



VIPP VALUES CREATED IN
FIBRE-BASED PROCESSES
AND PRODUCTS

Asif Javed

Effects of plasticizing and crosslinking on coatings based on blends of starch-PVOH and starch-lignin





Effects of plasticizing and crosslinking on coatings based on blends of starch- PVOH and starch-lignin

Asif Javed

Faculty of Health, Science and Technology

Chemical Engineering

DOCTORAL THESIS | Karlstad University Studies | 2018:14

Effects of plasticizing and crosslinking on coatings based on blends of starch- PVOH and starch-lignin

Asif Javed



VIPP VALUES CREATED IN
FIBRE-BASED PROCESSES
AND PRODUCTS



BILLERUDKORSNÄS

KK-stiftelsen ><

Effects of plasticizing and crosslinking on coatings based on blends of starch-PVOH and starch-lignin

Asif Javed

DOCTORAL THESIS

Karlstad University Studies | 2018:14

urn:nbn:se:kau:diva-66853

ISSN 1403-8099

ISBN 978-91-7063-844-2 (print)

ISBN 978-91-7063-939-5 (pdf)

© The author

Distribution:
Karlstad University
Faculty of Health, Science and Technology
Department of Engineering and Chemical Sciences
SE-651 88 Karlstad, Sweden
+46 54 700 10 00

Print: Universitetstryckeriet, Karlstad 2018

WWW.KAU.SE

Abstract

Fibre-based food packaging normally requires a barrier material to protect packed foodstuff from gases and moisture in order to ensure food quality. So far, the barrier materials used in food packaging applications have been mostly oil-based polymers. Over the last decade, efforts have been made to replace oil-based barrier materials with bio-based materials due to growing environmental concerns and due to the persistent increase in oil prices and oil scarcity. The work described in this thesis has focused on coatings based on blends of starch-poly(vinyl alcohol) (PVOH) and starch-lignin for their potential use as barrier materials in food packaging applications.

The effects of plasticizing and crosslinking on mechanical and barrier properties of coatings based on starch-PVOH blends were investigated, the plasticizers used being glycerol, polyethylene glycol and citric acid. The addition of PVOH to the starch increased the flexibility of the film, and the addition of a plasticizer further increased their flexibility. Curing of the films led to a decrease in flexibility and to an increase in brittleness of the films containing citric acid at high temperature. Citric acid acted as a compatibilizer for starch and PVOH blend and a low water vapour transmission rate through coatings containing citric acid indicated that citric acid also acted as a cross-linker. The oxygen-barrier properties of the coatings reflected the compatibility and cross-linking of the starch-PVOH blend containing citric acid.

Polyethylene was extruded onto a paperboard pre-coated with a starch-PVOH blend, and this lowered the oxygen transmission rate for all the pre-coating recipes containing plasticizer. The addition of a plasticizer to the pre-coating reduced the adhesion of polyethylene to the pre-coated board. The increase in brittleness of the pre-coating at a high temperature and the increase in wetting of the pre-coated board by the PE melt can affect the barrier properties developed by the extrusion coating. The polyethylene coated board had a lower oxygen transmission rate when the board was pre-coated with a polyethylene-glycol-containing recipe than when the board was pre-coated with a citric-acid-containing recipe.

In order to convert a board into a package, creasing and folding operations are usually necessary. The results showed that an increase in brittleness of the barrier coating layer can increase the cracking tendency of the layers after creasing and folding of the board. The base substrate can also affect the crack propagation in the barrier coating layer. Barrier coatings applied on the mineral-coated side of the board showed a greater tendency to crack than barrier coatings applied on the uncoated side of the board. The cracks in the barrier coating layers seemed to follow the fibres when the coating was applied on the board with a high susceptibility to fibre rising.

The addition of lignin to the starch decreased the migration of starch from the starch-lignin films into the model liquids viz. deionized water, alkaline buffer solution of pH 10 and food simulant B (3%, w/v, acetic acid solution). The addition of ammonium zirconium carbonate as a cross-linking agent to the starch-lignin blend increased the brittleness of the film and decreased the migration of both starch and lignin from the films in contact with a liquid. Ammonium zirconium carbonate was a better cross-linker for starch and lignin when the pH of the starch-lignin solution was adjusted with ammonia rather than with NaOH. The addition of starch to the lignin solution increased the solubility in the test liquid of the lignin in starch-lignin blends at low pH levels. The migration into the model liquids of lignin from the paper with a pre-coating of a starch-lignin blend containing ammonium zirconium carbonate decreased with decreasing pH of the coating solutions.

List of papers included in the thesis

- I. Javed, A., Ullsten, H., Ernstsson, M., Järnström, L. (2016) Study of starch and starch-PVOH blends and effects of plasticizers on mechanical and barrier properties of coated paperboard. *Nordic Pulp & Paper Research Journal*, 31(3), 499-510.
- II. Javed, A., Ullsten, H., Järnström, L. (2016) Effects on oxygen-barrier properties of pre-treatment of paperboard with starch-poly(vinyl alcohol) blends before polyethylene-extrusion. *Packaging Technology and Science*, doi/10.1002/pts.2210.
- III. Javed, A., Rättö, P., Järnström, L., Ullsten, H. (2018) Crack analysis of barrier coatings based on starch and starch-PVOH with and without plasticizer. *Accepted for publication in Nordic Pulp & Paper Research Journal*.
- IV. Javed, A., Ullsten, H., Rättö, P., Järnström, L. (2018) Lignin-containing coatings for packaging materials. *Submitted for publication*.
- V. Javed, A., Rättö, P., Järnström, L., Ullsten, H. (2018) Lignin-containing coatings for packaging materials-pilot trials. *Submitted for publication*.

Author's contribution

- I. Principal author. Prepared the samples and designed the experiment. Carried out all the experiments except for the X-Ray Photoelectron Spectroscopy.
- II. Principal author. Prepared the samples and designed the experiment. Performed all the laboratory work except for the PE-extrusion coating.
- III. Principal author. Planned and performed all the experimental work with the exception of SEM images.
- IV. Principal author. Planned and performed all the experimental work.
- V. Principal author. Planned and performed all the experimental work.

List of abbreviations and symbols

A	Interfacial area
AZC	Ammonium zirconium carbonate
A_c	Average crack area
C	Concentration
CA	Citric acid
CLA	Cylindrical laboratory coater
CTMP	Chemithermomechanical pulp
D	Diffusion coefficient
DiCA	Contact angle of diiodomethane
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
E	Elastic modulus
E'	Storage modulus
ESCA	Electron spectroscopy for chemical analysis
EVOH	Ethylene vinyl alcohol
F_x	Flux in x-direction
G	Energy
Gly	Glycerol
G_{mix}	Gibbs free energy of mixing
H_{mix}	Enthalpy of mixing
k	Boltzman constant
L_c	Crack length

L_t	Total measured length
MD	Machine direction
n	Number of molecules
OTR	Oxygen transmission rate
pph	Parts per hundred
P	Permeability
PA	Polyamide
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PVC	Poly(vinyl chloride)
PVDC	Poly(vinylidene chloride)
PEG	Polyethylene glycol
PVOH	Poly(vinyl alcohol)
RH	Relative humidity
SEM	Scanning electron microscope
S	Solubility coefficient
SP	Starch-to-PVOH ratio
S_{mix}	Entropy of mixing
t	Time
t_a	Average thickness
T	Absolute temperature
TMA	Thermo mechanical analysis

T_g	Glass transition temperature
U	Potential energy
v	Volume fraction
W_c	Average crack width
WCA	Contact angle of water
WVTR	Water vapour transmission rate
w	Average coat weight
x	Distance
XPS	X-ray photoelectron spectroscopy
ρ	Density
σ	Stress
ε	Strain
δ	Phase shift
ω	Angular frequency
γ^{TOT}	Total Surface Energy
γ^{Lw}	Lifshiz – van der Waals component of the surface energy
γ^-	Electron donor component of the surface energy
γ^+	Electron acceptor component of the surface energy

Table of Contents

Abstract	I
List of papers included in the thesis	III
Author's contribution	IV
List of abbreviations and symbols.....	V
1. Objectives of the study	1
2. Background.....	2
2.1 Food packaging	2
2.2 Polymeric materials as barrier materials	4
2.3 Barrier properties.....	6
2.4 Water resistance.....	7
2.5 Mechanical properties and the glass transition temperature..	8
2.6 Plasticization	10
2.7 Polymer solutions and polymer blends	11
2.8 Adhesion.....	13
2.9 Coating	14
2.10 Converting.....	17
3. Materials	17
3.1 Starch.....	17
3.2 Poly(vinyl alcohol)	21
3.3 Polyethylene	23
3.4 Lignin	23
3.5 Additives.....	24

4. Experimental techniques	26
4.1 Coatings.....	26
4.2 Self-supporting films	27
4.3 Extrusion	27
4.4 Oxygen transmission rate	28
4.5 Water vapour transmission rate.....	29
4.6 Mechanical properties of self-supporting films	29
4.7 X-Ray electron spectroscopy	31
4.8 Adhesion.....	33
4.9 Scanning electron microscopy (SEM)	34
4.10 Microscopic analysis	35
4.11 Contact angle determination	35
4.12 Surface roughness	36
4.13 Surface profilometry	37
4.14 Creasing and folding	38
4.15 Stability in water of self-supporting films.....	38
5. Barrier Properties.....	39
6. Crosslinking.....	43
7. Mechanisms of failure	45
8. Sustainability and socio-economic aspects	46
9. Summary of papers	47
10. Future perspectives	49
11. Conclusions	50

12.	Acknowledgement.....	52
13.	References	54

1. Objectives of the study

Barrier coatings are normally applied on fibre-based food packaging materials in order to shield the packaged food from gases, liquids and moisture. The barrier coating materials currently being utilized for food packaging are mostly oil-based polymers, but interest in environment-friendly bio-based polymers has developed in recent years, due to the expanding interest in replacing oil-based polymers with them. Currently, bio-based barrier materials have been surveyed under conditions that are far from being realistic, and there is thus a need to centre research endeavours in this field.

The main aim of this study was to gain detailed knowledge about bio-based barrier coatings, and to explore the possibility of using them to replace oil-based polymers in food packaging. The focus of this project is to improve the mechanical properties, barrier properties and stability in water of starch-based barrier layers. The aim of the project is also to understand the mechanism of failure of the layers during the converting operations typically performed in industry to convert a barrier-coated board into a package.

This work has explored how different plasticizers influence the properties of starch-based barrier layers with and without polyethylene extrusion, and how plasticizers affect the compatibility of starch-PVOH blends. The way in which plasticizers affect the mechanical and barrier properties of starch and starch-PVOH coatings was also investigated.

Furthermore, a crack analysis of board coated with starch and starch-PVOH blends was performed after creasing and folding of the coated board. The purpose was to investigate how the flexibility of barrier layers and baseboard properties can affect cracking in the layers after creasing and folding of the coated board.

Starch-lignin based barrier coatings were also studied. The major aim being to improve the water stability of starch films by adding lignin to starch films and further by cross-linking the starch-lignin coatings. Pilot trials were performed to investigate whether the good results obtained in the laboratory could also be achieved on a pilot-scale.

The overall goal of this project is to be able to demonstrate how a fibre-based food packaging provided with a bio-based barrier coating could be formed with functional applications leading to advances within the barrier-coatings field.

2. Background

2.1 Food packaging

Food items require a packaging in order to keep their quality for a long time, to prevent food spoilage and wastage, and to handle and transport the food items easily and safely. The principal roles of food packaging are to contain the food, to protect packed food from the outside effects and damage, and to inform the consumer about the contents and ingredients (Coles, 2003). Over the past decades, efforts had been made to measure worldwide how much food is wasted before and after it reaches the consumer. It is reported that as much as half of the global food that is produced is generally wasted (Lundqvist et al., 2008, FAO, 2013). In the modern society, packaging of foodstuff is inescapable and vital in order to reduce financial losses and food shortage for the growing world population. One way to reduce the food wastage is to enhance the shelf life of the packed food.

Shelf life is the time during which the quality of the food should not deteriorate, and this time starts when the food item is packed (Singh and Singh, 2005). Exposure to moisture and gases can influence the quality of the packed food and can reduce the shelf life. An increase in the moisture content inside the package facilitates the growth of microorganisms such as mould, bacteria and yeast which can damage the food (Andersson, 2008, Gram et al., 2002). Dry snacks lose their crispiness through moisture adsorption, and they become soggy and unacceptable to the consumer (Katz and Labuza, 1981). Odours, off-flavours and colour changes can develop when oxygen enters packed food (Kerry et al., 2006). For instance, milk can develop off-flavour due to lipid oxidation (Moyssiadi et al., 2004). Oxidation of meat can result in a colour change, loss of flavour and the degradation of meat proteins, pigments and lipids (Liu et al., 2010a). Thus, it is essential to protect packed foods from water, water vapour and oxygen in order to maintain their quality for a longer time.

Materials such as metals, glass, plastics, paper and paperboard are commonly used in food packaging. Aluminium metal is mostly used in food packaging applications and it is an excellent barrier to water, water vapour and gases, but it has a high cost. Aluminium films with a thickness greater than 25 μm can provide a total gas and moisture barrier in flexible package (Robertson, 2006, Lange and Wyser, 2003). Glass has a long history in food packaging and is impermeable to gases and moisture, but it is susceptible to breakage due to its brittleness and the transportation costs are high due to its heavy weight. Plastics are low-cost materials and are widely used in food packaging. They are moldable and light weight, but are mostly oil-based polymers and have a variable permeability to water vapour and gases. Paper and paperboard are inexpensive renewable materials, and about 97% of paper and paperboard is produced from wood. Paper for packaging of any kind was first used in China (200 BC). Paper is often treated, laminated or coated with other materials to improve its barrier properties. Different types of papers such as Kraft paper, Sulphite paper, Greaseproof paper, Glassine and Parchment paper having different properties are often used to package food such as, for example, flour, dried fruits, confectionery, fast foods, baked goods and butter (Marsh and Bugusu, 2007). According to the ISO (International Organization for Standardization), paper is called paperboard when its grammage is about 200 g/m^2 or more. In the early 20th century, paperboard-based packaging came onto the market with several advantages over glass bottles for the transportation and distribution of milk (Kirwan, 2008). Paperboard can provide a physical protection to the packed food and can shield the contents from mechanical damage during distribution. It is commonly used to make boxes, cartons or trays in order to transport food items or other goods. Paperboard is a porous material and is therefore not a good barrier against water vapour and oxygen, paperboard is therefore often coated or laminated with other materials for use in food packaging. A scanning electron microscopy image of a paperboard is shown in Figure 1.

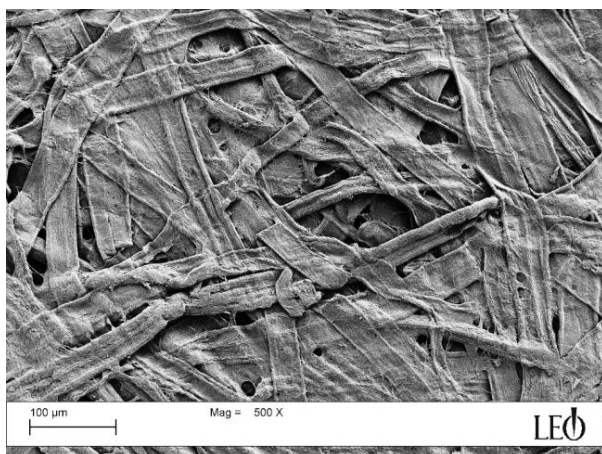


Figure 1. Scanning electron microscopy image of a typical paperboard.

White board, solid board, chipboard and fibreboard are different types of paperboard used in combination with aluminium or plastics to package food such as, for example, fruit juices, soft drinks, cereals, milk powder, tea and coffee (Marsh and Bugusu, 2007).

To date, most of the materials used together with paperboard for food packaging applications are metals or oil-based polymeric materials such as aluminium, ethylene vinyl alcohol (EVOH), polyamide (PA) and polyethylene (PE), but their overall impact on the environment is a major concern (Marsh and Bugusu, 2007, Lange and Wyser, 2003). Bio-based materials such as chitosan (Kjellgren and Engström, 2006), protein (Rhim et al., 2006, Olabarrieta et al., 2001), wheat gluten (Mangavel et al., 2002), starch (Olsson et al., 2013b, Javed et al., 2016), lignin (Johansson et al., 2012b, Bhat et al., 2013) and hemicellulose (Hartman et al., 2006) have recently been studied for their possible use as barrier materials in food packaging applications.

2.2 Polymeric materials as barrier materials

Polymers are mostly synthesised by a chemical process called polymerization and are building blocks of repeating units called monomer to form a chain. Polymers can be divided into groups based on their structures such as linear polymers, straight and long chains, branched polymers, linear chains having some branches, and cross-linked polymers, linear chains are joined together by covalent bonds. Polymer materials can be classified according to the ordering of their chains such as crystalline polymers, ordered molecular chains,

amorphous polymers, random molecular chains, and semi-crystalline polymers, both ordered and random molecular chains. A polymer containing a single type of monomer is known as a homo-polymer and those containing more than one type of monomer are known as co-polymers or block co-polymers (Figure 2).

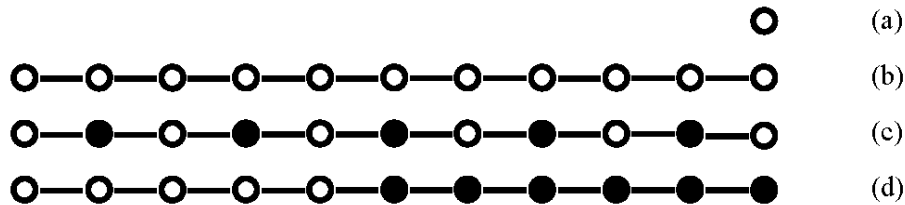


Figure 2. (a) Monomer (b) homo-polymer (c) co-polymer (d) block co-polymer.

Polymeric materials can be divided into two groups, thermoplastics and thermosets. Thermoplastic polymers are mainly used in packaging as barrier materials, while thermosetting polymers are commonly used in automobiles and the construction industry (Piringer and Baner, 2008). Thermoplastic polymers can easily be moulded into various products and can be remoulded upon heating. Paperboard used in food packaging applications is often coated or laminated with a polymeric barrier material, the primary function of which is to reduce the transport of gases, moisture, fat and aroma both from and into the packed food, but mechanical strength and flexibility can also be required of the material to avoid food deterioration. In addition, polymeric materials should have several other features such as, gloss, transparency, printability, puncture resistance, heat resistance, chemical resistance and agreement with pertinent food contact regulations (Sidwell, 1992). Multilayer structures of different polymeric materials are normally used in food packaging applications in order to meet these requirements. Polymeric materials such as polyvinylidene chloride (PVDC), polypropylene (PP), polyethylene terephthalate (PET), polyethylene (PE), polyamide (PA), poly(vinyl chloride) (PVC), ethylene vinyl alcohol (EVOH), polystyrene (PS) and poly(vinyl alcohol) (PVOH) are most commonly used as barrier materials in food packaging applications (Lange and Wyser, 2003, Lau and Wong, 2000, Mokwena and Tang, 2012).

