



# **Polymers used in papermaking industry process**

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Bioproduct and Process Engineering

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## ABSTRACT

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This thesis is accomplished in Tampere University of Applied Sciences. Polymers used in paper making process are discussed in this thesis. This thesis is divided into two parts. One part lists polymers applied in different sections on a paper machine. Another part is about polymers in paper grades.

Mainly used polymers in papermaking industry process are listed below:

Polyethylene, known as PE, is used in extrusion coating and lamination. Products like film, packaging bags, containers are made widespread over the world. Besides, Polyethylene is also used in paper machine as polyethylene covers.

Polypropylene (PP) is similar to polyethylene and also used in similar products. Besides, PP can also against aromas and solvents, which cannot be reached by PE.

Polyethylene terephthalate, known as PET, has the similar application as PP. Polyethylene terephthalate's abrasion resistance and dimensional stability make it the dominate material for fabrics in paper machines.

Polyamide (PA) is used in the manufacture of clothing and carpets, and also can be used as a barrier polymer. With the same properties, EVOH is another barrier polymers used for the same reason. Besides, PA is also used in producing fabrics in paper machines.

Rubber is used in produce roll cover nowadays, especially synthetic rubber.

Other polymers such as PAE (polyamide-epichlorohydrin) and PAAE (polyaminoamide-epichlorohydrin) are used as wet strength additives while another polymer called polyacrylamide is used as dry strength additive.

Rosin can be used mostly in internal sizing. And starch can be also used for papermaking; especially in sizing and wet end chemistry to improve the paper quality. All of rosins used in papermaking are natural products. As for surface sizing, apart from starch, there is another four different polymers underutilization: SMA (Styrenen maleic anhydride), SAE (Styrene acrylate emulsions), PUD (Polyurethanes), and EAA (Ethylene acrylic acid).

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Key words: paper machine, polymers, papermaking, paper grade

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**ABBREVIATIONS AND TERMS**

TAMK	Tampere University of Applied Sciences
cr	Credit
MD	Machine direction
CD	Cross machine direction
PA	Polyamide
PET	Polyethylene terephthalate (polyester)
NR	Natural rubber
PAE	Polyamide-epichlorohydrin
UF	Urea-formaldehyde
MF	Melamine-formaldehyde
PAAE	Polyaminoamide-epichlorohydrin
C-PAM	Cationic polyacrylamide
PE	Polyethylene
PP	Polypropylene
EVOH	Ethylene vinyl alcohol
LDPE	Low density polyethylene
HDPE	High density polypropylene
SBR	Styrene-butadiene rubber
ASA	Alkyl succinic anhydride
AKD	Alkyl ketene dimer
SMA	Styrenen maleic anhydride
SAE	Styrene acrylate emulsions
PUR	Polyurethanes
PUD	Polyurethanes dispersion
EAA	Ethylene acrylic acid

## **1 Introduction**

The purpose of this thesis is to list how and where polymers are used in papermaking process. This thesis will mainly introduce what kinds of polymers are used in paper industry, including in paper machine and in different paper grades. How polymers affect paper machine and paper properties are also discussed.

This thesis is a survey to tell about the important role of polymers in industry today. We will focus on paper industry and divide this thesis into two parts. The first part mainly introduced about where and how polymers used in paper machine. During this part, basic information about different sections in paper machines, type of polymers and how polymers are used in different sections are discussed. The second big part talks about polymers used in papermaking process in different paper grades. Sizing, coating and additives are mainly talked during the second big part.

This thesis is based on different articles, books and journals.

## 2 Basic introduction about polymers

Polymers are very large molecules that consist of several independent molecules combined together. For example, an ethylene molecule attaches itself to another ethylene molecule and when several thousands or millions of single ethylene molecules join with each other, a polyethylene molecule is formed. 'Poly' means large amount and 'mer' means part or unit. A polymer means that many parts chemically linked together. The basic individual unit from which it is synthesized is called a monomer, 'mono' meaning one. Polymers are also called macromolecules. (Suhas K., 9)

The process of converting monomers to polymers is called polymerization. Polymers can also be synthesized from more than one type of monomers. For example, ABS is synthesized from three different monomers, acrylonitrile, butadiene, and styrene. Polymers have been around since the beginning of time. DNA, (Figure 2.1) the basic and critical unit of life, is a polymer found in all lives as a naturally occurring polymer. (Suhas K., 9)

Nowadays, almost all available polymers for business are synthesized from natural materials. Polymers are synthesized by a chemical process. There are mainly two types of polymerization processes, the addition polymerization process and the condensation polymerization process. In the addition polymerization process, the polymerization reaction is initiated by a catalyst and each monomer adds onto the next monomer until all the monomers are polymerized. An additional polymerization example is polyethylene. Polyethylene is combined from ethylene unit, which is a gas at room temperature. The double bond in the ethylene molecule breaks and a bond with an adjacent ethylene molecule is formed. The polymerization process is shown in Figure 2.2 (Suhas K., 9)

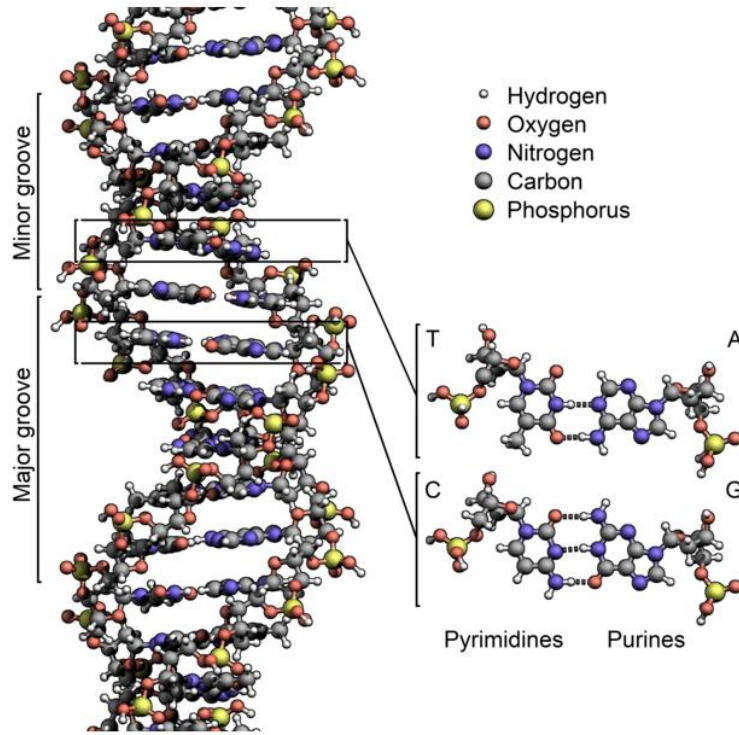


Figure 2.1 DNA structure (Wikipedia, DNA)

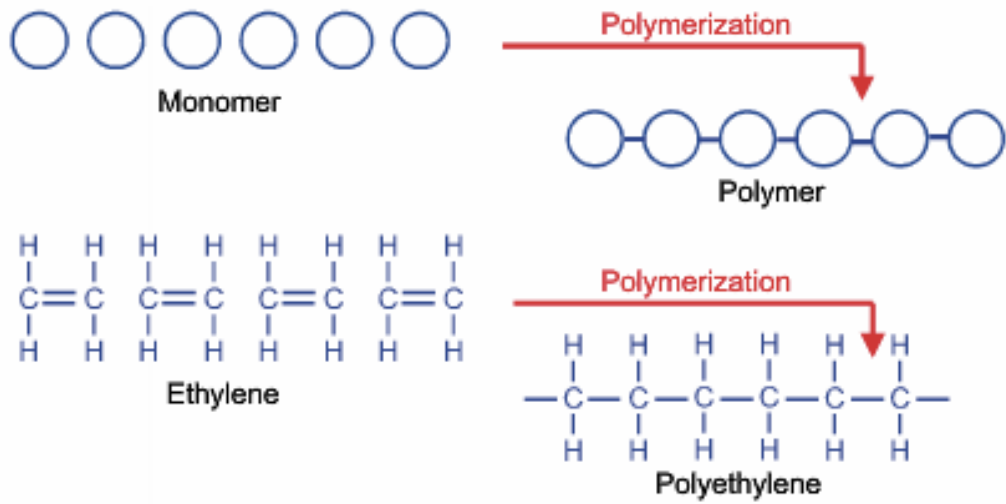


Figure 2.2 The process of polymersization and formation of polyethylene (Suhas K., 10)



### 3 Polymers used in paper machines

#### 3.1. Basic introduction about paper machines

##### 3.1.1 Paper machine structure

Paper machines produce different kinds of paper, including printing paper, tissue paper and packaging paper. Paper machine consists of different units. They are forming section (wet end), press section, drying section and finishing section (calendering section). ( Figure 3.1.1.1 and Figure 3.1.1.2)

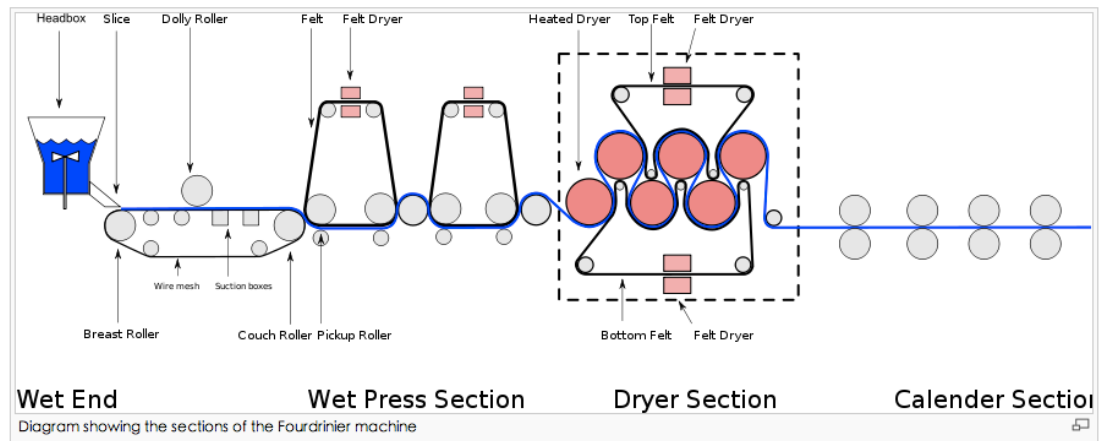


Figure 3.1.1.1 The basic paper machine structure (Wikipedia, Paper Machine)

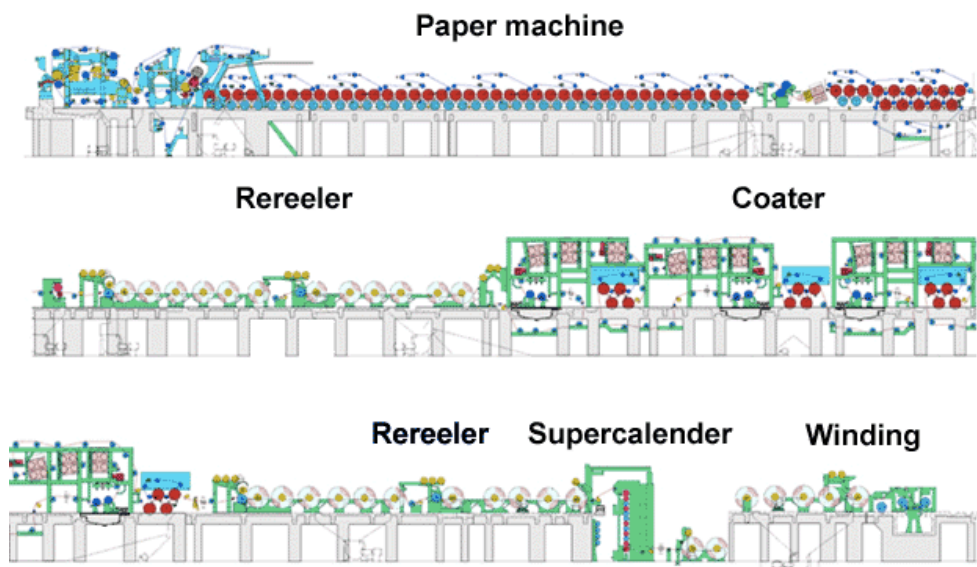


Figure 3.1.1.2 Coating fine paper machine (Knowpap, paper and board production)

## **3.2. Polymers applied in forming fabrics**

Almost all the fabrics used in paper machines are synthetics and made from polymers. These are forming fabrics in forming section, press fabrics in press section and dryer fabrics in dryer section.

### **3.2.1 Introduction about forming section**

The headbox approach piping, headbox and wire section on paper machine make the web forming section. The most important properties of paper are created in web forming section. In the following process stages, formation will be affected only marginally. The tasks of a web forming section are to remove water from stock by draining it through the forming fabric, to prevent fiber floc in the web by producing enough hydrodynamic forces, to control dewatering and hydrodynamic forces in such a way that fiber and filler retention are uniform and at a desired level and to ensure the web a sufficient dry solid content so as to enable it's easy to transfer into press section. (Knowpaper, Forming section, 2014)

There are three basic kinds of forming section. They are fourdrinier (Figure 3.2.1.1), hybrid former (Figure 3.2.1.2) and gap former (Figure 3.2.1.3.) Fourdrinier is the oldest web forming section type, which is still widely used especially in special papers and paperboards.

## Fourdrinier

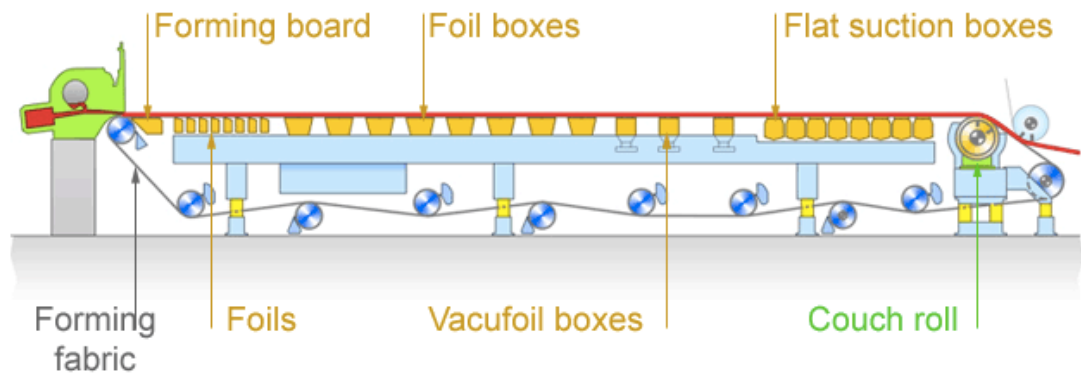


Figure 3.2.1.1 Fourdrinier—one kind of web forming section. (Knowpap, web forming)

## SymFormer MB

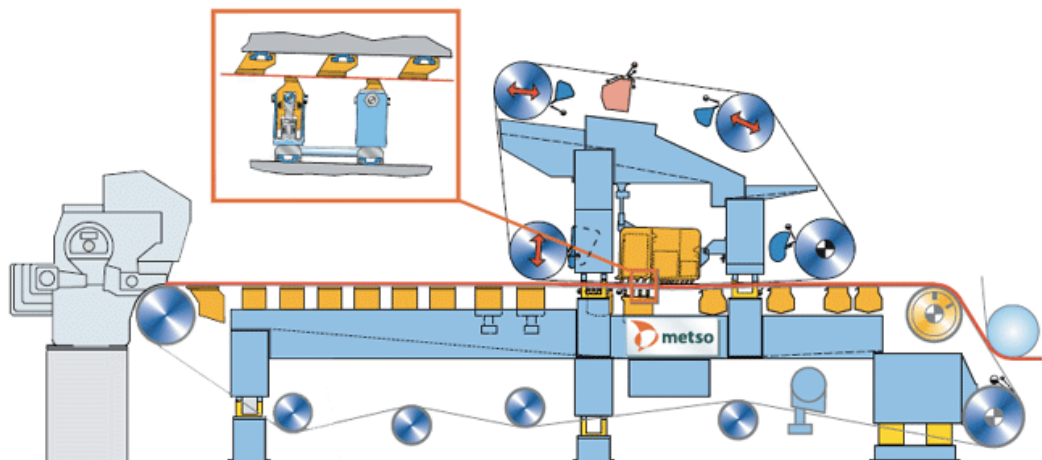


Figure 3.2.1.2 Hybrid former—one kind of web forming section.

