Welcome to COST ActInPak "Active and Intelligent Packaging Solutions Summer School"

Dr. Johanna Lahti, WG2 leader

June 12-16 2017, TUT, Tampere, Finland

COST FP1405

ACTIVE AND INTELLIGENT FIBRE-BASED PACKAGING – INNOVATION AND MARKET INTRODUCTION

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Welcome to Tampere!

- The third largest city in Finland with over 200,000 inhabitants. One of Finland's fastest growing urban centres and, according to a survey, the most popular city to live and study in.
- Two universities: **Tampere University of Technology** and the **University of Tampere** with ~30,000 students.

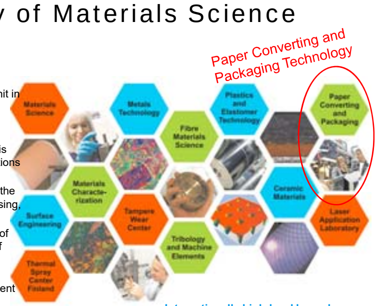
TAMPERE UNIVERSITY OF TECHNOLOGY

Tampere University of Technology (Finland)

TAMPERE UNIVERSITY OF TECHNOLOGY

Laboratory of Materials Science

- The only higher education unit in Finland covering all material groups
- Over 1000 M.Sc. (Eng.), 80 Lic.Tech., and 70 Ph.D. thesis and more than 6000 publications since 1969
- High-level basic research of the structure, properties, processing, and use of materials
- Researcher with knowledge of and expertise in all groups of materials
- Versatile and up-to-date research and testing equipment
- Strong collaboration with industry and academic units



Internationally high-level know-how on ALL materials based on strong interdisciplinary basic research

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Paper Converting and Packaging Technology (Research group)

- The research group offers teaching and research on **paper, paperboard and polymer processing, converting and packaging technology, materials (wood-, fibre- and plastic-based) and products.**
- R&D is focused on **extrusion coating, laminating, dispersion coating, wet and melt spinning and their applications.**
- The development challenges of today include **high-barrier and thin coatings, materials from renewable resources and sustainable packaging materials.**

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Current research topics

- ❑ High-barrier co-extruded coatings and films
- ❑ High-barrier paper and paperboard packages
- ❑ Biodegradable and bio-based coatings and materials
- ❑ Wood-based materials (*e.g.* lignin, cellulose) for various applications
- ❑ Active and intelligent packages solutions
- ❑ Surface functionalization of plastic films and fiber-based materials and their coatings
- ❑ Thin coatings and surface modification based on different techniques (ALD, Atomic Layer Deposition; LFS, Liquid Flame Spray; Atmospheric Plasma Deposition)
- ❑ Barrier dispersion coating

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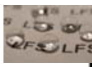
Our facilities

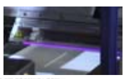
YouTube video: "NanoMEND pilot line"

Versatile Roll-to-Roll pilot lines

- **Production of packaging materials via**
  - **(co)extrusion coating and lamination**
  - **dispersion coating**
  - **cast film (co)extrusion**
  - **Max. speed ~400 m/min, max. width 550 mm**

Coatings, treatments and functionalisation of surfaces, e.g. plasma, IR, UV, LFS





Well-equipped laboratory for packaging materials and packages

- **Barrier properties (WVTR, OTR, CO2, grease)**
- **Sealability & hot tack**
- **Surface energy**
- **Adhesion etc. etc.**

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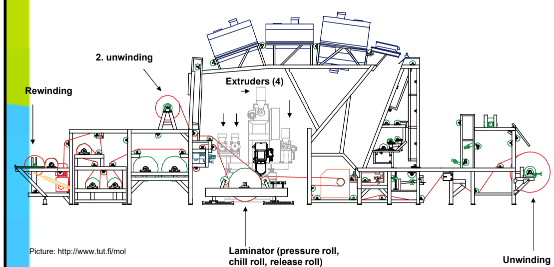
Extrusion coating and lamination pilot line (TUT)



Picture: http://www.tut.fi/mol

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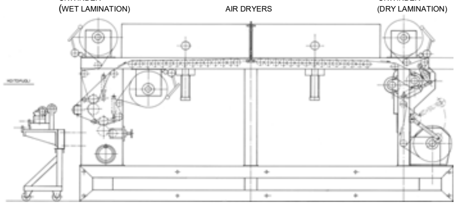
Laminating Pilot Line



Dry and wet lamination, dispersion coating, and 1-colour flexo printing

- Web width max. 400 mm
- Line speed 10-115 m/min
- Drying temp. max. 200°C

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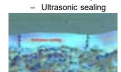
TUT Paper Converting and Packaging Technology Laboratory

- Two environmental test chambers (23-38°C / 50-90%RH, volume 120l)
- Barrier measurements:
  - O_2TR: MOCON Ox-Tran 2/21 MH and Ox-Tran 2/21 SS
  - WVTR: MOCON Aquatran 1G and Cup test (ASTM E96-10)
  - CO_2TR: MOCON Permatran-C 4/41
  - Grease resistance (ASTM F119-82)
  - HVTR
- Dual column material testing machine: Strength properties and adhesion measurements (90°and 180°peel)
- Contact angle and surface energy
- Heat sealability:
  - Hot bar sealing and hot tack (KOPP SGPE 20 laboratory sealer)
  - Hot air sealing
  - Ultrasonic sealing
- Coefficient of friction (Qualitest FX7100-V)
- FTIR with ATR unit
- Optical microscope with polarisation contrast + microtome
- Extrusion rheometer
- Lab-scale sheet coater
- Brookfield viscometer
- Creasing – perforating machine (Cyklos GPM4 50)
- Package testing:
  - Hydrogen leak detector H2000
  - PBI Dansensor CheckPoint O2/CO2



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ActInPak

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"Active and intelligent packaging solutions – Summer school

"Production methods of fiber- and polymer-based packaging materials"

TUT, Tampere, Finland
June 12, 2017

Dr. Johanna Lahti
Senior Research Fellow
Tampere University of Technology (Finland)

Laboratory of Materials Science
Paper Converting and Packaging Technology

Content of the lectures

paper converting

PART 1

- **Production technologies of fiber- and polymer-based packaging materials**
  - Extrusion coating, coextrusion
  - Lamination techniques
  - Cast film and blown film technology
  - Dispersion coating

PART 2

- **Multilayer technology, barrier, adhesion**
- **Surface treatments** and nanoscale R2R surface modification and novel thin film technologies

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Introduction

- Extrusion coated materials, plastic films and polymers are used in various applications – **packages** and **packaging materials** and **printable electronics etc**. These include **flexible packages** (such as wrappings, pouches and bags), **liquid packages** (folding cartons, bottles etc.), **rigid packages** (cups, trays, etc.) and **other products like labels.**
- In packages, the most important function of a packaging material is to shield the product inside the package, i.e. barrier.
- Usually packaging materials are **multilayer structures**
- Depending on the polymer type, extrusion coating or plastic film generally give a **barrier** against water, water vapor, aroma, grease, oxygen, etc.
- Good **adhesion** between extrusion coating and fiber-based substrate and different layers in multilayer structure is essential in packaging materials.
- In addition to barrier and adhesion properties, **sealability** is one of the most important properties of packaging materials.