Polymeric materials can be further divided into groups according to source such as oil-based polymers and bio-based polymers, and

according to their bio-degradation such as biodegradable polymers and non-biodegradable polymers. The polymeric materials such as PE, PP, EVOH, PVDC, PVOH, and PET, used as barrier materials in food packaging applications are mostly oil-based polymers. Bio-based and biodegradable polymers such as polysaccharides, proteins, polylactic acids or polyhydroxyalkonates have shown a potential for use as barrier materials in packaging applications. So far, polylactic acids have made the highest impact in the packaging market. Bio-PE and bio-PET are also derived from bio sources, but are not bio-degradable (Johansson et al., 2012a). Bio-PE and Bio-PET have the same physical and chemical properties as those of PE and PET derived from oil.

2.3 Barrier properties

The permeation of gases and water vapours through a barrier coating depends on their diffusion and solubility coefficients and on defects such as cracks or pinholes in the barrier layer. The free volume, and amorphous and crystalline regions in the polymer structure affect the transport of gases and water vapours through the material. Molecules pass through the polymer material in three steps; adsorption of the molecules at the surface and the absorption of some of the molecules, diffusion of the molecules through the polymer matrix by a random molecular motion, and desorption from the other side of the material.

In general, the permeability, P , of the water vapour or gas molecules through a barrier layer is a function of the product of the diffusion coefficient, D , and the solubility, S , (Crank, 1975):

$$P = D \times S \quad (1)$$

Diffusion can be defined as “transportation of molecules from one part of the system to another by random molecular motion” (Crank, 1975).

The phenomenon of diffusion through the material was first explained by Fick (1855), adapted from the mathematical equation for heat conduction defined by Fourier (1822), where the flow rate through the cross-sectional area of the material is proportional to the concentration gradient. This is known as Fick’s law of diffusion and is given by:

$$F_x = -D \frac{\partial C}{\partial x} \quad (2)$$

where F_x is the flux in the x-direction, C is the concentration, and the negative sign indicates that the diffusion occurs from higher to lower concentration and x is the distance. For uni-dimensional diffusion, Fick's first law of diffusion leads to the conclusion that the change in concentration with time, t , is dependent on the flux (Crank, 1975):

$$\frac{\partial C}{\partial t} = - \frac{\partial F_x}{\partial x} \quad (3)$$

For uni-dimensional diffusion, if the diffusion coefficient is constant, Fick's second law of diffusion can be expressed (Crank, 1975) as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (4)$$

The diffusion coefficient depends on the size of the solute molecule. The activation energy of diffusion increases, and the diffusion in a given polymer matrix thus decreases with increasing size of the solute molecule (Hedenqvist, 2002). Activation energy of diffusion is the energy required to form a hole in the polymer matrix of sufficient size for the solute to jump into. The solubility of small molecules in a polymer material depends on the solubility parameters of the solute molecules and the polymer, on the solute-polymer intermolecular forces and interaction energies, and on changes in the free energies between the solute and solvent molecules. The greater the difference in solubility parameter, the lower is the solubility, due to a low interaction between the solute molecules and the polymer (Hedenqvist, 2002). Solubility also depends on the degree of crystallinity, the size of the crystallites, and the voids and free volume in the polymer material (Choudalakis and Gotsis, 2009).

2.4 Water resistance

Natural polymers such as starch, cellulose, and hemicellulose are generally hydrophilic and their films or coatings have a low resistance to water, which severely limit their use in food packaging applications. Water can form a hydrogen bond with hydrophilic groups such as hydroxyl, carboxyl and carbonyl groups. Water can plasticize the polymer matrix and a polymer can become swollen in the presence of excess water. Food packages are often exposed to high moisture contents and polymer materials intended to be used as a barrier

material in a food package must therefore have a good resistance against water. The resistance to water of the films and coatings can be assessed by measuring the degree of swelling or by measuring the contact angle of water on the surface of a material. The absorption of moisture by a film or coating of a polymeric material reduces the mechanical strength and the film can lose its barrier properties. Moisture acts as a plasticizer for polymeric materials and the absorption of water by a material lowers its glass transition temperature. The resistance to water of natural polymer materials can however be increased through crosslinking or blending with synthetic polymers.

2.5 Mechanical properties and the glass transition temperature

The mechanical properties of polymeric materials are usually dependent on the rate of applied stress, resultant strain and temperature conditions. Polymeric materials used as barrier materials in packaging applications are generally described as viscoelastic materials i.e. they experience elastic and viscous (time-dependent) deformations when subjected to a stress. At low temperatures or high frequencies of measurement and at high temperatures or low frequencies of measurement, a given polymer may be respectively glass-like and rubber-like. An intermediate temperature or frequency range is normally known as the glass transition range of the polymer. The glass transition temperature (T_g) is a narrow temperature range in which a polymer passes through a transition from a brittle, glassy and rigid solid to a rubbery and softer state (Ebewele, 2010). Differential scanning calorimetry (DSC), thermo mechanical analysis (TMA) and dynamic mechanical analysis (DMA) are commonly used methods to measure T_g . In this work, DMA was applied to starch, starch-PVOH and starch-lignin. A sharp decrease in storage modulus occurs in the glass transition region during dynamic mechanical analysis of a material.

A tensile stress applied to a ductile material deforms the material elastically and then plastically as the stress increases, and failure occurs when the local stress exceeds the local strength. The real strength of the material is usually much lower than the theoretical strength, because of the presence of flaws or cracks where the local stress exceeds the

local strength (Souheng, 1982). Fracture can be a cohesive fracture where the fracture energy creates two similar surfaces or an adhesive fracture where the fracture energy creates two dissimilar surfaces. The fracture energy is affected by the loading mode such as tensile mode, in-plane shear mode or anti-plane shear mode as shown in Figure 3.

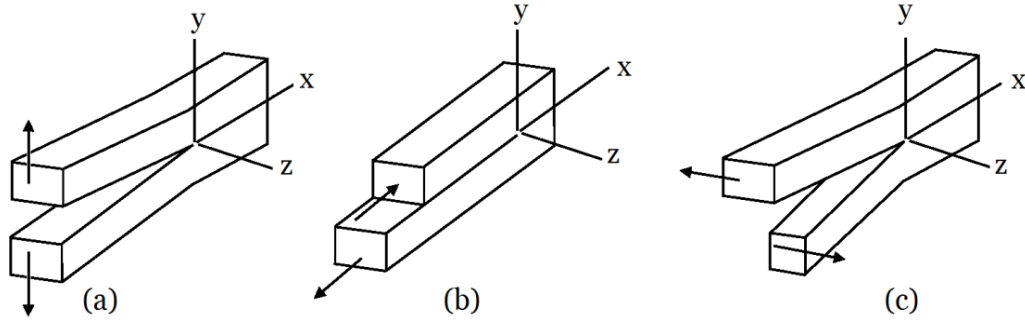


Figure 3. Typical modes of loading (a) tensile mode (b) in-plane shear (c) anti-plane shear.

The fracture continues to propagate if the potential energy released by the growth of the crack is adequate to produce a new fracture surface (Souheng, 1982). When the local stress exceeds the yield strength of the material, a plastic flow, the deformation of a material beyond the point of recovery, occurs around the crack tip and this can increase the crack length, but in an ideal brittle material no plastic flow occurs.

According to the Griffith Theory, the criterion for fracture to occur is:

$$-\left(\frac{\partial U}{\partial A}\right) \geq G \quad (5)$$

where U is the potential energy, A is the interfacial area, and G is the energy required to separate one unit interfacial area.

Rivlin and Thomas proposed a theory for fracture to occur in a viscoelastic material:

$$-\left(\frac{\partial U}{\partial A}\right)_L \geq G \quad (6)$$

where U is the elastically stored energy, A is the interfacial area, G is a typical fracture energy per unit interfacial area, and L indicates that no

external work is done on the system during the interchange of energy between the body of the specimen as a whole and the crack.

As described in section 2.2, paperboard is usually coated with a polymeric material to create a barrier. The process of converting a coated paperboard into a package involves cutting, creasing and folding operations during which complex shear and tensile forces act on the coated paperboard (Andersson, 2008). As a result, cracks can occur in the coating layer, and these can negatively affect the barrier properties of the coated paperboard. It is, therefore, important to investigate thoroughly the formation of cracks in the coating layers. Coating layers with a high flexibility have shown a greater resistance to cracking during the creasing and folding of a coated paperboard (Kim et al., 2010).

In an amorphous or semi-crystalline polymer, the T_g is associated with the onset of segmental mobility of the amorphous phase of the polymer (Turi, 1997b). In order to move a polymer segment a certain activation energy is needed to increase the free volume surrounding the polymer segment (Bueche, 1953). As a general rule, any structural feature in a polymer such as chain stiffness, chain length, attractive forces in the polymer and cross-linking that reduces the free volume surrounding a polymer segment will lead to an increase in T_g (Bueche, 1953, Turi, 1997b). The T_g increases with increasing degree of cross-linking of the polymer, since the mobility of the amorphous chains is reduced by the cross-linking (Chung et al., 2004). The T_g also increases with increasing molecular weight up to a certain limit and this effect is more evident for shorter chains (Cowie and Henshall, 1976).

2.6 Plasticization

The flexibility of a polymer film can be increased by adding a plasticizer that can reduce the defects such as cracks or pinholes in the films. The addition of a plasticizer to a polymeric material improves its processability and decreases its T_g . A plasticizer acts as a lubricant and reduces the frictional forces between the polymer chains and thus increases the flexibility of the film (Cadogan and Howick, 2012). Low volatility, compatibility with the polymer, ability to interact with the polymer and low crystallinity at ambient temperatures are important

requirements of a plasticizer (Brydson, 1995). Inert organic materials such as esters are commonly used as plasticizers to increase the workability and flexibility of polymeric materials (Cadogan and Howick, 2012). Plasticizers usually act either externally, where they do not react chemically with the polymer, or internally, where they attach to the polymer chain through a chemical reaction (Videki et al., 2007, Fringant et al., 1998). Plasticizers can be primary plasticizers or secondary plasticizers. Secondary plasticizers usually have a low compatibility with the polymer and work as a plasticizer only in the presence of a primary plasticizer (Cadogan and Howick, 2012).

The plasticizer composition, molecular weight, and compatibility with the polymer affect the degree of flexibility of the polymer (Cao et al., 2009, Donhowe and Fennema, 1993). Low molecular weight plasticizers are usually more efficient in increasing the flexibility of a polymer film than high molecular weight plasticizers but they adversely affect the barrier properties (Mathew and Dufresne, 2002, Donhowe and Fennema, 1993).

At low plasticizer contents, the plasticizer can hinder the mobility of the polymer chain, making it less flexible. This phenomenon is called anti-plasticization and has been reported for various plasticizers when they are added to polymers in small amounts (Lourdin et al., 1997a, Gaudin et al., 2000). Anti-plasticization can lead to a low oxygen permeability of the polymer film (Gaudin et al., 2000). With a high plasticizer content, phase separation can occur between the plasticizer and the polymer in the plasticizer-polymer blend. Two glass transition temperatures may then exist, one for the polymer-rich phase and another for the plasticizer-rich phase (Lourdin et al., 1997b).

2.7 Polymer solutions and polymer blends

The Bragg-William model, also known as regular solution theory, is based on a lattice model and describes the processes in the liquid mixture. According to this model, each site of the lattice is occupied and accommodates only one molecule. This model assumes that the volume of the system does not change, that the mixing is random and that interactions take place only between neighbouring molecules. The

Flory-Huggins theory of polymer solutions is also based on the theory of regular solutions.

In the Flory-Huggins theory, polymer molecules are first positioned in the lattice cell followed by filling of the remaining cells by the solvent molecules, but polymer molecules and solvent molecules can replace one another in the lattice. Each lattice cell is occupied by a polymer chain segment or by a solvent molecule.

The solubility of a material in a solvent generally depends on the entropy and enthalpy of mixing. The entropy of mixing usually dominates the system for small molecules having different polar characteristics but it is less important for macromolecules. The entropy of mixing is much higher for small molecules in the regular solution theory than the large polymer molecules in the Flory-Huggins theory, because segments of polymer chains are connected to each other and mixing is not random. The entropy of mixing decreases as the number of possible ways of arranging the molecules in the space decreases.

According to the Flory-Huggins lattice model (Flory, 1953), the entropy of mixing polymer and solvent, assuming no specific interactions between neighbours, can be expressed as:

$$\Delta S_{mix} = -k(n_1 \ln v_1 + n_2 \ln v_2) \quad (7)$$

where , ΔS_{mix} is the entropy of mixing, k is the Boltzman constant, n_1 and n_2 are respectively the numbers of solvent and polymer molecules, and v_1 and v_2 are respectively the volume fractions of solvent and polymer molecules.

Equation (7) can be generalized for heterogeneous polymers as:

$$\Delta S_{mix} = -k(n_1 \ln v_1 + \sum_i' n_i \ln v_i) \quad (8)$$

where prime suffix indicates that only polymer species are included in summation, although the solvent term $n_1 \ln v_1$ can also be included.

The enthalpy of mixing of a polymer and a solvent, assuming that the polymer does not affect the heat of mixing, can be expressed as:

$$\Delta H_{mix} = k T \chi_1 n_1 v_2 \quad (9)$$

where ΔH_{mix} is the enthalpy of mixing, T is the absolute temperature, χ_1 is the dimensionless Flory-Huggins interaction parameter, n_1 is the number of solvent molecules, and v_2 is volume fraction of polymer molecules. Equation (9) can also be used for heterogeneous polymers where $v_2 = \sum_i' v_i$. In a ternary system, where two different polymers are mixed in a single solvent, the interaction between solvent and polymer is not important, on condition that they are completely miscible and that phase separation is merely caused by polymer-polymer interaction (Flory, 1953). Two polymers immiscible in one solvent were also found to be immiscible in another solvent, which indicated that the interaction between polymers is of primary importance (Flory, 1953).

Polymer-polymer mixing, blending of polymer melts, can occur if the Gibbs free energy of mixing is negative (Olagoke and Llyod, 1979b, Turi, 1997a), according to:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (10)$$

where ΔG_{mix} is the Gibbs free energy of mixing, ΔH_{mix} is the enthalpy of mixing, ΔS_{mix} is the entropy of mixing, and T is the absolute temperature.

The solubility parameter theory of mixing “like dissolves like” is not always applicable to polymer-polymer blends, since it predicts an endothermic energy of mixing, but the solubility parameter theory can be applicable for low molecular weight polymers (Turi, 1997a). The most common way to measure the miscibility of a polymer-polymer blend is to measure the T_g . If only one T_g exists for a polymer-polymer blend, it is probable that the polymers in the blend are miscible (Olagoke and Llyod, 1979a, Turi, 1997a).

2.8 Adhesion

The adhesion between the barrier coating and the substrate, including any pre-coating, and the adhesion between the barrier coating and the PE extrusion coating is important for the barrier properties. Dole et al. (2005) showed that, in a multi-layered structure, good adhesion between the different layers is a prerequisite for achieving synergetic effects of the different barrier layers. “Adhesion refers to the state in

which two dissimilar bodies are held together by intimate interfacial contact such that mechanical force or work can be transferred across the interface and cohesion refers to adhesion or attraction within a bulk phase (Souheng, 1982)."

In practice, adhesion is a combination of several effects. The adhesion phenomenon can be explained by mechanical interlocking, physico-chemical interaction or inter-diffusion processes between polymers with equal solubility parameters (Vähä-Nissi and Kuusipalo, 1997). Mechanical interlocking due to the penetration of a coating in a fluid state into a substrate plays a major role for practical adhesion when a substrate is highly porous (Vähä-Nissi and Kuusipalo, 1997). It has been shown by Steffner et al. (1995) that the adhesion between coating and substrate increases with increasing porosity of the substrate, due to mechanical interlocking. The physico-chemical interactions are the result of acid-base interactions and Lifshitz-van der Waals forces or may be the result of covalent bonding between the two components. Berg (1993) demonstrated the importance of physico-chemical interactions for the adhesion and reported that the work of thermodynamic adhesion is a combination of acid-base interactions and Lifshitz-van der Waals forces. Thermodynamic adhesion is promoted if the surface energies of the substrate and the coating are equal (or rather if the apolar components of the free energy are equal and the asymmetric electron-acceptor – electron-donor interactions match each other) (Bonnerup and Gatenholm, 1993, Kaczinski and Dwight, 1993). The surface energy is the energy required to bring one atom from the bulk of the material to the surface.

2.9 Coating

A coating can be applied to a paperboard as a dispersion where the coating material is dispersed in water, as a solution where the coating material is dissolved in water or other solvent, by extrusion where the coating material is a thermoplastic polymer melt, or by lamination. These coating techniques are discussed below.

A typical dispersion coating is a pigment coating which contains binders, additives, pigments and water, and which is usually applied to a paperboard in order to enhance the printing and optical properties.

Coating with, for example, a nano-clay dispersion can be used to improve the barrier properties. Material produced by dispersion/solution coating can easily be repulped and this technique is therefore advantageous for recycling (Christer and Johan, 2007), and the increasing environmental concerns mean that the use of dispersion/solution coating to improve barrier properties is increasing. Dispersion/solution coating can be applied in-line or off-line. In laboratory-scale dispersion/solution coating, various laboratory coating methods such as a reel-to-reel coater, Helicoater, cylindrical lab coater (CLC) or a conventional bench coater can be used. In a laboratory reel-to-reel coater, a web width of 200 mm can be handled and drying can be achieved with an infrared (IR) dryer followed by a hot air dryer (Blankenburg et al., 2009). CLC is a high speed, maximum at 2200 m/min, laboratory blade coater generally equipped with an IR dryer (Guerrero et al., 2011). The Helicoater is also a high-speed, about 2000 m/min, laboratory-scale coater equipped with pond, short dwell and rod coating heads, and both IR and hot air impingement drying systems are used. In the present study, a conventional laboratory-scale bench coater, equipped with wire-wound rods (K202 Control Coater, RK Coat Instruments Ltd., Royston, UK), and a pilot-scale coater (UMV Coating Systems AB, Säfte, Sweden) were used, as shown in Figure 4, and barrier solution coatings based on a starch, starch-PVOH and starch-lignin were applied to a paper or paperboard substrate.