(Knowpap, Forming section)



Figure 3.2.1.3 Gap former—one of three kind of web forming section. (Knowpap, web forming)

### 3.2.2 Introduction about dryer section

The paper drying process is one of the few papermaking operations, which have remained relatively unchanged since the invention of the paper machine. The drying section consumes the most energy among papermaking operations and it is the longest part of the paper machine, often with more than 50 rotating cylinders (M. Kuuslpalo & J. Paltakari, 14).

The higher running speeds enabled by dryer section, the energy-efficient technology, and the dryer section's impact on the quality of paper and board together constitute to affect the efficiency of the entire machine. (Knowpap, Drying section, 2014) (Figure 3.2.2.1)

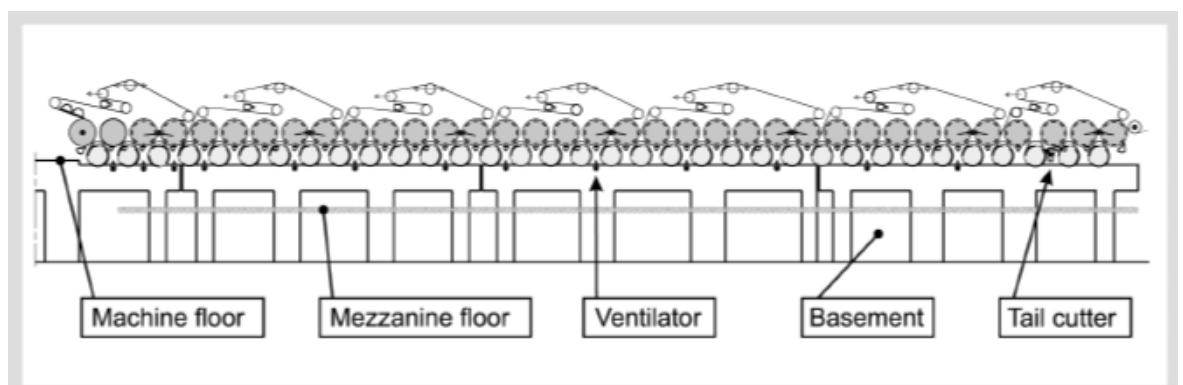


Figure 3.2.2.1 Top-felted, closed-draw drying section with high basement floor. (M. Kuuslpalo & J. Paltakari, 18)

The purpose of the dryer section is to remove water from the web through evaporation by heating. Evaporation must occur efficiently, economically, evenly and without damaging paper quality.

Raising the web dry content to 50 % could be reached economically and technically by using mechanical drying methods (by means of centrifugal force and under pressure at the wire section and by pressing at the press section). Water is then removed by evaporation, in order to reach the desired final dry content. At the dryer section, paper can also be coated and surface-sized with a separate coating and surface-sizing equipment. (Knowpap, Drying section, 2014)

### **3.2.3 Forming fabrics**

Forming fabric, also called wires, are used in forming section for stock drainage. Formation is the most typical and important property that should be achieved in forming sections with the help of fabrics. (Matthias W. Schmitt, 592)

A forming fabric is a woven, endless fabric, through which the water could be drained from slurry, a furnish of a paper, paperboard machine. (Figure 3.2.3.1) While functioning as a filtration medium and as a smooth base for the paper web flowing from headbox, forming fabric also have the duty to transfer paper to press section. (P. Kortelainen, R. Kilpeläinen, S. Taipale, A. Martin, S. Metsäranta, S. Lohm, E. Sjöblom, 310) Sheet support refers to the ability to retain fibers and other furnish components on the fabric components on the fabric surface. Obviously, all kinds of fabric functions are related with each other optimization of one function may be at the expense of another. Depending on the paper grade and their special properties, different fiber fabrics are needed. (Gary A. Smook, 241)



Figure 3.2.3.1 Forming fabric in wire section (Albany international)

Forming fabrics are used in varying conditions and its minimum speeds may vary from about 100 m/min to more than 1900 m/min. The type of fabric is varied from different paper grade, and the design of forming section. The critical properties of forming fabrics are its dewatering and retention characteristics, stability, wear resistance and non-marking structure. ( P. Kortelainen, R. Kilpeläinen, S. Taipale, A. Martin, S. Metsäranta, S. Lohm, E. Sjöblom, 310)

The main requirements of forming fabrics:

- Uniform and controlled dewatering of the fiber suspension spaying from headbox and uniform buildup of paper web.
- Support paper web uniformly and gently during intensified web dewatering at blades, foils, and vacuum suction boxes.
- Transfer paper safely and guide ability
- Easy web release (Matthias W. Schmitt, 592 )
- Good wear resistance
- Resistance to high pressure shower and other damages
- Easy cleaned and have the sheet knocked off

A good forming fabric may prove paper:

- Good formation
- Good strength properties and less two sidedness

- Excellent first pass retention
- Reduced offset linting and save energy (Sabit Adanur, 38)

A fabric could be single-layer, double-layer or triple-layer structure. A compromise fabric is named a double – layer extra (or sometimes two and a half layer). (Figure 3.2.3.2) Single-layer fabrics have one layer of warp yarns and one layer of filling yarns. Double-layer has one layer of warp yarn in MD and two layers of filling yarn in CD. (Figure 3.2.3.4) The two-and-half layer has two filling yarns on the top side for each filling yarn on the wear side. Triple-layer fabrics consist of one MD yarn system and three layers of CD strands.

The three layers of CD yarns consist of two separate fabrics, top and bottom, using a binder yarn as a connection. The double-layer and triple-layer constructions provide progressively better sheet support; improved formation and stability, also longer used time because of larger diameter wear yarns. Single-layer fabrics are the cheapest and oldest but still in using. And for the simple constructions of the single-layer fabrics, they are used on intermediate-speed paper machines. Double-layer and triple-layer fabrics are used in high-speed paper machines instead of single-layer fabrics. (Gary A. Smook, 241)

Besides, there is another kind of fabric named Sheet support binder fabric (SSB) being often used presently. (Figure 3.2.3.3) A sheet support binder (self-support binder) is a multi-layer forming fabric in which the binding yarns become a part of the structure linking top to bottom and having the supporting function. These SSB designs integrate the binding yarn of a triple layer in the structure of the top layer. Binding yarns of SSB could be warp yarns and these designs are called warp bound SSBs.

But SSBs has a more popular version which has wefts for binding. In addition to binding, the SSB fabrics differ from each other in, for example, weft ratio. (Figure 3.2.3.5) “The weft ratio is the ratio between the paper side weft yarn paths to the wear side weft yarn paths.” ( P. Kortelainen, R. Kilpel änen, S. Taipale, A. Martin, S. Mets ärantta, S. Lohm, E. Sjöblom, 315) The weft ratio of forming fabric could affect paper properties

such as retention. For example, a fabric with the ratio 2:1 usually gives better retention than the 1:1 ratio fabric. Typical weft ratios can be 1:1 to prove thin caliper, 2:1 to prove better fiber support ability, 3:2 to give the balance between good fiber support and lifetime as well. (Matthias W. Schmitt, 594)

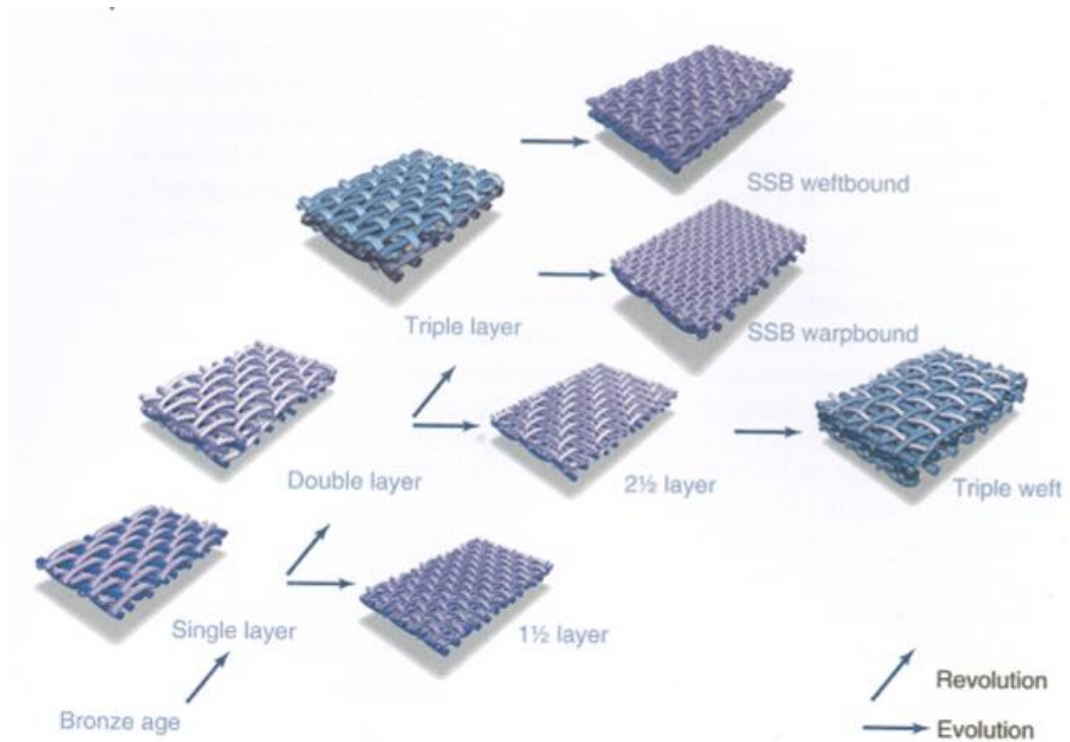


Figure 3.2.3.2 Evolution and revolution in the design development of forming fabrics (Matthias W. Schmitt, 594)



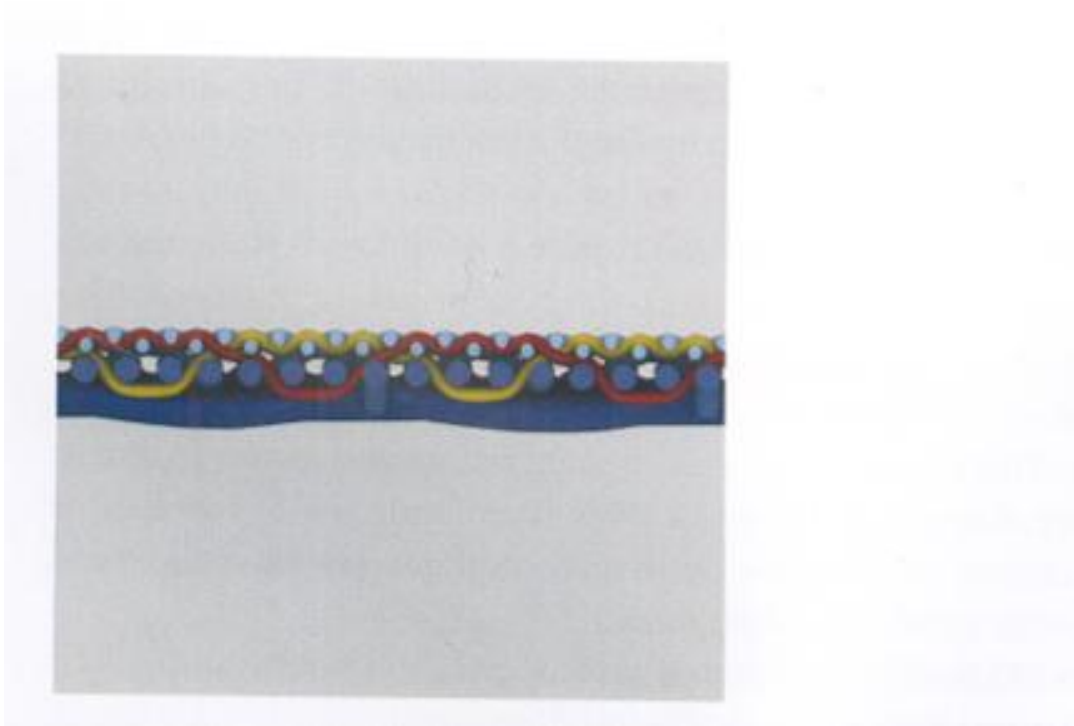


Figure 3.2.3.3 Weft path of a modern SSB design (Matthias W. Schmitt, 594)

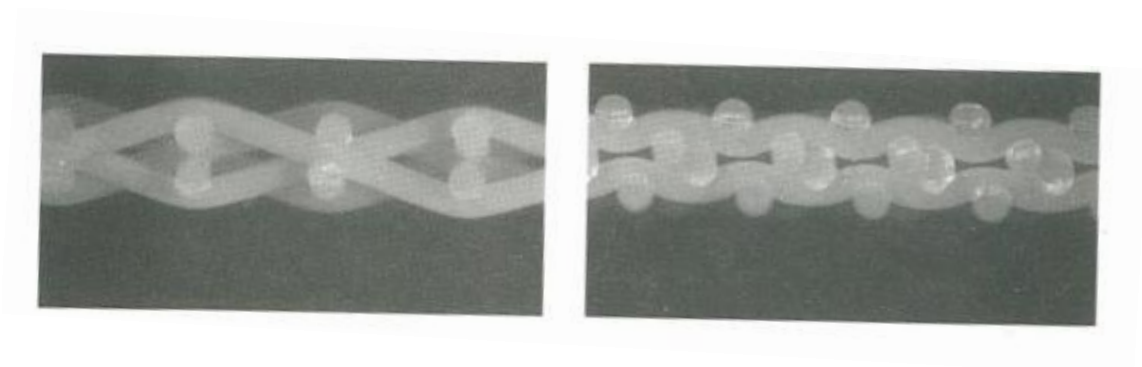


Figure 3.2.3.4 Warp and filling profiles of a four harness two layer fabrics (Sabit Adanur, 46)

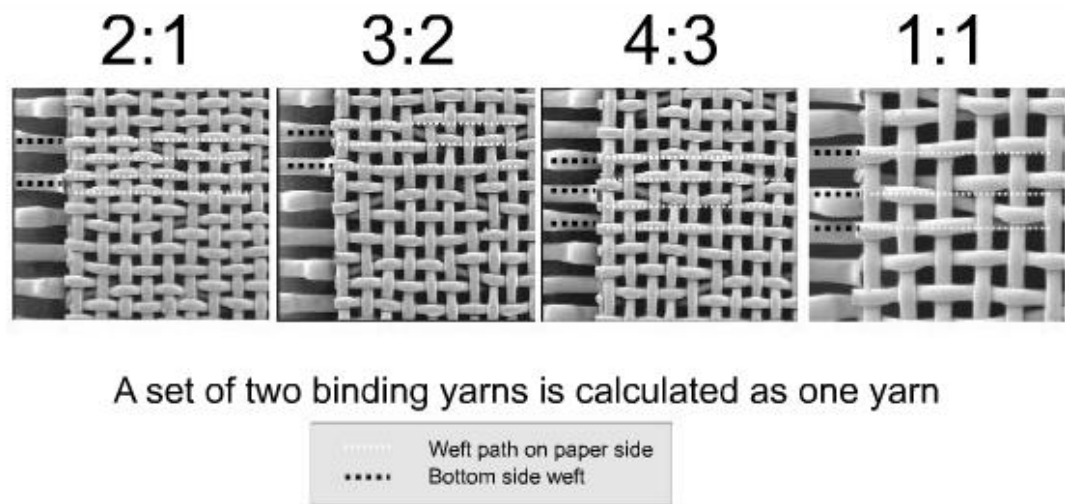


Figure 3.2.3.5 Weft ratio ( P. Kortelainen, R. Kilpeläinen, S. Taipale, A. Martin, S. Metsäranta, S. Lohm, E. Sjöblom, 316)

Typically, forming fabrics are made of round polyethylene terephthalate (PET, which is often called polyester) and polyamide (PA) monofilaments, whose diameters vary from 0.10 to 0.50 mm. Different shapes and even diameters below 0.10 mm are being studied. ( P. Kortelainen, R. Kilpeläinen, S. Taipale, A. Martin, S. Metsäranta, S. Lohm, E. Sjöblom, 311)

Usually different materials are used in different directions for its properties. Polyester is used in machine direction because of its good behavior under load in high tensile strength property and low elongation. But in cross direction, both polyester and polyamide are used.

