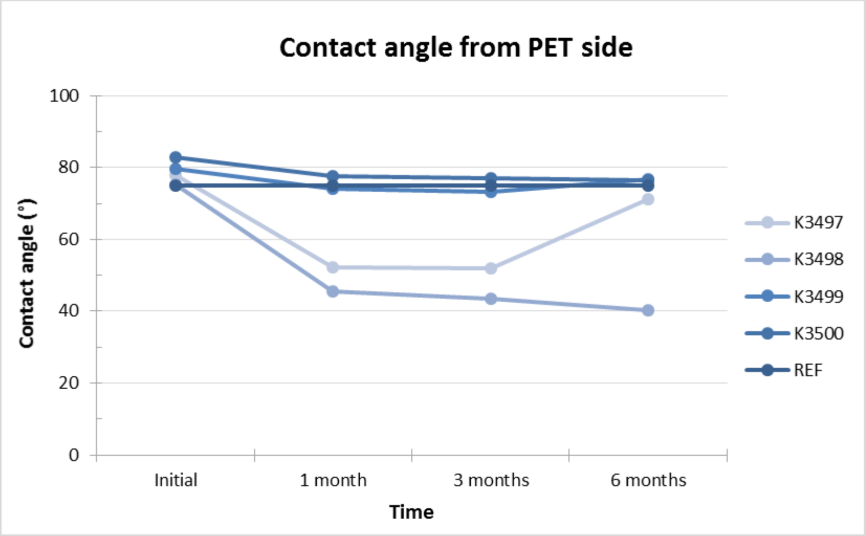

Figure 60. *Contact angles from PET side of the films throughout the six months ageing period.*

Table 14. *Surface energy measurements from PET side of the films throughout the six months ageing period.*

	Surface energy (mJ/m²)				
Time	**K3497**	**K3498**	**K3499**	**K3500**	**REF**
Initial	36,9	37,8	36,3	35,1	38,0
1 month	46,2	48,6	38,2	36,9	38,0
3 months	46,3	49,3	38,5	37,2	38,0
6 months	39,3	50,5	37,3	37,5	38,0

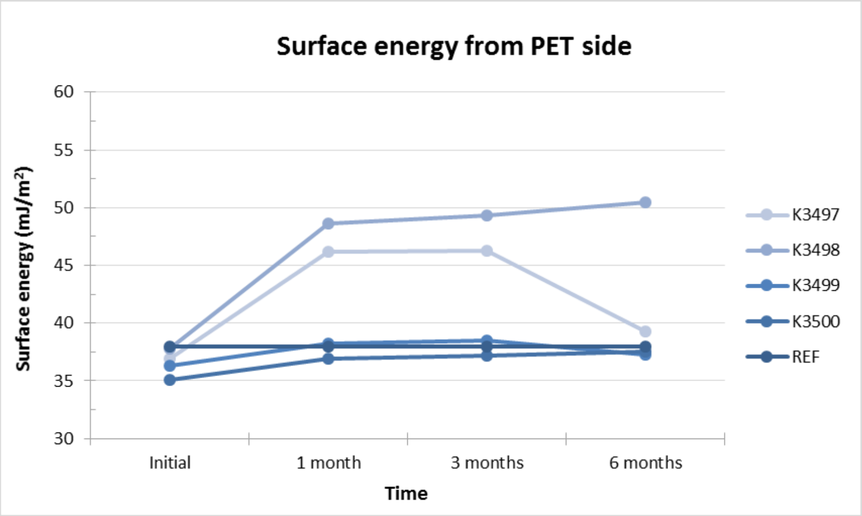

Figure 61. *Surface energy results from PET side of the film throughout the six months ageing period.*

When measuring surface energy and contact angles it was detected that AF lacquer no. 2 activates faster than AF lacquer no. 1. The activation of lacquer was studied by measuring the time from the moment when the water droplet drops on the surface of the film to the moment when the droplet spreads as uniform layer on the surface. It was observed that water droplets on the surface of the film samples coated with AF lacquer no. 2 spread as uniform layer in less than one minute. In the case of AF lacquer no. 1 water droplets maintained their shape for a longer time and spread as uniform layer in six to ten minutes.