➢ Sealability affects the ability of the material to form hermetic seals, which is a necessity in different packages.

Production of multilayer products

- **Extrusion coating**
  - Extrusion coating
  - Co-extrusion coating
- **Film manufacturing** (Co-extrusion)
  - Cast film
  - Blown film
- **Lamination**
  - Extrusion
  - Dry
  - Wet
  - Solventless
  - Hot melt/wax
- **Dispersion coating**
  - Barrier coatings
  - Functional coatings

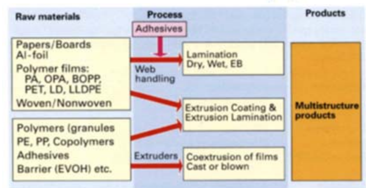


Figure 3. Multistructure product flow

Materials in extrusion coating, film manufacturing and lamination

- Extrusion coating and lamination aim to combine properties of different materials, e.g. paper or paperboard and thermoplastic polymer, into a same multilayer structure
- Fiber-based substrates gives:
  - Mech. properties (stiffness, strength, "shape")
  - Light barrier
  - Excellent printability
  - Certain barrier properties week, which restricts usage especially as a primary package for food ➔ Converting with extrusion coating / lamination
- Polymer coating/film gives:
  - Barrier properties (gas, vapours, liquid, grease…)
  - Heat sealability
  - Adhesion properties
  - Surface properties (food contact, outlook)

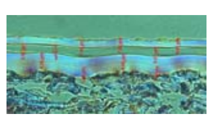
Selection of a plastic

Process, application & product → Required process and end-use properties:

- Tightness (barrier-properties)
  - → water vapour, water, grease, aroma, gas, light
- Heat sealability
- Suitable friction properties for converting operations
- Toughness, resistance to abrasion
- Heat resistance
- Adhesion
- Printability
- Food contact
- Appearance, clarity
- Processability (processing temperatures - in coating around 300°C)
- Suitable viscosity (rhelogical properties of the polymer are very important)
- Biodegradability, recyclability..
- Price
- …

Examples of polymers used in extrusion coating and film manufacturing

- **Polyolefins**
  - PE (polyethylene)
    - PE-LD, PE-MD, PE-HD
  - PP (polypropylene)
- **Copolymers**
  - E/VAC (ethylene vinyl acetate)
  - E/BA (ethylene butyl acrylate)
  - E/MA (ethylene methyl acrylate)
  - E/EA (ethylene ethyl acrylate)
- **Adhesives (TIE-layers)**
  - Acid copolymers (Ionomers, E/AA)
  - Grafted polyolefins (MAH grafted)
  - Modified polyolefins (e.g. Bynel, Admer)
- **Barrier polymers**
  - EVOH (ethylene vinyl alcohol)
  - Polyamide
    - PA 6, PA 66, PA 11, PA 12
    - MXD-6 (amorphous polyamide)
  - COC (Cyclo-olefin copolymer)
- **Other special polymers**
  - Polyester (PET); Polymethylpentane (PMP)…
- **Biopolymers**
  - Polylactic acid (PLA), Polyhydroxyalkanoate (PHA),…

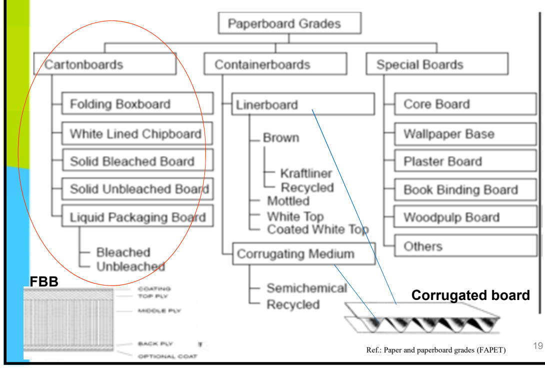


Examples of packaging papers

- **Kraftpaper**
  - Based on virgin brown sulphate pulp or bleached chem. pulp (➔ strength)
  - Grammage 60 – 120 g/m²
  - Wrappings, bags, pouches, laminates, sacks, etc.
- **MG-paper (machine glazed)**
  - One side is glossy
  - Grammage 20 – 120 g/m²
  - Wrappings, labels, flexible packages (laminates), etc.
- **C1S, coated one side**
  - Bleached chem. pulp
  - High quality
  - Grammage 45 – 120 g/m²
  - Cosmetic packages, lid laminates, pet food packages, soup and spice packages, etc.

➡ *Papers*: good printability, good adhesion, solvents are absorbed quickly by the paper, fast drying but porosity of paper can have a negative effect on conductivity.

Paperboard & Cartonboard grades

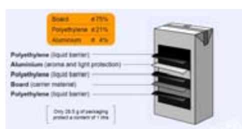


Ref.: Paper and paperboard grades (FAPET)

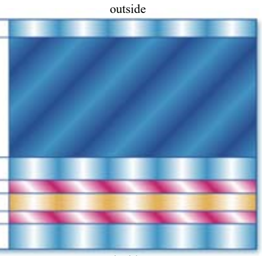
Other packaging materials (examples)

- **Al-foil**
  - Easily deformable
  - Thickness usually 6-20µm; max. web width ca. 2m
  - Very good barrier, especially light barrier
  - Dead fold property
  - Usually used together with some other flexible packaging material like plastic film
- **Metallized films**
  - Mainly to replace Al-foil
  - Good barrier properties
- SiOx coated materials (like plastic films)
  - Very expensive; Good gas barrier
- Cellophane
  - Clear and stiff; good dead fold-property
  - Usually coated with e.g. PVCD or vinylchloride/vinylacetate copolymer

Typical construction of extrusion coated multilayer packaging



layers	g/m2
PE-LD	15
Board	300
PE-LD	20
Adhesive (tie layer)	6
Barrier (EVOH)	6
Adhesive (tie layer)	6
PE-LD	20



Extrusion → Product examples

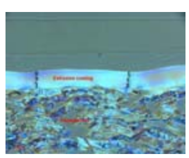
Liquid packaging: milk and juice gable top cartons, aseptic rectangular shaped drink boxes

Flexible packaging: snack foods, condiment packs, food, dry goods, medical packages, toothpaste type collapsible tubes, liquids, "bag-in-box"

Paperboard packaging: bakery boxes, microwaveable trays, frozen food boxes, detergent boxes, animal food boxes

Industrial wraps: drum liners, ream wrappers, composite cans, soap wrappers

Extrusion coating



- *Coating situation where molten thermoplastic film is combined with web substrate*

<u>Main demands of extrusion coating:</u>

- very high processing temperatures (around 300°C)
- suitable viscosity of a polymer (rhelogical properties of the polymer are very important)