Polyamide yarns are typically used as wefts on the wear side for the reason that they improve the wear resistance of forming fabrics. Polyamides yarns cannot be used as MD yarns or as the sole material of wear side CD yarns, because of their tendency to absorb water and their high elongation under load. So polyamide is usually used together polyester. Typically, every second wear side CD yarn is polyamide and every second is polyester. This kind of mixing two polymers materials together form could give high wear resistance and good stability to the forming fabric. Besides, adding other polymers or additives into polyester polymers can also improve the wear resistance before extru-

sion of the filament. ( P. Kortelainen, R. Kilpeläinen, S. Taipale, A. Martin, S. Metsäranta, S. Lohm, E. Sjöblom, 312)

Table 1 below shows the typical properties of PET and PA monofilaments for fabrics. Those properties are typical for monofilament yarns used in forming fabrics. Depending on the monofilament type, properties change a lot within the limits showed in the table (Table 1)

Table 1. Typical properties of PET and PA monofilaments ( P. Kortelainen, R. Kilpeläinen, S. Taipale, A. Martin, S. Metsäranta, S. Lohm, E. Sjöblom, 312)

Abbreviation	PET	PA6
Chemical name	Polyethylene terephthalate	Polyamide 6
Density, g/m <sup>3</sup>	1.38	1.14
Melting point, °C	c. 260	c. 220
Shrinkage (180 °C), %	2–15	2–15
Tenacity, cN/tex	35–65	30–60
Elongation at break, %	10–45	25–60
Moisture content (20 °C 65 RH %), %	c. 0.4	c. 4
Abrasion resistance	Good	Excellent
Acid resistance	Good	Moderate
Alkali resistance	Moderate	Good

### 3.2.4 Press fabrics

Press fabrics are used in press section (Chapter 3.3.1) in paper machines and are tailor-made for each particular position in the different press nip.

Paper contact with press felt directly and is strongly influenced in both paper surface properties and economy of papermaking process. The thickness of press felt varies from 3-4mm, and the range of length is from 15 to 75 m. (Matthias W. Schmitt, 598-599)

In general, the press felt (press fabric) need to:

- Accept the water that is expressed from the sheet in the press nip

- Provide the proper protection for the sheet to:
  - Resist crush and shadow mark
  - Resist groove mark and base fabric mark
- Provide the proper surface to the sheet to meet certain paper smoothness
- In case of closed draws, transfer the sheet from one position to another
- Low abrasion at the roll-side surface
- Excellent dimensional stability among life time (Sabit Adanur, 158-159)

The actual requirements of press fabric differ from positions in the press section. All press nips in modern paper machines are using single felts or double felts. Shoe press mainly use double felt. The pick-up felt is in the first press nip and its function is to transfer wet paper web from wire section to press section. The diameter of pick-up press felt fiber on the paper side surface goes down, because of the increasing load between forming section and press section. During the lifetime, press felts run several million times and felt thickness, abrasion, as well as contamination is reduced. Because of these factors, press felts have to be replaced into new after long time used. (Matthias W. Schmitt, 600)

In 1930s, press felts appeared and made from woolen. In the early 1960s, woolen felts were replaced by improved designs based on high-tech textiles. Improved press fabrics had long running time and used under higher machine speed.

Figure 3.2.4.1 Illustrates the basic structure of press fabric. The base weave exist in the middle layer of felts. Base press felts are woven circularly. The weft yarn during weaving is the yarn in the machine direction (length direction) of the press felt and warp yarn is in the cross direction. This kind of press felts are called seamless felts and could be used in all applications. Besides, there is another kind of press felts called seamed felts, which is used in packaging and board. (Figure 3.2.4.2 and 3.2.4.3) The difference between seamless and seamed felt is that seamed felt are not endless. Seamed felts are closed in paper machine with a seam and popular in North America (about 80% of all press fabrics are seamed felts). Seamed felts are easier to install in paper machine, as

well as safer. But seamed felts give marking to paper boards and packaging easily and have effect on printability. (Matthias W. Schmitt, 600)

Almost all the press felts are synthetics, and use polyamide (chapter 5.1.3.2) as the primary material. Press felts consist of batt (nonwoven layer) and base fabrics (woven layer). The nonwoven layers are on the top and bottom layer of the base fabric. Mainly used material is staple fiber. The nonwoven bottom layer contact to the roll surface and protect press felt against abrasion. The top layer contact with paper surface and ensure a low and uniform water flow resistance during the drainage process in press nips. (Matthias W. Schmitt, 600) The base fabric can be single-layer or multilayer. The fabrics can be woven endless or flat and also joined with a seam (chapter 3.2.3). The base fabric weave have an effect on the pressure uniformly, flow resistance and compression properties. (Sabit Adanur, 159)

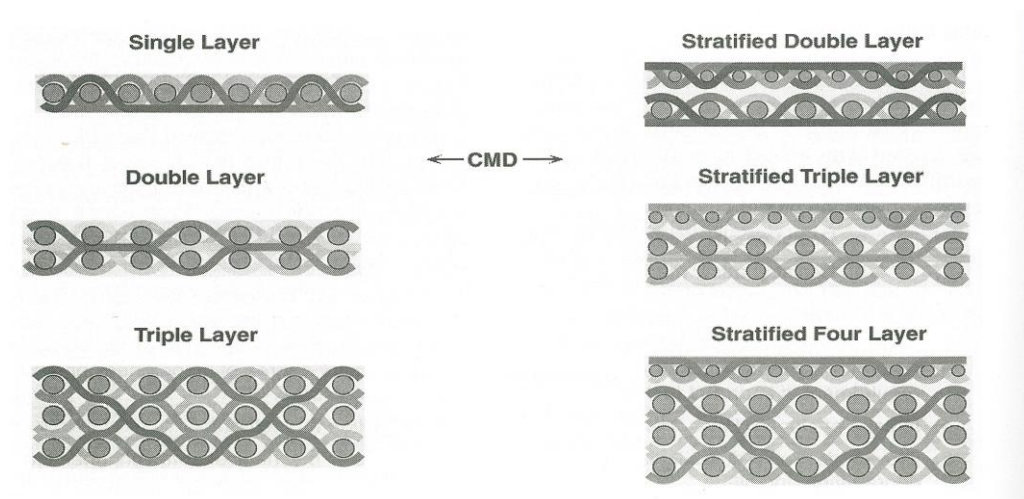


Figure 3.2.4.1 Major types of basic structure used in press fabrics. (Sabit Adanur, 160)

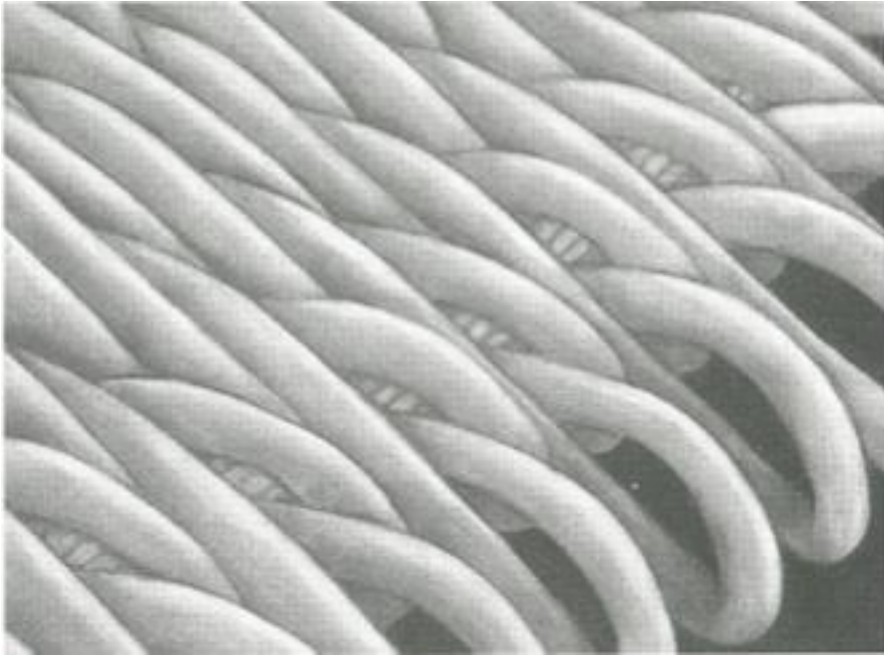


Figure 3.2.4.2 Pin seam press fabric (Sabit Adanur, 167)

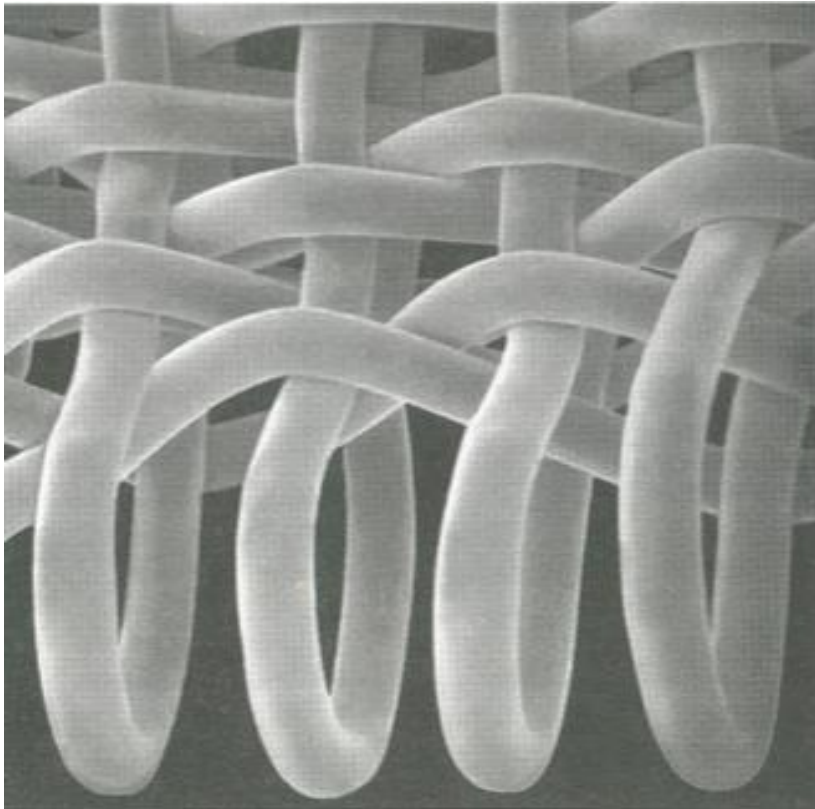


Figure 3.2.4.3 Woven loop seam fabric (Sabit Adanur, 167)

### **3.2.5 Dryer fabrics**

After press section, paper web will be transferred in to dryer section. Dryer fabrics play the role that guide the paper web through dryer section.

The requirements that dryer fabrics should have are listed below.

- One side which contact with paper surface should have a high contact density to ensure the heat to be uniformly transferred to paper web from cylinder.
- Paper-contact side should be smooth enough and inline seam technology for nonmarking of paper.
- High performance and quality running lifetime at a high temperature and humid conditions, as well as excellent dimensional stability.
- Optimized and sufficient vapor permeability are needed to ensure evaporative drying to occur freely
- Assistance the safe transfer from unit to unit inside dryer section
- Allow the water to be evaporated through fabric and a clean run, also keep the permeability up by contamination resistance.

Dryer fabrics are woven as a continuous, also flat fabric. They comprise MD (warp) and CD (weft) yarns. These yarns might comprise single-filament, multi-filament, spun, and plied and so on. (Figure 3.2.5.1 and 3.2.5.3) Besides, dryer fabrics also can be finished by contacting a series of alternating left-handed and right-handed spiral monofilaments (Figure 3.2.5.2). Those spirals are linked together by connecting monofilament. (Figure 3.3.5.4)

At first, cotton was used as the natural material to produce dryer fabrics. With technology developed, dryer fabrics have become synthetic. Nowadays, usually used materials are polyesters and polyamides. These materials could be spun and contacted into monofilaments. Comparing these two materials, good abrasion resistance and dimensional stability make polyester (PET) (chapter 5.1.4) a better choice. And there are PPS and another polymers system like poly (cyclohexylenedimethylene terephthalate) (PCTA). Among these three different materials, PET, PCTA, and PPS, PET is the mainly used material.



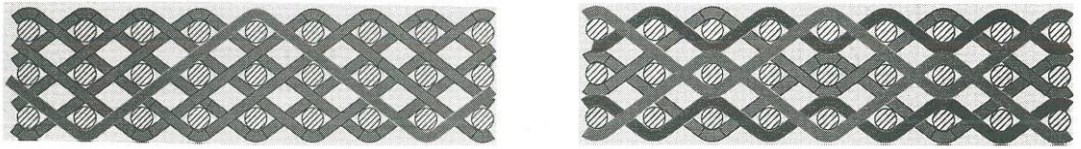


Figure 3.2.5.1 One (left) and four MD yarns fabrics (Sabit Adanur, Ph.D. 215)

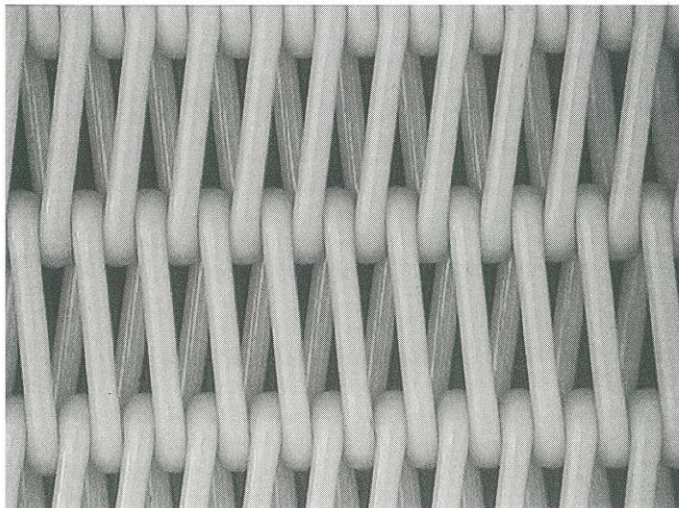
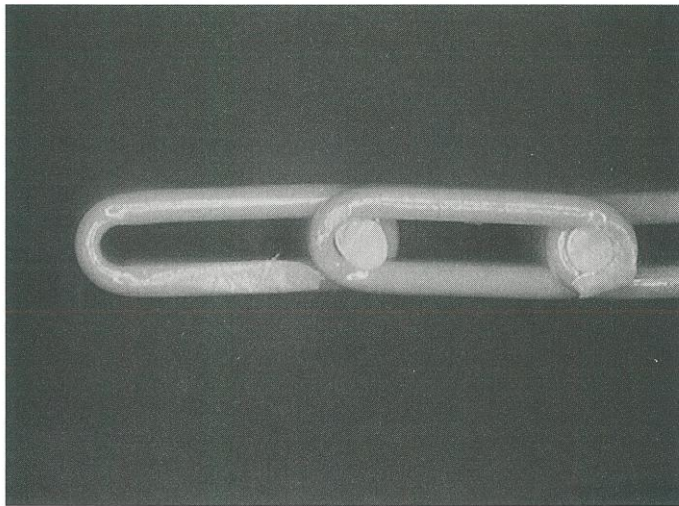


Figure 3.2.5.2 Spiral fabrics, coil: round PET, pintle: round PET (Sabit Adanur, 215)