Table 15 presents the test results of AF coldpool tests from the whole six-month ageing period. AF performances of film samples coated with AF lacquer no. 2 (K3499 and K3500) do not show signs of weakening during six months. The AF performance of film sample K3498 reduces significantly during the first month after which it remains almost constant and after six months of ageing its AF performance is still at acceptable level. The AF performance of film sample K3497 reduces during the whole six-month ageing period. The film sample aged for three months has a result of E, but the AF performance is slightly improved after being stored in coldpool for one week. The film sample aged for six months has really weak AF performance, even though after being stored in coldpool for one week, the AF performance is slightly improved again.

Table 15. *AF coldpool test results of film samples throughout the six months ageing period.*

Instantly after AF coating process				
Time	**K3497**	**K3498**	**K3499**	**K3500**
1 hour	2	2	1	1
4 hours	2	2	0	1
1 day	2	1	0	1
3 days	2	1	0	0
1 week	2	0	0	0
After one month of ageing				
Time	**K3497**	**K3498**	**K3499**	**K3500**
1 hour	3	3	0	0
4 hours	3	3	0	0
1 day	3	3	0	0
3 days	3	3	0	0
1 week	2	2	0	0
After three months of ageing				
Time	**K3497**	**K3498**	**K3499**	**K3500**
1 hour	E	3	0	0
4 hours	E	3	0	0
1 day	3	3	0	0
3 days	2	2	0	0
1 week	2	2	0	0
After six months of ageing				
Time	**K3497**	**K3498**	**K3499**	**K3500**
1 hour	E	3	1	1
4 hours	E	2	0	0
1 day	E	2	0	0
3 days	E	2	0	0
1 week	2	2	0	0

When observing the contact angle and surface energy results performed on PE surface (Figures 58 and 59), it is detected that after one month of ageing the results were equal with both lacquers. Nevertheless, the AF performances were not the same. In other words, contact angles and surface energies do not correlate with AF performances. It can be assumed that in the case of AF lacquer no. 1 there is not enough AF agent on the PE surface that could absorb into condensed water vapor and make the water droplet spread as a uniform layer on the substrate surface. AF lacquer changes the surface of the

PE film into hydrophilic ($\theta < 90°$). Still, there is not enough AF additive to change dropwise condensation into filmwise condensation. Even though contact angle and surface energy measurements show hydrophilicity of the film, they do not show how many droplets form on the surface of film. In general, the number of droplets formed on the surface of the substrate defines the AF performance of the film.

It is noticed from the results that the film samples coated with AF lacquer no. 2 (K3499 and K3500) have again excellent AF performance across the whole six-month ageing time. Nevertheless, the contact angles of these samples were 60° which is quite high value. In the case of film samples coated with AF lacquer no. 1 (K3497 and K3498) there was significant change in the AF performance which could also be detected from the contact angle and surface energy measurements.

5. CONCLUSIONS

5.1 Key results

The purpose of this research was to explain backgrounds and theory of AF phenomenon by literature survey. Additionally, AF phenomenon was studied through an experimental study. Fogging is an undesirable phenomenon observed in the plastic films of food supply packages. It is undesirable because it affects the visual appearance of packed food products and makes the product unattractive from the point of view of consumer. Fog appears on a film when water vapor condenses on the surface of it. Condensation is enabled when enclosed air mass cools down to temperature, which is under the dew point of water. At this temperature, the air cannot contain all the water vapor anymore and condensed water vapor starts forming small discrete water drops on the surface of plastic film. The fogging phenomenon is influenced by temperature and relative humidity of enclosed air mass, and temperature of plastic film. [29] [30] Situation, in which water does not condense in the shape of water droplets on the surface of film but spreads as continuous and transparent layer, is called the antifogging effect. AF effect can be achieved by creating hydrophilic surface on the polymer film either by using different AF additives, liquid coatings or by taking advantage of physical methods. The studied problem behind this AF effect is that good AF properties are difficult to achieve and maintain on PE surfaces.