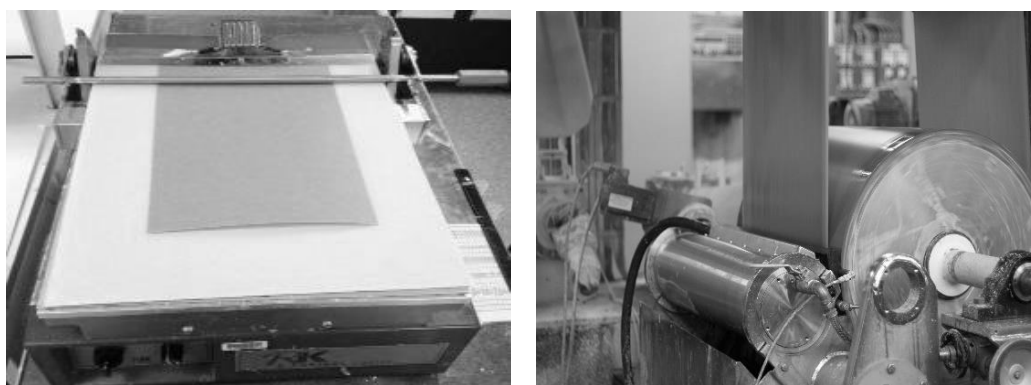


Figure 4. Conventional laboratory-scale bench coater (left side) and a pilot-scale coater at UMV Coating Systems AB, Säfte, Sweden.

The pilot-scale coater at UMV consists of two coating stations equipped with blade and film coaters have blade and rod metering units. In the present study, Invo-Coater having an Invo-Tip metering element, a soft

polymeric metering element that provides good surface coverage and smoothness, and smooth rod metering element were used. It is possible to apply two coating layers on a substrate in one run and to use multiple coater configurations. It is a high speed coater, up to 2200 m/min, equipped with Infra dryers of installed effect 346 kW at station 1 and 1036 kW at station 2, and with three drying hoods of air velocity 70 m/s and temperature 300°C.

A schematic diagram of an extrusion coating process and a photomicrograph of the cross-section of a pre-coated and extrusion-coated paperboard are shown in Figure 5.

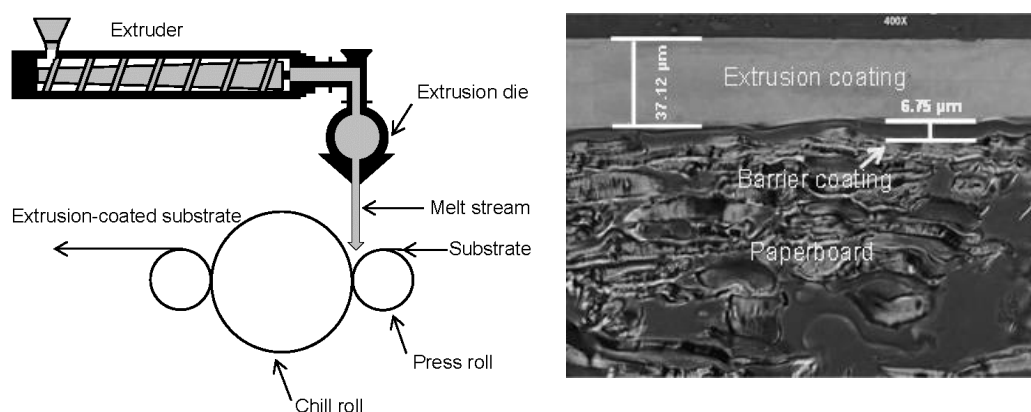


Figure 5. Schematic description of an extrusion coating process (left side), and a photomicrograph of the cross-section of a pre-coated and extrusion-coated paperboard (right side).

Extrusion coating of a thermoplastic polymer is usually performed in a food packaging application in order to improve the barrier properties and to make the package heat-sealable. Thermoplastic polymers commonly used in extrusion coating are PVOH, EVOH, PVDC, PE, PP, PA etc. (Lange and Wyser, 2003, Schott et al., 2010). A synthetic petroleum-based PE is the most common polymer used in extrusion coating (Schott et al., 2010). A typical extruder consists of three zones, the feeding zone, the compression zone and the metering zone. Solid thermoplastic polymer is fed into the extruder where the polymer is melted and metered in a die, and then compressed by a press roll followed by cooling on a chill roll. Parameters such as line speed, extrusion temperature and die jaws can be adjusted depending on the application. The extrusion temperature can affect the extruded

polymer layer. Extrusion coating is usually carried out off-line and the line speed ranges between 600 and 1000 m/min.

2.10 Converting

Converting a paperboard into a package requires cutting, creasing and folding operations, which involve forces acting on the paperboard. The creasing operation can cause plastic deformation and delamination of the substrate, which improves the foldability of the board by reducing its folding resistance. A board with a lower resistance to cutting, creasing and folding operations is generally considered to be a better substrate to convert into a package (Cavlin, 1988). These operations involve tension, compression and shear stresses. High mechanical loading during the creasing and folding of a coated paper or coated board can develop cracks in the coatings or in the substrate (Andersson, 2008, Barbier et al., 2002, Cavlin, 1988). Coating layers with a high mechanical strength and flexibility that can withstand high mechanical loading when the paperboard is converted into a package are therefore needed.

3. Materials

3.1 Starch

Starch is a highly abundant, high molecular weight natural polymer with repeating units of alpha D-glucose, which provides reserve energy for plants. It is available in high purity at a relatively low cost. The molecular formula of a glucose unit is $C_6H_{10}O_5$ and the general formula for the starch polymer is thus $(C_6H_{10}O_5)_n$ where n is the number of glucose units. The molecular weight ranges from 10^5 to 10^6 g/mole for linear and 10^7 to 10^8 g/mole for branched starch chains (Mua and Jackson, 1998). Wheat, potato, corn and maize are commercially important natural sources of starch. In Europe, potato starch is commonly used in the paper coating industry (Kearney and Maurer, 1990). Most starch derivatives have shown good barrier properties against oxygen and fat at low RH, and they are therefore excellent candidates for use as a renewable barrier material.

Starch occurs in the form of tiny granules having two molecular forms: amylopectin and amylose. The amount of each fraction depends on the

starch source. The amylose: amylopectin ratio is normally about 1:3 but amylose-free starch and varieties of starch with a high amylose content, 60%-80% amylose, also occurs (Whistler and Daniel, 1984).

The amylose and amylopectin contents of starches from different botanical sources are shown in Table 1.

Table 1. Amylose and amylopectin contents of starches (John and Leonard, 1990).

Starch source	Amylose	Amylopectin
Waxy maize	0	100
Tapioca	17	83
Rice	17	80
Potato	21	79
Wheat	28	72
Corn	28	72

Amylose has a linear structure with 1-4 alpha glucosidic linkages, while amylopectin has a branched chain structure with 1-6 and 1-4 alpha glucosidic linkages (Wurzburg, 1986b). The molecular structures of amylose and amylopectin are shown in Figure 6.

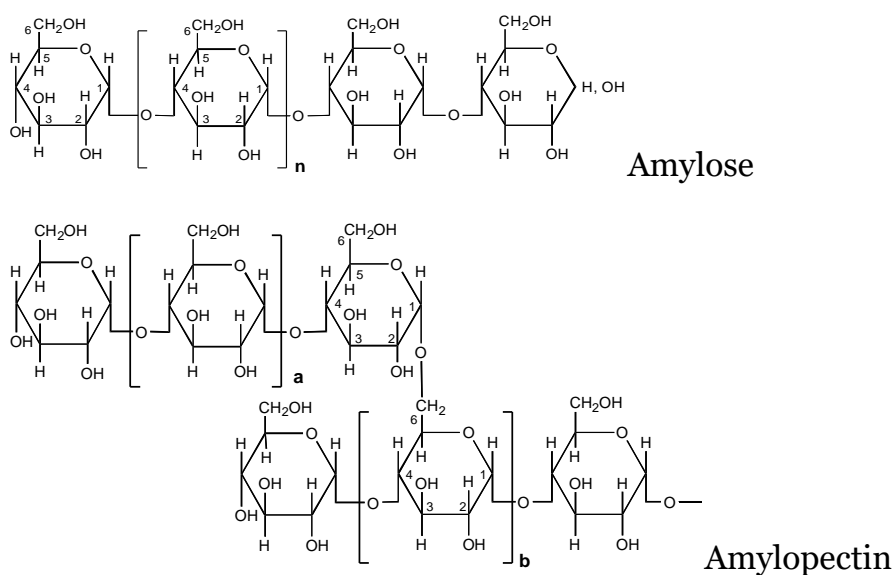


Figure 6. Molecular structures of amylose and amylopectin.

In nature, starch exists in a granular form having a semi-crystalline structure, with both crystalline and amorphous phases. The crystallinity of the starch affects its barrier or mechanical properties. With a high degree of crystallinity, starch films have good oxygen-barrier properties (Arvanitoyannis et al., 1994), but an increase in crystallinity reduces the flexibility of the film. Drying temperature and RH during film forming can affect the crystallinity. Starch films formed at a high temperature and low humidity have been shown to have a low crystallinity (Rindlava et al., 1997). An increase in crystallinity reduces the flexibility of an amylopectin film. Stading et al. (1998 and 2001) have reported that an increase in crystallinity of an amylopectin film can lead to a decrease in its flexibility, and a decrease in the water vapour and oxygen permeability through the films. Water can enter the amorphous regions of starch and attach to hydroxyl groups, and this can lead to a high oxygen permeability at high relative humidities (Dole et al., 2004, Masclaux et al., 2010).

The glass transition temperature of amylose starch is usually higher than that of amylopectin starch (Yu and Christie, 2001). The T_g also depends on the crystal structure of the starch (Liu et al., 2010b). At high moisture contents, the amorphous part of a starch film passes through the transition phase from a glassy to a rubbery state at a higher temperature (Lazaridou and Biliaderis, 2002). The addition of a plasticizer facilitates the mobility of polymer chains and the T_g of starch decreases with an increase in glycerol or water content (Mali et al., 2006).

In most starch applications, such as paper coating and sizing and adhesive formulations, the first step is starch gelatinization. When starch granules are heated in an excess of water above a certain temperature, hydrogen bonds within the granules start to become weaker, and this allows water to penetrate into the granules. Some of the granules then collapse leading to a leakage of amylose from the granules. This process is known as gelatinization. Hydration of the granules takes place and the viscosity of the solution increases. High amylose corn starch is more difficult to gelatinize and disperse than potato starch, and corn starch pastes may revert upon cooling. When a starch suspension is subjected to heat, the starch granules start to

swell, and it is reported that below 60°C this swelling is reversible (Zobel, 1984). Swelling increases with increasing temperature and the subsequent change in granule size subjects more molecules to hydration. Above 60°C, the changes are generally irreversible and this is the initiation of gelatinization. For homogeneous heat transfer, agitation is needed throughout the process. It is important to know the starch paste viscosity, gel strength and gel rigidity in order to be able to judge the starch viscosity and flow behaviour during application. Retrogradation or recrystallization of starch gels can occur during cooling or storage. The extent of retrogradation depends on the botanical source (Tuschhoff, 1986) and it usually occurs below 70°C (Liu et al., 2007). Small side chains can be introduced by chemical substitution on the starch backbone to prevent retrogradation from taking place (Hermansson and Svegmarm, 1996). Retrogradation occurs due to hydrogen bonding of the hydroxyl groups on the starch molecule, while substituent groups introduced onto the starch backbone act as steric hindrance and limit the chain interactions, resulting in reduced hydrogen bonding (López et al., 2010). Amylopectin has less tendency to retrograde due to the branched chain polymer and its lower mobility than the amylose polymer. Hydroxypropylated, cross-linked and acid-modified starches have shown a lower degree of retrogradation than native starches due to a reduction in the hydrogen-bond interactions and steric hindrance (Tuschhoff, 1986, Jiugao et al., 2005, Delville et al., 2003). Retrogradation can also be reduced by adding a plasticizer (Ma and Yu, 2004). The degree of retrogradation depends on the storage time, a higher percentage retrogradation being observed after a longer storage time (Hermansson and Svegmarm, 1996). Retrogradation in a starch suspension affects the flexibility of the starch film and results in an increase in brittleness (Ma and Yu, 2004, Delville et al., 2003). Recrystallization in a starch film also reduces the water uptake of the film (Mathew and Dufresne, 2002).

Native starches are usually modified by chemical/and or physical conversion or derivatization, where the structure of the starch is altered to reduce the chain length or molecular weight by oxidation, enzymatic conversion, dextrinization or acid conversion. Acid modification and oxidation of starch are also used to shorten the chain length and to

lower the viscosity of the starch (Wurzburg, 1986a). In derivatization, substituent groups such as hydroxyethyl, hydroxypropyl or acetate that can react with the starch hydroxyl groups are introduced into the starch molecule. Enzymatic conversion reduces the molecular weight of the starch and the starch paste viscosity by reducing the polymer chain length, and this makes it possible to prepare starch suspensions at higher solids contents.

Starches for commercial use or paper coating applications are often oxidized with sodium or calcium hypochlorite at a reasonably high pH. Under alkaline conditions, this treatment results in carboxyl groups on the starch chains, and these groups reduce retrogradation and increase the stability of the linear amylose molecules (Schmorak et al., 1962). Hydroxypropylated starches are hydrophilic in nature and are manufactured by the reaction of propylene oxide with the starch. These starches have a lower gelatinization temperature and better film-forming properties than unmodified starches (Rutenberg and Solarek, 1984). Hydroxylpropylated potato starch has a lower water vapour permeability than normal potato starch (Jansson and Järnström, 2005). Most of the hydroxypropylated starches are approved by the Food and Drug Administration as indirect food additives, and they are thus appropriate for use in coatings on food packaging.

3.2 Poly(vinyl alcohol)

Poly(vinyl alcohol), usually abbreviated as PVOH or PVA, is manufactured by the hydrolysis of polyvinyl acetate. The molecular structure of PVOH is shown in Figure 7.

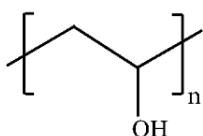


Figure 7. Molecular structure of Poly(vinyl alcohol)

PVOH is an important water-soluble polymer which is usually insoluble in organic solvents, and it is used in a wide range of industrial fields, for instance in packaging, in coating, as a protective colloid, as an adhesive, emulsifier etc. PVOH is commercially available with trade names such as Elvanol, Moviol, POVAL, Moviflex etc. Different PVOH

grades vary in solution viscosity and in the degree of hydrolysis being either fully hydrolysed or partially hydrolysed. PVOH grades with a degree of hydrolysis greater than or equal to 98 % are usually considered to be fully hydrolysed grades. PVOH is manufactured by the hydrolysis of polyvinyl acetate in an alcoholic solution and the degree of hydrolysis is the number of acetate groups removed (Goodship and Jacobs, 2009). The physical properties of PVOH and its application in different areas depend on the degree of hydrolysis, the degree of polymerization, the type of plasticizer used etc. The melting point of PVOH ranges from 180°C to 240°C depending on the degree of hydrolysis and is high for fully hydrolysed grades (Marten, 2002). Thermal degradation of PVOH occurs above 150°C and this may result in discoloration (Marten, 2002). The T_g of fully hydrolysed PVOH is 74°C at 0% RH (Konidari et al., 2011). PVOH has a crystalline structure because smaller hydroxyl groups present in PVOH do not destroy the crystalline lattice structure. However, residual acetate groups can hinder crystal formation so that fully hydrolysed PVOH grades have been shown to have a higher degree of crystallinity than partially hydrolysed PVOH grades (Goodship and Jacobs, 2009). Commercially produced PVOH is an almost atactic linear polymer in which the repeating units have no regular stereochemical configuration. Highly hydrolysed PVOH has shown a high tendency to crystallise (Assender and Windle, 1998). PVOH films have been shown to have good barrier properties against oxygen and good resistance to grease and oil, but poor moisture barrier properties. PVOH is hydrophilic, having an affinity for water, in nature and a synthetic polar polymer. Water diffuses into the amorphous region of PVOH and bonds with the hydroxyl group of PVOH leading to an increase in polymer chain mobility (Hodge et al., 1996). The crystallinity of PVOH decreases and the oxygen permeability of PVOH films consequently increases at high RH (Grunlan et al., 2004). PVOH is claimed to be a biodegradable synthetic polymeric material. Nevertheless, the biodegradation of PVOH films is slower than that of cellulose (Solaro et al., 2000). PVOH/nano-cellulose and PVOH/starch films degrade more rapidly, measured as weight loss with time, than pure PVOH films when exposed to compost mud (Ibrahim et al., 2010, Krochta and De Mulder-Johnston, 1997).

3.3 Polyethylene

Polyethylene (PE) is a semi-crystalline synthetic polymer, which is non-polar, hydrophobic, odourless and heat-sealable. It is used in numerous applications due to its low cost, abundant supply and good processability. PE has a low surface energy i.e. 33 mJ/m² (Van Oss, 1994a) and the surface properties of PE are therefore often modified in order to improve printability, adhesion to other surfaces and paintability. PE has excellent water and water vapour barrier properties but is a poor barrier against oxygen (Park et al., 1993). There are two main types of polyethylene, high density polyethylene (HDPE) and low density polyethylene (LDPE). LDPE is a branched chain polymer which is widely used in packaging as a moisture barrier and heat-sealable material (Li et al., 2001, Laiho, 1994).

3.4 Lignin

Lignin is a three-dimensional network polymer consisting of phenyl propane units with different substituents on the phenolic groups (Figure 8).

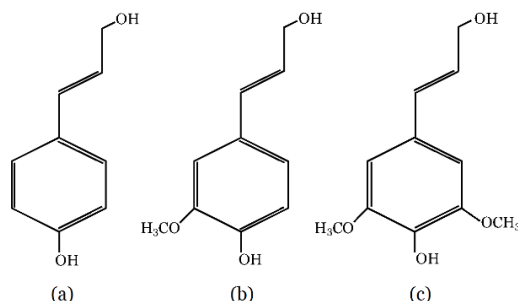


Figure 8. Chemical structure of building blocks of the lignin polymer (a) p-coumaryl alcohol (b) coniferyl alcohol and (c) sinapyl alcohol.