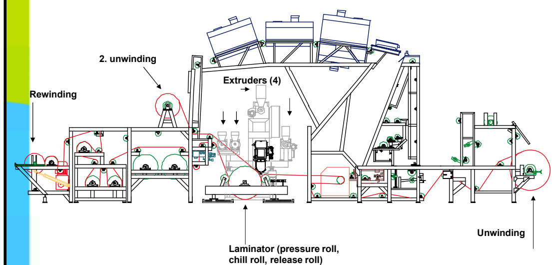
Extrusion coating

- **Extruding a high molecular weight, high melt temperature polymer in film form onto a rapidly moving web**
- Web (substrate) can be, e.g. paper, paperboard, Al-foil, plastic film
- Co-extrusion technology provides a multilayer extrusion coated product for more demanding applications, particularly food packaging applications, e.g. liquid packaging board (milk, juice, soup) and flexible packages

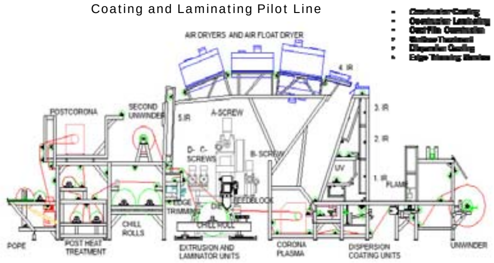
Extrusion coating pilot line at TUT

Video available in YouTube: "Nanomend pilot line"

Extrusion coating and lamination pilot line (TUT)



Coating and Laminating Pilot Line



Extrusion coating:

Winders
Main unwind
Second unwind
Rewind

Extruders
Extruder A
D 60, L/D 30
Extruder B
D 40, L/D 24
Extruder C
D 30, L/D 25
Extruder D
D 30, L/D 25
Die: EBR (Cloeren)
+Encapsulation
Feedblock:
5-layer possibility

Laminator
Working width:
max 550 mm
Max.speed: 400 m/min
Press roll
Chill roll (matte/glossy)
Release roll
Surface treatments
Corona (Vetaphone)
Flame (Hill GmbH)

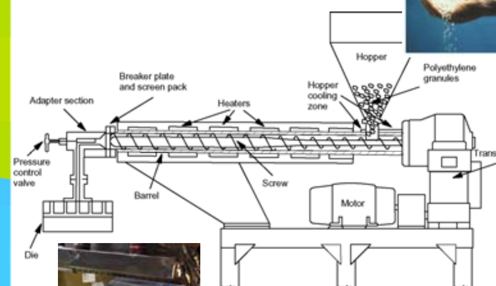
Other units
Relaxation

Dispersion coating:

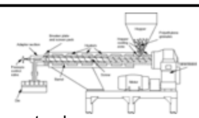
Coating units
Dispersion coating unit
-Blade or Rod

Other units
Chill rolls
Dryers
IR-dryers
Air dryers

Main parts of an extruder



Process technology includes

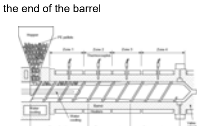


- ✓ **infeed (hoppers);** granulates to the extruders
- ✓ **barrel and screw;** polymer is melted and homogenised
- ✓ **screen pack** filters the impurities and **breaker plate** creates smooth laminar flow
- ✓ **adapter;** adjusts the back pressure in the extruder
- ✓ **feedblock;** forms the film structure
- ✓ **die;** widens the film to the desired width
- ✓ **laminator** (pressure, release and chill rolls); polymer film is pressed to the web

- **Processing temperatures vary depending on the polymer concerned**
- Usually temperature increases from the beginning to the end
For example PE-LD:
  screw: 220-250-280-300 °C
  adapter: 280-290
  die: 300-310

Function of the screw

- **As the screw rotates, it conveys plastic granules and converts them into a homogeneous melt.**
- **Granulates melt because of friction that is generated and heating of the extruder**
- A screw typically consists of feed, compression, and metering zones.
- The barrel zone temperature settings, screw speed, back pressure, adapter melt temperatures, and the adapter and die temperature settings control the melt temperature and homogeneity.
- In the feed zone, water cools the screw and barrel to avoid bridging due to premature melting of the pellets.
- The feed section of the barrel can have grooves to provide optimum output.
- Processing temperatures vary depending on the polymer concerned
  – Processing temperatures are much higher than the melting temperatures of the polymers
  – Usually temperature increases from the beginning to the end of the barrel
  – For example PE-LD:
    screw: 220-250-280-300 °C
    adapter: 280-290
    die: 300-310

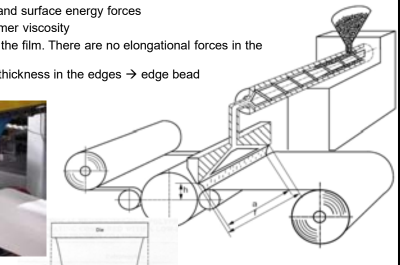


Feedblock: Selector plug

- **Co-extrusion combines two or more polymer layers into one film or layer structure.**
- The adhesion between the polymers must be sufficient
- Selector plug organises the polymer melts coming from the extruders to the desired order before the die
- A converter usually has several selector plugs to put together structures of various layers
- For example:
  - 3 extruder (A, B, and C) line has a possibility to use three polymer materials
  - By changing the selector plug, the following coating structures are possible:
    - web / A / B / C / C / C (3 layers)
    - web / A / A / C / B / B (3 layers)
    - web / A / B / C / B / A (5 layers)

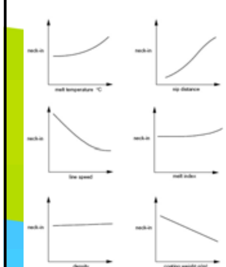
Neck-in (Filmin kurouma)

- Caused by gravitation and surface energy forces
- Is affected by e.g. polymer viscosity
- Occurs in the edges of the film. There are no elongational forces in the middle of the film.
- Neck-in increases film thickness in the edges → edge bead (reunapaksunnos)

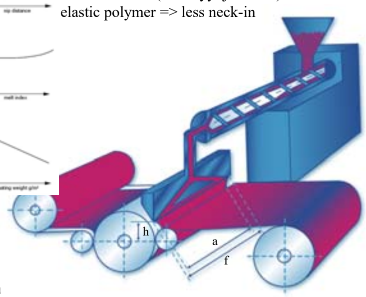


h = ilmaväli, nip distance (air gap)

f - a = kurouma, total neck-in



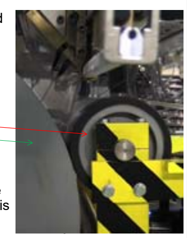
- The smaller the neck-in, the less waste (Less material has to be cut from the edges)
- Broad MWD (molekyylijakauma) => more elastic polymer => less neck-in



- **h = nip distance**
- **total neck-in = f - a**

Laminator

- The purpose of the laminating operation is to create adhesion between the resin and the moving web and to solidify the resin
- The surface properties of the chill roll affect the surface properties of the final coating
- Laminating system consists of:
  - **pressure and stripping (release) rolls**
  - **chill roll**
- The pressure or nip roll has a rubber covering and is water cooled. Pressure rolls strongly influence adhesion, coating integrity, appearance, and caliper.
- Double-walled, spiral chill rolls can provide adequate cooling. The temperature range of the cooling water is often 15-25°C.