The aim of this research was to find out, how functionality of AF lacquer could be improved on the surface of polyethylene. The dilemma was approached by studying functionality of AF lacquers of two different suppliers. The AF lacquers used in experimental part were AF lacquer no. 1 and AF lacquer no. 2. Test results of this research point out that AF lacquer no. 1 does not adhere on the surface of PE film as effectively as AF lacquer no. 2. Contact angle and surface energy measurements showed that AF lacquer no. 1 transferred from PE surface to PET side of film, while the film reel was being stored. The transfer of lacquer was the most intense during the first month. The same kind of transfer was not detectable in the case of AF lacquer no. 2. This is a significant difference between the two studied lacquers.

Changes in the AF performance of AF lacquer no. 1 are the most intense during the first month of ageing, when the AF performance reduces significantly. After this, the AF performance remains almost unchangeable until the end of the research period of six months. The durability of AF performance with AF lacquer no. 1 depends clearly on the AF dry coating weight. Some of the film samples maintained their AF properties even after six months. However, the activation of AF lacquer no. 1 after the condensation of water droplets on the surface of film is slower in comparison with AF lacquer no. 2. The AF performance of AF lacquer no. 2 is altogether better and maintains its excellent level throughout the whole six-month shelf life of the product. Sealability and re-tack properties of all film samples were at acceptable level for the whole research period and considerable differences between the studied lacquers could not be detected. It can also be stated that printing had no significant influence on the test results. It was detected that dilution ratio of AF lacquer no. 2 somewhat affected the re-tack property. The re-tack force was greater in diluted version than in undiluted. The sealing curve tests pointed out that AF lacquering affects the sealability of films. The AF lacquer applied on the sealing surface increases the seal initiation temperature by approximately 20 °C comparing to uncoated film.

Based on these results, it can be stated that good AF and sealability properties can be maintained over the ageing period of six months, if AF lacquer no. 2 is selected. However, in such case it must be considered that dilution ratio affects the re-tack property of the film. Thus, to minimize the risk of reduced re-tack properties, a recommended dilution ratio of AF lacquer no. 2 is 2:1. A significant improvement in AF performance can also be attained by the optimal AF dry coating weight with AF lacquer no. 1. With the dilution ratio of 1:1 the AF performance with it was maintained for the whole research period of six months reaching the level 2 in coldpool test in one week. With the dilution ratio 1:2, the AF performance was lost in approximately three months. Another solution to improve the AF performance of films is reducing the winding tension of the film reels. In that case, the transfer of AF agents from PE side to PET side of film can be prevented or at least slowed down. Also, slowing down the process speed of lacquering could be one solution to improve the adhesion between AF lacquer and the surface of film. In that case, the film spends more time in the oven and the lacquer has more time to dry out. Effective evaporation of solvents enhances the adhesion of lacquer. However, infinite slowing down of processes is not possible because of productivity requirements.

A potential method to create AF property on the surface of polymer film could be plasma treatment. Plasma treatment is a suitable alternative, because it is solventless method and thus environmental friendly and therefore safer to use in food packaging. The method functions as gas primer that replaces both the use of corona treatment and liquid primer. Plasma treatments do not affect the bulk properties of substrates, especially the mechanical properties. With gas plasma the properties of all polymer surfaces can be processed regardless of their structure and chemical reactivity. A lot of material can be saved and the need for drying can be eliminated. AF coating created with plasma treatment does not wear out in the same way as coatings that are made in traditionally. [86] [87]

When measuring contact angles, it was detected that test results vary a lot between individual samples. The surface of hydrophilic film is sensitive to contamination and even small changes in surrounding conditions make a large difference in wettability. Since air quality in each lab can vary from day to day, the results from contact angle measurement can be poorly reproducible. Laboratory air is exposed to contamination also already because of exhaled air, which contains volatile organics. Results from contact angle measurements are however very useful in understanding of the changes in hydrophilicity of film altogether. Test results would be more accurate if all the tests were possible to perform in standardized conditions.