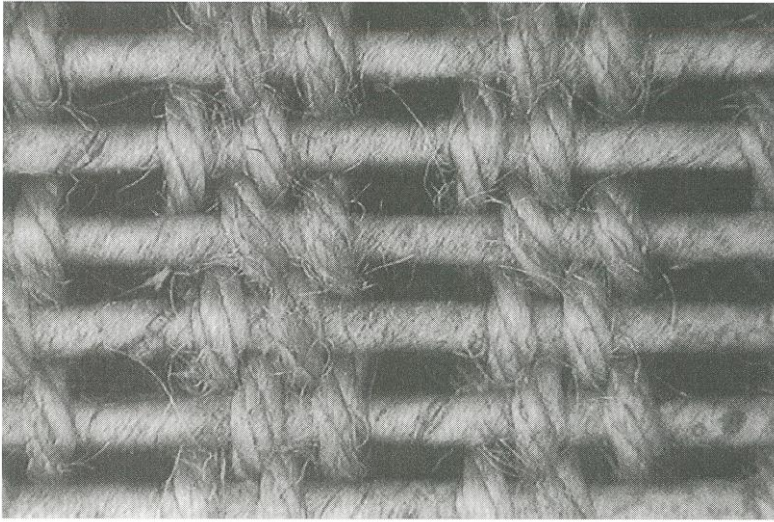


Figure 3.2.5.3 Hydrolysis resistant multifilament fabric. MD: spun Nomex aramid, CD acrylic wrapped glass (Sabit Adanur, 211)

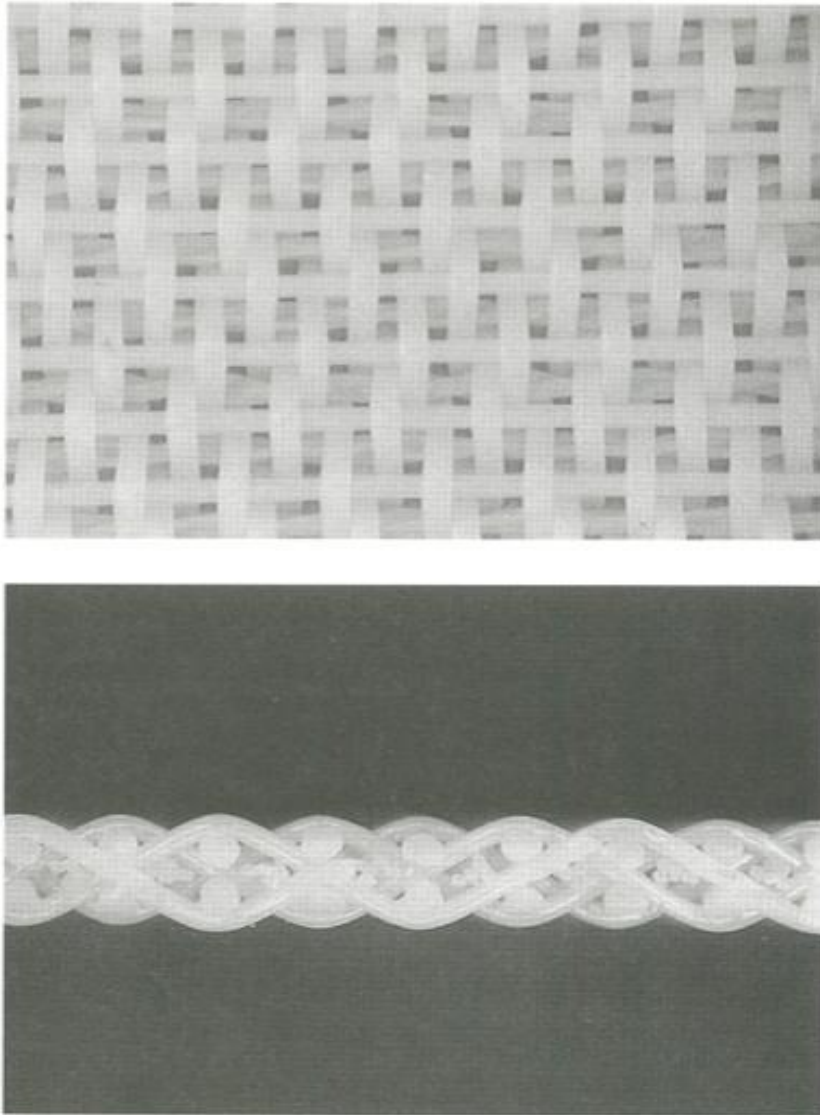


Figure 3.3.5.4 Top view and MD profile of a monofilament fabric with stuffer yarn (Sabit Adanur, 207)

### 3.2.6 Brief information about PET and PA

Polyethylene terephthalate, which is one kind of polyester, is the full name of PET. Polyethylene terephthalate is a thermoplastic polymers resin of the polyester family and is used in synthetic fibers. PET consists of polymersized units of the monomer ethylene terephthalate, with repeating  $C_{10}H_8O_4$  units. PET is commonly recycled. PET can be used as liquid package, flexible food package, substrate in thin film and solar cell. When filled with glass particles or fibers, it becomes significantly stiffer and more durable. (Wikipedia, Polyethylene terephthalate) More properties and details about PET please see chapter 5.1.4.

A polyamide is a macromolecule with repeating units linked by amide bonds. Polyamide could be both natural and synthetic. Artificially made polyamides can be made through step-growth polymerization or solid-phase synthesis, examples being nylons, aramids, and sodium poly (aspartate). Synthetic polyamides are commonly used in textiles, automobiles, carpet and sportswear due to their extreme durability and strength. (Wikipedia, Polyamide) Polyamide has excellent tensile strength, good spin ability and good properties, which have very positive effects on the affinity of impregnation. (Sabit Adanur, 196) More properties and details about PA please see chapter 5.1.3.2.

### **3.3. Polymers used as roll covers in paper machines**

#### **3.3.1 Introduction about press section**

Press section removes much of the remaining water via a system of nips and felts. The nip system is formed by rolls pressing against each other aided by press felts that not only support the sheet, but absorb the pressed water. (Wikipedia, Paper Machine) The dryness is usually about 40% when paper web leave press section. (Figure 3.3.1.1. and 3.3.1.2)

The press section also has a major impact on sheet surface properties such as roughness, smoothness and absorption properties, and also effect indirectly on bulk. Removing water from the paper web is the basic function of the press section, but some paper qualities are also often mentioned, such as web porosity and bonding strength. In any condition, dry solid content after the press section is the most typical value by which press section performance is judged. (Knowpap, Pressing section, 2014)

With long felt and roll change intervals, a good press section may give paper web high dryness. It could provide even moisture profiles and is not easy to cause network failure or runnability problem during the drying section. A good press section also should be safe for operators in that it minimizes the need for interfering with the operating of machine. (Knowpap, Pressing section, 2014)

## SymPress B

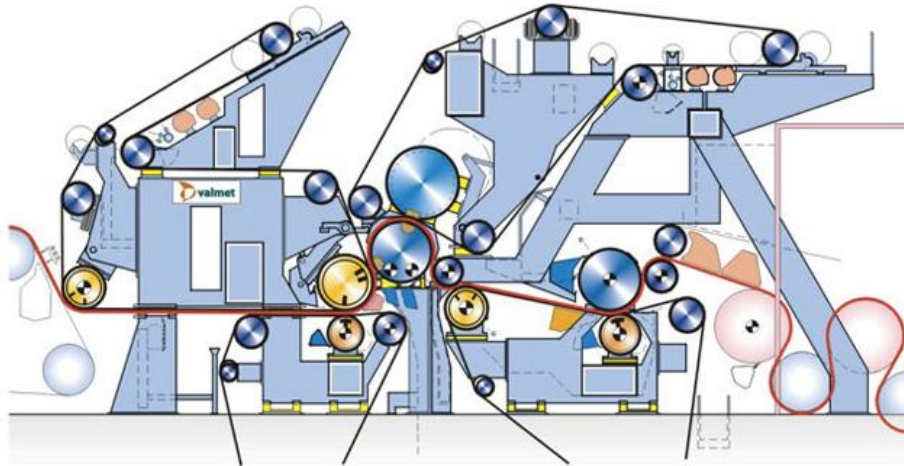


Figure 3.3.1.1 A typical press section for printing papers—SymPress B (Knowpap, Pressing section, 2014)

## OptiPress

Double-nip press with a closed draw

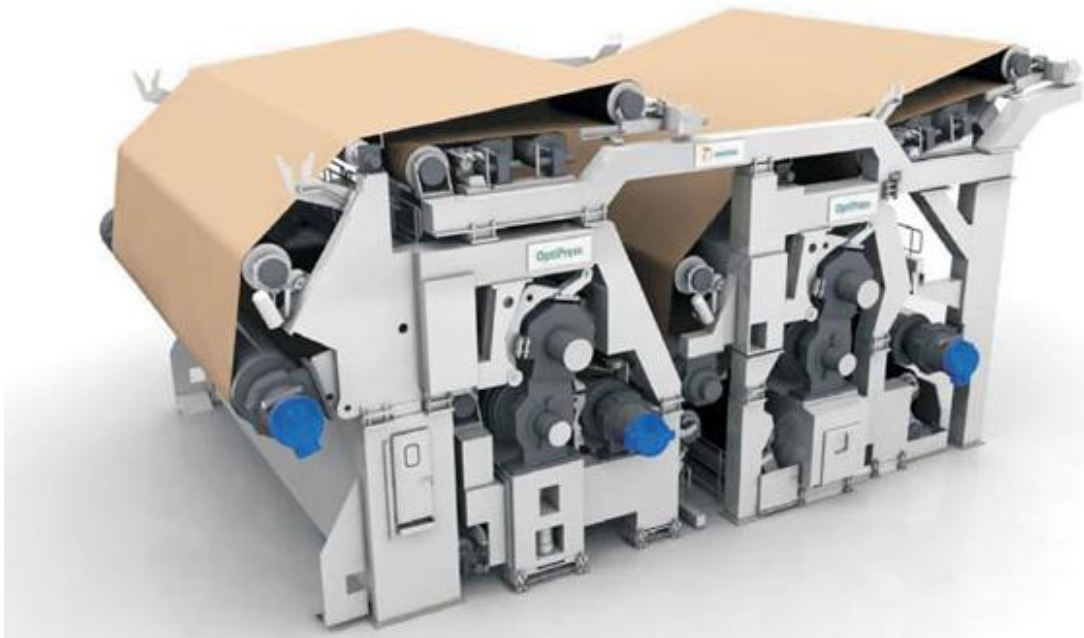


Figure 3.3.1.2 One type of press section—OptiPress, a kind of double-nip press with a close draw. (Knowpap, Press section, Read Feb, 09<sup>th</sup>, 2014) (Knowpap, Pressing section, 2014)

### 3.3.2 Introduction about calender section

The paper in the web leaving the paper machine is usually not as such suitable for its intended use but it requires further processing. The most common additional process is calendering. Calendering is implemented by means of leading the paper through a system of nips between two or more rolls. (Knowpap, calender section, 2014) (Figure 3.3.2.1)

The paper may be calendered at:

- The paper machine, in an on-machine calender in the dryer section .
- At the finishing department, in an off-machine calender.

Calendering has three main functions:

- Improving paper surface properties (smoothness, gloss), to improve printing properties, or other factors related to further processing
- Adjusting paper thickness, or caliper, to obtain paper of desired density
- Leveling the paper caliper profile, to obtain smooth and even rolls at the winder.

Moreover, calendering may be used for various special purposes, e.g., for stamping relief designs on the paper with patterned rolls.

## Calendering

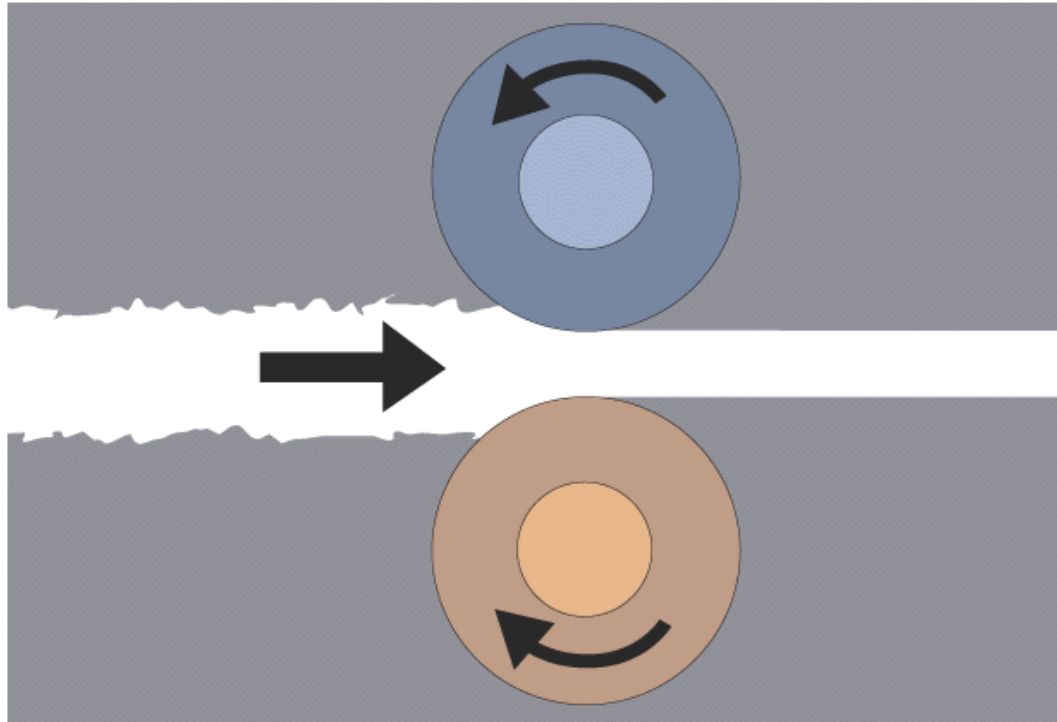


Figure 3.3.2.1 Principle of calender section and how rolls work on paper (Knowpap, Calender section, Read Feb 11<sup>th</sup>, 2014)

There are different types: soft calender, hard nip calender, multiple nip calender. Their difference is in the roll cover materials and number of nips. (Figure 3.3.2.2)

Hard nip calenders are well suited for pre-calendering of coated paper and board grades to prepare the paper surface for coating. This is called intermediate calendering. It can also be the final calendering application like for uncoated woodfree papers and newspaper. This is called machine calendering. And it consists of hard rolls and hard nips. (Knowpap, calender section, 2014)

A soft calender refers to a calender where at least one of the rolls forming each nip is furnished with a soft polymers cover and where each nip is separately loaded. To be sure, the soft calenders are usually arranged as on-line calenders, i.e., integrated with a paper or board machine or a coater. The number of nips in a soft calender varies from one to four. (Knowpap, calender section, 2014)

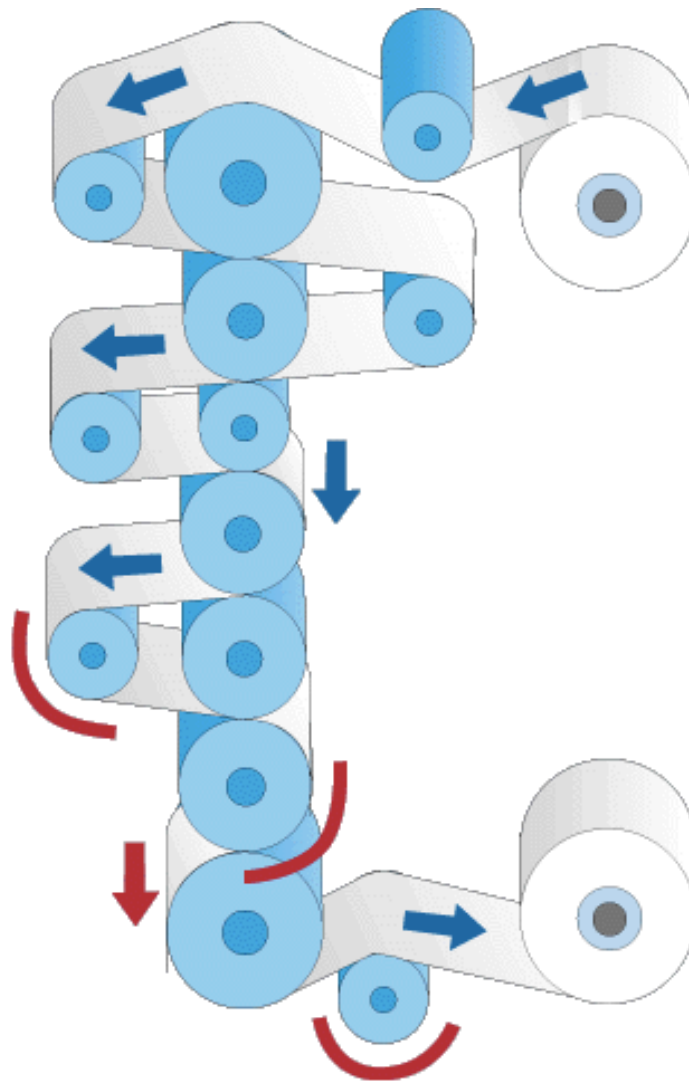


Figure 3.3.2.2 Supercalender structure, one of calender ways (Knowpap, Calender section, 2014)

### 3.3.3 Roll covers in press section and in calender section

Polymers are usually used as roll covers in press section. There are four base material groups used as press roll cover: 1) hard coatings; 2) fiber-reinforced epoxy covers; 3) polyurethane covers; 4) rubber covers.