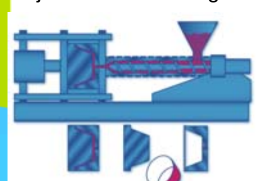


Chill roll

- The surface finish of the chill roll is critical. It determines the release characteristics, the optical properties, and the coefficient of friction (COF) of the coating.
  - A glossy or polished finish: high optical properties of excellent gloss, good transparency, and low haze. Polished finishes also provide high COF.
  - Matte rolls: the poorest optical properties of low gloss, poor transparency, and high haze. Good release properties. Produce coatings with low COF.
  - Tacky resins such as ionomers and methyl acrylate modifications of polyethylene normally use matte rolls because of their good release properties.
  - Other chill roll finish types are satin or semi-glossy and mirror pockets.

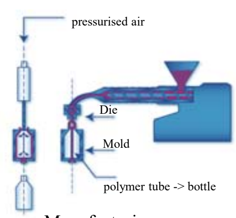
Other extrusion processes (examples)

Injection molding



Very precise products by using a mold

Blow molding



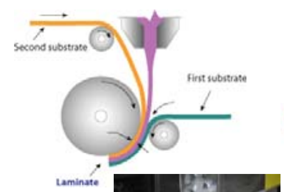
Manufacturing of hollow products

LAMINATION

- **Lamination is used to achieve properties that cannot be achieved by a single material**
- **Lamination method depends on e.g. materials to be combined**
  - In lamination process two or more webs will be glued and pressed together to get a board grade with a higher grammage level.
  - The lamination can be:
    - wax lamination (molten wax is applied to board surface)
    - glue lamination (two or more webs are glued together)
      - wet lamination
      - dry lamination
      - solventless lamination
    - extrusion lamination
    - hot melt
  - Wax or resin modified wax are used as a hot melt adhesive in wax lamination. The wax will be heated, applicated to the surface and cooled.

Johanna Lahti

(CO)EXTRUSION LAMINATION



Extrusion lamination is similar to extrusion coating except that it combines two webs with the molten plastic film.

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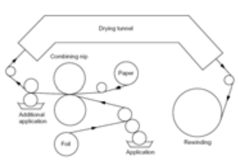
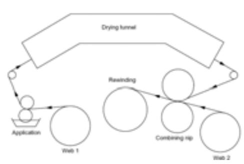
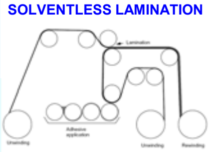
WET LAMINATION



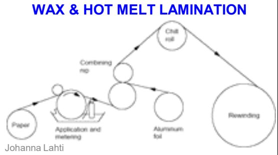
DRY LAMINATION



SOLVENTLESS LAMINATION



WAX & HOT MELT LAMINATION



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Manufacturing of plastic films/foils: Cast and blown film technologies

Plastic films

- *'rough' definition: less than 250 μm thick; sealable to itself hermetically*
- *uses/advantages: especially in food packaging; protection (barrier); printable; clarity/transparency; easy handling and package forming*
- *Flexible and rigid plastic products*
- *other uses: wraps in building and construction, agricultural, waste/shopping bags, labels, etc.*
- *packaging: overwrap, blister packaging, shrink packaging, stretch packaging, etc.*
- *Two production technologies:*

  Blown films vs. cast film
  - *Blown film technology saves space due to vertical configuration*
  - *With cast film technology, higher speeds can be used and the clarity of the films is slightly higher*

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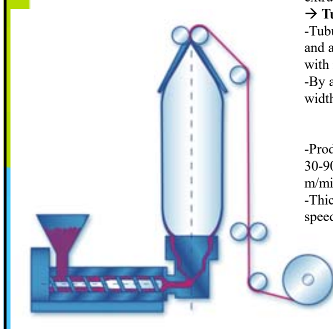
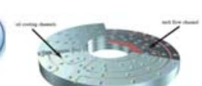
Blown film technology

Polymer granulates are fed into the extruder → heating, melting and mixing
→ **Tubular die**
-Tubular polymer melt is cooled with air and at the end the cooled film is pressed with rolls into web
-By adjusting the amount of air, the web width can be adjusted

-Production speeds with thin films 30-90 m/min, and rarely even 300 m/min.
-Thicker films are produced with lower speeds.





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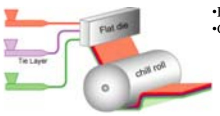
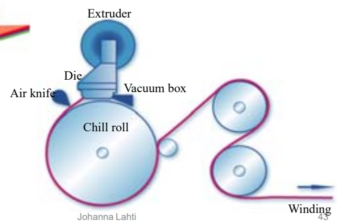
Cast film

- **Target is a short air gap → fast cooling**
- Web widths usually 1-3m, production speeds ~100-300 m/min
- Can be combined to deep drawing
- Film thickness ~0,2 -2,5 mm
- Can be single or multilayer structure



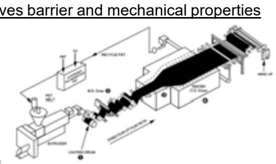


Film orientation

= **Orientation of the plastic film (at temperature below polymer's melting temperature)** in

a) cross direction,
b) machine direction, or
c) in both directions (=biaxial)

- For example: OPP=oriented polypropylene, BOPP=biaxially oriented PP
- Polymer chains are oriented in the direction of the draw → strength is improved
- Orientation improves barrier and mechanical properties



DISPERSION COATING

- Barrier dispersion (i.e. polymer dispersion) coating is understood to mean the **application, metering and drying of latex on a paper or paperboard to form a solid, uniform and nonporous polymer film with certain barrier properties.**
- Most latexes have the appearance of milk. The word latex describes the class of surfactant stabilized, water borne emulsion polymers that have small particles of polymer in water. The particle diameter is typically 50-300 nm.
- Dispersion coating process:
  - Application
  - Coat weight control
  - Drying
- Latex particles must coalesce upon drying, when water is removed
  → Uniform, pore free film
- Composition of the dispersion coating and the coating method affect the properties of the final product (coating)
- General coat weights: 4-15g/m²

Advantages and applications of dispersion coatings

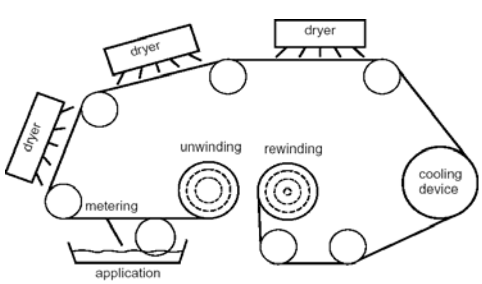
- Depending on the polymer and fillers used: grease, oxygen and moisture barrier
- Environmentally friendly (compostable, repulpable)
- Usually modest heat sealability properties (e.g. compared to extrusion coatings)
- Lack of speed and width limitations
- In-line or off-line process

- In paper recycling dispersion coatings are removed using techniques similar to treating inks and varnishes

- Different kinds of wrappings, ream wrappings, sacks, disposables, frozen and chilled food cartons and corrugated board, candy wrappings and boxes as well as bakery products and other packages containing greasy food could be latex coated. Also as pre-coating under extrusion coating.
- In packaging applications, dispersion coatings mainly compete with PE-LD

Picture: www.plastirol.fi

Dispersion Coating
Process



DISPERSION COATING
Dispersion coatings i.e. latexes

- Latexes are dispersions of water and polymer particles. The most widely used polymers are various polyacrylates, polymetacrylates, polystyrene (PS), polybutadiene, polyvinylacetate, and polyolefins (PE, PP).