5.2 Recommended future research and actions

Test results clearly showed the differences between studied AF lacquers. Understanding of how these lacquers function on the surface of PE film was also obtained. Exact analyses of the AF lacquers that were being studied are difficult to make. This is due to the fact that suppliers do not inform about the compositions of AF lacquers. With some chemical analyses it could be possible to get more information and clarity of the compositions of lacquers.

Effects of printing on the performance of AF lacquer should be studied more carefully. Effects of printing have not been previously treated in literature or in other surveys, and hence there is barely information about it. According to suppliers, AF lacquer does not interact with inks. However, in practice that is not the truth. During this research, it was detected that AF lacquer adhered on inks when the film was stored as reel. In other words, printed surface absorbed AF agent from the reverse side of the film. One affecting factor can be the binder included in AF lacquer. Depending on the composition of binder some binders tend to strongly adhere to inks. There is not enough information about how common this problem with inks is.

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APPENDIX A: THE SEALABILITY AND RE-TACK TEST RESULTS OBTAINED FOR THE SAMPLES ACROSS THE 6-MONTH AGEING PERIOD

The number in parentheses shows the starting peak value of strength.

Table 16. *Sealing curve results of all clear film samples instantly after the coating process.*

	Seal strength (N/m)				
Temperature (°C)	**K3451**	**K3452**	**K3453**	**K3454**	**REF**
100	0	0	0	0	23
110	164	69	19	12	527 (677)
120	489 (562)	519 (649)	490	495 (585)	529 (692)
130	501 (589)	492 (616)	462 (475)	504 (613)	525 (655)
140	483 (508)	488 (505)	475 (491)	467	537 (623)
150	485 (513)	492 (627)	439 (404)	458 (486)	523 (640)
160	478	477	450	475	525 (560)
170	489 (551)	495 (543)	465 (518)	493	514 (517)
180	462	455	395 (394)	444	500 (509)
190	500	464	426 (427)	429 (476)	490 (486)
200	461	423 (488)	366	447	489 (595)

Table 17. *Sealing curve results of all printed film samples instantly after the coating process.*

	Seal strength (N/m)				
Temperature (°C)	**K3451**	**K3452**	**K3453**	**K3454**	**REF**
100	0	0	0	0	23
110	149	159	9	0	527 (677)
120	510	488 (636)	512 (599)	482 (552)	529 (692)
130	511 (541)	445	456 (506)	423	525 (655)
140	485 (521)	472 (482)	484	462 (490)	537 (623)
150	484 (500)	469 (577)	491	471	523 (640)
160	477	463 (480)	478	455 (502)	525 (560)
170	477	472	454	429 (493)	514 (517)
180	469 (470)	461	428 (421)	401	500 (509)
190	446	476 (489)	390 (394)	369	490 (486)
200	468	445 (466)	390	385 (398)	489 (595)

***Table 18.** Sealing curve results of all clear film samples after one month of ageing.*

	Seal strength (N/m)				
Temperature (°C)	**K3451**	**K3452**	**K3453**	**K3454**	**REF**
100	0	0	9	7	23
110	36	27	16	52	527 (677)
120	478 (639)	460	471	451	529 (692)
130	475	452	466	430	525 (655)
140	494 (584)	457	467	493	537 (623)
150	460 (576)	465 (487)	435 (483)	436 (481)	523 (640)
160	462 (475)	439 (470)	479 (515)	419	525 (560)
170	492 (507)	404	476	362	514 (517)
180	423	370 (437)	417 (468)	395	500 (509)
190	492	395	397 (388)	362	490 (486)
200	340	344	372 (412)	402	489 (595)

***Table 19.** Sealing curve results of all printed film samples after one month of ageing.*

	Seal strength (N/m)				
Temperature (°C)	**K3451**	**K3452**	**K3453**	**K3454**	**REF**
100	10	12	11	14	23
110	482	498 (610)	477	484 (548)	527 (677)
120	418	428	442	436	529 (692)
130	485 (491)	433 (428)	490 (518)	454	525 (655)
140	468	453	441	482	537 (623)
150	419	463 (441)	442 (465)	448 (421)	523 (640)
160	429	470 (532)	445 (549)	460 (520)	525 (560)
170	452	484	454 (484)	429 (448)	514 (517)
180	388	410 (411)	442	415	500 (509)
190	406	421 (469)	430 (484)	410	490 (486)
200	389	490	340	395	489 (595)