Besides press section, other sections in paper machines are also using polymers roll covers, like suction rolls in forming section, sizer roll in sizing and coater backing rolls in coating section. In this chapter, press section, and calender roll cover will be used as an example to illustrate these roll cover material groups.

Roll covers are quite crucial for paper quality and paper machine runnability. The first generation of roll is made from wood, steel or other metals. With technology and science developing, rubber was introduced in the 1920s, polyurethanes in the 1970, and various composites in the 1980s. Besides, chromium-plating technology was known by paper makers in the 1930s in the areas of hard coating. In the 1980s, novel carbide and ceramic coating technology was developed. (H. Kettunen, 10)

The main effects of roll covers may be

- To protect roll body from corrosion when machine is running;
- To protect the roll against wear from fabrics, felts or wires;
- To generate a soft and wide nip compared to a hard and narrow nip
- To reduce the hydraulic force in a nip of press section
- To increase drainage ability
- To ensure good release of paper web
- To give sizing or coating color to paper (in coating or calendering section)

(H. Holik & J. Moser, 575)

### 3.3.3.1. Rubber cover

Polyisoprene (Figure 3.3.3.1) is the main component of rubber which found in a tree named *Hevea braziliensis* in the jungles of Brazil. Polyisoprene has a special ability to return its original shape after being stretched, especially when being chemically modified by vulcanization. And materials that have the remarkable ability have entitled to be named rubber.

NR (natural rubber) is the polyisoprene extracted from *Hevea braziliensis*. Rubber's remarkable elastic ability eventually develops into a billion-dollar business and affected million people's normal life. Besides NR, synthetic rubbers are manufactured artificially and playing important rules in nowadays life. (Ciesielski A., 3-6)



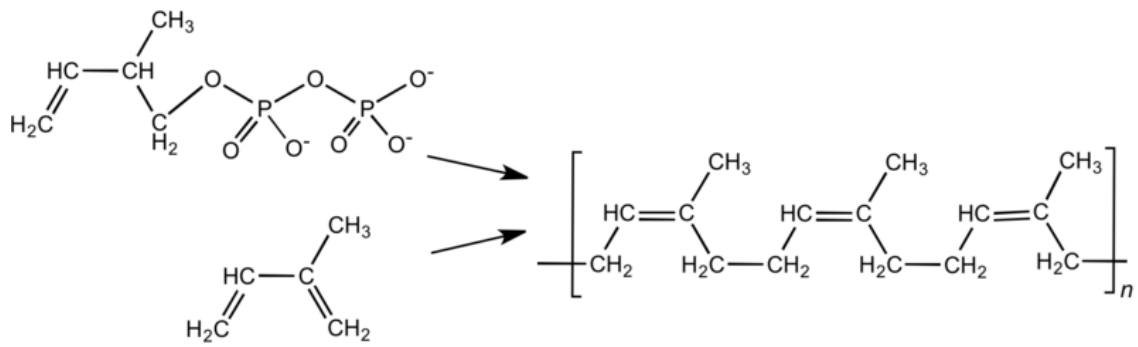


Figure 3.3.3.1 Chemical structure of cis-polyisoprene, the main constituent of natural rubber. Synthetic cis-polyisoprene and natural cis-polyisoprene are derived from different precursors by different chemical pathways. (Wikipedia, Synthetic rubbers)

When the properties of rubber are discussed now, the final vulcanized compound properties are always referred to. The attributes of the final vulcanized compound which are almost always referred to. The primary component of the compound is the raw gum elastomer (for NR this would be the dried latex from the tree) whose nature is the driving force for many of these properties. (Ciesielski A., 11)

As a usual material for rolls cover, rubber has an upper temperature aging limits, which means it has a heat aging resistance at certain temperature range. Also, synthetic rubbers have good resistance to ozone at room temperature, but not the NR. With temperature rising, rubber's mechanical properties changed. When a higher temperature reached, most types of rubbers' elasticity ability are weaker. NR has good mechanical strength and can be compounded to have excellent elasticity to keep its original shape. Besides, NR's good great abrasion resistance which, with its low relative cost, makes it a typical choice for applications like slurry pumps. (Ciesielski A., 11-16)

Many rubber products are used in situations where a load is applied to them, like roll cover in press section of paper machines or the wheel of vehicle. (Ciesielski A., 116) Modern rubber covers are based on synthetic rubber compounds (like chloroprene nitrile, hydrogenated nitrile, chlorosulphonated polyethylene, styrene butadiene). Synthetic polymers such as chlorosulfonated polyethylene (CSPE) synthetic rubber provide excellent aging and good chemical resistance. And another example is nitrile rubbers, which lead to very abrasion resistance and good mechanical properties. Properties like dampening, roughness and low compression set for marking resistance have to be con-

sidered for development of the compound in these applications. (H. Holik & J. Moser, 2013, 582)

Generally, rubber has a high coefficient of heat generation in the loading cycle and its characteristic cause reduction of rubber's use in where mechanical load is small or the paper machine has a low speed. The most typical applications are various guide rolls for the paper web and fabrics, sizing press rolls, backing rolls of blade coaters, soft calender rolls and also soft reeling cylinders. In some occasion, rubber rolls covers are also used as primary press rolls covers. The typical rang of rubber cover hardness from 2 to 200 P&J units and thickness range various from 10 to 50 mm. In ordinary, the limit temperature of cover is 90 °C, but HNBR tolerates temperature up to 160 °C or even 170 °C. (H. Kettunen, 11)

### **3.3.3.2. Polyurethane covers**

Polyurethane covers (such compounds as TDI and MDI based polyether and polycarbonate, PPDI) (Figure 3.3.3.1.) have mostly been developed for the same applications as rubber covers.

The key properties of polyurethane rolls cover are smaller internal heat generation and better wear resistance. For all the types of roll covers in paper machines, only polyurethane covers have the capacity to give enough wear resistance to reach acceptable grinding intervals. High quality polyurethane roll cover formulations give the required mechanical strength and elasticity, also the excellent hydrolytic stability. (H. Holik & J. Moser, 2013, 584) Polyurethanes roll cover has less desire of interior cooling of rolls and is used in both press section and calender section.

Comparing with rubber roll cover, polyurethane does not need as high curing temperature as rubber. This advantage has made polyurethane more economical. Besides, polyurethane roll covers will absorb some water during papermaking process, which must be considered in roll maintenance. Typically, the operating temperature could go up to 90 °C in wet condition and in dry condition; the limit temperature is 110 °C to 120 °C. (H. Kettunen, 11)



Figure 3.3.3.1 Polyurethane PressFox (Metso) cover-feature a new type of undulating structure providing improved durability and safety performance (H. Kettunen, 11)

The functional polyurethane layer is manufactured by casting process. This can ensure that the layer get homogeneous material properties. The polyurethane elastomer itself is a reaction polymer, which is created by the mixing of pre-polymers and chain extenders. (H. Holik & J. Moser, 2013, 584) More details about polyurethane please see chapter 6.2.3.

### 3.3.3.3. Hard coatings

Hard coatings can be subdivided into carbide and ceramic coatings and chromium plating. But those coating materials do not belong to polymers family. (H. Kettunen, 12). In this chapter, not so much information about its material is mentioned.

Usually, hard coating rolls are applied in center rolls, dryer cylinders, thermo rolls and guide rolls. Hard coating roll cover has high hardness, which could give paper better smoothness. (H. Kettunen, 12) But hard coating roll cover is not the point we will discuss in the paper.

### 3.3.3.4. Composite covers

Composite covers for roll's hardness are higher than rubber or polyurethane roll covers. Typical hardness of composite roll cover ranges from 85 ShD to 95 ShD and operating temperature could up to 100 °C. The most useful composite cover rolls are in calender section, where pressure levels can reach 100 MPa. Indeed, development of composite covers gives possibility for online calender technology.

Besides, various types of guide rolls, backing rolls, spreader rolls, press rolls and reeling cylinders are also use composite covers because of better wear resistance being provided than softer materials. Usually, composite covers are made of matrix material (mostly epoxy resins), fillers (various hard particles) and reinforcement fibers (various) in different proportions. (H. Kettunen, 11)

### **Reinforcement fiber roll cover layer**

Composite covers in the functional layer are mainly applied in calender section. The most significant advantage of reinforcement fiber roll cover is very good mechanical and thermal robustness of the cover. (H. Holik & J. Moser, 2013, 585)

The concept of reinforcement is that the fibers offer composites some extra purpose to give enough functional properties to the products, which like strength, stiffness and other mechanic properties. Reinforcement fibers include glass fibers, carbon fibers, aramid fibers and boron fibers, also ceramic fibers and steel fibers. (Guo Yuanzheng & Zhao Hanqing, 26)

High-performance materials, like aramid fibers are used in the place, which a high damage tolerance is needed. Besides, glass fiber-reinforced is mostly used in the base layer of multilayer roll covers. For soft calendering, different hardness of the roll covers is asked in order to ensure the required paper properties. This purpose can be achieved by using different amount and combination of fillers in the fiber-reinforced composite. (H. Holik & J. Moser, 2013, 585)

Class fibers can be used in a many applications, especially for the production of large composite structures. Glass fibers provide a high strength and light weight in a low price which make glass fibers more economical. Furthermore, glass fiber is one of inorganic fibers, which will not cause burning itself, and the thermal conductivity of it is

typical low. This property make glass fiber has a good high temperature resistance. Besides, glass fiber is good at avoiding corrosion from acid, alkali and some solvents, that means it has excellent chemical resistance. Additionally, glass fiber is electrically insulating and has moisture resistance and high tensile strength. But everything has two sides. Glass fiber also has its own disadvantages: the material is not quite stiff and has poor wear resistance, flexibility and bend resistant. (Guo Yuanzheng & Zhao Hanqing, 26)

Compared with glass fibers, carbon fibers can have little elastic deformation when they are under a certain stress. Moreover, the thermal expansion of carbon fiber is basically zero, which means carbon fiber can remain its basic form when heating. But for carbon fibers, a strong acid condition may cause it oxygenated easily. (Guo Yuanzheng & Zhao Hanqing, 28)

### **Resin covers**

Resin covers are usually used in press section and calender section. Typically, mineral-filler resin covers are applied as a base layer of fiber reinforced functional layer. The positive effects of resin layer are extreme homogeneity of the functional layer and excellent abrasion resistance. Those mentioned properties are critical for rolls used in soft calender or center press roll positions. Special formulations of resins make the adjustment of sheet release properties possible, also the wear resistance. (H. Holik & J. Moser, 2013, 586)

Thermosetting resins include polyesters, vinyl ester, epoxies and polyamides. The most used resin in roll cover is epoxy (Figure 3.3.3.4). Epoxy resin traditionally are made by reacting epichlorohydrin with bisphenol A, which are linear polymers that cross-link, forming thermosetting resins basically by the reaction with amine-type compounds. (Guo Yuanzheng & Zhao Hanqing, 15)

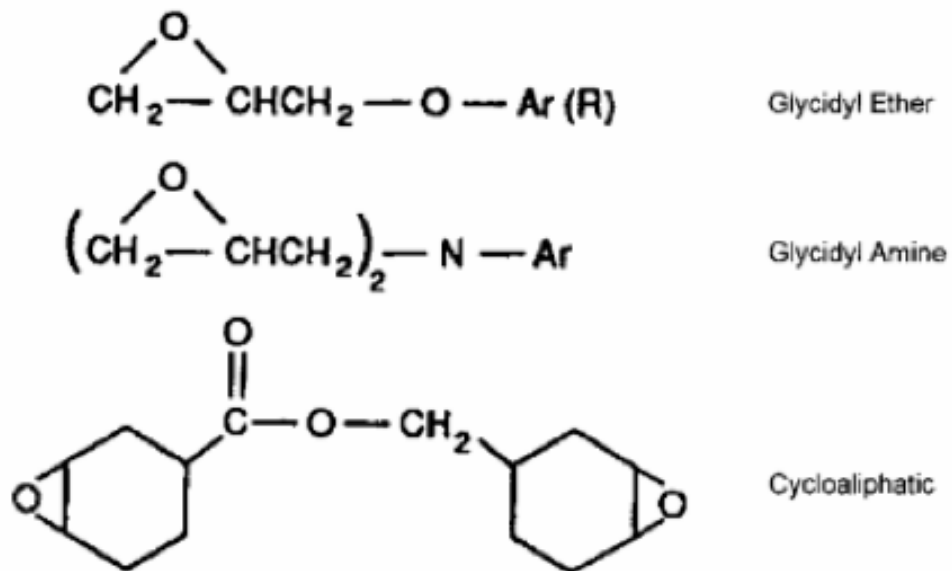


Figure 3.3.3.4 Three types of different epoxy (Guo Yuanzheng & Zhao Hanqing, 15)

### 3.3.4 Innovation

Usually, large amount of energy consumption is a continuous problem for papermakers. Energy efficiency, reliability and production efficiency are demanded of the paper machines still running. Based on this phenomenon, innovations about roll covers are necessary.

#### 3.3.4.1. PressPolar and PressKodiak

##### PressPolar

Metso Company designs Presspolar for Long Nip Pressure (LNP) positions. (Figure 3.3.4.1) It is designed to outperform other premium polyurethane covers in LNP applications. PressPolar could be operated under the temperature of 121°C and the load of 525 KN/m. What's more, the surface structure of this roll cover could be plain, grooved or blind drilled. Typically, the structural geometry of the polyurethane is perfect so that the internal work loss could almost be avoided. (Paper 360°, October 2013, Brown paper goes green)

During the development of PressPolar, a new kind of material for roll cover was manufactured to meet certain customer's needs. This new material is kept in solid condition at room temperature and at normal processing temperature. So to get the resin flow and high even viscosity, high process temperature is necessary. This high temperature equates very high system pressure. The newly installed roll cover has 44 °F lower than before. The new PressPolar worked for two years and the mill was run without problems for more than 4 years. (Paper 360°, October 2013, Brown paper goes green)

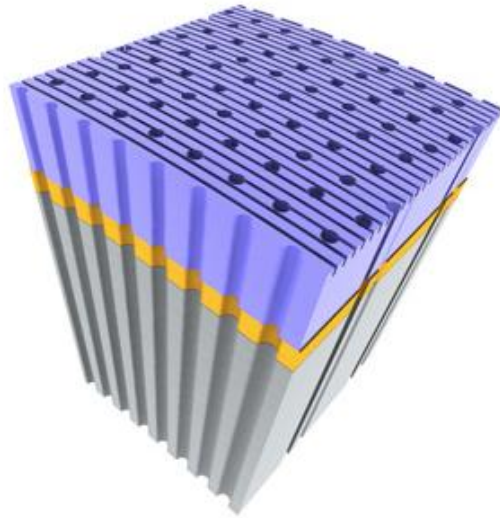


Figure 3.3.4.1 PressPolar polyurethane roll cover – valmet  
(Paper 360°, October 2013, Brown paper goes green)

### **PressKodiak**

Such a lot of applications like suction rolls mated to high impact profiling steam boxes, multiple nipped press rolls, may need to be worked at a high temperature and high load condition. For these applications, PressKodiak series, which available in common thickness for suction rolls and blind drilled positions with hardness ranging from 12-25 P&J, was designed by Metso. This cover material also allows for greater open area previously not available using other premium polyurethane covers. (Paper 360°, October 2013, Brown paper goes green)

### **Comparison**

With PressKodiak and PressPolar, less internal friction, lower temperature inside the cover and less energy consumption was realized. Due to the load limitation of the roll cover, seldom paper mill would like to use LNP. Now those limitations have been eliminated. PressPolar and PressKodiak could help paper machine perform better and reduce environmental impact as well. (Paper 360°, October 2013, Brown paper goes green)

#### **3.3.4.2. MajorSoft and MegaSoft**

Voith Paper changed manufacture technology for rubber roll covers and especially, improved the polymers matrix of the base layer and the intermediate layer. After improving, the bonding force between cover layers is four times stronger than conventional rubber roll because of more contact points in and between these layers. Meanwhile, higher dewatering capacity, more energy savings and longer grinding intervals could be achieved. (New roll covers with improved polymers matrix, TWOGETHER, 34/2013, 36)

MajorSoft and MegaSoft are mainly used in tissue paper machine. (Figure 3.3.4.2.1 and Figure 3.3.4.2.2) New cover of these two innovations is a newly developed functional layer that consists of an improved rubber polymers matrix. MajorSoft and MegaSoft may improve machine speed and save energy. The MegaSoft roll cover ones show its ability in a tissue machine. The machine used virgin and recycled fibers to produce tissue paper at a speed of 1600-1850 m/min. By using MegaSoft, the production speed was increased by 25m/min and the dry content was improved by up to 1.2%. MegaSoft helped paper mill save 63 kWh/t energy. Because of the new cover, production was increased by 1.3-1.5% and saves almost 180,000 € annually. (New roll covers with improved polymers matrix, TWOGETHER, 34/2013, 37)





Figure 3.3.4.2.1 MajorSoft, rubber roll cover in press section—Voith (TWOGETHER, 34/2013, 37)



Figure 3.3.4.2.2 MegaSoft, rubber roll cover in press section—Voith (TWOGETHER, 34/2013, 37)

Besides, MajorSoft and MegaSoft could wear on half or less load comparing with previous rubber roll cover at the same load. The multi-layer cover structure absorbs the nip press and reduces shear force down to the shell. This advantage causes less and less damage of cover and then less production stoppage.