Wood consists mainly of cellulose, hemicellulose and 20-30% of lignin depending on the biological source (Sjöström, 1993). In order to make high quality cellulose-based materials such as paper, paperboard, viscose and many other products, lignin is separated from the wood fibres during the pulping process and is usually removed as a by-product from the black liquor from the pulping process. In a pulp mill, the black liquor is often used as fuel to recover energy, but lignin is also a renewable heterogeneous thermoplastic polymer with a glass

transition temperature (T_g) ranging from of 90°C to 170°C, depending on the plant species and on the process used for lignin extraction (Wang et al., 2016). Many processes exist to isolate the lignin polymer such as, for example, the kraft lignin, lignosulfonate, organosolv lignin, hydrolysis lignin, enzymatic isolation and LignoBoost processes (Gellerstedt and Henriksson, 2008, Zhu et al., 2016, Wang et al., 2016, Tomani, 2010). The LignoBoost process to extract lignin from the black liquor in kraft mills has many advantages over other technologies, such as lower investment costs, lower operational costs and higher yield (Tomani, 2010). The LignoBoost lignin has lower ash and carbohydrate contents and a higher content of dry lignin solids than other lignin polymers. The LignoBoost lignin can also be extracted as a dry lignin powder, which means that the lignin can be used outside the pulp mill with a high capacity without investing in a new boiler. The most obvious example is to use the lignin as a biofuel in boilers or burners (Tomani, 2010), but lignin has also shown a potential for use as an antioxidant in food packaging (Domenek et al., 2013).

3.5 Additives

Plasticization of polymeric materials is discussed in chapter 2.6. Starch and PVOH are hydrophilic in nature and a change in RH affects the plasticization of starch and PVOH films. The addition of a plasticizer to the polymeric material increases the polymer chain mobility, lowers the T_g and increases the flexibility of the film (Cadogan and Howick, 2012). It has been shown that the T_g of starch and PVOH films decreases if the amount of plasticizer or the moisture content of the films is increased (Lourdin et al., 1997b, Mohsin et al., 2011). Jansson and Järnström (2005) and Konidari et al. (2011) have shown that T_g of the starch and PVOH films decreases if the RH of the surrounding environment is increased, due to an increase in moisture content of the films.

A number of plasticizers such as glycerol, polyethylene glycol (PEG), sorbitol, xylitol, maltitol, urea and citric acid (CA) have been used to increase the flexibility of starch and PVOH films (Garcia et al., 1998, Mathew and Dufresne, 2002, Lourdin et al., 1997b, Mohsin et al., 2011, Shi et al., 2008). CA can be used as a cross-linker for starch and PVOH

where it reacts with the hydroxyl groups present ((Shi et al., 2008). In the present study, glycerol, PEG and CA plasticizers have been used. These plasticizers are approved by the American Food and Drug administration (FDA) for use in contact with food (Jiugao et al., 2005, Cao et al., 2009, Shi et al., 2008). The molecular structures of glycerol, PEG, CA are shown in Figure 9.

Ammonium zirconium carbonate (AZC) is a soluble alkaline salt of zirconium that has been used as an insolubilizer in paper coating colours. An alkaline solution of AZC contains anionic species with bridging hydroxyl groups with carbonate groups bonded to the zirconium. In aqueous solution, AZC has the ability to interact with carboxyl and hydroxyl groups present on the polymer species. Structure of AZC in an aqueous solution is shown in Figure 9.

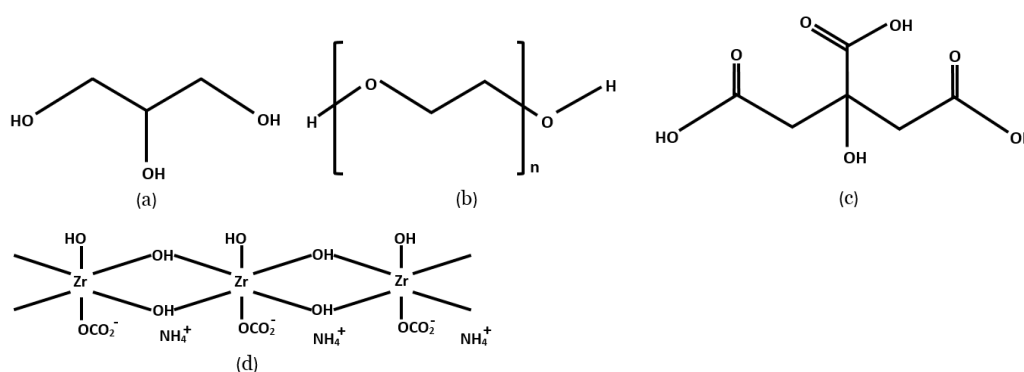


Figure 9. Molecular structures of (a) glycerol, (b) polyethylene glycol, (c) citric acid and (d) ammonium zirconium carbonate in solution.

AZC is generally classified as safe, and is approved by the American Food and Drug Administration (FDA) for use in paper and paperboard in contact with food (Moles and Chemicals, 2002). The addition of AZC to starch solution can affect the rheology of the solution due to weak hydrogen bonding interactions and its active pH range is 5-10. McAlpine (1982) found that AZC increased the viscosity of oxidized starch solutions at 40°C and low pH (pH=5). An increase in pH and an increase in storage time further increased the viscosity of a starch solution containing AZC (McAlpine, 1982). The increase in viscosity of starch solutions containing AZC can however be inhibited in the presence of tartrate ions and at a pH of about 9. Song et al. (2009) have shown that the viscosity of a starch solution containing AZC can increase slightly (ca. 2 cp in about 2 hrs) at 23°C and pH 9, but starch

solutions containing AZC were found to be stable at room temperature and pH 9-9.5 (Solam, unpublished data). The stability of a starch solution containing AZC also depends on the concentration of the solution (Solam, unpublished data). Self-crosslinking of AZC and crosslinking of AZC with starch in an aqueous solution can occur at an elevated temperature, 80-90°C, and at pH 9 (Song et al., 2011).

It is reported that AZC can react with starch during drying when water is removed and the curing at high temperature is not necessarily needed (Robert, 1990). During the drying of polymer coatings containing AZC, ammonia and carbon dioxide are released and reactive sites on AZC react with carboxyl and/or hydroxyl groups present on the polymer in a cross-linking reaction (William and Susan, 1995, Wang et al., 2013).

4. Experimental techniques

4.1 Coatings

In laboratory trials, the starch suspension and PVOH solution were prepared separately from dry starch and PVOH to different final concentrations. Starch granules were pre-dispersed in deionized water with magnetic stirring for ca. 30 minutes. The starch suspension and the PVOH solution were immersed in a bath of boiling water under continuous stirring at 300-400 rpm with a dispersion blade impeller for 60 minutes. In pilot trials, the starch was cooked in a steam boiler for 60 minutes under vigorous stirring. For starch-PVOH blends, starch and PVOH solutions were cooled to room temperature and mixed at a starch-to-PVOH ratio of 70:30 on a dry basis, followed by the addition of a plasticizer such as glycerol, PEG or CA. For the starch-lignin blends, a starch solution at a temperature of ca. 90° was added to the lignin solution followed by the addition of glycerol and AZC and the mixture was then cooled to room temperature.

The paper or paperboard was coated in a bench coater equipped with wire-wound rods (K202 Control Coater, RK Coat Instruments Ltd., Royston, UK). The coating speed was set at 5 m/min. Different numbers of coating layers were applied on paper or paperboard and the coated samples were dried at 105°C for 90 s or at 70°C for 5 min after

each layer had been applied. The base paper was also coated in pilot trials at UMV Coating Systems AB (Säffle Sweden) with starch/lignin blends. The coatings were applied with an Invo-Coater using an Invo-Tip metering element at different tip angles. The machine speed was 280 m/min and the coated board was dried online in Infra dryers, followed by drying in three Spooner dryers at different temperatures. Prior to testing, the samples were conditioned at 23°C and 50% RH for at least one week.

4.2 Self-supporting films

Self-supporting films were cast by pouring 10 ± 0.1 g of the mixture into 88 mm diameter polystyrene Petri dishes (Figure 10). The films were subsequently dried at 70°C for 5h in a self-ventilated oven or at 23°C and 50% RH for at least 3 days. For curing at a high temperature, the dried films were placed in a desiccator for 24 h which were then put into a ventilated oven at 105°C for 10 minutes.

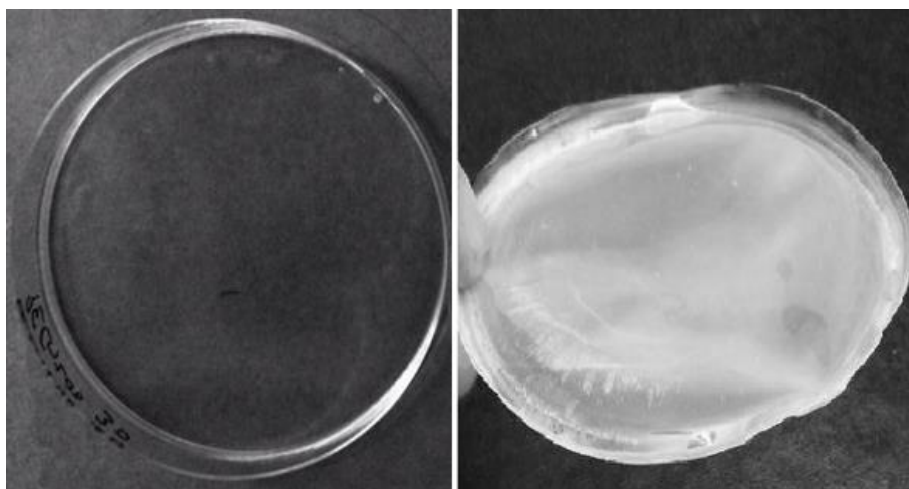


Figure 10. Petri dish (left) and self-supporting film (right)

4.3 Extrusion

The extrusion coating was performed on paperboard pre-coated with a barrier coating based on starch and PVOH. No other pre-treatment, such as corona, plasma, ozone or flame treatment, was applied prior to the extrusion coating. The extrusion coating was performed on the pilot line at Tampere University of Technology, Tampere, Finland (Figure 11). The extrusion coating parameters were adjusted to apply 40 g/m²

on the barrier-coated side and 20 g/m² on the other side of the board. The extrusion temperature was 310°C and the line speed was 100 m/min.

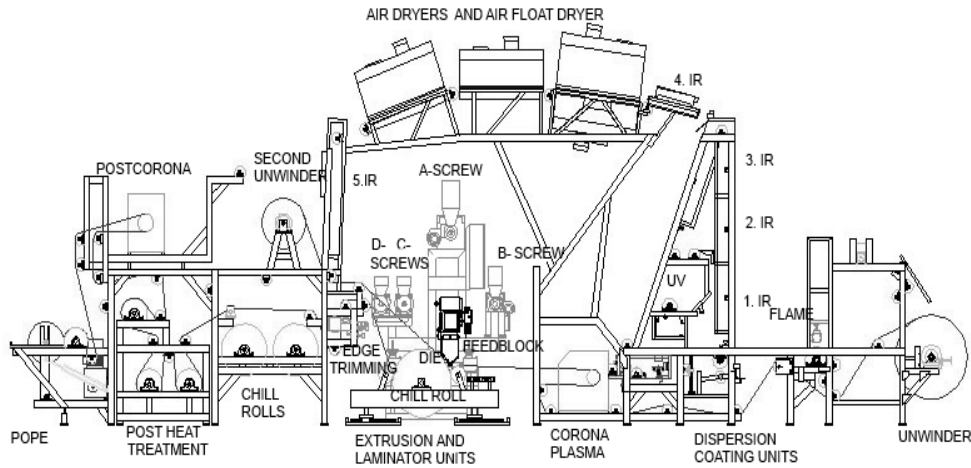


Figure 11. Pilot line at Tampere University of Technology.

4.4 Oxygen transmission rate

The oxygen transmission rate, OTR, is defined as the volume of gas passing through a unit thickness and unit area per unit time at the given temperature and RH. The units of OTR are cm³ m⁻² day⁻¹. The OTR was measured according to the ASTM standard test method D 3985-05 with Ox-Tran 2/21 MH (Mocon Inc., Minneapolis, USA). The films or coated papers to be tested were mounted between the two chambers and flushed with nitrogen (Figure 12).

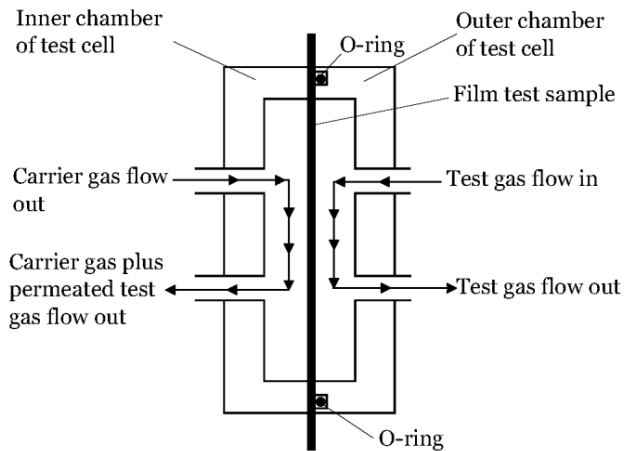


Figure 12. Illustration of permeation through a film

One side contained the test gas, oxygen, and the other side the carrier gas, nitrogen. The oxygen permeates through the sample due to the concentration difference between the two sides. The carrier gas transports the permeated oxygen to the calorimetric detector sensor. The relative humidity and temperature conditions in the chamber can be adjusted but are stabilized before the measurements are performed.

4.5 Water vapour transmission rate

The water vapour transmission rate, WVTR is given as the number of grams of water vapour permeating through unit area per unit time at a given temperature and RH. The units of WVTR are $\text{g m}^{-2} \text{ day}^{-1}$. ASTM E 96, DIN 53122-1, ISO 2528, TAPPI 448 and T 464 are common standards used for the measurement of WVTR (Andersson, 2008). The WVTR of the coated samples was measured according to ISO 2528 using the gravimetric (dish) method. The films or coated-board samples to be tested were mounted onto a cup containing silica gel as a desiccant or water (Figure 13). The water vapour is transported through the sample due to a moisture gradient across the samples created by the difference in RH on the two sides of the sample. The barrier-coated side of the sample was exposed to the high RH, and the increase or decrease in weight over time was measured.



Figure 13. Coated-board samples mounted on WVTR measurement cups

4.6 Mechanical properties of self-supporting films

Tensile tests on the self-supporting films were carried out according to DIN ISO 1924-3 using a tensile tester Zwick/Roell Z005 (Ulm,

Germany), in which the sample is fixed between the grips with a constant initial grip separation and constant cross-head speed (Figure 14). The applied tensile stress and dimensional change in the sample are measured continuously.

The maximum tensile strength, elastic modulus and elongation at break can be evaluated from the stress-strain curve. The elastic modulus (E) is calculated from the linear elastic region of the stress-strain curve where the ratio of stress to strain is constant:

$$E = \frac{\sigma}{\varepsilon} \quad (11)$$

where σ is the stress and ε is the strain.

Dynamic mechanical analysis was performed using a DMA instrument (DMA/SDTA861, Mettler Toledo, GmbH, Schwerzenbach, Switzerland) in the tensile mode (Figure 14). Menard (2008) has described the basic principle of DMA as: “applying an oscillating force to a sample and analysing the material’s response to that force”. DMA is often used to analyse the mechanical properties of viscoelastic materials as a function of temperature, time and frequency. In this study, the dynamic mechanical properties, storage modulus, of the materials were recorded as a function of temperature and as a function of frequency in the tensile mode.

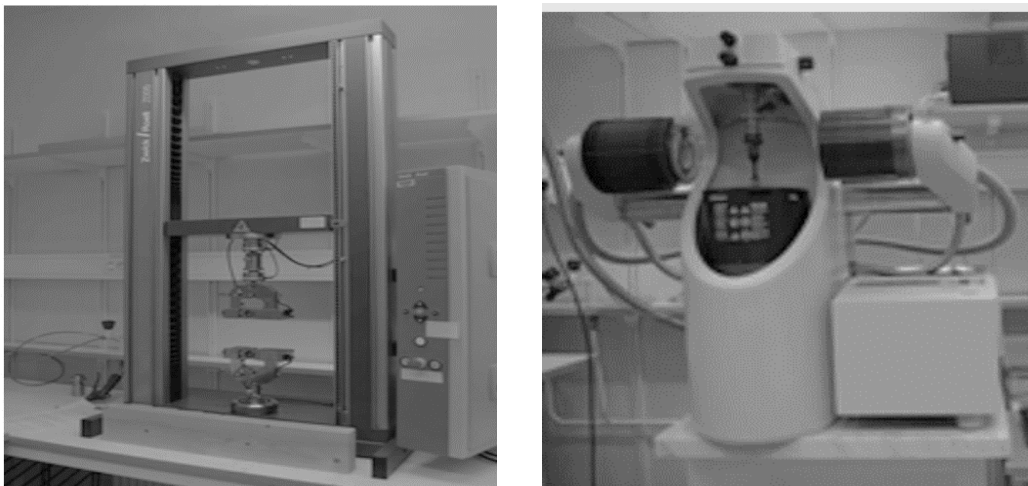


Figure 14. Tensile tester (left) and DMA instrument (right).

In a temperature scan, the polymer material is oscillated at a constant frequency while the temperature is varied at a constant rate. A material response can also be measured over time with a constant temperature. In a frequency scan, the material response is measured at a range of frequencies while the temperature, force and relative humidity are kept constant (Menard, 2008).

In DMA, a sinusoidal force is applied and the material response is recorded. Several properties of the material can then be calculated such as storage modulus, loss modulus and complex modulus. The strain (ε) and stress (σ) are given by:

$$\varepsilon = \varepsilon_0 \sin \omega t \quad (12)$$

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad (13)$$

where, t is the time, ω is the angular frequency, ε_0 is the initial strain, σ_0 is the initial stress and δ is the phase shift.

The storage modulus (E') is given by:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad (14)$$

DMA of the polymeric materials gives valuable information about the crosslinking of polymers and it is often used to determine the glass transition (Menard, 2008). E' modulus of the polymeric materials is increased by cross-linking of polymers and a decrease in E' modulus is observed at the glass transition (Schlesing et al., 2004, Yin et al., 2005).

4.7 X-Ray electron spectroscopy

X-Ray electron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), was used to characterise the top nanometre surface of the films and coatings. XPS spectra were recorded using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK) with a monochromatic Al X-ray source. The analysis area was $< 1 \text{ mm}^2$, with most of the signal from an area of $700 \times 300 \text{ }\mu\text{m}$.

