CHAPTER FIVE

5. FABRICATION OF POLYMERS

Fabrication of polymers Depending on the type of resin, whether thermoplastic or thermosets, many methods of fabrication of polymers are used. In this polymers are heated and molded into different required shape. The methods of fabrications are given below.

METHODS OF POLYMER FABRICATION:

They are six methods of polymer fabrication, Thermoforming, Extrusion of polymers, Injection molding of polymers, Blow molding, Compression molding of polymers and Transfer molding of polymers

THERMOFORMING: Thermoforming is a process of shaping flat thermoplastic sheets which includes two stages: Softening the sheet by heating. Forming it in the mold cavity. Elastomers and thermosets can be formed by the thermoforming methods because of their cross-linked structure.

Thermoplastics formed by thermoforming method: Thermoplastics formed by thermoforming method Polypropylene(PP) Polystyrene(PS) Polyvinyl Chloride(PVC) Low Density Polyethylene(LDPE) High Density Polyethylene(HDPE) Cellulose Acetate Polymethylmethacrylate(PMMA) Acrylonitrile-Butadiene-Styrene(ABS).

Uses of thermoforming: Thermoforming is widely used in the food packaging industry for manufacturing ice cream and margarine tubes, meat trays microwave containers, snack tubes sandwich packs etc. It is also used for manufacturing some pharmaceutical and electronic articles, small tools, fasteners, toys, boat hulls, blister and skin packs.

There are three thermoforming methods: Vacuum thermoforming, Pressure thermoforming and Mechanical thermoforming.

Vacuum thermoforming: The process involves shaping a preheated thermoplastic sheet by means of vacuum produced in the mold cavity space. The atmospheric pressure forces the soft sheet to deform in conformity with the cavity shape. When the plastic comes into the contact with the mold surface it cools down and hardens.

Pressure thermoforming: This process involves shaping a preheated thermoplastic sheet by means of air pressure. The air pressure forces the soft sheet to deform in conformity with the cavity shape. When the plastic comes into the contact with the mold surface it cools down and hardens.

Mechanical thermoforming: The process involves shaping a preheated thermoplastic sheet by means of a direct mechanical force. A core plug forces the soft sheet to fill the space between the plug and the negative mold. The process provides precise dimensional tolerance and surface detailing.

Extrusion of polymers: Extrusion is a process of manufacturing long products of constant cross-section forcing soften polymer through a die with an opening. Polymer material in form of pellets is fed into an extruder through a hopper. The material is then conveyed forward by a feeding screw and forced through a die.

Uses of extrusion: Extrusion is used mainly for thermoplastics but elastomers and thermosets are also may be extruded. In this case cross-linking forms during heating and melting of the material in the extruder. The thermoplastic extruded products may be further formed by the thermoforming methods.

Injection molding of polymers: Injection molding is a process in which molten polymer is forced under high pressure into a mold cavity through an opening. Polymer material in form of pellets is fed into an injection molding machine through a hopper. The material is then conveyed forward by a feeding screw and forced into a split mold, filling its cavity through a feeding system with spruce gate runners. Thermoplastics used in injection molding: Polypropylene(PP) Polycarbonate(PC) Acrylonitrile-Butadiene-Styrene(abs) Nylon 6(N6).

Uses of injection molding of polymers: Injection molding is used for thermoplastics, but elastomers and thermosets are also may be extruded. In this case cross-linking occurs during heating and melting of the material of the heated barrel. Injection molding is highly productive method providing high accuracy and control of shape of the manufactured parts. It is profitable in mass production of large number of identical parts.

Blow molding: Blow molding is a process in which a heated hollow thermoplastic tube is inflated into a closed mold conforming the shape of the mold cavity.

Uses of blow molding: Disposable containers of various sizes and shapes, drums, recyclable bottles, automotive fuel tanks, storage tank..etc are produced by blow molding method. Materials used for blow molding: Low Density Polyethylene(LDPE) High Density Polyethylene(HDPE) Polyvinyl Chloride(PVC) Polyethylene Terephtalate(PET).

Three principal techniques of blow molding method for parisons preparation: Extrusion Blow molding Injection Blow molding Stretch Blow molding. Extrusion Blow Molding involves manufacture of parison by conventional extrusion method using a die similar to that used for extrusion pipes. The production cycle consists of the following steps: The parison is extruded vertically in downward direction between two mold halves. When the parison reaches the required length the two mold halves close resulting in pinching the top of parison end and sealing the blow pin in the bottom of the parison end. Injection blow molding method a parison is produced by injecting a polymer into a hot injection mold around a blow tube or core rod. Then the blow tube together with the parison is removed from the injection mold and transferred to a blow mold and Stretch blow molding is similar to injection blow molding. Stretch blow molding involves injection molding of parison, which is then stretched in the downward direction by means of the blow tube. The extended parison is then inflated in a blow mold.