## 4 Additives

Additives act an extremely significant role in modern paper manufacturing industry. In fact, date back to the period of handmade paper; additives have already been involved. The main purpose of using additives is to improve the properties of the final paper products and provide an economical process at the same time.

In papermaking, additives can be divided in different ways. In general, two groups are classified, either functional additives or process additives. Functional additives are materials that enhance or alter specific properties of the paper product, for example, fillers, sizing agents, hydrophobicity, dyes, optical brighteners, and wet-strength and dry-strength additives. They may be added internally or to the surface of the sheet, improving some paper properties or even bringing totally new properties. Process additives, on the other hand, are materials that improve the operation of the paper machine, such as retention and drainage aids, biocides, dispersants and defoamers. They are primarily added to the wet end of the paper machine for improving the runnability, for example, by improving retention and dewatering and controlling pitch problems. There is no a clear boundary between functional and process additive, which means some functional additives may also be able to be utilized as a process additives, or have a significant impact of process additives' performance. (Margaret A. Dulany, George L. Batten Jr., Michael C. Peck, Charles E. Farley, Apr 15<sup>th</sup> 2011)

### 4.1. Functional additives

In general, there are two main purposes to employ wet end chemistry and practices:

- a. Achieve some specific paper properties. (Scott, W.E, 1996, 1) As we all know, every paper grades has to meet the specification properties that are wanted by the costumers and manufacturers. Of primary importance in this regard is the efficient application of functional additives. However, there are a number of inherent limitations in paper, so wed end chemistry enables paper to overcome many of these limitations and deficiencies.
- b. Enhance runnability of paper machine. (Scott, W.E, 1996, 1) Indeed, on one hand, wet end chemistry can be used to enhance drainage, minimize entrained air and foam,

keep machines clean and keep the solids levels down in recycled white water streams. On the other hand, the same wet end chemistry will destroy the paper machine if they are out of control.

#### **4.1.1 Wet strength additives**

The tensile strength of paper and paperboard falls down dramatically when it becomes wet, however, various products such as packaging paper, paper sacks, wall and poster paper, liquid packaging, etc. require higher retention properties in the wet sheet. Therefore, wet strength additives are employed.

Wet strength additives are polymeric materials, which must be adsorbed so that they can act effectively. In addition, all common wet strength resins must also undergo a curing step before add another layer of complexity in wet end chemistry interactions. (Scott, W.E, 1996, 61)

In the early twentieth century, some certain water soluble synthetic resins that can impart wet strength to paper was found, which lead to a dramatically growth in use of these synthetic wet strength resins in paper industry since then.

There are four properties which must be contained by the effective wet strength resins. First, the resins must be polymeric, and can provide mechanical strength to protect fiber-fiber bonds against swelling and disruption. Second, it must be cationic and provide the attraction to negative cellulose fibers needed for rapid and complete retention. Third, it must be water-soluble or water-dispersible to insure uniform distribution throughout the furnish. Last, the must be chemical network-forming and provide paper with resistance against swelling by water. (Scott, W.E, 1996, 62)

Four resins are discovered the most effective application, including polyamide-epichlorohydrin (PAE), polyamide-epichlorohydrin, which are most effective in neutral and alkaline systems. Whereas in acid systems, urea-formaldehyde (UF) and melamine-formaldehyde (MF) are the main wet strength resins. The last two resins are also used in paper mill. Apart from these resins, there are also other synthetic polymers used as wet strength additives, such as polyureas, polymelamines, polyaminoamide-epichlorohydrin

(PAAE) resins, amine polymers, and polyethylene imine (PEI) etc. (Scott, W.E, 1996, 62).

#### 4.1.1.1. PAE

In today's papermaking process, the most common wet strength additive materials are polyamide resins used under neutral or alkaline conditions, which was invented nearly thirty years ago.

Basically, PAE resins, also called polyamide-epichlorohydrin, are acidified to a pH of 3.5-6 and the end of their preparation in order to make them stable. However, the perfect range for using PAE resins is 6-8, but also available in the range of 5-9 with decreased reactivity. (Scott, W.E, 1996, 65) They are often added at the fan pump, or earlier in the system when people want longer retention time.

#### 4.1.1.2. PAAE

Another high effective wet strength agent, PAAE, has been accepted by papermakers and has become one of the dominant wet strength additives, especially in alkaline systems. Reasons for it are numerous, for example, its excellent cost-effectiveness, wide versatility and easy usage. At high retention levels, adding polycarboxylic acid can improve the retention of products. (Raimo Alén, 2007, 94) Table 1 shows the advantages and disadvantages of different wet strength resins

Table 1. The advantages and disadvantages of different wet strength resins (Raimo Alén, 2007, 96)

Resin	Advantages	Disadvantages
UF	Low cost, easily reworkable broke, compatible with rosin + alum sizing	Low off-machine cure, semipermanent wet strength, low pH working range, formaldehyde vapours (health hazard)
MF	High off-machine cure, very high wet strength, dry strength	Sensitive to sulphate ion, low total solids content, formaldehyde release
Glyoxal	Dry strength, high off-machine cure, easily repulpable	Temporary wet strength, sensitive to pH, short shelf life
Polyamide	Very cost effective, broad effective pH range, high off-machine cure	Not easily repulpable, AOX contributor
Polyamine	Low cost, good off-machine cure, high cationic	Not easily repulpable, AOX contributor
Epoxide	Extremely high permanent wet strength, very high off-machine cure	Requires in-mill activation, epichlorohydrin release, AOX contributor, not repulpable

### **4.1.2 Dry strength additives**

Dry strength is an inherent structural property of paper webs, which mainly derived from the formation of bonds in the fiber network during consolidation and drying. If a paper sheet failing under tensile load, some fibers fracture will be pulled out intact during failure. (Roberts, J.C, 1996, 119) But bonds between fibers, formation, fines retention, and drainage will be all improved when utilizing dry strength additives.

Many water soluble and hydrogen bonding polymers can be used as dry strength additives. In fact, natural dry strength additive, like hemicelluloses, are contained in wood fibers. Hemicelluloses are also polysaccharides as celluloses, but they contain several of sugars, linkages and linkage position, which is the difference from cellulose.

Hemicelluloses can interact strongly with water, contribute greatly to the swelling of wood fibers during beating and promote the development of fiber-fiber bonding in paper. So, removing hemicelluloses from wood fiber would make it more difficult for the bonding development. However, there is also another example of difficult to achieving interfiber bonding in paper produced from cotton fibers, which is no hemicellulose contained itself. (Scott, W.E, 1996, 51) In that case, dry strength additives have to be employed to improve the paper bonding. Commercially, the most important dry strength additives are starch, natural gums and polyacrylamides. Other polymers such as carboxymethylcellulose, polyvinyl alcohol, latex are also used in some specific applications.

#### **4.1.2.1. Starch**

Starch derivatives, according to the book principle of wet end chemistry by William E. Scott, occupy 95% of commercial dry strength additives types' market share in today because of its low cost, along with gums and synthetic dry strength agents, which only take approximately 2% of each. Other substances, for example, polyvinyl alcohol and latex, account for the rest of 1% of dry strength additives, since they are usually used for specifically paper grades.



Figure 4.1.2.1 Starch in a spoon (Wikipedia, Starch)

Starch is a carbohydrate consisting of glucose polymers, amylopectin and a large number of glucose units, which is also called amylose. This polysaccharide is produced by most green plants as an energy store. (Wikipedia, Starch) Before the invention of paper machine, starch has already been used for paper additives. Nowadays, the application of starch including wet end additions, paper dry strength, and surfacing sizing, which will be also introduced in this paper.

In wet end process, in order to gain good starch retention on papermaking fibers, cationic starches are applied in a wide range of paper grades to have a positive charge bound to the starch polymers. These starch derivatives associate with the anionic or negatively charged paper fibers / cellulose and inorganic fillers. Cationic starches together with other retention and internal sizing agents help to provide strength to the final paper sheet. (Wikipedia, Starch, Papermaking). Moreover, starch enhances interfiber bonding due to its free glucose hydroxyls participate in hydrogen bonds that would naturally occur in the bonded area between two fibers. (Scott, W.E, 1996, 52-53)

Papermakers usually need to provide conditions which can promote the rapid and complete adsorption of starch on fibers and minimize adverse reactions with other additives or interfering substances so that they can use starch effectively.

#### **4.1.2.2. Polyacrylamide dry strength resins**

Besides starch, there is another well known retention and drainage dry strength synthetic additives used widespread, polyacrylamide. These polymers contain primary amide group so that they can form hydrogen bonds with surface cellulose molecules in fibers and improve interfiber bonding as starches do. However, polyacrylamide is a nonionic material according to its structure. As a consequence of it, polyacrylamide cannot be retained to any significant degree and has only a little attraction to papermaking fibers. So, in order to make it more beneficial in papermaking process, some kinds of charge groups are involved and incorporated, for example, anionic polyacrylamide and cationic polyacrylamide, which can promote their retention. (Scott, W.E, 1996, 56-57)

Cationic derivatives of polyacrylamide are prepared by the application of Mannich reaction in order to expand the range of its possible uses in the pulp and paper industry. Cationic polyacrylamide(C-PAM) is used as strengthening agent and as flocculants. The polymers used in these two applications differ in molecular weight. (Scott, W.E, 1996, 57)

#### 4.2. Process additives

Retention and drainage polymers type are discussed below.

Different synthetic and natural polymers are used as the retention polymers in papermaking processes. Table 2 shows some typical fixation and retention polymers used nowadays.

Table 2. Some typical fixation and retention polymers used nowadays (Raimo Alén, 2007, 106)

Polymer type	Abbr.	Typical molecular weight, million Da	Typical charge density*, meq/g active substance	Purpose / use
Polyaminoamide-epichlorohydrin	PAE	0.02–0.1	+7	Fixative
Polyamidoamine	PAMAM	Medium	Cationic	Fixative
Polyethylene imine	PEI	0.8–2	+5...+15	Fixative, retention aid (by "patch flocculation")
Dicyandiamide formaldehyde	DCD	Low	Cationic	Fixative
Starch-based compound	St	High	+2.5	Fixative
Polydiallyldimethylammonium chloride	PDADMAC	0.5–1	+6...+8	Fixative
Polyacrylamide	PAM	4–16	-4...+3.4 An-, non- and cationic types.	Main polymer in retention aid systems (by "bridging flocculation")
Polyethylene oxide	PEO	7–10	Neutral	Fines retention (by "network flocculation")
Polyvinyl amine	PVAm	0.03–5	0... +15	Fixative and retention aid

\*Also depending on pH and ion strength.

In water, their ionisable groups are dissociated into polyvalent macroions poluions and a large number of small ions of opposite charge counterions the strong interaction between the polyions and counterions, which is a source of the characteristic properties of polyelectrolytes.



## 5 Coating

### 5.1. Extrusion coating

Extrusion coating is the most common coating method, which high molecular weight, high melting temperature synthetic resin is being extruded in film, and combined onto a rapidly moving substrate material. Various plastics, notably polyethylene, polypropylene are used for the economic application in this versatile coating technique. In speaking of substrate material, paper, paperboard, corrugated board, aluminum foils, cellulose and plastic films can be used as the moving web.

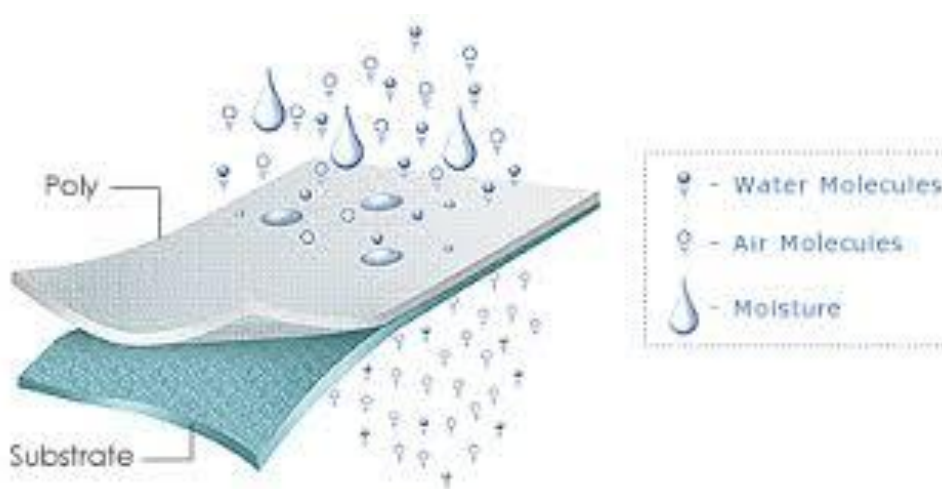


Figure 5.1 Functions of coated polymers (Clopayplastics, Extrusion laminate)

In the converting industry, the actual process of extrusion coating involves placement of polymers in pellet form into a hopper, conveying and converting them into a homogeneous melt temperatures at around 300 °C by a rotated screw, extruding resin from a slot die directly onto the moving web which may then passed through a nip consisting of a rubber covered pressure roller and a chrome plated cooling roll. The latter cools the molten film back into the solid state and also imparts the desired finish to the plastic surface. The web is normally run faster than the speed at which the resin is extruded from the die, creating a coating thickness which is in proportion to the speed ratio and the slot gap. (Wikipedia, Extrusion coating)

Not surprisingly, polymers used in extrusion coating must have some certain characteristics that allow it to meet the demanding properties and functions of the final products while offering the necessary economics simultaneously. These characteristics are the

direct result of selecting different polymers for different coating products. Here are some factors that affecting polymers selection for extrusion coating.