The XPS method illustrated in Figure 15 is based on the photoelectric effect discovered by Thomson (1899) and Einstein (1905). The measurement principle is that the solid surface of the sample is irradiated in ultra-high vacuum with X-ray energy causing the emission of electrons ionized as photoelectrons. Only those photoelectrons from the outer surface of the sample reach the detector. The number and kinetic energy of the photoelectrons are analysed and used to calculate their binding energy. The binding energy is very specific for the atom from which the electron originated. XPS detects all the elements except hydrogen and helium. It is not possible to detect highly volatile samples with the XPS method due to the ultra-high vacuum used during the analysis. XPS has been used in the pulp and paper industry to study the surface chemistry of pulp, the migration of binder from coated paper, and the adhesion between the paper and coating layers (Beamson and Briggs, 1992, Istone, 1995). XPS provides quantitative data about the elemental composition on the surface and the chemical states of those elements i.e. functional groups, chemical bonding, oxidation state, and information about the relative states of the elements. It is highly surface sensitive and a powerful tool for chemical surface analysis, providing the surface chemical composition in atomic % for the outermost 2-10 nm of the surface (Istone, 1995). The analysis depth for papers and polymers is about 10 nm, but for metal oxides and metals it is less.

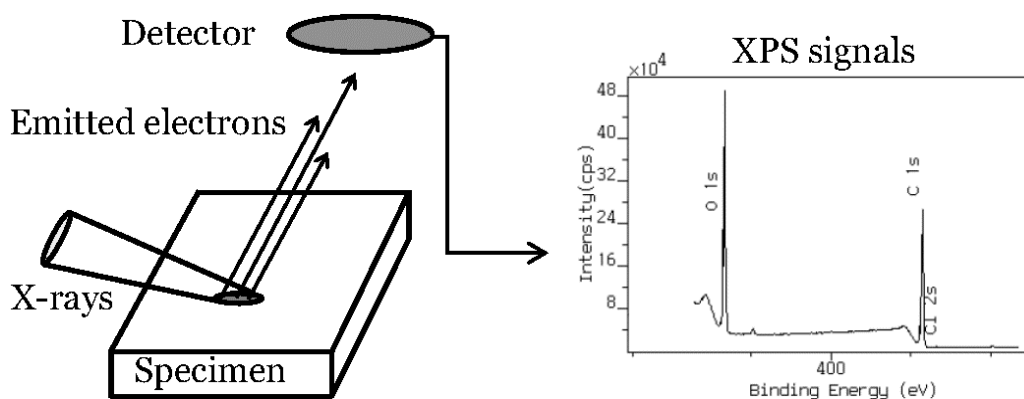


Figure 15. Illustration of the XPS method.

In this work, wide (survey) spectra were run to detect elements present in the surface layer. The relative surface compositions expressed in atomic % were then obtained by quantification of the detailed spectra

for each element. From the atomic % of carbon and oxygen, the O/C was calculated. The relative sensitivity factors (RSF) used for quantification were 0.278 for C1s, 0.780 for O1s, 1.685 for Na1s and 0.486 for P2p (RSF data supplied by Kratos Analytical, Manchester, UK). In addition, a chemical bond analysis of the carbon was accomplished by de-convoluting the C1s peak into four sub peaks with chemical shifts relative to the C1-carbon. These are given in Table 2.

Table 2. Deconvoluted peak assignments with corresponding shifts in binding energy relative to the C1 carbon and bond type for high-resolution XPS scan of the C1s region. C1 carbon is at binding energy of 285.0 eV.

Carbon group	Chemical shift (eV)	Bond
C1	-	C-C, C=C or C-H
C2	1.6-1.7	C-O or C-O-C
C3	3.0-3.2	O-C-O or C=O
C4	4.2-4.4	O-C=O or C(=O)OH

4.8 Adhesion

The adhesion of the extrusion coating to the substrate was determined by a peeling test as shown in Figure 16, using a standard tensile tester Zwick/Roell Zoo5 (Ulm, Germany).

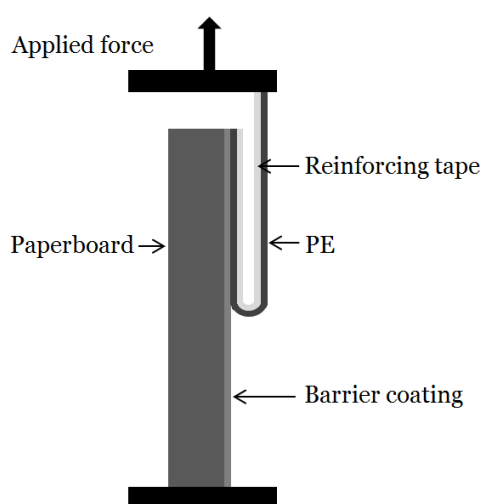


Figure 16. The set-up for measuring adhesion.

A sample was fixed between the grips and the cross-head speed was kept constant. The adhesive strength was measured by drawing the coating off the paperboard at an angle of 180° from its original position on the board. The initial strength (N/m) at the point of separation was recorded. To avoid stretching the coating during the adhesion test it was laminated with a reinforcing tape.

After the coating had been peeled off from the paperboard, the nature of the failure was examined. The presence of starch was determined with an iodine solution (KI to I₂ ratio 3:1 according to TAPPI standard method T419) on both the detached PE layer and the paperboard.

4.9 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to characterize the cracks and flaws in the coatings. The samples were coated with gold in a sputter coater. Micrographs were obtained in a SEM (FE-SEM, Leo 1530, Carl Zeiss GmBH; Vienna, Austria) under low vacuum at 20 kV with a secondary electron detector. The cross-section of samples was studied after creasing and folding, and the samples were prepared using a free cut. A SEM from Hitachi; (modelSU3500) was used to study the samples, with a pressure of 40 Pa, and an accelerating voltage of 10 kV. The basic principle of scanning electron microscopy is shown in Figure 17.

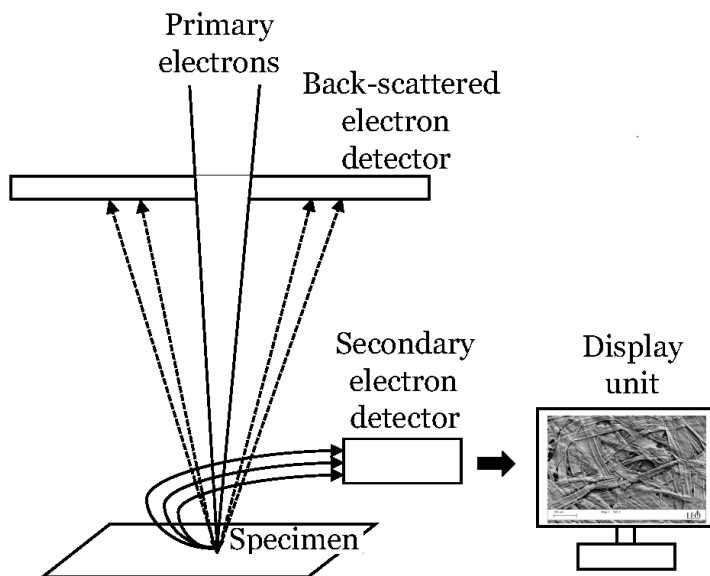


Figure 17. The basic principle of SEM.

A specimen is bombarded with an electron gun and the scattered primary and secondary electrons are detected. The back-scattered electrons are caused by the direct collision of primary electrons with the nuclei of the specimen. Secondary electrons are low-energy electrons which are produced when primary electrons transfer energy to the specimen. Both back-scattered and secondary electrons can be detected to produce SEM images.

4.10 Microscopic analysis

Cross-section images of extrusion-coated samples were obtained with an optical microscope (Zeiss Axioskop 40, Thornwood, NY, USA) using a magnification of 400. Images of the creased and folded samples were obtained using a Nikon SMZ-U zoom 1:10 stereo-microscope equipped with a ProgRes CT5 camera.

4.11 Contact angle determination

The contact angles of three test liquids on the substrates were captured with a CCD camera (sanyo VCB-3512T) using the FTA 200 Dynamic Contact Angle Analyzer (First Ten Angstroms, USA). The contact angles were plotted verses time and the linear region of the curve was extrapolated to zero time. The three test liquids used were deionized water, ethylene glycol (Merck, Germany) and diiodomethane (Fluka Chemie DmbH, Switzerland). The surface energy parameters of the test liquids are shown in Table 3.

Table 3. Surface energy parameters of test liquids (mJ/m^2).

	Water	Ethylene glycol	Diiodomethane
γ^{Lw}	21.8	29	50.8
γ^+	25.5	1.92	0
γ^-	25.5	47	0

In Figure 18, high and low contact angles of a liquid on a solid surface are shown. θ is the contact angle i.e. the angle formed between the plane of the solid surface and the tangent to the droplet at the point of

contact. In general, if the contact angle of liquid on a solid surface is less than 90°, it wets the solid.

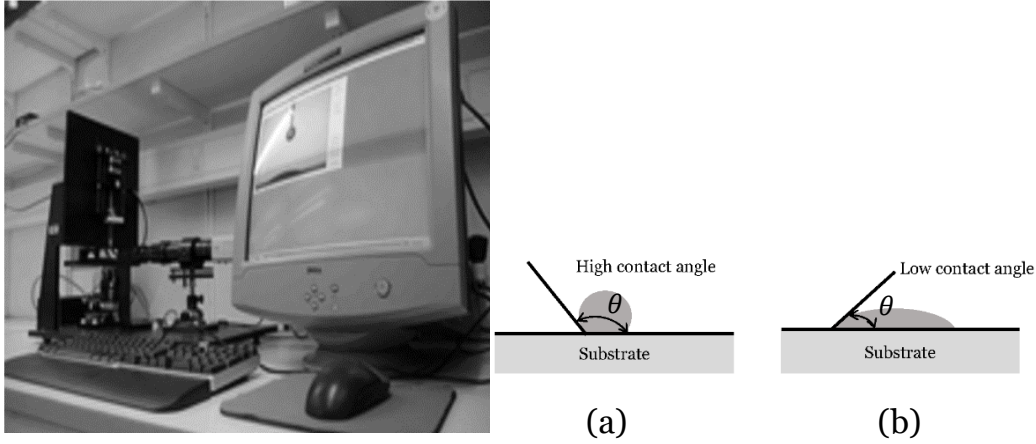


Figure 18. The dynamic contact angle analyser used (left) and illustration of (a) high and (b) low contact angle (right)

The surface energy parameters and the total surface energy of the substrate were calculated according to the method proposed by Van Oss (Van Oss, 1994b) from the contact angles of the three test liquids according to:

$$\gamma_l(\cos \theta + 1) = 2\left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + 2\sqrt{\gamma_s^+\gamma_l^-} + 2\sqrt{\gamma_s^-\gamma_l^+}\right) \quad (15)$$

$$\gamma^{TOT} = \gamma^{LW} + 2\sqrt{\gamma^-\gamma^+} \quad (16)$$

where the suffixes s and l stand for the solid and liquid phases, respectively, θ =the contact angle, γ =surface energy, γ^{LW} =Lifshitz – van der Waals component, γ^+ =electron acceptor component, γ^- =electron donor component and γ^{TOT} =total surface energy.

4.12 Surface roughness

The surface roughness of the uncoated sides of the pre-coated board and duplex board was measured with a Bendtsen tester at different pressures before and after treatment with water. Water was applied by a bench coater on the uncoated side of the board samples followed by subsequent drying at 105°C for 90 s.

4.13 Surface profilometry

The cracks in the coating layers were studied by Vertical Scanning Interferometry by a surface profiler, Model 831-567-1, Bruker Nano GmbH, Berlin, Germany, with a scanning speed of 5X. The measurements were performed using an objective lens 50X*0.55X, green light and a threshold frequency of 2%.

The microscope is generally used to obtain information about the lateral features of an object but it does not give information about the height of an object. A combination of microscope and interferometer in a single instrument can be used to measure the height of engineering surfaces with high resolving power. An interferometer is an optical device that splits and recombines a beam of light to produce an interference pattern. A typical interferometer is shown in Figure 19 in which a beam of light is separated into two beams using a beam splitter.

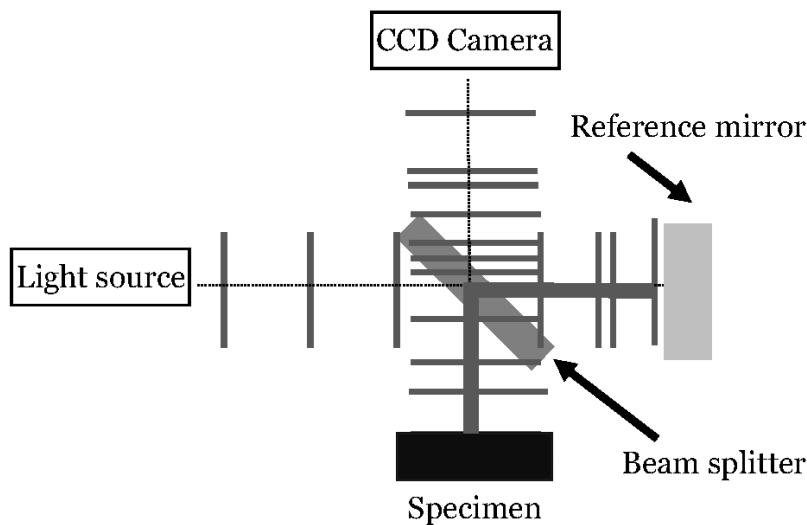


Figure 19. Illustration of a typical interferometer.

One beam is reflected from the specimen and the other from a reference mirror, and they are recombined by the beam splitter to interfere. The difference in optical path length creates a phase difference between the two reflected beams. The interference can be either constructive interference resulting in a bright band or destructive interference resulting in a dark band.

4.14 **Creasing and folding**

The coated board samples were printed with a cyan ink (Sun Chemical offset, cyan, Toplith B 6210) in an IGT laboratory printing press in order to show the surface cracks more clearly in the optical microscopy. The samples were then creased in a Marbach laboratory crease tester (Marbach, Heilbronn, Germany) with a male ruler having a width of 0.71 mm and a female die with a width of 1.4 mm. A crease depth of 0 mm was used. After creasing, the samples were folded 180 degrees by hand in the machine direction (MD) with the coating on the inside of the fold and then unfolded prior to crack analysis.

4.15 **Stability in water of self-supporting films**

The migration of starch and lignin from the films/coated papers into the aqueous phase of three different model liquids was studied in order to investigate their stability in water. The liquids used were deionized water, an alkaline buffer solution of pH 10 ($\text{NaHCO}_3 + \text{NaOH}$), and 3% (w/v) acetic acid solution at pH 2.43, at a temperature of 25°C. 3% (w/v) acetic acid solution is food simulant B according to Commission Regulation (EU) No 10/2011. Pieces of the films, 20 mg of films with an exposed area of ca. 2cm², and pieces of coated papers, 4 mg of dry coating with an exposed area of ca. 5cm², were put in 15 ml plastic test tubes containing 5 ml of the liquid. The tubes were rotated at 22 rpm and the concentration of the polymer in the aqueous phase was measured after different times.

McCready et al. (1950) have described the anthrone method to detect the amount of starch in the aqueous phase. According to their method, the absorption at 630 nm was used to determine the amount of starch that had migrated to the liquid after 5 minutes, the absorbance being measured using a spectrophotometer, UV-1800 240V IVDD, Shimadzu, Canby, U.S.A. All the measurements were performed in six replicates. The absorbance at 630 nm was also measured for pure starch and lignin solutions separately at different concentrations ranging from 0 to 100 (µg/ml) and it was found that the influence of dissolved lignin on the starch analysis was negligible within the investigated concentration range.

The migration of lignin to the liquid was measured at 380 nm after different times using the same spectrophotometer. Experiments were performed in six replicates, and the results are shown with 95% confidence intervals. The wavelength of 380 nm was chosen after studying the absorption spectra between 100 and 1100 nm. Absorption at 380 nm gives a strong signal from lignin without any significant influence of starch within the range of polymer concentrations investigated in this study. Johansson et al. (2012) have also indicated that 380 nm gives the highest selectivity for lignin. For starch/lignin films, the absorbance after 5 minutes contact time was 0.9 % of the total absorbance in deionized water, 0.7 % in alkaline buffer solution and 4 % in food simulant B.

5. Barrier Properties

As described in sections 2.1 and 2.3, a paperboard package is usually barrier coated to protect the inside contents from gases and moisture, and most of the materials used today as barrier materials in food packaging applications are oil-based polymers. Oxygen and water vapour permeabilities of oil-based polymeric materials normally used in packaging are shown in Table 4.

PE and PP are the polymeric materials most commonly used in food packaging. Both are easy to process, highly flexible and have good water barrier properties (Marsh and Bugusu, 2007). EVOH and PVDC are both good gas barrier polymers. PVDC also has low water vapour permeability and its oxygen barrier properties are not affected by the relative humidity, but EVOH films have shown a low oxygen permeability only in the dry state (Marsh and Bugusu, 2007, Mokwena et al., 2009). Oxygen permeability of EVOH films can increase about one hundred times when the relative humidity is increased from 0% RH to 90% RH (Muramatsu et al., 2003). EVOH is normally used in combination with other polymeric materials such as PE, PP or PET combined by a lamination or co-extrusion process in order to provide a barrier against both water and oxygen permeability in food packaging applications. In lamination, two or more polymer films are bonded together or to paperboard with an adhesive and pressing between rolls at a certain pressure. In co-extrusion, molten polymer layers are combined together during a film-forming process in an extruder.

Although, PVDC has good water and oxygen barrier properties, its cost, environmental issues and difficulties in processing are major concerns (Massey, 2003).

Table 4. Oxygen and water vapour permeabilities of polymeric materials commonly used in packaging (Lange and Wyser, 2003).