- Besides water and polymer, latexes typically contain several different additives and fillers. A typical latex may contain 10-20 components. The additives can be stabilizers, thickeners, waxes, antifoamers, etc. The latexes can also contain a small percentage of monomers and emulsifiers.

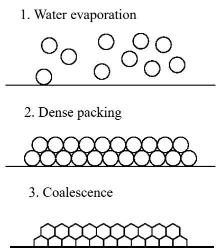
- The typical fillers are those used in coating colors and some polymer particles. The fillers improve barrier properties, runnability, blocking resistance, optical properties, or price competitiveness.
- Typical fillers are kaolin, calcium carbonate, talc and titanium dioxide.

- All polymer dispersion coated applications require a latex that can form a film.

Dispersion Coating
Film formation

•Film formation means a coalescence of polymer particles upon drying

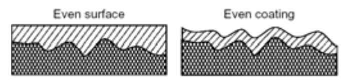
• During drying, as water is removed, spherical polymer particles flotating in water start to coalescence together forming an even polymer layer.
• If polymer particles are elastic enough, they can form non-porous film, in this case, barrier properties are significantly improved.
•During film formation, polymer particles must diffuse into adjacent particles so that the shape of the individual particles disappears.
• Polymer particles do not totally fuse together but instead, they adhere to each other (honeycomb) (Diffusion theory)
➢ Solid, uniform, pinhole free barrier layer



Dispersion Coating
Coating methods

•Dispersion coating can be done to reach either an even coating thickness or even surface.
•In typical dispersion coated applications, the intent is to achieve even coating thickness instead of an even surface
•A coating with even thickness gives better barrier properties than a coating layer with a thin covering over the hills of a fibrous network. If it is necessary to print on the dispersion coated side, a compromise is usually necessary between the barrier properties and printability.
•The most widely used coating methods are blade coaters, rod/bar coaters, air doctor coaters, roll coaters, and presses

• Blade coating
  → even surface
• Air knife coating
  → even thickness
• Rod coating
  → compromise of the two



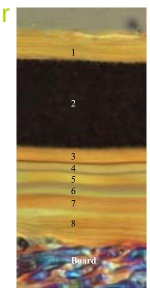
PART 2

Multilayer technology &

Coextrusion

Adhesion

Selection of polymer(s) for multilayer structures



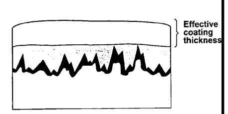
- Material selection is a compromize between
  - Adhesion
  - Friction properties
  - Uniform coating profile (both in the whole coating and single layers)
  - Barrier properties
    - Water vapour
    - Oxygen
    - Light
    - Grease
    - Aroma
  - Heat sealability
  - Printability etc.
- Co-extrusion allows thin layers and minimizes the amount of expensive special polymers
- There are less pinholes in co-extrusion coated material because of multilayer structure (vs. one layer coating)
- In co-extrusion can be achieved very thin layers, because there are more layers supporting each other

Advantages of co-extrusion

- **Adhesion enhancement** can occur by selection of the proper polymer bonded to the substrate or by using higher temperatures
- **Thin layers:** minimization of expensive polymer use with thinner layers of cheaper polymers as support layers around the main polymer
- **Less pinholes** in the coating enhances the barrier properties: running only one polymer with co-extrusion into a two-layer structure improves the pinhole resistance compared to a one-layer coating
- **Better heat sealability**: extruding the surface layer at a lower temperature reduces the oxidation of the polymer. Selection of the heat-sealable skin polymer can provide good heat sealing properties by using, for example, an ionomer
- **Layers containing additives and pigments**: only the surface layer needs to contain any additives to reduce cost and protect the die metal. Two dissimilar colors are also possible.
- **Less manufacturing processes**: machine time savings
- Polymers that are difficult to process can be run supported by other polymers
- Increase in capacity
- Combine polymers having special barrier properties as thin layers as are necessary
- Non-slip surfaces or ultra low heat seal temperatures by the selection of the skin-polymer.

Pinholes

- **Pinholes are microholes and like other discontinuity or non-homogeniety they strongly reduce barrier properties**
- **Pinholes in material or coating layer can restrict or even prevent the usage of the material in certain applications ⇨ barrier properties become weaker**
- Formation of pinholes:
  - Before coating (thin films)
  - When the film and substrate meet
  - In the nip
  - During release from chill roll
  - During converting, (e.g. during sealing)



- Pinholes can be caused by:
  - Air/gas bubbles in the polymer melt
  - Impurities in the polymer melt, e.g. gels
  - Uneven or rough substrate (Fibers sticking from the substrate can puncture the thin film)
  - Impurities on the surface of the chill roll or other rolls
- Can be random or accumulate
- In real, leak is rarely an idealised "hole", it can be f.ex. a tear, slit, crack or combination of these

Pinholes

Visual testing of pinholes with coloured test liquid

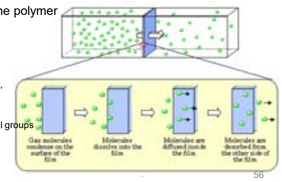
Barrier properties

•Polymers are usually classified as semi-permeable materials because they allow the passage of small molecular species such as carbon dioxide, oxygen, nitrogen or water, while restricting the flow of structurally larger organic molecules

•Barrier against: Water (vapour), oxygen, CO2, aroma, grease, light, etc.

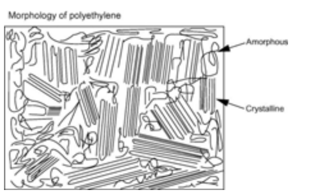
•Small molecules (H_2O, O_2) penetrate through polymer
- *Absorption* on the surface of polymer
- *Dissolution* in the polymer matrix
- *Diffusion* through the polymer
- *Desorption* from the other side of the polymer

•Factors affecting permeability
- Temperature, humidity
- Permeating species
- Thickness of the polymer layer
- Glass transition temperature, molecular weight, density
- Moisture content of the polymer
- Crosslinking, crystallinity, orientation, functional groups



Barrier

- Morphology: crystalline parts prevent penetration of water; water molecules penetrate through amourphous regions
- PE, PP, PTFE (teflon) hydrophobic polymers => good water vapour barrier, poor oxygen barrier
- PA, EVOH hydrophilic polymers (contain hydrogen bonds) => good oxygen barrier, poor water vapour barrier
  - O2-barrier of PA and EVOH decreases when moisture increases



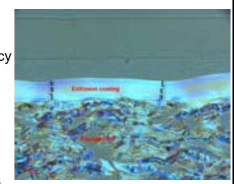
Adhesion

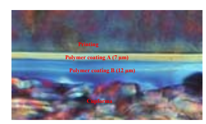
= **Adhesion is the tendency of dissimilar particles and/or surfaces to cling to one another** (vs. cohesion refers to the tendency of similar or identical particles/surfaces to cling to one another).