***Table 20.** Sealing curve results of all clear film samples after three months of ageing.*

	Seal strength (N/m)				
Temperature (°C)	**K3451**	**K3452**	**K3453**	**K3454**	**REF**
100	10	0	20	21	23
110	149	298	129	482	527 (677)
120	478	511	517 (639)	524 (439)	529 (692)
130	521	508 (636)	509 (525)	518 (639)	525 (655)
140	512 (636)	502 (452)	512 (680)	514	537 (623)
150	499 (510)	496 (530)	460 (437)	485 (507)	523 (640)
160	460	446	496 (489)	487	525 (560)
170	507 (478)	432 (356)	490 (466)	524	514 (517)
180	507 (509)	504	472 (529)	476	500 (509)
190	468 (619)	409 (490)	516 (626)	442	490 (486)
200	451	456	435 (426)	503 (534)	489 (595)

Table 21. *Sealing curve results of all printed film samples after three months of ageing.*

	Seal strength (N/m)				
Temperature (°C)	**K3451**	**K3452**	**K3453**	**K3454**	**REF**
100	16	24	17	13	23
110	468 (579)	501	270	535 (694)	527 (677)
120	444 (501)	508 (533)	488 (622)	526	529 (692)
130	501 (530)	473	507 (533)	493 (543)	525 (655)
140	474 (406)	510	507 (487)	519	537 (623)
150	504 (529)	485 (476)	492 (811)	480 (408)	523 (640)
160	443 (407)	468 (461)	468 (522)	496	525 (560)
170	507 (602)	515 (502)	490	511	514 (517)
180	479 (403)	429 (420)	498 (531)	461	500 (509)
190	450	434	495 (497)	478	490 (486)
200	426	443	459 (426)	500 (570)	489 (595)

Table 22. *Sealing curve results of all clear film samples after six months of ageing.*

	Seal strength (N/m)				
Temperature (°C)	**K3451**	**K3452**	**K3453**	**K3454**	**REF**
100	10	7	10	7	23
110	38	23	38	50	527 (677)
120	538	513	410	462	529 (692)
130	555 (681)	492 (527)	534 (630)	523 (631)	525 (655)
140	528 (656)	508 (579)	489 (527)	508	537 (623)
150	544 (716)	488	506	498	523 (640)
160	502	491 (570)	517 (534)	505	525 (560)
170	527 (594)	519	513 (525)	487 (506)	514 (517)
180	518 (648)	475	506 (528)	503	500 (509)
190	484	423	497 (542)	509	490 (486)
200	507	472 (580)	480 (501)	466	489 (595)

Table 23. *Sealing curve results of all printed film samples after six months of ageing.*

	Seal strength (N/m)				
Temperature (°C)	**K3451**	**K3452**	**K3453**	**K3454**	**REF**
100	7	12	11	10	23
110	54	23	39	44	527 (677)
120	538	514 (619)	514	528 (652)	529 (692)
130	487	524 (587)	534 (643)	512	525 (655)
140	493	505 (569)	489 (515)	543 (660)	537 (623)
150	497	508	504 (526)	500 (569)	523 (640)
160	481	483 (498)	497	494 (594)	525 (560)
170	478	504 (591)	500	438	514 (517)
180	505	460	479 (505)	512 (639)	500 (509)
190	473	495	484 (505)	518	490 (486)
200	474	408	444 (491)	459 (508)	489 (595)

Table 24. Peel strength test results of clear and printed samples instantly after the coating process.