- Good draw down
- Low neck-in
- Without edge waving
- Good heat sealability
- Good melt film appearance
- Good chill roll release

(Lahti, J, 2013)

### **5.1.1 Polyolefins**

Two typical and common types of polyolefins are used in worldwide scope, polyethylene and polypropylene. Polyolefins are thermoplastic resin polymersized from ethylene and propylene. Usually polyolefins are in granular form when used in extrusion coating. The pellets are normally additive-free, but sometimes they may contain antioxidants, antistats or slip additives. Occasionally the pellets will contain colorants. (Kuusipalo, J, 2008, 139)

#### **5.1.1.1. PE**

PE, as known as polyethylene, is the workhorse for extrusion coating. PE is available in different paper grades depending on end use. There are some kinds of PE type, including low-density, high-density, and linear low-density. (Bentley, David J, Jr, Jul 2000)

In the middle of twentieth century, the first commercial extrusion coating process was introduced, using low-density polyethylene for the coating plastic because of its easy process property. Meanwhile, adequate moisture barrier and excellent sealing properties are also outstanding advantages of PE. Combined with these advantages is low cost, so this highly branched polyethylene is the highest-volume polymers used in extrusion coating also in the modern coating industry. By contrast, high-density polyethylene makes it more difficult to extrude due to the tendency for increased neck-in, but blends of high-density and low-density polyethylene are commonly used nowadays. (Kuusipalo, J, 2008, 143) A development that originally began with a combination of low-density polyethylene to paper has since progressed to a very diverse and broad range of applications and material combinations. (Bentley, David J, Jr, Jul 2000)

Delivered as a film in a hot, molten state, the various grades of PE will flow onto and adhere to many substrates. Bonds are especially good to paper and board, because the molten mass can mesh with the fibrous surface. Enhanced adhesion and improvement in other properties are possible with the use of a primer on a substrate or flame or corona treatment to oxidize the surface.

### 5.1.1.2. PP

Another resin which is very similar to PE but used in a more demanding application is PP, also called polypropylene. Polypropylene finds use in extrusion coating process primarily because of its temperature and grease resistance.

Polypropylene is a thermoplastic polymers used in a wide variety of applications including packaging, labeling, textiles (e.g., ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymers banknotes. Addition polymers are made from the monomer propylene; it is rugged and unusually resistant to many chemical solvents, bases and acids. (Wikipedia, Polypropylene)

No matter polyethylene or polypropylene, there are some disadvantages for extrusion coating. In order to improve the processing efficiency, polypropylene often contains a polyethylene modification. To be more exact, approximately 15-20% of polyethylene addition can reduce the melting point of polypropylene by 10-15°C. (Kuusipalo, J, 2008, 144) Table 3 lists characteristics and primary uses of LDPE and PP.



Figure 5.1.1.2 (1) All kinds of products made from PE (Sabk, Polyethylene products)



Figure 5.1.1.2 (2) Products from PP (Petroquim)

Table 3 Characteristics and primary uses of LDPE and PP (Lottechem, Products, PP, and PE)

Low-Density Polyethylene (LDPE)	<ul style="list-style-type: none"> <li>• Easy to process</li> <li>• Good strength and clarity</li> <li>• Usually converted to plastic products by blown film or cast film extrusion</li> </ul>	<ul style="list-style-type: none"> <li>• Food packaging films</li> <li>• Plastic bottles for packaging food and personal care items</li> <li>• Bags - dry cleaning bags, ice bags, pallet shrink wrap, heavy-duty bags for mulch and potting soil, boil-in-bag bags, bag-in-box bags</li> <li>• Coatings on flexible packaging products, paper board such as milk cartons</li> <li>• Foamed sheets</li> <li>• Vacuum cleaner hoses</li> <li>• Medical tubing Clear sheet protectors</li> <li>• Flexible binders</li> </ul>
Polypropylene	<ul style="list-style-type: none"> <li>• Versatile</li> <li>• Lightweight</li> <li>• High optical clarity</li> <li>• Low moisture vapor transmission</li> <li>• Ability to be drawn and oriented into fibers</li> </ul>	<ul style="list-style-type: none"> <li>• Fibers for carpets</li> <li>• Rugs and upholstery</li> <li>• Housewares</li> <li>• Automotive battery cases</li> <li>• Automotive fascia</li> <li>• Running boards and bumpers</li> <li>• Grid-type flooring for sports facilities</li> <li>• Fishing tackle boxes</li> <li>• Bottle caps and closures</li> </ul>

### 5.1.2 Copolymers

Copolymers is a polymers derived from two (or more) monomeric species, as opposed to a homopolymers where only one monomer is used.

Using other polymers except PE or PE backbone modified with other ingredients provides a convenient route for increasing adhesion and improving the processing and performance of the polymers. (Bentley, David J, Jr, Jul 2000)

For example, preparing a polymer from a blend of vinyl acetate and ethylene monomers instead of all ethylene monomer produces EVA copolymers. This material has a lower processing temperature than PE and so might be more suitable for extrusion applications involving heat sensitive substrates. In addition, the presence of the vinyl acetate component generally improves adhesion to a variety of substrate. (Bentley, David J, Jr, Jul 2000)

### **5.1.3 Barrier polymers**

Modern synthetic polymers have been used for over 50 years as barriers to mass transport of liquids and gases. The growth in polymers-based packaging materials at the expense of metal and glass containers has seen the importance of barrier polymers keep growing. Traditionally, the definition of a barrier polymer has been strongly attached to the oxygen permeability. In packaging, any of a variety of thermoplastic materials, like barrier polymers, used in the packaging of foods, beverages, and other materials requires some degree of protection against environmental forces, such as water, oxygen, vapor, etc. Impeding the penetration of oxygen and other gases (such as carbon dioxide) into the package, as well as other substances (such as odors) out of the package must be achieved by these barrier materials. Another consideration of using barrier polymers is the extent to which the packaging material will leech the flavor or odor of the material being packaged, as well as the extent to which the packaged material will absorb the flavor and odor of the packaging. Some commonly used barrier polymers are Ethylene vinyl alcohol copolymers (EVOH), Polyamide (PA), polyvinyl alcohol, polyacrylonitrile, ethylene vinyl alcohol, and cellophane, as well as various polyvinyl chloride and polyethylene formulations. (Printwiki)

Polymersic packaging offers the advantages of weight reduction, formability into useful and attractive shapes, reduced breakage, transparency, and cost savings. Recently, emphases on longer-term storage and convenience factors such as microwavability have become important. Research remains strong in industry and academia to offer improved polymers properties and fabrication methods and to address environmental issues including recyclability, source reduction, sustainability, and degradability.

### **5.1.3.1. EVOH**

Ethylene vinyl alcohol copolymers (EVOH) are an expensive material to produce due to it required indirectly polymersization from component monomers. Instead of making an entire package out of EVOH, papermakers keep costs down by co-extruding or laminating it as a thin layer between cardboard, foil, or other plastics. Therefore, it is still a good barrier polymer because of the excellent gas and aroma barrier ability.

As copolymers, EVOH is formed by ethylene and vinyl alcohol. Because the vinyl alcohol monomer mainly exists as its tautomer acetaldehyde, the copolymers are prepared by polymersization of ethylene and vinyl acetate to give the ethylene vinyl acetate (EVA) copolymers followed by hydrolysis. With lower ethylene content grades, EVOH has higher barrier properties; however, higher ethylene content grades leads to lower temperatures for extrusion.

This plastic resin is commonly used as an oxygen barrier in food packaging. It is better than other plastics to keep air out and flavors in. Moreover, EVOH is highly transparent, weather resistant, oil and solvent resistant, flexible, moldable, recyclable, and even printable.

### **5.1.3.2. PA**

Polyamide (PA) is also another good barrier polymers with the similar cost as EVOH. It can occur either naturally, such as proteins, or artificially. Artificially made polyamides can be made through step-growth polymersization or solid-phase synthesis, examples being nylons, aramids, and sodium polyaspartate. Synthetic polyamides are commonly used in textiles, automotives, carpet and sportswear due to their extreme durability and strength. An aromatic ring structure in PA makes the polymersic backbone with higher stiffness and higher tensile strength. With as high as 220°C melting point, PA is also suitable for heat resistance application.

### **5.1.4 PET (Peltovuori, M.)**

Polyethylene Terephthalate (PET) is a thermoplastic polymers resin of the polyester family used in synthetic fibers; it is extruded or molded into plastic bottles and contain-

ers for packaging foods and beverages, personal care products, and many other consumer products. PET resins used in extrusion coating are usually in pellets form, which can be easily heated and extruded or molded into almost any shape. PET is produced in esterification reaction by ethylene glycol with a dibasic acid. Esterification reaction results water as by-product. Also it is a reversible reaction which means that if there is water present with PET is melted the process is reversed and PET will degrade into monomers. Polyester is normally hard, tough, high temperature resistance polymers.

PET is a highly valued packaging material because it is strong yet lightweight, non-reactive, economical, and shatterproof. PET's safety for food, beverage, and personal care, pharmaceutical and medical applications is recognized by health authorities around the world. PET's properties also offer a wide selection of applications for PET coated papers and paperboards. High temperature resistance of polyesters has generated a big business for PET coated boards in readymade meal trays. PET coated paperboard tray has a good image of environmental product and it has replaced aluminum in many cases. PET after coating is very amorphous which makes it very tough. This property of PET coated board has been utilized in package where high strength is required. For example folded box small hand resistant medical packages have been created. PET has also some polarity naturally which makes it a very good printing surface.

### **5.1.5 Biopolymers**

Biopolymers are polymers which are naturally found in nature. Like polymers biopolymers are chain-like molecules made up of repeating chemical blocks and can be very long in length. Biopolymers are produced by living organisms; in other words, they are polymeric biomolecules. Since they are polymers, biopolymers contain monomeric units that are covalently bonded to form larger structures.

Biopolymers can be classified in three groups according to the nature of the repeating unit they are made of: (i) polysaccharides are from sugars, which are often linear bonded polymeric carbohydrate structures. (ii) proteins of amino acids, and (iii) nucleic acids of nucleotides. The following substances are example-biopolymers for each group: cellulose (found in plants), myoglobin (muscle tissues), and DNA (genetic material of a given organism). At Novozymes, we produce macromolecules belonging to the two first classes, namely polysaccharides and proteins. (Novozymes)

## 5.2. Lamination

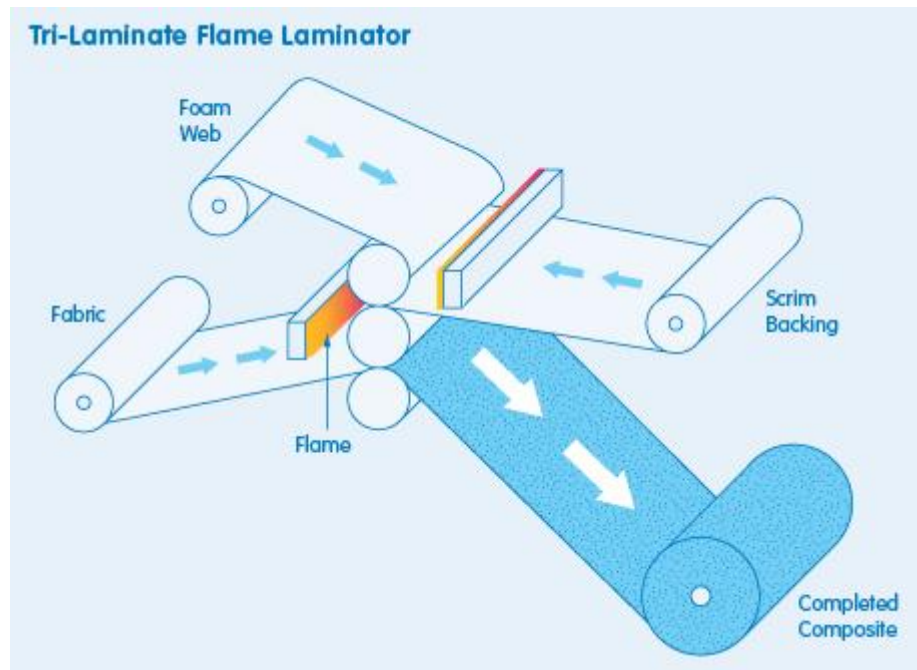


Figure 5.2 Lamination process (Fxi, Foam lamination)

Lamination is a similar process as extrusion coating except that the extruded hot molten resin acts as the bonding medium to a second web of material. In addition, it is the technique of manufacturing a material in multiple layers, so that the composite material achieves improved strength, stability, sound insulation, appearance or other properties from the use of differing materials. A laminate is usually permanently assembled by heat, pressure, welding, or adhesives. (Wikipedia, Lamination)

As well as extrusion coating, there are also a variety of polymers that are available in lamination: PE, PP, PET, and PA.

Polyethylene film is the most common material. As introduced in 5.1.1.1, there are many grades of PE including LDPE and HDPE. PE film has excellent water and water vapour resistance property, as well as good barrier against grease. PP film, similar to PE film, has excellent barrier properties against water, water vapour, greases and oil, but has better heat resistance than PE. PET films are usually semi-crystalline, which crystallinity level might over 40%. A lacquer layer is needed for semi-crystalline when it comes to heat application. PET also has excellent barrier properties against water, water vapour, greases and oil. In addition, it can also against aromas and solvents.



Nowadays, most of the ovenable trays are made by PET because of its good heat resistance. PA film, mostly from PA 6 or PA 66, has good mechanical properties, gases, aromas, grease and oil resistance, and excellent heat and cool resistance. However, unlike the other materials described above, PA has poor barrier against water and water vapour.

### **5.3. Dispersion coating**

Dispersion coating is a technique using latex on a paper or paperboard to form a solid, uniform and nonporous film with certain barrier properties. Dispersion coatings offer repulping advantages and the ability to apply them in line using a paper machine. Heat sealability of dispersion coatings is a critical characteristic due to blocking and a narrow sealing window. Most used polymers in dispersion coatings are styrene-butadiene, acrylates, vinyl acetate, and vinylidene chloride. They all have their own advantages for coating and end products. More exactly, styrene-butadiene materials provide good adhesion and moderate barrier properties. Acrylates give hydrophobicity and grease resistance. Polyvinylidene chloride has very good barrier properties. Incorporation of wax or fillers in dispersion gives extra water resistance and barrier. (Kuusipalo, Jurkka) Dispersion coatings polymers are applied as water dispersions by traditional pigment coating methods. 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 polymers in water.

#### **5.3.1 Styrene-butadiene**

During the period from 1930s to 1940s, the usage of Styrene-butadiene was increasing due to the limitation of natural rubber. (Kuusipalo, J, 2008, 77) Styrene-butadiene or styrene-butadiene rubber (SBR) describes families of synthetic polymers derived from styrene and butadiene. These materials have good abrasion resistance and good aging stability when protected by additives. About half of car tires are made from various types of SBR. The styrene/butadiene ratio influences the properties of the polymers: with high styrene content, the rubbers are harder and less rubbery. (Kuusipalo, J, 2008, 77) SBR is not to be confused with a thermoplastic elastomer made from the same monomers, styrene-butadiene block copolymers.

Apart from barrier properties, styrene-butadiene also has other important properties including sealing, blocking, creasing, and folding, etc. (Kuusipalo, J, 2008, 78)

### **5.3.2 Acrylates**

Acrylates are a type of vinyl polymers, which are of course made from acrylate monomers, with vinyl groups. Acrylate-based polymers are usually utilized as barrier dispersions, and have been suggested to be used by marine phytoplankton as a poisonous defense against predators such as protozoa. When attacked, DMSP lyase breaks down DMSP into DMS (g) and acrylate.

Comparing the different dispersion coatings, acrylate dispersion clearly gives better water absorption and water vapor barrier than styrene-butadiene dispersions. This is the substance forming the basis of many paints and inks and is a type of resin. It can remain as a liquid until a chemical reaction takes place, perhaps by oxidation, perhaps by introduced heat from a variety of sources. (Polyacrylates)

### **5.3.3 Synthetic polymers**

Besides styrene-butadiene and acrylate, there are many other barrier dispersion polymers, for instance, vinyl acetates, polyvinylidene chloride, polyvinyl alcohol, and polyolefin. The properties they have are quite suitable for barrier. (Kuusipalo, J, 2008, 77) Table 4 below releases some advantages and disadvantages of these materials as barrier polymers, except polyolefins, which have been introduced clearly before.

Table 4 Advantages and disadvantages of barrier polymers

Polymers	Advantages	Disadvantages
Vinyl acetates	Good bonding Low cost High solids	Poor moisture resistance
Polyvinylidene Chloride(PVDC)	Low pH Self stability	Poor moisture resistance Oxygen needed
Polyvinyl alcohol(PVOH)	Excellent oil resistance Oxygen barrier High hydroxyl content	Poor water barrier

## 6 Sizing

Papermaking fibers have a strong natural tendency to interact with water. This is significant to the development of strong interfiber hydrogen bonds during papermaking; in addition, it's also the reason that paper loses its strength when saturated with water. Even though this property is an advantage for some certain paper grades, tissue and toweling for instance, (Scott, W.E, 1996, 85) we still need a technique to prevent the other, most of, paper grades from water penetration and control wettability and absorbency.