= The state in which dissimilar bodies are held together by intimate interfacial contact so that mechanical force can be transferred across the interface

= **The force required to separate the bodies**

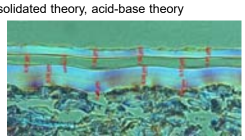
- The forces that cause adhesion and cohesion can be divided into several types.
- Adhesion is important in various interfaces and processes: e.g. between substrate and coating/adhesive, between coating layers multilayer structures, printing, sealing…





Adhesion theories

- There is no universally applicable adhesion theory. At least six adhesion theories are currently in use, and each of the theories describes the phenomenon of adhesion
- Theories of adhesion:
  1. **Mechanical interlocking** (e.g. extrusion coating of fiber-based substrate)
  2. **Diffusion theory** (e.g. heat sealing of polymeric surfaces)
  3. **Electrostatic theory**
  4. **Thermodynamic adsorption theory** (a.k.a. wetting theory: intermolecular forces on a surface, hydrogen and Van der Waals forces, surface energy)
  5. **Chemical adhesion** (ionic, covalent and metallic bonds)
  6. **Weak boundary layer theory (WBL)** (explains sites of failure)
  7. **Others:** consolidated theory, acid-base theory



➢ ***See**: Kuusipalo, J. (ed) Paper and paperboard converting, Chapter 2 for more details*

Mechanical interlocking

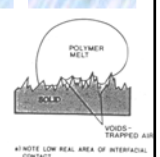
•Based on theory, the main mechanism in adhesion is the penetration of one component into irregularities in the other surface

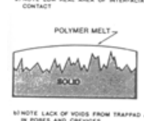
•Adhesive materials fill the voids or pores of the surfaces and hold surfaces together by interlocking

•Phenomenon occurs on porous substrates e.g. paper and paperboard

•The geometry of irregularities, the contact angle between materials, and the wettability of adhesives affect this phenomenon

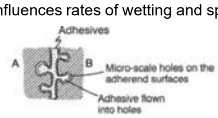
•If wetting is incomplete or entrapped air is present, sites for failures can occur





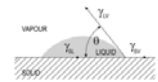
Mechanical interlocking

- Optimum contact area between the substrate and an adhesive can occur when the shape and size of irregularities are suitable and when the adhesive has sufficient time to penetrate into the irregularities
- Adhesion between a polymer and a wall of irregularities involves intermolecular forces and close contact with materials
- Mechanical interlocking is a macroscopic phenomenon
- Surface topography also influences rates of wetting and spreading



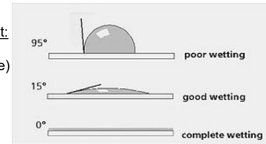
Contact angle (to define wetting & surface energy)

- Contact angle > 90° lyophobic (hydrophobic, oleophobic) surface
- Contact angle < 90° lyophilic (hydrophilic, oleophilic) surface
- Defined with water:
  - Contact angle > 0° low energy surface
  - Contact angle = 0° high energy surface



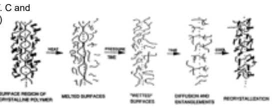
- The higher the surface energy, the smaller contact angle → the higher wetting

Properties affecting the measurement:
- Roughness of the surface
- Absorption (porosity of the surface)
- Contamination of the surface



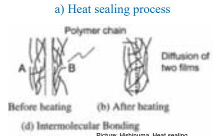
Ref. Stehling, F. C and Meka, P. (1994)

Diffusion theory



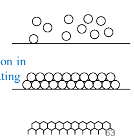
- **When the temperature becomes adequate, molecules or molecule segments become mobile. Under this condition, compatible materials with equal solubility parameters can form a transition zone where interdiffusion of macromolecules of molecule segments can occur.**
- This may occur when the molecules of both materials are mobile and soluble in each other.
- Close molecular contact by wetting is necessary for interdiffusion (keskinäinen diffuusio).
- Adhesion due to diffusion only occurs with identical or compatible polymers: in polymer-to-polymer adhesion, interdiffusion only occurs with identical or compatible polymers. E.g. between different layers in coextrusion or autohesion (layers of the same polymer).
- The temperature of the material should be above the glass transition temperature (T_g, lasinsiirtymälämpötila) for the diffusion to occur.
- **Diffusion also occurs in heat sealing of thermoplastics (a) and in the film formation of aqueous polymer dispersions (b)**

a) Heat sealing process



Picture: Hishinuma, Heat sealing technology and engineering for packaging

b) Film formation in dispersion coating



Weak boundary layer theory (WBL)

- The theory of weak boundary layers (WBL; heikko rajakerros) can explain the difference in bond strengths between the calculated bond strengths value and the occurrence of actual failure
- Theory states that a failure within a WBL near the interface causes poor adhesion
- Weak boundary layers at polymer interfaces could due to migration of additives on the surface, contaminants, or excessive treatments that create a low molecular weight layer by breaking polymer chains
  - WBL can be a) chemical or b) mechanical
- Reactions between the adherents and trapped air can create a WBL
- The surface of paper can have a WBL due to e.g. less bonded fibers
- WBL can affect the adhesion between coating and substrate or it can cause improper joints

Hand test

(käsitesti)

- A hand test can evaluate adhesion between polymers and fiber-based substrates
  - the polymer coating is separated from the fiber substrate
  - If fiber tear occurs, the adhesion can be evaluated by determining the extent of fiber tear.
  - If cohesive failure occurs in one of the materials, the interface is not the weakest point, and good adhesion is achieved
  - With coated grades -> Evaluation of force required to separate materials

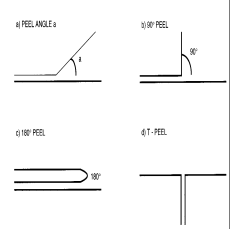
EVALUATION OF FIBER TEAR (KUITUREPEÄMÄN ARVIOINTI)

Value	Criteria of evaluation
0	layers do not adhere
1	layers peel off each other
2	layers peel off each other, some fibers are removed
3	fiber tear < 50% of surface area
4	fiber tear > 50% of surface area
5	total fiber tear

Peel test (vetotesti)

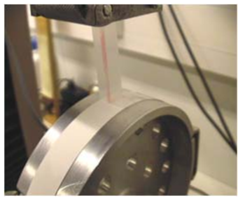
- **Peel test can measure the force to peel the layers apart**
- Results will vary with the peel angle
- Three commonly used methods are:
  - The 90°-peel test (L-peel test)
  - The 180°-peel test (U-peel test; ASTM D 903)
  - The T-peel test (ASTM D 1876)