Polymer	Permeability	
	Water vapour	Oxygen
	23°C 85% RH (g mm/m ² day)	23°C 50% or 0% RH (cm ³ mm/m ² day atm)
Polyvinylidene chloride	0.1	0.01-0.3
Polypropylene	0.2-0.4	50-100
Polyethylene terephthalate	0.5-2	1-5
Polyethylene	0.5-2	50-200
Polyamide	0.5-10	0.1-1 (0% RH)
Polyvinyl chloride	1-2	2-8
Ethylene vinyl alcohol	1-3	0.001-0.01 (0% RH)
Polystyrene	1-4	100-150
Polyvinyl alcohol	30	0.02 (0% RH)

Bio-based materials such as proteins and polysaccharides are potential candidates to replace oil-based barrier materials in fibre-based food packaging. Olabarrieta et al. (2001), Rhim et al. (2006) Rindlav-Westling et al. (2002), Hartman et al. (2006), Österberg et al. (2013) and Kjellgren et al. (2006) have reported that most of the polysaccharides and proteins such as wheat gluten, whey protein, chitosan, starch, alginates and hemicellulose have shown good film-forming and oxygen-barrier properties but poor resistance to moisture. The water vapour permeability through films or coatings based on bio-based materials is usually high because of their hydrophilic nature, and the oxygen permeability was higher at a high relative humidity

(Forssell et al., 2002). Bio-based polymers are hydrophilic in nature due to the abundance of hydroxyl groups present in their molecules. The blending of bio-based polymers with other polymers can overcome these limitations. Olabarrieta et al. (2001) have shown that when chitosan was blended with the hydrophobic poly (ϵ -caprolactone), the water vapour transport through the films decreased significantly.

Films produced with pure starch are usually brittle, the elongation-at-break of a starch film being about 5% (Jansson and Järnström, 2005), and this limits the use of starch as barrier material in fibre-based food packaging. Brittle barrier coating layers cannot withstand mechanical loading during the converting process creating packages from a barrier-coated paperboard. Defects such as cracks can occur in the barrier-coating layers through which the transportation of gases or water vapours is to take place. The flexibility of the starch films can be increased by adding a plasticizer to the starch or by blending with other polymers.

The addition of a plasticizer to a polymer increases the polymer chain mobility, increases the free volume surrounding the polymer chains and decreases the crystallinity of the material, and results in high oxygen and water vapour permeabilities (Bialecka-Florjanczyk and Florjanczyk, 2007, Donhowe and Fennema, 1993). The WVTR and OTR through a paperboard coated with starch and starch-PVOH blends with and without plasticizer were measured in Paper I, and it was found that both the WVTR and OTR of the coatings increased when glycerol or PEG was added to the starch and starch-PVOH formulations. The OTR-values for the coated-board were less than 1 cm³/m²day when four layers of coating with a total thickness of about 14 μ m were applied using starch-PVOH without any plasticizer, but the OTR values for the coated board were about 2000 and out of the measurable range (i.e. OTR>10000 cm³/m²day) when glycerol and PEG respectively were added to the coating recipe.

Starch films have shown a remarkable increase in flexibility and barrier properties when films were formed from blends containing PVOH (Mao et al., 2000, Katerinopoulou et al., 2014). It has been shown that the addition of PVOH to a starch film decreases the moisture uptake of the film (Liu et al., 1999), and starch-PVOH-based materials formed by

a baking process have been shown to have a higher tensile strength and greater water resistance than starch (Cinelli et al., 2006). Jansson and Järnström (2006) showed that plastisol coatings based on starch-PVOH showed a potential to give a low OTR when applied to a paperboard substrate, but defects such as pinholes in the coatings must be reduced to give high oxygen-barrier properties. Foamed particles formed with starch-PVOH blends have been shown to have a greater resistance to water than starch (Cinelli et al., 2006, Shogren et al., 1998). However, both starch and PVOH are hydrophilic in nature and films and coatings based on starch have poor barrier properties against oxygen at high relative humidities. Starch-PVOH blend films have shown a decrease in flexibility at high starch contents (Ramaraj, 2007).

Lignin has shown a potential for use as an antioxidant and antimicrobial agent in food packaging (Domenek et al., 2013). Lignin blends with other polymers, such as poly (vinyl alcohol) (Kadla and Kubo, 2004), polypropylene (Pouteau et al., 2003), polyethylene (Alexy et al., 2000) and starch (Kaewtatip and Thongmee, 2013) have been studied for use in different applications. Johansson et al. (2012b) and Bhat et al. (2013) have recently studied starch-lignin blends for their promising use in food packaging applications. In the present work, it has been shown that the addition of lignin can significantly increase the stability in water of starch films and coatings (Papers IV and V).

In food packaging applications, paper or paperboard are usually extrusion coated with PE to provide a protection against moisture (Kjellgren and Engström, 2008, Savolainen et al., 1998), and it has been shown that PE extrusion coating on a pre-coated or uncoated board can also decrease the OTR of the board (Vähä-Nissi et al., 2001, Furuheim et al., 2003, Stolpe, 1996, Dole et al., 2005, Olsson et al., 2014). Kjellgren and Engström (2008) have shown that the OTR through greaseproof paper was reduced after extrusion coating and the OTR values were found to be much lower than that of PE or greaseproof paper itself. Olsson et al. (2014) have also reported the same result when a pre-coated board with a starch-based coating was extrusion coated with PE. Similar effects of extrusion coating on a pre-coated board with starch-PVOH blends with and without plasticizer were observed (Paper II). In a multilayer structure, good adhesion between

the different barrier coating layers is a prerequisite for achieving the synergetic effects of different barrier layers (Dole et al., 2005). PE melt extrusion coatings on paperboard can seal small pores and result in a lower OTR, and the wetting of the substrate by the PE melt during the extrusion process is therefore also vital to achieve low oxygen barrier properties (Furuheim et al., 2003). The results in Paper II showed that the addition of PEG to the pre-coating recipes can increase the wetting of PE melt on the pre-coated board during the extrusion process. During the extrusion coating process mechanical and temperature loads are applied and a pre-coating layer with high brittleness can therefore be damaged.

6. Crosslinking

Starches have been cross-linked with a range of substances such as boric acid (Yin et al., 2005), sodium trimetaphosphate (Hirsch and Kokini, 2002), sodium tripolyphosphate (Deetae, et al., 2008), monochloroacetic acid, dichloroacetic acid (He, et al., 2007) epichlorohydrin (Kuniak and Marchessault, 1972), glutaraldehyde (Ramaraj, 2007) CA (Olsson et al., 2013a) and AZC (McAlpine, 1982). In the cross-linking of starch, a multi-functional chemical containing two or more functional groups can react with hydroxyl groups of starch making a covalent or ionic bond. The crosslinking of starch with covalent bonds can occur intra-molecularly within the same polymer chain or inter-molecularly between different polymer chains. Cross-linking between starch and other reagents can reduce the number of hydroxyl groups present on the starch. It also reduces the mobility of the polymer chain and make the film brittle. Crosslinking of polymers can also reduce their moldability and recyclability (Stephens, 1999). The crosslinking of starch reduces its solubility, increases the starch paste viscosity and reduces the swelling in water.

In the present work, CA was added to the starch and starch-PVOH formulations and AZC to the starch-lignin formulations as potential cross-linkers. Olsson et al. (2013b) have demonstrated that the cross-linking of starch with citric acid occurs at a low pH between 4 and 6.5, but pH levels between 7 and 11 are recommended for the cross-linking of AZC with starch/cellulose (Song et al., 2011, McAlpine, 1982, Yoon and Deng, 2006).

Olsson et al. (2013b) have shown that the crosslinking of starch with CA suppressed the increase in oxygen permeability through the coated paper at high relative humidity by reducing the moisture sorption of the coatings. Javed et al. (2016) have shown that the WVTR through paperboard coated with starch and starch-PVOH blends decreased when CA was added. Starch-PVOH blends, like starches, also have the ability to be cross-linked by bi- or multi-functional agents. Yin et al. (2005) have shown that cross-linking of starch-PVOH films with boric acid increased the water resistance of the films. Shi et al. (2008) have reported that CA can react with both starch and PVOH. Some researchers have reported poor compatibility and phase separation in starch and PVOH blends (Mao et al., 2000, Liu et al., 1999). The compatibility of a starch-PVOH blend can be increased by crosslinking (Lee et al., 2007). In Paper I, it was shown that CA acted as a compatibilizer for starch-PVOH blends.

Crosslinking of a polymer can increase the brittleness of the polymer films/coatings due to the strong attraction between the polymer chains and the cross-linking agent. An increase in brittleness of starch and starch-PVOH films by crosslinking has been reported by many researchers (He, et al. 2005, Yin et al., 2005, Shi, et al., 2008, Javed et al., 2016). Artefacts in the films or coatings such as cracks may arise during mechanical loading, leading to high oxygen transmission rates.

Gröndahl et al. (2013) have studied the effect of cross-linking of xylan coatings on the water resistance and oxygen barrier properties of the films. AZC was added in an amount of 0-20% by weight based on the total amount of dry polymer. It was reported that xylan films have shown a greater water resistance with even small amounts of AZC, and the water resistance of the films increased substantially with increasing AZC content (Gröndahl et al., 2013). The oxygen permeability at 23°C and 80% RH through xylan films containing 10% of AZC was ca. 7 times lower than the film containing 5% of citric acid (Gröndahl et al., 2013). Starch can be cross-linked with AZC, and the water resistance of starch-based coatings can be increased through cross-linking with AZC (McAlpine, 1982). In papers IV and V, it was shown that the addition of AZC to the starch-lignin blends increased the stability of the films and coatings in water.

7. Mechanisms of failure

Creasing and folding operations are performed to convert board materials into a package, and this involves the action on the substrate of complex tensile, compressional and shear forces. A material with little resistance to creasing and folding operations which does not crack is generally considered to be a better material from a converting point of view. The crack resistance of paperboard is generally high compared to that of materials such as ceramics, glass, plastics, fibre composites and paper, but problems may arise if the board is cracked. The mechanical properties of the coating layers and properties of the base substrate can affect the tendency of the coating layers to crack during creasing and folding (Jopson and Towers, 1995). Rättö et al. (2012) have shown that the creasing of paperboard and folding of paper result in different types of cracking behaviour, probably because of differences in the stress field during the two operations. Barbier et al. (2002) and Nygåards et al. (2009) have suggested that in-line stresses are important during the folding of paper but that out-of-plane tensile stresses and shear stresses are important in the creasing of paperboard. Strains at the surface of the board can decrease if forces applied during creasing operation delaminate the bulk of the board (Beex and Peerlings, 2009, Nagasawa et al., 2003). Beex and Peerlings (2009) have proposed that cracking in the top coating layer tends to follow the creasing line due to the development of high strains at the creasing borders. Barbier et al. (2002) have reported that cracking occurs near the fold during the folding of a paper. Kim et al. (2010) have shown that fibre orientation and the stiffness of the base board affect the cracking in the coating layers. In multiple coating layers, failure in one coating layer can initiate cracking in the adjacent coating layer (Alam et al., 2009, Carlsson et al., 2007). Ductile barrier coating layers can fail due to large stresses, and brittle coating layers can fail due to large strains in the coating layers during the creasing and folding operations. Tensile stresses applied to a ductile layer deform the layers elastically and then plastically, and failure occurs when the local stress exceeds the local strength. Local plastic flow in the ductile barrier coating layers can further initiate cracks in pre-existing defects such as small cavities and voids in the coating layers leading to a large number of cracks. Alam et al. (2009) have proposed that multiple coating layers consisting of a

thin and stiff inner layer, a thick middle layer of low stiffness and a thin outer layer of low stiffness can be a good strategy to reduce cracking during the folding of a coated paper. In this strategy, a thick middle layer of low-stiffness can act as a buffer and reduce the impact of forces on the outer layer.

In this thesis (Paper III), failure in the coating layers based on starch and starch-PVOH with and without plasticizer was studied on two different substrates. The effects on crack formation of the flexibility and thickness of the coating layers, the fibre orientation and the pre-coating, mineral coating, on the baseboard were investigated. The results have shown that the crack area in the barrier coating layer increased with increasing brittleness of the barrier coating layer. Barrier coatings on the mineral-coated side of the board showed a greater cracking tendency than barrier coatings on the uncoated side of the board. It was shown that a thicker ductile barrier coating layer could resist stresses caused by cracking in the mineral coating layer. In the case of the uncoated board, fibre rising seemed to be one possible mechanism leading to cracking.

8. Sustainability and socio-economic aspects

Over the last few decades, efforts have been made by academia and industry to replace oil-based polymers with bio-based polymers in packaging, considering that recyclability and sustainability are major issues. Bio-based polymers derived from renewable resources are essentially more sustainable than oil-based polymers which are derived from non-renewable resources (Shen and Patel, 2008). Life cycle assessments of starch-based materials have shown a lower energy use, a higher energy recovery and a lower emission of greenhouse gases than oil-based materials (Shen and Patel, 2008, Narayan, 2004). Ståhl et al. (2014) have shown that by adding starch to the wood pellets, the use of energy, the emission of greenhouse gases and the product losses in the production of wood fuel pellets can be reduced. However, the cost of new bio-based materials compared to the cost of their traditional oil-based counterparts, the use of agricultural land to grow materials for industrial purposes and the overall impact on the global environment are major concerns (FP1003-BioMatPack). In food packaging applications, conventional non-renewable materials such as

aluminium or EVOH and PE are usually applied on a paperboard to create a barrier against oxygen and moisture (Lange and Wyser, 2003). In the present study, barrier coatings based on starch-PVOH and starch-lignin and PE-extrusion coating have been applied to a paperboard. Eriksson et al. (2009) have made life cycle assessments of various packages used for the retail distribution of milk or juice. Paperboard packages with a larger amount of plastic have been shown to make a greater contribution to greenhouse gas emissions but to have a relatively low impact on global warming compared with packages containing a layer of aluminium. It is reported elsewhere that the impact on the environment was lower when less material was used for a paperboard package with an aluminium-polymer barrier layer than a plastic package with an aluminium-EVOH barrier layer (BioIntelligent, 2010). Starch and lignin have been shown to have less impact on the environment and lower greenhouse gas emissions than the traditional non-renewable polymers such as PET, PE and PVOH (Shen and Patel, 2008).

The development of bio-based materials can add value to the industry through e.g. a better green profile, new product areas, a pro-active approach to finding alternative materials, fulfilling social responsibility by reducing greenhouse gas emissions, increasing the recyclability of packaging waste and increasing profits.

9. Summary of papers

Papers I and II

In papers I and II, the effects of plasticizers such as glycerol, PEG and CA on the mechanical and barrier properties of starch and starch-PVOH blends were studied. PE extrusion coating was also applied on paperboard pre-coated with a starch-PVOH blend with and without plasticizer. It was found that the elongation-at-break was higher in the glycerol- and PEG-containing starch and starch-PVOH blend films than in the CA-containing films. The addition of PVOH to starch increased the flexibility of the starch films, and this was further increased by adding a plasticizer to the formulation. Curing of the films containing plasticizers led to a decrease in flexibility and an increase in tensile strength of all the films, although the effect of curing was greater

for the starch films containing CA. The XPS analysis of starch-PVOH blend films containing PEG and CA revealed an enrichment of PVOH at the surface of films with both the plasticizers. A stratified structure was observed in the starch-PVOH-PEG films but not in the starch-PVOH-CA films, which indicated that CA may act as a starch-PVOH compatibilizer. The WVTR of starch and starch-PVOH coatings decreased substantially when CA was added to the coating formulation. The addition of a plasticizer to the coating formulation considerably increased the OTR through starch-PVOH coated board when two layers were applied. With four layers, coatings based of starch-PVOH has the same OTR-values with citric acid as without citric acid.

After PE extrusion, samples with a CA-containing coating had a higher OTR than those with a PEG-containing coating. The E' of starch-PVOH films containing CA increased substantially at high temperatures and this had a dominating effect on the barrier properties of these samples. On the other hand, the low contact angle of diiodomethane on a paperboard pre-coated with a starch-PVOH blend containing PEG indicated a greater wetting by the PE melt during the extrusion process than with the CA-containing pre-coating. The high degree of wetting of the PEG-containing samples may have sealed the small pores and voids and resulted in low OTR values

Paper III

In this paper, cracks were studied in the coating layers based on starch and starch-PVOH with and without plasticizer after the creasing and folding of two different substrates, a pre-coated board and a duplex board. The OTR through the coated samples was above the measurable range after creasing and folding, which indicated failure in the coating layers. The optical microscopy revealed small cracks in the barrier layers, probably related to an increase in flexibility of the coating layers. Cracking of the mineral coating layer led to cracking in the coating layer, and the cracks seemed to follow the fibres in MD when the coating layers were applied on the board with a high compressibility and which was more susceptible to fibre rising. A thicker coating layer did not necessarily increase the resistance to failure in the coating layer during creasing and folding. The coating layers with a higher coat weight mostly exhibited large crack areas.

Papers IV and V

In these papers, the effects of addition of lignin and AZC on the mechanical properties and stability of starch films in contact with three model liquids viz. deionized water, alkaline buffer solution of pH 10 and Food simulant B (3%, w/v, acetic acid solution) were studied. Paperboard was also coated with starch/lignin blends on laboratory and pilot scales and the effects of AZC on the stability in water of coatings at different pH levels were studied when the pH of the solutions was adjusted with ammonia or NaOH solution. It was shown that the addition of lignin increased the stability of starch films in contact with the three liquids. The addition of AZC to the formulations as a cross-linking agent reduced the migration of starch from the films, and it also reduced the migration of lignin from the starch-lignin films. The lignin migration from the films was less when the pH was adjusted with ammonia than with NaOH solution. The presence of a large number of sodium ions could restrict the interaction between AZC and starch-lignin. Lignin became soluble in water at lower pH levels when starch was added to the solution. It was shown that stability of coatings in water can be increased by adding AZC to the coating recipe or by lowering the pH level of the coating formulation. The addition of starch to the lignin increased the solubility in the test liquid of the lignin in starch-lignin blends at low pH levels. The migration into the model liquids of lignin from the paper with a pre-coating of a starch-lignin blend containing AZC decreased with decreasing pH of the coating solutions. Paperboard coated with a starch-lignin solution showed no significant decrease in WVTR when AZC was added to the coating recipe. The OTR through the coated paperboard increased after the addition of AZC to the coating formulation.

10. Future perspectives

Good adhesion between the separate layers is essential to achieve the desired properties of a multilayer structure. Strategies to improve the adhesion between different layers and how it affects the barrier properties of the multilayer structure require further studies.

It is necessary to study the effects of cross-linking of starch-PVOH and starch-lignin films/coatings on their bio-degradability.

In future work, it would be of great value to further investigate the mechanisms of failure of barrier coating layers in converting process and how the process can be improved without affecting the barrier properties negatively.

Pilot-coatings of starch-lignin have shown defects in the coatings, and optimization of the large-scale process is therefore needed. A future study should also focus on how the kinetics of the drying process can affect the barrier properties of coatings.

11. Conclusions

The flexibility of the starch films was increased by adding PVOH to the starch and it was further increased by adding a plasticizer to the recipe. Curing of the films decreased their flexibility and the films containing CA showed an increase in brittleness of the films at elevated temperature.