Generally speaking, the processes that can impart resistance to water penetration in paper and paperboard are called sizing processes. Sizing agents are applied into the paper to impart certain desirable qualities. The main function of sizing agent is to increase the resistance to penetration of water or other liquids into the paper so that the paper is suitable for printing, writing and other purpose. (Scott, W.E, 1996, 89) It can be achieved either by using wet-end additives or by applying a suitable coating to the surface of the dried paper. Sometimes a combination of treatments is required. The wet-end sizing agents also decrease dusting, control spreads of inks, improve dewatering, retention of filler and fibers, improve paper quality, smoothness, dimension stability, abrasion, decrease porosity and improve paper machine runnability.

### 6.1. Internal sizing

Internal sizing agents are added to the papermaking furnish and get incorporated into the web when it is formed. There is no doubt that a good internal sizing agent must meet some criteria so that it can make a paper surface more hydrophobic by reducing its surface tension, or surface energy. Five criteria following are compulsory for good internal sizing agents according to the *principle of wet end strength* by Scott, W.E.

- ✧ High retention on fibers
- ✧ Uniformly distributed on fiber surfaces
- ✧ Can produce hydrophobic fiber surfaces
- ✧ Strongly adhere to fibers
- ✧ Chemically inert to the penetrants of interest

The most important internal sizing chemicals are alkyl ketene dimer (AKD), alkyl succinic anhydride (ASA) and rosin. The internal sizing agents should have some basic

characteristics, for example high hydrophobicity, good retention on fibers, uniform distribution throughout the fiber surfaces, and must strongly bond with fibers.

The internal sizing agents can also be classified into acidic type sizing chemical and basic or neutral type sizing chemical. Rosin and its derivatives are acidic type sizing agent. On the other hand AKD and ASA are basic or neutral type sizing agent.

### **6.1.1 Rosin sizing**

Rosin is the oldest internal size used in papermaking, and rosin internal sizing was introduced in the beginning of 19<sup>th</sup> century. For rosin sizing usage, retention of size in the web, attachment of size to fiber, distribution of size of fiber and anchoring of size on fiber are extremely important elements. In the case of internal sizing, there is another chemical needed as a key additive in three of these elements, alum. (Batten, G.L., Jr, 2005)

Alum was found that facilitating greatly the attachment of negatively-charged molecules (Smook 1982). Thus, alum acts as a mordant to bind together the different components of paper. Optimum performance of alum-rosin size during paper manufacture occurs at a pH of 4 to 5.5 (Arnson 1982). However, unfortunate consequence of such a low pH level is acidic paper, which promotes acid hydrolysis and scission of cellulose molecules.

Alum was also often used without rosin for the control of pH (i.e., to reduce pH), and to increase the retention of materials other than rosin (e.g., fines, fillers, and pigments) in the paper. Rosin is reportedly of little significance in the physical deterioration of paper, but the acidity associated with alum is a major cause of paper deterioration. In fact, the pH of paper is the most significant factor influencing strength loss over time (Casey 1981). (Thurn, J, December 3<sup>rd</sup>, 2003)

### **6.1.2 Sizing with ASA**

ASA, alkenyl succinic anhydride, is a sizing agent which can increase resistance to water penetration when paper is formed under neutral or alkaline systems. ASA is especially used where full cure is desired before the size press and where it is important to

maintain a high frictional coefficient in the paper product. In addition, ASA is beneficial for paper machine runnability and preserve paper's dimensional stability because it can limit penetration of size-press solution into the sheet. Holding the size-press starch out nearer to the paper surface also makes the surface-applied additives more effective for such purposes as promoting surface strength, reducing dusting, reducing picking of vessel segments during offset printing, and even improving the performance of hydrophobic polyelectrolytes added with the size-press starch solution. (Thurn, J, December 3<sup>rd</sup>, 2003)

### **6.1.3 Sizing with AKD**

AKD, alkyl ketene dimer, is other common sizing agents used in neutral/ alkaline systems. Structurally, it is unsaturated lactones and it is synthesized from fatty acids. Physically it is waxy like milky emulsion chemicals. The waxy solid tiny particles are dispersed into water and the emulsification. AKD is stabilized by the cationic starch or another cationic polyelectrolyte stabilizer. The function of AKD sizing agent depends on different technological parameters such as pH value of the fiber suspension, raw materials, method of drying, temperature, time etc. AKD is much less reactive than ASA; hence it is more flexible for papermakers during usages. It means that it can be add to the thick or thin stock. However the presence of PCC in the system can lessen the efficiency of the sizing agent. Alkaline sizing agent improves surface conditions of paper. AKD also reduces paper machine breakdown and water recycling difficulties compare to acidic sizing agent. (Pulp Paper Mill, AKD Sizing Agent, June 16, 2013)

## **6.2. Surface sizing**

In surface sizing, the paper web is formed and dried. Sizing agents is applied to the paper surface by a size press, coater or calendar box. There are both hydrophilic and hydrophobic ends contained in sizing agents. It forms a thin film on paper web, the hydrophilic tail of it joined with the fiber, whereas hydrophobic tail facing outwards. The thin film reduces paper dust and improves surface strength, printability and water resistance of the paper. There are different chemicals are used as surface sizing agent such as modified starches, Styrene Maleic Anhydride (SMA), Styrene Acrylic Emulsion (SAE), Styrene Acrylic Acid (SAA), Ethylene Acrylic Acid (EAA), gelatin and Polyurethane (PUR). These polymersic sizing agents can provide significant improvements in paper

properties, for instance, surface strength, coefficient of friction, smoothness, porosity and print quality. It is also normally applied in a paper mill though the sizes press at dry end section. (Pulp Paper Mill, Sizing Agent, June 16<sup>th</sup>, 2013.)

Starch, as described in the dry strength additives part, can be also employed in surface sizing. The principle uses of starch for surface sizing are improved printability, surface strength and internal strength. The sources of the strength improvements from starch are its strong hydrogen bonding ability with cellulose and its good film forming ability.

Starch can be modified or converted by enzymes, thermal treatment or chemical treatment so that forms with better handling properties through reduction of molecular weight and/or derivitization with functional groups can be produced. Another way to modify starch is done through reaction with ethylene oxide under an alkaline condition. Ethylated starch is nonionic and is retained better on fiber compared to oxidized starch. The result of this modification is forming strong, flexible and cleat surface films, and a low tendency toward retrogradation.

Apart from starch, there is a variety of polymersic sizing additives, which have been mentioned above, available to the papermaking for enhancing operational efficiency and paper properties for end use performance.

### **6.2.1 SMA**

Styrenen maleic anhydride copolymers are produced by the copymertization of styrene with maleic anhydride in various molar rotios. Using sodium, potassium or ammonium hydroxide can opened to improve its water solubility. The properties of SMA copolymers can be altered by changing the styrene to maleic anhydride ratio, the molecular weight, salt type and the presence or esterification type.

Broadly speaking, SMA dispersions provide excellent sizing response, improve inkjet printability, stabilize foam, reduce linting and milking on offset presses, improve toner adhesion, increase coefficient of friction and are compatible with most anionic and nonionic size press additives.

### **6.2.2 SAE**

Styrene acrylate emulsions (SAE) have become more popular polymeric sizing agents nowadays due to the advantages they offer for improving inkjet printability. They can be supplied in either anionic or cationic form depending on the ionicity of the emulsifier used.

SAE polymers offer excellent sizing response, because of their lack of hydrophilic monomers in composition. In addition, they are extremely versatile because of the wide range of compositions and available emulsifiers. They can also improve toner adhesion, coefficient of friction surface strength and inkjet printability as SMA.

### **6.2.3 PUD**

Polyurethanes dispersion are known for excellent sizing response, and reducing linting during offset printing, even though they are not good film formers. On the other hand, advanced PUD was found can handle hot or cold end-use extremes, while providing improved printing characteristics. It has an excellent barrier effect at low dosage levels, gaining in part from base sheet improvements made possible by silica nanoparticle technology. PUDs are compatible with most size press co-additives including salt. They are still available at a wider pH range than solution surface sizing agents. Compared to SAEs, they need less energy to fix size to fiber and do not contribute to foaming much.

The PUD products attaches directly to the fibers. Their hydrophobic groups rotate away from the sheet under heat condition, with a consequence of hydrophobic penetrating liquids, but hydrophilic to liquids being released from the sheet, which lead to a highly hydrophobic surface. (Osby, D, Jan 2001)

### **6.2.4 EAA**

Ethylene acrylic acid is an excellent film-forming polymer which can provide moderate sizing responses. EAA copolymers have only a moderate stabilizing effect on foam and produce a slight lowering in the coefficient of friction. Moreover, it promotes polyethylene adhesion in grade.



## 7 Lignin

Lignin is a complex aromatic polymer with unclear structures which has two different distributions for trees. (Stenius, P, 2000, 39) Firstly, in the case of wood, it provides the tree with unique strength and elastic properties, which means it acts as a strengthening agent in the composite wood structure. Secondly, it is also a component which assists in the resistance of the wood towards attack by micro-organisms and decay. Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components, especially in xylem tracheids, vessel elements and sclereid cells. There are now some strong evidences proving that formal covalent link between lignin and carbohydrates components of the wood structure. (Roberts, J.C, 1996, 26-27)

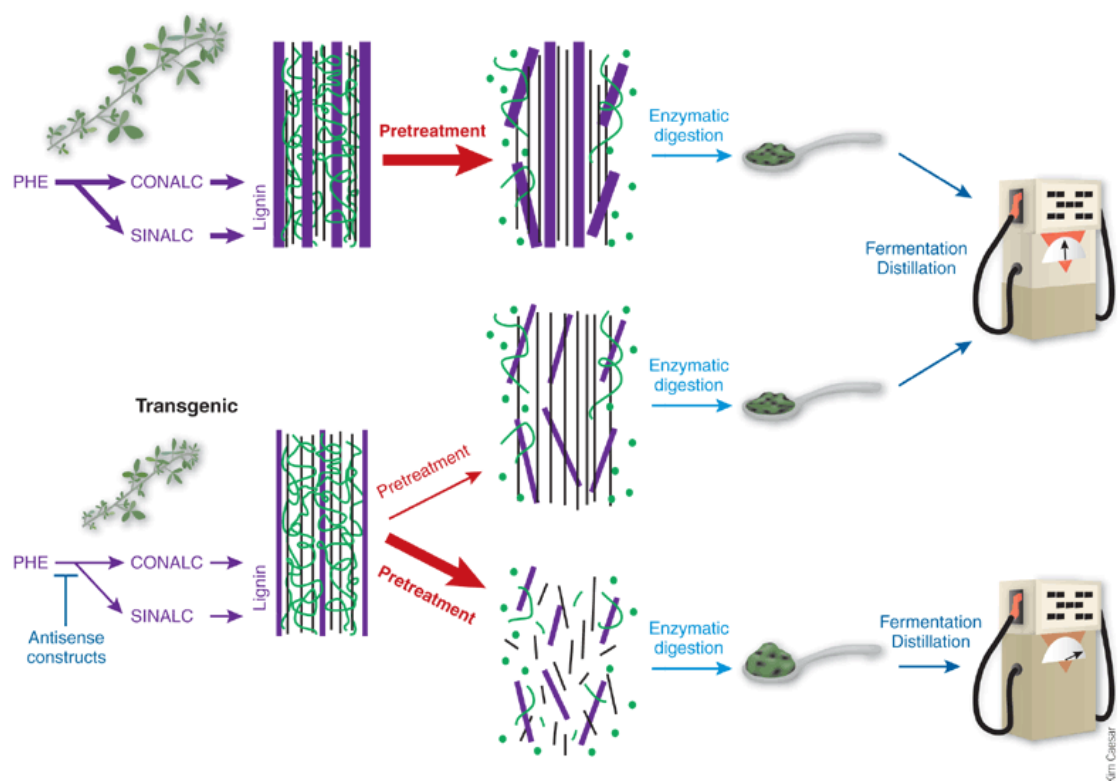


Figure 7 Loosing lignin's grip in biofuel production (Nature)

In papermaking process, removing lignin from the wood or fiber matrix is necessarily for producing high quality paper with good structure properties, because lignin discolors with age and involves lignin making the sheet become brittle. (Roberts, J.C, 1996, 26)

### 7.1. Suggestions from Yang and Rui

Actually, lignin is similar as gel, which sticks fibers together. Lignin also has a similar advantage as sizing chemicals. As lignin can resist water, we have been wondering whether it could be used in sizing part in papermaking in the future. That could happen by a physical treatment like heating, or chemical treatment to make the lignin as a film and applied on the surface of paper, or maybe the sizing effect could occur in the dryer section by heated applications.

By using lignin, papermaking could be more economical and a more environmental friendly process. Besides, using natural components from trees instead of processed chemicals is another idea that papermaking industry could be interested in.

## 8 Conclusion

From the beginning of papermaking history, chemicals were involved by papermakers in order to produce higher quality paper and adapt to different end-use. Among that wide range of chemicals, polymeric additives are the most used component and they dominate more than half of the papermaking chemicals. This article introduced several types of polymers used in papermaking process. Besides, polymers are utilized a lot in paper machine which improves efficiency and paper quality. In the whole papermaking process, PE, PP, PET, PA and starch are the most common polymers as materials in paper furnish and in paper machines. They have a lot of properties in common: especially the first three polymers have excellent barrier against water, vapour, greases and oil as well as good heat resistance which makes them useful materials in processes such as lamination. However, there are also some differences among these polymers.

Polyethylene, with countless features, becomes one of the most widely used plastics with production in the billions of pounds each year. Apart from the advantages mentioned above, it has more good properties including food contact acceptable, good processability, antioxidant, high ESCR (Stress Crack Resist.), good impact resistance, good toughness and good stiffness, etc. Polyethylene are used in extrusion coating and lamination, therefore, thousands of polyethylene domestic and industrial products like film, packaging bags, piping, containers, food packaging, laminates, wire and cable are made widespread over the world.

Polyurethane is used in paper machine. Usually, it is a kind of material for roll cover called polyurethane covers. Because of its mechanical strength and elasticity, as well as hydrolytic stability, polyurethane are quite popular and useful roll covers. Polyurethane covers have the advantage of less desire of interior cooling, enough wear resistance and in used in both press section and calender section.

Polypropylene is similar to polyethylene, in properties aspect. For example, PP is non-toxic material as well as PE, so both of them can be used for food packaging sources. However, its heat resistance is better than PE, so PP is usually applied in some products which require higher heat resistance. Besides, PP can also against aromas and solvents, which cannot be reached by PE.

PET gives the products an excellent heat resistance, and most of the ovenable trays are made by PET. With the nearly same properties as PP, PET also can be used in extrusion coating and lamination processes, with the similar application as PP. Polyethylene terephthalate is a thermoplastic polymers resin of the polyester family and is used in synthetic fibers. Its abrasion resistance and dimensional stability make it the dominate material for fabrics in paper machines.

PA has good mechanical properties, gases, aromas, grease and oil resistance, and excellent heat and cool resistance. PA, can be used as a barrier polymers which gives the product the ability to barrier liquids and gases during transportation. With the same properties, EVOH is another barrier polymers used for the same reason. Because of its excellent tensile strength and good spin ability, PA is also utilized in producing fabrics in paper machines in forming section, press section or dryer section.

Starch is the most common in our daily life, which can be also used for papermaking, especially in sizing and wet end chemistry to improve the paper quality.

Rubber is used in produce roll cover nowadays, especially synthetic rubber. Rubber has remarkable elastic ability, which made it work at a higher-pressure condition.

Other polymers such as PAE (polyamide-epichlorohydrin) and PAAE (polyaminoamide-epichlorohydrin) are used as wet strength additives while another polymer called polyacrylamide is used as dry strength additive. All of these polymers can enhance the strength of paper either in wet or dry condition.

In papermaking processes, there is sizing involved, where rosin is used most in internal sizing chemicals. Rosins used in papermaking are natural products. By modified rosin, the amount of chemicals can be reduced and therefore get the process simplified and less expensive.

Besides starch, there are other four different polymers used in surface sizing: SMA, SAE, PUD, and EAA. All of them can improve the moderate stabilizing effect on foam and produce a slight lowering of friction.

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