(Peel-testiä voidaan käyttää jos materiaalit ovat erotettavissa siten, että kummassakaan materiaalissa ei ilmene koheesiovirheitä)



Peel test (Vetotesti)

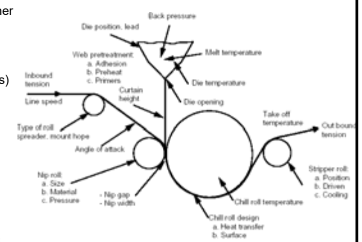
- Several factors affect the measurement result:
  - The separating speed
  - The direction of separating
  - The material properties
- Sometimes ethanol or another solvent is necessary to separate the layers (before the measurement)



Peel-test at TUT laboratory: Defines adhesion between polymer coating and fiber-based substrate

The effect of process parameters on adhesion

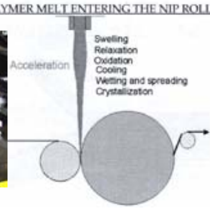
- Extrusion process parameters have significant influence on adhesion between polymer and substrate
- They also define several other qualities of the final product
- Parameters e.g.
  - Cooling
  - Coating weight (thickness)
  - Pre-treatments
  - Melt temperature
  - Oxidation, air gap
  - Line speed
  - Nip pressure
  - Polymer grade



Adhesion mechanisms in extrusion coating

Adhesion between the extruded polymer and the substrate is the principle criteria by which the quality of the final product will be judged. Fig. 5.1 illustrates the events taking place in the air gap as the molten polymer is drawn from the die and combines with the substrate in the chill roll nip. The melt is stretched and begins to cool and crystallise as it enters the nip.

Fig. 5.1 POLYMER MELT ENTERING THE NIP ROLL ASSEMBLY



Surface treatment methods

- **Ozone** treatment of polymer melt (in extrusion coating)
- **Corona** discharge treatment
- Atmospheric **plasma** treatment
- **Flame** treatment
- **Priming** (i.e. application of adhesion promoter on the substrate)

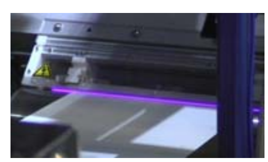
- ➢ Each method can have several effects that improve adhesion
- ➢ A modern extrusion coating line usually has both pre-treatment and post-treatment units

- In addition, there are **several thin layer technologies available** for grafting/coating/surface modification; CVD processes, sol-gel coating, etc.

Flame treatment

- **Flame treatment is used to change the chemical composition of the surface, increase the surface energy, modify surface topography, or remove the contaminants and weak boundary layers**
- Substrate is exposed to direct flame, which modifies the surface of substrate. In the combustion reaction different thermally activated atoms and molecules, e.g. oxygen ions and atoms, as well as free electrons are formed
- These react with the surface of substrate composing carbonyl, carboxyl and hydroxyl groups among others
- Consequently polarity and oxidation of the surface increases and leads into improved wetting and adhesion
- The flame treatment clearly improves adhesion on surfaces of paperboard or polymer
- However, the mechanism behind this adhesion improvement is not necessarily the same
  - In the surface of polymer occurs crosslinking, breaking of the long-chain molecules and some micro roughening
  - In the surface of paperboard micro roughening as well as surface activation takes place. Additionally, the flame treatment removes possible contaminants or sticking fibers from the surface of substrate

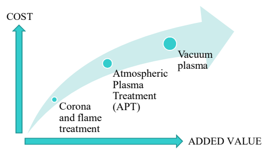
Target of corona treatment



- To activate the surface
- As a pre-treatment, to improve adhesion between substrate and coating
- As a post-treatment, to improve ink adhesion, especially with coated materials
  - Depending on the printing method and ink, the required surface energy level is usually around 30-42 mN/m
  - Thumb rule: surface energy of the substrate should be 7-10 mN/m > surface tension of the printing ink

Plasma surface modification

- Plasma is the fourth state of matter (solid, liquid, gas, plasma), and can be seen in nature e.g. as lightning
- A plasma is a (partially) ionised gas in which ions and electrons are present as well as radicals and molecules in an excited state
- Non-thermal plasmas based on atmospheric Dielectric Barrier Discharge (DBD) are typically used for surface treatment of polymers, metals and textiles



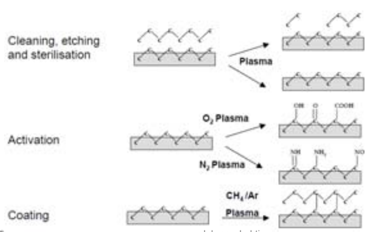
Ref. AFS and VITO

Atmospheric Plasma Treatment	Corona & Flame Treatment
+ operate in atmosphere (no vacuum/chambers), possibility to select treatment gas → tailored surface chemistry	+ operate in atmosphere → no vacuum or chambers - operate in atmosphere → fixed chemistry (air)
+ high energy densities → effective treatment	- relatively low energy densities
+ longer lasting treatment	- decay of treatment level (aging)
+ more uniform treatment (uniform flame)	- limited treatment uniformity, possible pin holes (corona)
+ no reverse side treatment (no breakdowns through the material)	- reverse side treatment → blocking problems (corona)
+ on-line, roll-to-roll process	+ on-line, roll-to-roll process
- more complex process → control and scale up more difficult	+ simple and acknowledged methods
- certain treatment gases quite expensive	+ relatively low cost and high speeds

Plasma surface modification

- Plasma activation

Functional chemical groups are created to the surface of the treated material → For packaging materials e.g. to enhance adhesion properties, wettability and printability of surfaces

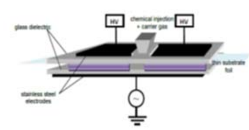


Ref. Vangeneugden, D., 2007

Plasma surface modification

- Plasma deposition

- A completely new surface is created which enables the possibility to create barrier coatings from precursor such as e.g. sol-gels chemistry.
- The desired surface properties can be obtained by injecting the precursor to the plasma discharge.
- Plasma discharge is chemically very reactive environment which causes the precursor to be fragmented into reactive species. These reactive species react with each other and also with the surface to produce a coating to the surface of the treated substrate.
- Depending on the chemistry used, various plasma deposited coatings can be produced, for example with grease/WV/oxygen barrier



Ref. VITO

- Example: UV inkjet printability of PP film
  - Argon plasma treatment enhances ink wetting and uniformity of the printed lines
  - In addition, adhesion properties of ink are improved

PP film / 1 pixel line width / 300 dpi / UV ink

Ref. Lahti, J. et al. 2011

Plasma systems can be used for:

- **Chemical functionalisation** (~1-100 nm)
  - O-containing groups
  - N-containing groups
  - F-containing groups
  - SiOx-like coatings
  - Acrylate/acrylic/ester/vinyl…. functionalities
- **Deposition of thin functional coatings** (~10-500 nm)
  - Adhesion
  - Release
  - Antibacterial
  - Corrosion protection
  - Reduced friction
  - Barrier
  - …..