Sample	RC-Peel Strength 150°C (N/m)		RC-Peel Strength 160°C (N/m)	
	Clear	Printed	Clear	Printed
K3451	455 (487)	494 (551)	493 (533)	476 (505)
K3452	467 (529)	465 (552)	466 (475)	470 (524)
K3453	508 (520)	466 (485)	479 (593)	483 (450)
K3454	509 (487)	466 (556)	486 (571)	479 (509)
REF	523 (640)		525 (560)	

Table 25. Peel strength test results of clear and printed samples after one month of ageing.

Sample	RC-Peel Strength 150°C (N/m)		RC-Peel Strength 160°C (N/m)	
	Clear	Printed	Clear	Printed
K3451	509 (599)	503 (525)	469 (499)	510 (582)
K3452	480 (537)	486 (490)	481 (466)	507 (521)
K3453	477 (572)	444 (460)	471 (466)	469 (475)
K3454	445 (429)	467	467 (474)	475 (445)
REF	523 (640)		525 (560)	

Table 26. Peel strength test results of clear and printed samples after three months of ageing.

Sample	RC-Peel Strength 150°C (N/m)		RC-Peel Strength 160°C (N/m)	
	Clear	Printed	Clear	Printed
K3451	522	484 (499)	490	475 (528)
K3452	472	512 (572)	505 (587)	482 (630)
K3453	480 (489)	475 (485)	499 (509)	495 (521)
K3454	473 (489)	486	498 (599)	478 (514)
REF	523 (640)		525 (560)	

Table 27. Peel strength test results of clear and printed samples after six months of ageing.

Sample	RC-Peel Strength 150°C (N/m)		RC-Peel Strength 160°C (N/m)	
	Clear	Printed	Clear	Printed
K3451	493 (523)	467 (568)	503	485 (715)
K3452	486 (522)	498 (546)	483	499 (523)
K3453	520 (549)	483 (562)	530	497 (521)
K3454	494 (497)	497	519	493 (500)
REF	523 (640)		525 (560)	

Table 28. *Re-tack test results of clear film samples instantly after the coating process (sealing temperature 150 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	195	187	170	142	111	110	102	100	85	75
K3452	201	187	151	99	99	90	75	67	65	66
K3453	224	210	211	184	161	140	120	109	107	90
K3454	221	196	175	151	142	120	108	102	100	89
REF	253	241	227	190	156	129	120	117	107	90

Table 29. *Re-tack test results of printed film samples instantly after the coating process (sealing temperature 150 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	162	199	166	176	144	126	110	94	78	90
K3452	178	170	150	111	100	89	80	78	70	79
K3453	178	200	175	121	114	95	86	75	76	75
K3454	163	169	135	99	80	98	89	80	73	63
REF	253	241	227	190	156	129	120	117	107	90

Table 30. *Re-tack test results of clear film samples instantly after the coating process (sealing temperature 160 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	219	218	211	175	145	124	99	96	81	80
K3452	205	191	152	127	122	106	80	80	74	70
K3453	207	156	174	159	120	98	103	77	68	64
K3454	215	199	176	156	120	108	103	100	99	80
REF	237	197	136	98	92	77	69	63	67	58

Table 31. *Re-tack test results of printed film samples instantly after the coating process (sealing temperature 160 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	212	196	190	173	139	119	109	83	71	82
K3452	157	191	157	111	101	92	92	91	64	56
K3453	223	211	187	159	143	126	120	93	91	82
K3454	193	183	174	140	142	128	90	90	80	84
REF	237	197	136	98	92	77	69	63	67	58

Table 32. *Re-tack test results of clear film samples after one month of ageing (sealing temperature 150 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	252	234	233	199	160	147	129	120	120	88
K3452	249	244	211	150	129	110	106	101	99	82
K3453	245	232	222	200	175	172	151	148	133	120
K3454	235	161	153	150	131	129	127	118	117	100
REF	253	241	227	190	156	129	120	117	107	90

Table 33. *Re-tack test results of printed film samples after one month of ageing (sealing temperature 150 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	251	247	179	141	111	92	91	87	84	73
K3452	235	201	167	158	124	117	100	93	90	82
K3453	240	197	202	181	152	149	121	120	108	104
K3454	205	201	180	158	125	128	114	101	70	80
REF	253	241	227	190	156	129	120	117	107	90