The mechanical tests and XPS analysis of the films revealed that CA acted as a compatibilizer for starch and PVOH and increased the compatibility of the starch-PVOH blends. The WVTR results indicated that CA acted as a cross-linker for starch and PVOH. The increase in compatibility and cross-linking of starch-PVOH coatings was reflected in their barrier properties, and the coatings containing CA showed OTR-values similar to those of pure PVOH when a sufficient number of coating layers were applied.

The adhesion between PE and the pre-coating layer decreased when a plasticizer was added to a pre-coating based on starch-PVOH blend. The reduction in OTR was less when CA was added to the pre-coating than when PEG was added. The increase in brittleness of the starch-PVOH-CA films at elevated temperatures was shown to effect the oxygen permeability of the pre-coating during the extrusion coating process. A pre-coating containing a PEG resulted in lower contact angle of diiodomethane and indicated that the wetting of the coating by the PE melt had increased.

CA could be used as a compatibilizer and cross-linker for starch-PVOH blends. The contact angle of diiodomethane could be used as a test

method to analyse the PE adhesion and PE melt wetting on paperboard.

It was shown that the crack area in the coating layer decreased with increasing flexibility of the coating layer. A coating applied on the mineral-coated side of the board showed greater cracking tendency than a coating applied on the uncoated side of the board. Flexible coating layers could resist the stress leading to cracking in the mineral-coating layer. The results indicated that fibre rising could be one possible mechanism behind cracking and the cracks seemed to follow the fibres in MD when the coating layers were applied on a board with high compressibility that was more susceptible to fibre rising.

The addition of lignin to starch decreased the migration of starch from the films to liquids and the addition of AZC to the recipes decreased the migration of both lignin and starch from the films. The DMA of the films indicated that AZC acted as a cross-linker for starch and lignin. The presence of a large number of sodium ions could restrict the interaction between AZC and starch-lignin. The addition of starch to the lignin lowered the minimum pH at which lignin is still soluble in water. A decrease in the pH of the coating solution decreased the migration of lignin from a paper coated with a starch-lignin-AZC blend.

12. Acknowledgement

Many people contributed to the completion of this work. It was their guidance, support and collaboration throughout this study which encouraged me to achieve this goal.

First and foremost, I should like to thank my main supervisor Professor Lars Järnström for all his help. This work would never have been possible without your invaluable guidance, advice, research ideas and great knowledge. Thank you for encouraging me, for always pushing me to work hard and for believing in me.

I thank my co-supervisors, Professor Peter Rättö and Dr. Henrik Ullsten, for sharing their time with me and believing in me. I really appreciate your support, advice, knowledge and all the discussions we had.

I would like to thank Associate Professor Caisa Johansson for all her help and guidance, especially at the start of this project.

My co-author Marie Ernstsson is deeply thanked for her invaluable guidance in the writing of paper I.

Pia Eriksson and Birgitta Gustafsson are thanked for their laboratory help. Micke Andersen is greatly thanked for providing materials needed for the experimental work.

Christer Burman is gratefully thanked for his assistance with SEM images and Mikael Sundin for his help with the XPS analysis. Ann-Catrine Hagberg and Thomas Trost at RISE Bioeconomy (Stockholm, Sweden) are thanked for their help with the optical microscopic and SEM images, and the creasing of the samples.

Dr. J. A. Bristow is greatly acknowledged for the linguistic revision of this thesis and the papers and for his valuable suggestions to improve the content.

This work was performed within a multidisciplinary Industrial Graduate School VIPP (Value Created in Fibre-based Processes and Products) at Karlstad University. I would like to thank all my colleagues

at VIPP for the fun time that we spent during the lunches, the coffee breaks and the courses.

The financial support from the Knowledge Foundation (Sweden), grant registration number 20100268, and from Vinnova (Sweden's innovation agency), grant registration number 2015-05023, is gratefully acknowledged. I would like to thank testbed LignoCity operated by RISE LignoDemo AB for delivery of kraft lignin.

To all my colleagues at the Department of Engineering and Chemical Sciences, thank you for creating an excellent environment at the department.

To all my friends, thank you for your help and support. Pyry, Chaudhary, Sir and Murshad are especially thanked for fun times and all the laughs we shared together.

Finally, this would have not been possible without the love, support, prayers and encouragement of my family. I should like to thank my brothers, sisters, nephews and nieces for everything. I wish my parents were here to see this happening, but I am sure you will be proud of me in heaven. I am thankful to my wife, Ummara, and daughter, Hajra, for unconditional love, affection, support and prayers. I love you both.

13. References

- Alam, P., Toivakka, M., Carlsson, R., Salminen, P. and Sandås, S. 2009. Balancing between fold-crack resistance and stiffness. *Journal of Composite Materials*, 43, 1265-1283.
- Andersson, C. 2008. New ways to enhance the functionality of paperboard by surface treatment—a review. *Packaging Technology and Science*, 21, 339-373.
- Arvanitoyannis, I., Kalichevsky, M., Blanshard, J. M. and Psomiadou, E. 1994. Study of diffusion and permeation of gases in undrawn and uniaxially drawn films made from potato and rice starch conditioned at different relative humidities. *Carbohydrate Polymers*, 24, 1-15.
- Assender, H. E. and Windle, A. H. 1998. Crystallinity in poly (vinyl alcohol). 1. An X-ray diffraction study of atactic PVOH. *Polymer*, 39, 4295-4302.
- Barbier, C., Larsson, P.-L. and Östlund, S. 2002. Experimental investigation of damage at folding of coated papers. *Nordic Pulp & Paper Research Journal*, 17, 34-38.
- Beamson, G. and Briggs, D. 1992. High Resolution XPS of Organic Polymers, John Wiley and Sons.
- Beex, L. and Peerlings, R. 2009. An experimental and computational study of laminated paperboard creasing and folding. *International Journal of Solids and Structures*, 46, 4192-4207.
- Berg, J. C. 1993. The importance of acid-base interactions in wetting, coating, adhesion and related phenomena. *Nordic Pulp and Paper Research Journal*, 8, 75-85.
- Bhat, R., Abdullah, N., Din, R. H. and Tay, G.-S. 2013. Producing novel sago starch based food packaging films by incorporating lignin isolated from oil palm black liquor waste. *Journal of food engineering*, 119, 707-713.
- Bialecka-Florjanczyk, E. and Florjanczyk, Z. 2007. Solubility of Plasticizers, Polymers and Environmental Pollution. Chapter 22. *Thermodynamics, Solubility and Environmental Issues*, 397-407.

- BioIntelligent 2010. Nordic Life Cycle Assessment Wine Package Study - Final report – ISO Compliant, BioIntelligent, 2010.
- Blankenburg, L., Schultheis, K., Schache, H., Sensfuss, S. and Schrödner, M. 2009. Reel-to-reel wet coating as an efficient up-scaling technique for the production of bulk-heterojunction polymer solar cells. *Solar Energy Materials and Solar Cells*, 93, 476-483.
- Bonnerup, C. and Gatenholm, P. 1993. The effect of surface energetics and molecular interdiffusion on adhesion in multicomponent polymer systems. *Journal of adhesion science and technology*, 7, 247-262.
- Brydson, J. A. 1995. *Plastics materials*, Butterworth-Heinemann Ltd., 72-105.
- Bueche, F. 1953. Segmental mobility of polymers near their glass temperature. *The Journal of Chemical Physics*, 21, 1850-1855.
- Cadogan, D. F. and Howick, C. J. 2012. Plasticizers. In *Anonymous Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 599-618.
- Cao, N., Yang, X. and Fu, Y. 2009. Effects of various plasticizers on mechanical and water vapor barrier properties of gelatin films. *Food Hydrocolloids*, 23, 729-735.
- Carlsson, R., Alam, P., Toivakka, M., Salminen, P. and Sandås, S. 2007. Balancing between fold-crack resistance and stiffness-Part 2, Experimental Studies. *PTS Coating Symposium*. Baden-Baden, Germany.
- Cavlin, S. 1988. The unique convertibility of paperboard. *Packaging Technology and Science*, 1, 77-92.
- Choudalakis, G. and Gotsis, A. 2009. Permeability of polymer/clay nanocomposites: a review. *European Polymer Journal*, 45, 967-984.
- Christer, S. and Johan, T. 2007. Packaging. In: Monica, E., Göran, G. and Gunnar, H. (eds.) *Ljungberg textbook part 4*. Universitetsservice US-AB, Stockholm Sweden.

- Chung, H.-J., Woo, K.-S. and Lim, S.-T. 2004. Glass transition and enthalpy relaxation of cross-linked corn starches. *Carbohydrate Polymers*, 55, 9-15.
- Cinelli, P., Chiellini, E., Lawton, J. and Imam, S. 2006. Foamed articles based on potato starch, corn fibers and poly (vinyl alcohol). *Polymer Degradation and Stability*, 91, 1147-1155.
- Coles, R. 2003. *Introduction*. In: Coles R, McDowell D, Kirwan MJ, editors. *Food packaging technology*. London, U.K.: Blackwell Publishing, CRC Press. p 1–31.
- Cowie, J. and Henshall, S. A. 1976. The influence of chain length and branching on the glass transition temperature of some polyglucosans. *European Polymer Journal*, 12, 215-218.
- Crank, J. 1975. *The Mathematics of Diffusion: 2d Ed*, Clarendon Press.
- Delville, J., Joly, C., Dole, P. and Bliard, C. 2003. Influence of photocrosslinking on the retrogradation of wheat starch based films. *Carbohydrate Polymers*, 53, 373-381.
- Dole, P., Averous, L., Joly, C., Valle, G. D. and Bliard, C. 2005. Evaluation of starch-PE multilayers: Processing and properties. *Polymer Engineering & Science*, 45, 217-224.
- Dole, P., Joly, C., Espuche, E., Alric, I. and Gontard, N. 2004. Gas transport properties of starch based films. *Carbohydrate Polymers*, 58, 335-343.
- Donhowe, I. G. and Fennema, O. 1993. The effects of plasticizers on crystallinity, permeability, and mechanical properties of methylcellulose films. *Journal of Food Processing and Preservation*, 17, 247-257.
- Ebewele, R. O. 2010. *Polymer science and technology*, CRC press.
- Einstein, A. 1905. A. Einstein, Ann. Phys.(Leipzig) 17, 132. *Ann. Phys.(Leipzig)*, 17, 132.
- Eriksson, E., Jelse, K., Einarson, E. and Ekvall, T. 2009. Life cycle assessment of consumer packaging for liquid food—Results for the Danish market. September 2, 2009, Copenhagen (Denmark). IVL Swedish Environmental Research Institute, on commission of Tetra Pak.

- FAO 2013. *Food Wastage Footprint: Impacts on Natural Resources, in Food Agriculture Organization of the United Nations*, FAO.
- Forssell, P., Lahtinen, R., Lahelin, M. and Myllärinen, P. 2002. Oxygen permeability of amylose and amylopectin films. *Carbohydrate Polymers*, 47, 125-129.
- FP1003-BIOMATPACK, C. A. Impact of renewable materials in packaging for sustainability - development of renewable fibre and bio-based materials for new packaging applications , 09 December 2010 - 08 December 2014.
- Fringant, C., Rinaudo, M., Foray, M. and Bardet, M. 1998. Preparation of mixed esters of starch or use of an external plasticizer: two different ways to change the properties of starch acetate films. *Carbohydrate Polymers*, 35, 97-106.
- Furuheim, K. M., Axelson, D. E. and Helle, T. 2003. Oxygen barrier mechanisms of polyethylene extrusion coated high-density papers. *Nordic Pulp & Paper Research Journal*, 18, 168-175.
- Garcia, M. A., Martino, M. N. and Zaritzky, N. E. 1998. Plasticized starch-based coatings to improve strawberry (*Fragaria× ananassa*) quality and stability. *Journal of Agricultural and Food Chemistry*, 46, 3758-3767.
- Gaudin, S., Lourdin, D., Forssell, P. M. and Colonna, P. 2000. Antiplasticisation and oxygen permeability of starch–sorbitol films. *Carbohydrate Polymers*, 43, 33-37.
- Goodship, V. and Jacobs, D. 2009. *Polyvinyl alcohol: materials, processing and applications*, Smithers Rapra Technology.
- Gram, L., Ravn, L., Rasch, M., Bruhn, J. B., Christensen, A. B. and Givskov, M. 2002. Food spoilage—interactions between food spoilage bacteria. *International journal of food microbiology*, 78, 79-97.
- Grunlan, J. C., Grigorian, A., Hamilton, C. B. and Mehrabi, A. R. 2004. Effect of clay concentration on the oxygen permeability and optical properties of a modified poly (vinyl alcohol). *Journal of applied polymer science*, 93, 1102-1109.

- Gröndahl, M., Bindgard, L., Gatenholm, P. and Hjertberg, T. 2013. Polymeric film or coating comprising hemicellulose. Google Patents.
- Guerrero, M. P., Bertrand, F. and Rochefort, D. 2011. Activity, stability and inhibition of a bioactive paper prepared by large-scale coating of laccase microcapsules. *Chemical Engineering Science*, 66, 5313-5320.
- Hartman, J., Albertsson, A. C., Lindblad, M. S. and Sjöberg, J. 2006. Oxygen barrier materials from renewable sources: Material properties of softwood hemicellulose-based films. *Journal of Applied Polymer Science*, 100, 2985-2991.
- Hedenqvist, M. S. 2002. Transport properties of polymers. Universitetservice US AB, Stockholm, Sweden.
- Hermansson, A.-M. and Svegmärk, K. 1996. Developments in the understanding of starch functionality. *Trends in Food Science & Technology*, 7, 345-353.
- Hirsch, J. B. and Kokini, J. L. 2002. Understanding the Mechanism of Cross-Linking Agents (POCl₃, STMP, and EPI) Through Swelling Behavior and Pasting Properties of Cross-Linked Waxy Maize Starches 1. *Cereal Chemistry*, 79, 102-107.
- Hodge, R., Bastow, T., Edward, G., Simon, G. and Hill, A. 1996. Free volume and the mechanism of plasticization in water-swollen poly (vinyl alcohol). *Macromolecules*, 29, 8137-8143.
- Ibrahim, M. M., El-Zawawy, W. K. and Nassar, M. A. 2010. Synthesis and characterization of polyvinyl alcohol/nanospherical cellulose particle films. *Carbohydrate polymers*, 79, 694-699.
- Istone, W. K. 1995. "X-ray Photoelectron Spectroscopy", in: Surface Analysis of Paper, T.E. Connors and S. Benerjee (eds.) CRS press.
- Jansson, A. and Järnström, L. 2005. Barrier and mechanical properties of modified starches. *Cellulose*, 12, 423-433.
- Jansson, A. and Järnström, L. 2006. Barrier and film properties of plastisol coatings, a water free coating application based on mixtures of starch, poly (vinyl alcohol) and poly (alkyl

- methacrylate). *Nordic Pulp and Paper Research Journal*, 21 (5), p 690-696,(2006).
- Javed, A., Ullsten, H., Ernstsson, M. and Järnström, L. 2016. Study of starch and starch-PVOH blends and effects of plasticizers on mechanical and barrier properties of coated paperboard. *Nordic Pulp & Paper Research Journal*, 31(3), 499-510.
- Jiugao, Y., Ning, W. and Xiaofei, M. 2005. The effects of citric acid on the properties of thermoplastic starch plasticized by glycerol. *Starch-Stärke*, 57, 494-504.
- Johansson, C., Bras, J., Mondragon, I., Nechita, P., Plackett, D., Simon, P., Svetec, D. G., Virtanen, S., Baschetti, M. G. and Bbreen, C. 2012a. Renewable fibers and bio-based materials for packaging applications—a review of recent developments. *BioResources*, 7, 2506-2552.
- Johansson, K., Winstrand, S., Johansson, C., Järnström, L. and Jönsson, L. J. 2012b. Oxygen-scavenging coatings and films based on lignosulfonates and laccase. *Journal of biotechnology*, 161, 14-18.
- John, A. W. and Leonard, F. V. D. B. 1990. *Unmodified starches: sources, composition, manufacture, and properties*, In: *Starch and Starch Products in Paper Coating: Edited by Robert L. Kearney and Hans W. Maurer*, Tappi press, 1-13.
- Jopson, R. and Towers, K. Improving fold quality in coated papers and boards-The relationship between basestock and coating. Coating Conference-TAPPI, 1995. Tappi Press, 459-477.
- Kaczinski, M. B. and Dwight, D. W. 1993. Enhancement of polymer film adhesion using acid-base interactions determined by contact angle measurements. *Journal of adhesion science and technology*, 7, 165-177.
- Katerinopoulou, K., Giannakas, A., Grigoriadi, K., Barkoula, N. M. and Ladavos, A. 2014. Preparation and characterization of acetylated corn starch–(PVOH)/clay nanocomposite films. *Carbohydrate polymers*, 102, 216-222.

- Katz, E. and Labuza, T. 1981. Effect of water activity on the sensory crispness and mechanical deformation of snack food products. *Journal of Food Science*, 46, 403-409.
- Kearney, R. L. and Maurer, H. W. 1990. Unmodified starches, sources, composition, manufacture and properties. *Starch and Starch Products in Paper Coating*. Tappi Press.
- Kerry, J., O'Grady, M. and Hogan, S. 2006. Past, current and potential utilisation of active and intelligent packaging systems for meat and muscle-based products: A review. *Meat science*, 74, 113-130.
- Kim, C.-K., Lim, W.-S. and Lee, Y. K. 2010. Studies on the fold-ability of coated paperboard (I): Influence of latex on fold-ability during creasing/folding coated paperboard. *Journal of Industrial and engineering Chemistry*, 16, 842-847.
- Kirwan, M. J. 2008. *Paper and paperboard packaging technology*, John Wiley & Sons.
- Kjellgren, H. and Engström, G. 2006. Influence of base paper on the barrier properties of chitosan-coated papers. *Nordic Pulp and Paper Research Journal* 21 (5) pp 685-689.
- Kjellgren, H. and Engström, G. 2008. Oxygen permeability of polyethylene-extrusion-coated greaseproof paper. *Nordic Pulp & Paper Research Journal*, 23, 272-276.
- Kjellgren, H., Gällstedt, M., Engström, G. and Järnström, L. 2006. Barrier and surface properties of chitosan-coated greaseproof paper. *Carbohydrate polymers*, 65, 453-460.
- Konidari, M., Papadokostaki, K. and Sanopoulou, M. 2011. Moisture-induced effects on the tensile mechanical properties and glass-transition temperature of poly (vinyl alcohol) films. *Journal of Applied Polymer Science*, 120, 3381-3386.
- Krochta, J. M. and De Mulder-Johnston, C. 1997. Edible and biodegradable polymer films: challenges and opportunities. *Food technology (USA)*.
- Kuniak, L. and Marchessault. 1972. Study of the crosslinking reaction between epichlorohydrin and starch. *Starch-Stärke*, 24, 110-116.