Benefits of plasma deposition process:
- Dry surface treatment
- Cold plasma
- Versatile due to broad range of precursor technologies
- Atmospheric process

Ref. VITO

Liquid Flame Spray (LFS) process

Ref. Tuominen, M. et al 2013

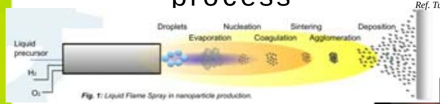


Fig. 1: Liquid Flame Spray in nanoparticle production.

- Generate nanoparticles with flame process, i.e. liquid flame spray
- Particle material: TiO_2, SiO_2, ZrO_2, Al_2O_3, Ag, Pd, Pt, Au, oxides of Na, Mg, Sr, Si, Ti, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Mo, Ag, W, Pt, Nd, Pr, Yb, Se ... and mixtures/composites
- Particle size range: 2-200 nm
- Develop thin layer -coatings (~20 nm-1 µm) on e.g. fiber-based packaging materials
- Porous coatings: porosity >80%

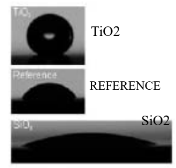
LIQUID FLAME SPRAY

Ref. Teisala, H., 2010

Liquid Flame Spray (LFS) process

- Liquid Flame Spray (LFS) can be used to generate
  - ***superhydrophobic*** CA > 150°(nano-titania, TiO_2) and
  - ***superhydrophilic*** CA < 10°(nano-silica, SiO_2)

  surfaces onto different substrates like paperboard and paper



TiO2

REFERENCE

SiO2

- LFS has great potential for industrial scale method because of its continuous nature, low coating amounts (30-50 mg/m2) and high line speeds
- The different amount of carbonaceous material on the TiO_2 and SiO_2 coatings is the main reason for the opposite wetting behaviour of the surfaces

Ref. Teisala, H., 2010; Mäkelä, J., 2008.

Functional nanoparticle coatings using Liquid Flame Spray (LFS)

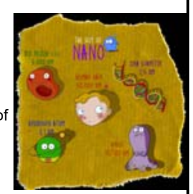
<u>LFS/TiO_2 coating properties:</u>

- Gas permeable (breathable)
- Transparent
- **Multifunctional:**
  - ✓ Superhydrophobicity/(philicity)
  - **LFS/TiO_2: >150°**
  - **LFS/SiO_2: <10°**
  - ✓ Adjustable wettability by surface stimulation
  - ✓ Self-cleanability

Ref. Tuominen, M. et al 2013

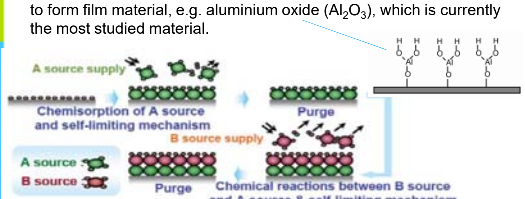
Atomic Layer Deposition (ALD)

- ALD is a CVD (Chemical Vapour Deposition) process, which enables deposition of highly conformal and uniform thickness thin films with monolayer precision
- <u>Purpose</u>: **thin, tight and stable coating** from gaseous precursors
- <u>Main advantage</u>: **the conformality and uniformity** which can be obtained regardless of the orientation or shape of the substrate; i.e., there are no pinholes in the film
- In ALD process, thin films of material are deposited one atomic layer at a time
- Thickness of a typical ALD layer can vary from 1 to over 100 nm



Atomic Layer Deposition (ALD)

- ALD coating consists of several reaction cycles. One cycle is able to achieve ~0.1 nm layer depending on the coating material and process parameters.
- Typically uses two precursors (TMA, trimethyl aluminium and water) to form film material, e.g. aluminium oxide (Al_2O_3), which is currently the most studied material.

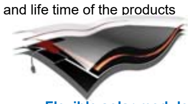


NanoMend EU project

NANOMEND

- €7.25million FP7 funded, 4 year long project from Jan 2012, in total 14 partners from Finland, Germany, Switzerland, Netherlands and UK.
- "Enhanced in-line Detection, Cleaning and Repair of Nano-scale Defects for Large Area Substrates„ (NANOMend)

  www.nanomend.eu
- The goal of the project is to bypass the state-of-the-art level of defect detection, cleaning and repair technologies in **fibre-based packaging material** and **flexible solar panel productions**
- Defects within these materials reduce the yield (in production), performance and life time of the products



Flexible solar modules

Food packaging

Consortium includes 14 partners from Finland, Germany, Switzerland, Netherlands and UK

NPL National Physical Laboratory · cpi ...the future inspired · IBS Precision Engineering · University of Huddersfield · Fraunhofer IVV · Open your mind. LUT. Lappeenranta University of Technology · Flisom Flexible Solar Modules · Tampere University of Technology · KITE Innovation Europe · TNO innovation for life · Isovoltaic · ISRA Vision · storaenso · tscent

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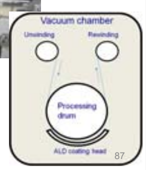
- NanoMend was a collaborative, end user led project aimed at pioneering novel technologies for in-line detection, cleaning and repair of micro and nano scale defects on thin films deposited on large area substrates in fibre-based packaging and flexible solar panel productions.
- The aim was to integrate these technologies into systems that work at speeds required for continuous production, thus enabling the new technologies to improve product yield and performance, while keeping manufacturing costs low.
- Defects like pinholes are microholes and like other discontinuity or non-homogeniety they strongly reduce barrier properties of (packaging) materials
  - Pinholes in material or coating layer can restrict or even prevent the usage of the material in certain applications
- **Role of TUT and LUT was research and demonstration of detection and cleaning systems relating to production of packaging materials.** Furthermore, target was to study use of **(R2R) ALD technology** in production of packaging materials and to create improved properties.

Roll-to-Roll Atomic Layer Deposition (R2R ALD)

- A new R2R ALD process opens up a possibility to perform high-throughput ALD processing for flexible substrates



Beneq WCS 500 Roll-to-Roll ALD system at LUT in Mikkeli (Finland)
Process description available in YouTube

ALD (Atomic Layer Deposition) as part of a package

- The targets for ALD technology as part of a packaging can be:
  - **Decrease the amount of other materials by extra ALD layer** (if the barrier properties of the structure is the reason for thicker layer).
  - **Replace the whole layer in the package** (e.g. aluminium foil in ultimate case)
  - To create hydrophopic / hydrophilic –surface
  - Improve optical properties of the surface
- Concerning of barrier properties, the ALD process on moving substrate has been a success. The oxygen and water vapor barrier of paper / polymer / Al_2O_3 -structures has improved significantly. In addition, UV barrier properties have been achieved.

Ref. Johansson, P., 2010

Acknowledgements & Further information

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- www.nanomend.eu
- www.tut.fi/plasmanice
- www.tut.fi/mol
- www.actinpak.eu/

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ActInPak · COST European Cooperation in Science and Technology · COST is supported by the EU Framework Programme Horizon 2020

Thank you for your attention!

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