Table 34. *Re-tack test results of clear film samples after one month of ageing (sealing temperature 160 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	249	208	177	169	130	145	123	105	102	93
K3452	254	208	176	133	114	100	100	88	73	69
K3453	243	235	200	180	148	123	115	99	100	102
K3454	234	202	163	149	107	108	93	91	85	83
REF	237	197	136	98	92	77	69	63	67	58

Table 35. *Re-tack test results of printed film samples after one month of ageing (sealing temperature 160 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	229	204	183	150	143	99	97	95	81	72
K3452	207	184	188	155	132	108	87	78	94	100
K3453	228	199	178	147	125	108	97	99	107	91
K3454	187	145	108	108	108	106	101	84	81	70
REF	237	197	136	98	92	77	69	63	67	58

Table 36. *Re-tack test results of clear film samples after three months of ageing (sealing temperature 150 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	271	237	231	207	182	169	156	153	139	115
K3452	287	249	216	175	156	112	101	95	90	88
K3453	251	230	228	208	175	147	129	120	114	116
K3454	210	206	198	151	125	111	97	96	92	90
REF	253	241	227	190	156	129	120	117	107	90

Table 37. *Re-tack test results of printed film samples after three months of ageing (sealing temperature 150 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	246	219	199	167	155	153	120	130	118	81
K3452	256	230	214	190	170	150	138	120	115	107
K3453	262	225	222	178	178	153	151	120	117	100
K3454	241	240	222	163	148	139	117	108	104	81
REF	253	241	227	190	156	129	120	117	107	90

Table 38. *Re-tack test results of clear film samples after three months of ageing (sealing temperature 160 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	250	248	207	161	134	110	96	87	86	86
K3452	247	192	158	139	133	94	92	90	80	76
K3453	240	190	171	162	143	117	113	99	99	77
K3454	255	219	191	150	127	105	106	102	92	87
REF	237	197	136	98	92	77	69	63	67	58

Table 39. *Re-tack test results of printed film samples after three months of ageing (sealing temperature 160 °C).*

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	224	166	142	120	108	100	100	80	66	60
K3452	231	193	157	128	100	106	80	82	81	65
K3453	212	196	187	164	140	117	114	98	89	72
K3454	231	190	154	143	140	93	79	76	72	70
REF	237	197	136	98	92	77	69	63	67	58

Table 40. Re-tack test results of clear film samples after six months of ageing (sealing temperature 150 °C).

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	200	198	200	139	111	97	79	77	77	70
K3452	237	178	122	107	85	78	73	69	73	69
K3453	259	198	187	186	148	118	107	96	105	79
K3454	242	198	175	146	133	117	93	79	76	70
REF	253	241	227	190	156	129	120	117	107	90

Table 41. Re-tack test results of printed film samples after six months of ageing (sealing temperature 150 °C).

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	242	185	181	147	128	111	91	100	70	63
K3452	229	195	177	134	112	90	82	76	68	67
K3453	231	180	159	142	109	99	82	66	65	62
K3454	242	196	178	146	130	116	100	94	70	66
REF	253	241	227	190	156	129	120	117	107	90

Table 42. Re-tack test results of clear film samples after six months of ageing (sealing temperature 160 °C).

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	235	188	165	147	102	92	86	68	67	57
K3452	225	180	154	113	92	80	70	68	64	56
K3453	243	211	194	185	140	111	97	79	79	66
K3454	236	200	184	165	124	103	98	85	78	63
REF	237	197	136	98	92	77	69	63	67	58

Table 43. Re-tack test results of printed film samples after six months of ageing (sealing temperature 160 °C).

	Re-tack force (N/m)									
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
K3451	242	195	160	146	117	120	84	73	68	63
K3452	230	192	151	135	115	92	85	70	75	60
K3453	239	198	178	151	117	94	81	73	71	66
K3454	240	195	171	118	95	80	79	66	70	60
REF	237	197	136	98	92	77	69	63	67	58