- Laiho, E. 1994. Flexible and Liquid Packaging in 1990's—Conference. Tampere University of Technology Paper Converting, Tampere.
- Lange, J. and Wyser, Y. 2003. Recent innovations in barrier technologies for plastic packaging—a review. *Packaging Technology and Science*, 16, 149-158.
- Lau, O.-W. and Wong, S.-K. 2000. Contamination in food from packaging material. *Journal of Chromatography A*, 882, 255-270.
- Lazaridou, A. and Biliaderis, C. G. 2002. Thermophysical properties of chitosan, chitosan–starch and chitosan–pullulan films near the glass transition. *Carbohydrate polymers*, 48, 179-190.
- Lee, W.-J., Youn, Y.-N., Yun, Y.-H. and Yoon, S.-D. 2007. Physical properties of chemically modified starch (RS4)/PVA blend films—part 1. *Journal of Polymers and the Environment*, 15, 35-42.
- Li, D., Garmestani, H., Kalidindi, S. and Alamo, R. 2001. Crystallographic texture evolution in high-density polyethylene during uniaxial tension. *Polymer*, 42, 4903-4913.
- Liu, F., Dai, R., Zhu, J. and Li, X. 2010a. Optimizing color and lipid stability of beef patties with a mixture design incorporating with tea catechins, carnosine, and α -tocopherol. *Journal of Food Engineering*, 98, 170-177.
- Liu, H., Yu, L., Chen, L. and Li, L. 2007. Retrogradation of corn starch after thermal treatment at different temperatures. *Carbohydrate polymers*, 69, 756-762.
- Liu, P., Yu, L., Wang, X., Li, D., Chen, L. and Li, X. 2010b. Glass transition temperature of starches with different amylose/amylopectin ratios. *Journal of cereal science*, 51, 388-391.
- Liu, Z., Feng, Y. and Yi, X. S. 1999. Thermoplastic starch/PVAI compounds: preparation, processing, and properties. *Journal of Applied Polymer Science*, 74, 2667-2673.
- Lopez, O. V., Zaritzky, N. E. and Garcia, M. A. 2010. Physicochemical characterization of chemically modified corn starches related to

- rheological behavior, retrogradation and film forming capacity. *Journal of food engineering*, 100, 160-168.
- Lourdin, D., Bizot, H. and Colonna, P. 1997a. "Antiplasticization" in starch-glycerol films? *Journal of Applied Polymer Science*, 63, 1047-1053.
- Lourdin, D., Coignard, L., Bizot, H. and Colonna, P. 1997b. Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials. *Polymer*, 38, 5401-5406.
- Lundqvist, J., De Fraiture, C. and Molden, D. 2008. *Saving water: from field to fork: curbing losses and wastage in the food chain*, Stockholm International Water Institute Stockholm, Sweden.
- Ma, X. and Yu, J. 2004. Formamide as the plasticizer for thermoplastic starch. *Journal of Applied Polymer Science*, 93, 1769-1773.
- Mali, S., Grossmann, M. V. E., Garcia, M. A., Martino, M. N. and Zaritzky, N. E. 2006. Effects of controlled storage on thermal, mechanical and barrier properties of plasticized films from different starch sources. *Journal of Food Engineering*, 75, 453-460.
- Mangavel, C., Barbot, J., Bervast, E., Linossier, L., Feys, M., Gueguen, J. and Popineau, Y. 2002. Influence of prolamin composition on mechanical properties of cast wheat gluten films. *Journal of Cereal Science*, 36, 157-166.
- Mao, L., Imam, S., Gordon, S., Cinelli, P. and Chiellini, E. 2000. Extruded cornstarch-glycerol-polyvinyl alcohol blends: mechanical properties, morphology, and biodegradability. *Journal of Polymers and the Environment*, 8, 205-211.
- Marsh, K. and Bugusu, B. 2007. Food packaging—roles, materials, and environmental issues. *Journal of food science*, 72, R39-R55.
- Marten, F. L. 2002. Vinyl Alcohol Polymers. *Encyclopedia of Polymer Science and Technology*, 399-437.
- Masclaux, C., Gouanve, F. and Espuche, E. 2010. Experimental and modelling studies of transport in starch nanocomposite films as

- affected by relative humidity. *Journal of Membrane Science*, 363, 221-231.
- Massey, L. K. 2003. *Permeability Properties of Plastics and Elastomers: A Guide to Packaging and Barrier Materials. PDL Handbook Series. Plastic Design Library/William Andrew Publishing, Norwich, New York.*
- Mathew, A. P. and Dufresne, A. 2002. Plasticized waxy maize starch: effect of polyols and relative humidity on material properties. *Biomacromolecules*, 3, 1101-1108.
- McAlpine, I. 1982. Ammonium zirconium carbonate , an alternative insolubilizer for coating binders. *1982 Coating Conference, TAPPI*, 165-179.
- Menard, K. P. 2008. *Dynamic mechanical analysis: a practical introduction*, CRC press.
- Mohsin, M., Hossin, A. and Haik, Y. 2011. Thermal and mechanical properties of poly (vinyl alcohol) plasticized with glycerol. *Journal of Applied Polymer Science*, 122, 3102-3109.
- Mokwena, K. K. and Tang, J. 2012. Ethylene vinyl alcohol: a review of barrier properties for packaging shelf stable foods. *Critical reviews in food science and nutrition*, 52, 640-650.
- Mokwena, K. K., Tang, J., Dunne, C. P., Yang, T. C. and Chow, E. 2009. Oxygen transmission of multilayer EVOH films after microwave sterilization. *Journal of Food Engineering*, 92, 291-296.
- Moles, P. J. and Chemicals, M. E. L. 2002. The use of zirconium in Surface Coatings. *Data sheet*, 117776-1780.
- Moyssiadi, T., Badeka, A., Kondyli, E., Vakirtzi, T., Savvaidis, I. and Kontiminas, M. G. 2004. Effect of light transmittance and oxygen permeability of various packaging materials on keeping quality of low fat pasteurized milk: chemical and sensorial aspects. *International dairy journal*, 14, 429-436.
- Mua, J. P. and Jackson, D. S. 1998. Retrogradation and gel textural attributes of corn starch amylose and amylopectin fractions. *Journal of cereal science*, 27, 157-166.

- Muramatsu, M., Okura, M., Kuboyama, K., Ougizawa, T., Yamamoto, T., Nishihara, Y., Saito, Y., Ito, K., Hirata, K. and Kobayashi, Y. 2003. Oxygen permeability and free volume hole size in ethylene–vinyl alcohol copolymer film: temperature and humidity dependence. *Radiation Physics and Chemistry*, 68, 561-564.
- Nagasawa, S., Fukuzawa, Y., Yamaguchi, T., Tsukatani, S. and Katayama, I. 2003. Effect of crease depth and crease deviation on folding deformation characteristics of coated paperboard. *Journal of Materials Processing Technology*, 140, 157-162.
- Narayan, R. 2004. Drivers & rationale for use of biobased materials based on life cycle assessment (LCA). *GPEC Paper abstract*.
- Nygårds, M., Just, M. and Tryding, J. 2009. Experimental and numerical studies of creasing of paperboard. *International Journal of Solids and Structures*, 46, 2493-2505.
- Olabarrieta, I., Forsström, D., Gedde, U. and Hedenqvist, M. 2001. Transport properties of chitosan and whey blended with poly (ϵ -caprolactone) assessed by standard permeability measurements and microcalorimetry. *Polymer*, 42, 4401-4408.
- Olagoke, O. and Llyod, M. R. 1979a. *Introduction, In: Polymer-polymer miscibility, Academic Press, Inc. New York, 3-18, Elsevier.*
- Olagoke, O. and Llyod, M. R. 1979b. *Thermodynamics of polymer-polymer mixing, In: Polymer-polymer miscibility, Academic Press, Inc. New York, 19-116, Elsevier.*
- Olsson, E., Hedenqvist, M. S., Johansson, C. and Järnström, L. 2013a. Influence of citric acid and curing on moisture sorption, diffusion and permeability of starch films. *Carbohydrate polymers*, 94, 765-772.
- Olsson, E., Johansson, C., Larsson, J. and Järnström, L. 2014. Montmorillonite for starch-based barrier dispersion coating—Part 2: Pilot trials and PE-lamination. *Applied Clay Science*, 97, 167-173.
- Olsson, E., Menzel, C., Johansson, C., Andersson, R., Koch, K. and Järnström, L. 2013b. The effect of pH on hydrolysis, cross-

- linking and barrier properties of starch barriers containing citric acid. *Carbohydrate polymers*, 98, 1505-1513.
- Park, H., Weller, C., Vergano, P. and Testin, R. 1993. Permeability and mechanical properties of cellulose-based edible films. *Journal of Food Science*, 58, 1361-1364.
- Piringer, O. G. and Baner, A. L. 2008. *Plastic packaging: interactions with food and pharmaceuticals*, John Wiley & Sons.
- Ramaraj, B. 2007. Crosslinked poly (vinyl alcohol) and starch composite films. II. Physicomechanical, thermal properties and swelling studies. *Journal of Applied Polymer Science*, 103, 909-916.
- Rhim, J.-W., Lee, J.-H. and Hong, S.-I. 2006. Water resistance and mechanical properties of biopolymer (alginate and soy protein) coated paperboards. *LWT-Food Science and Technology*, 39, 806-813.
- Rindlav-Westling, Å., Stading, M. and Gatenholm, P. 2002. Crystallinity and morphology in films of starch, amylose and amylopectin blends. *Biomacromolecules*, 3, 84-91.
- Rindlava, Å., Hulleman, S. H. and Gatenholma, P. 1997. Formation of starch films with varying crystallinity. *Carbohydrate Polymers*, 34, 25-30.
- Robert, E. M. 1990. *Improving of water resistance of starch coatings, Starch and Starch Products in Paper Coating: A Project of the Coating Binders Committee of the TAPPI Coating and Graphic Arts Division. Ed. by Robert L. Kearney*, Tappi press.
- Robertson, G. L. 2006. *Food packaging: principles and practice*. CRC press, Boca Raton, FL.
- Rutenberg, M. and Solarek, D. 1984. Starch derivatives: Production and uses. *Starch chemistry and technology*, 2, 311-366.
- Rättö, P., Hornatowska, J. and Barbier, C. 2012. Influence of the distribution of the shape and size distribution of pigment particles on cracking in coating layers during creasing. *Nordic Pulp & Paper Research Journal*, 27, 714-720.

- Savolainen, A., Kuusipalo, J., Laiho, and Penttinen, T. 1998. Extrusion coating and product applications, in Savolainen, A. (ed.) *Paper and Paperboard Converting*, Fapet, Helsinki, Finland, pp. 124-187.
- Schlesing, W., Buhk, M. and Osterhold, M. 2004. Dynamic mechanical analysis in coatings industry. *Progress in organic coatings*, 49, 197-208.
- Schmorak, J., Mejzler, D. and Lewin, M. 1962. A study of the mild oxidation of wheat starch and waxy maize starch by sodium hypochlorite in the alkaline pH range. *Starch-Stärke*, 14, 278-290.
- Schott, N., Rosato, M. and Rosato, D. 2010. *Plastics Technology Handbook : Introduction, Properties, Fabrication, Processes*, New York, N.Y., Momentum Press, eBook Collection (EBSCOhost), EBSCOhost, viewed 11 October 2015, 85-412.
- Shen, L. and Patel, M. K. 2008. Life cycle assessment of polysaccharide materials: a review. *Journal of Polymers and the Environment*, 16, 154-167.
- Shi, R., Bi, J., Zhang, Z., Zhu, A., Chen, D., Zhou, X., Zhang, L. and Tian, W. 2008. The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature. *Carbohydrate polymers*, 74, 763-770.
- Shogren, R. L., Lawton, J. W., Tiefenbacher, K. F. and Chen, L. 1998. Starch–poly (vinyl alcohol) foamed articles prepared by a baking process. *Journal of Applied Polymer Science*, 68, 2129-2140.
- Sidwell, J. A. 1992. *Food contact polymeric materials*. Vol. 6(1). Report 61. *Rapra Technology*, England.
- Singh, R. K. and Singh, P. 2005. In: *Innovations in food packaging* (J. H. Han ed), Elsevier, Amsterdam, Holland, 24-44.
- Solaro, R., Corti, A. and Chiellini, E. 2000. Biodegradation of poly (vinyl alcohol) with different molecular weights and degree of hydrolysis. *Polymers for Advanced Technologies*, 11, 873-878.
- Song, D., Breedveld, V. and Deng, Y. 2011. Rheological study of self-crosslinking and co-crosslinking of ammonium zirconium

- carbonate and starch in aqueous solutions. *Journal of Applied Polymer Science*, 122, 1019-1029.
- Song, D., Zhao, Y., Dong, C. and Deng, Y. 2009. Surface modification of cellulose fibers by starch grafting with crosslinkers. *Journal of applied polymer science*, 113, 3019-3026.
- Souheng, W. 1982. Polymer interface and adhesion. *Marcel Decker, New York*.
- Stading, M., Hermansson, A.-M. and Gatenholm, P. 1998. Structure, mechanical and barrier properties of amylose and amylopectin films. *Carbohydrate Polymers*, 36, 217-224.
- Stading, M., Rindlav-Westling, Å. and Gatenholm, P. 2001. Humidity-induced structural transitions in amylose and amylopectin films. *Carbohydrate polymers*, 45, 209-217.
- Steffner, O. E., Dickson, R. and Lepoutre, P. 1995. Mechanical interlocking in coated paper. *Nordic Pulp & Paper Research Journal*, 10, 80-82.
- Stolpe, L. 1996. Greaseproof paper as a barrier material in packaging. *Inv. T  c. Papel*, 128, 415-426.
- St  hl, M., Berghel, J. and Williams, H. 2014. Sustainable improvements in the wood fuel pellet chain. *Proceedings of SEEP2014, Dubai-UAE*, 23-25., 6, 7.
- Thomson, J. 1899. J.J Thomson, *Philos. Mag.* 5:48, 547 *Philos. Mag.*, 5, 547.
- Turi, E. 1997a. *Thermal characterization of polymeric materials*. San Diego: Academic Press, 745-886., Elsevier.
- Turi, E. A. 1997b. *Thermal characterization of polymeric materials*. San Diego: Academic Press, 235-337.
- Tuschhoff, J. 1986. Hydroxypropylated starches. *Modified starches: Properties and uses*, 89-96.
- Van Oss, C. 1994a. Interface Forces in Aqueous Media. Marcel Dekker, inc., New York, 170-186.
- Van Oss, C. J. 1994b. *Interfacial forces in aqueous media*, Marcel Dekker, inc., New York, pp. 18-45.

- Wang, S., Zhang, F., Chen, F. and Pang, Z. 2013. Preparation of a crosslinking cassava starch adhesive and its application in coating paper. *BioResources*, 8, 3574-3589.
- Whistler, R. and Daniel, J. 1984. Molecular structure of starch. *Starch: chemistry and technology*, 153-182.
- Videki, B., Klebert, S. and Pukanszky, B. 2007. External and internal plasticization of cellulose acetate with caprolactone: structure and properties. *Journal of Polymer Science Part B: Polymer Physics*, 45, 873-883.
- William, C. F. and Susan, F. B. 1995. Kane, R. J. (1995). Paper Coating Additives: A Project of the Coating Additives Committee of the Coating and Graphic Arts Division, Committee Assignment: 880102.01. Tappi Press. *Tappi journal*, 89-124.
- Wurzburg, O. B. 1986a. *Converted Starches*. In O.B. Wurzburg (Ed.). *Modified starches-properties and uses*. Boca Raton, Florida: CRC Press Inc., 17-40.
- Wurzburg, O. B. 1986b. *Introduction*. In O.B. Wurzburg (Ed.). *Modified starches-properties and uses*. Boca Raton, Florida: CRC Press Inc., 4-16.
- Vähä-Nissi, M. and Kuusipalo, J. 1997. Wetting and adhesion in paper and paperboard converting. *Papermaking science and technology, Book*, 12, 24-59.
- Vähä-Nissi, M., Kuusipalo, J. and Savolainen, A. 2001. Coated greaseproof paper as a barrier material, *Paperi ja Puu – Paper and Timber*, vol.83, no 2, pp. 138-141.
- Yin, Y., Li, J., Liu, Y. and Li, Z. 2005. Starch crosslinked with poly (vinyl alcohol) by boric acid. *Journal of Applied Polymer Science*, 96, 1394-1397.
- Yu, L. and Christie, G. 2001. Measurement of starch thermal transitions using differential scanning calorimetry. *Carbohydrate polymers*, 46, 179-184.
- Zobel, H. F. 1984. Gelatinization of starch and mechanical properties of starch pastes. *Starch: chemistry and technology*, 2, 285-309.

Österberg, M., Vartiainen, J., Lucenius, J., Hippi, U., Seppälä, J., Serimaa, R. and Laine, J. 2013. A fast method to produce strong NFC films as a platform for barrier and functional materials. *ACS applied materials & interfaces*, 5, 4640-4647.



VIPP VALUES CREATED IN FIBRE-BASED PROCESSES AND PRODUCTS

A barrier material is usually needed on a fiber-based food package to maintain quality by protecting packed food from gases and moisture. Over the last few decades, efforts have been made to replace petroleum-based materials with bio-based materials. The present work has focused on the possibility of using a natural barrier material on fiber-based food packaging materials, and the effects of plasticizing and cross-linking on the mechanical and barrier properties and on the stability in water of coatings based on starch-PVOH and starch-lignin blends have been evaluated.

Citric acid can act as a compatibilizer and cross-linker for starch and PVOH, and the use of citric acid may retard the diffusion of both oxygen and water vapor if a multilayer coating strategy is used. A polyethylene extrusion coating on a board pre-coated with a recipe containing polyethylene glycol resulted in a greater reduction in the rate of oxygen transmission than through a board pre-coated with a recipe containing citric acid. The addition of lignin to the starch solution decreased the migration of starch from the starch-lignin films, and the addition of ammonium zirconium carbonate as a cross-linker decreased the migration of both starch and lignin from the films.


BILLERUDKORSNÄS

KK-stiftelsen ><

ISBN 978-91-7063-844-2 (print)

ISBN 978-91-7063-939-5 (pdf)

ISSN 1403-8099

DOCTORAL THESIS | Karlstad University Studies | 2018:14