Compression molding of polymers: Compression molding is a process in which a molding polymer is squeezed into a preheated mold taking a shape of the cavity. This method is mostly used for molding thermosetting resins, but some thermoplastics parts may also be produced by compression molding. This method uses split mold mounted in a hydraulic press. Steps involved A pre-weighed amount of a polymer mixed with additives and fillers is placed into the lower half of the mold. The charge may be in the form of power, pellets, putty like masses or pre-formed blanks.The charge is usually preheated to placed into the mold. Preheated polymer becomes softer.

Materials processed by compression molding: Epoxies(EP) Urea Formaldehyde(UF) Melamine Formaldehyde(MF) Phenolics(PF) and it is used for manufacturing electrical wall receptacles, brush and mirror handles, meter cases, trays, circuit breakers, cookware knobs, clothes dryer blower fan blade, electronic and cooking utensils, milling machine adjustment wheel..etc

Transfer molding of polymers: Transfer molding is a process in which a pre-weighted amount of a polymer is preheated in a separate chamber. Then it is forced into a preheated mold through a sprue, taking the shape of the mold cavity. It is used for molding thermosetting resins, but some thermoplastic parts may also be produced.

Transfer molding process involves the following steps- A pre-weighed amount of a polymer mixed with additives and fillers is placed into the transfer pot. The plunger, mounted on the top plate, moves downwards, pressing on the polymer charge and forcing it to fill the mold cavity through the sprue. The mold is opened and the part is removed from it by means of the ejector pin.

Materials processed by compression molding: Epoxies(EP) Unsaturated Polyesters(UP) Phenolics(PF) Vinyl ester and transfer molding is used for molding parts encapsulating metal inserts, wear plates, pins, studs, electronic components with molded terminals. It is also used for manufacturing radio and television cabinets and car body shells.

5.1. Preparation of Polymer films

Thin and ultrathin polymer films are of interest both from an application oriented perspective, and for the fundamental understanding of poly-mer morphology and properties in confinement. Their structure and properties can differ substan-tially from bulk materials, and also the prepara-tion of submicron films requires different techni-ques than the melt processing most often applied to semicrystalline bulk polymers.

For the preparation of semicrystalline (ultra)-thin films, the polymer is commonly applied to a substrate in a nonordered state, usually as a dilute solution in an organic solvent and often at elevated temperatures. Formation of crystalline order occurs only upon evaporation of the solvent and cooling, which therefore pronouncedly influ-ences the crystallization process. As a completely different approach, we have recently communi-cated the preparation of polyethylene (PE) ultra-thin films from aqueous dispersions of prefabri-cated nanocrystals. Film formation occurs at room temperature, and water rather than organic solvents is evaporated.

5.2. Production of fibres

Most synthetic and cellulosic manufactured fibers are created by "extrusion" — forcing a thick, viscous liquid (about the consistency of cold honey) through the tiny holes of a device called a spinneret to form continuous filaments of semi-solid polymer.

In their initial state, the fiber-forming polymers are solids and therefore must be first converted into a fluid state for extrusion. This is usually achieved by melting, if the polymers are thermoplastic synthetics (i.e., they soften and melt when heated), or by dissolving them in a suitable solvent if they are non-thermoplastic cellulosics. If they cannot be dissolved or melted directly, they must be chemically treated to form soluble or thermoplastic derivatives. Recent technologies have been developed for some specialty fibers made of polymers that do not melt, dissolve, or form appropriate derivatives. For these materials, the small fluid molecules are mixed and reacted to form the otherwise intractable polymers during the extrusion process (if you are interested in the latest information on extrusion.

The Spinning

The spinnerets used in the production of most manufactured fibers are similar, in principle, to a bathroom shower head. A spinneret may have from one to several hundred holes. The tiny openings are very sensitive to impurities and corrosion. The liquid feeding them must be carefully filtered (not an easy task with very viscous materials) and, in some cases, the spinneret must be made from very expensive, corrosion-resistant metals. Maintenance is also critical, and spinnerets must be removed and cleaned on a regular basis to prevent clogging.

As the filaments emerge from the holes in the spinneret, the liquid polymer is converted first to a rubbery state and then solidified. This process of extrusion and solidification of endless filaments is called spinning, not to be confused with the textile operation of the same name, where short pieces of staple fiber are twisted into yarn. There are four methods of spinning filaments of manufactured fibers: wet, dry, melt, and gel spinning.

Wet spinning

Wet spinning is the oldest process. It is used for fiber-forming substances that have been dissolved in a solvent. The spinnerets are submerged in a chemical bath and as the filaments emerge they precipitate from solution and solidify. Because the solution is extruded directly into the

precipitating liquid, this process for making fibers is called wet spinning. Acrylic, rayon, aramid, modacrylic and spandex can be produced by this process.

Dry Spinning

Dry spinning is also used for fiber-forming substances in solution. However, instead of precipitating the polymer by dilution or chemical reaction, solidification is achieved by evaporating the solvent in a stream of air or inert gas. The filaments do not come in contact with a precipitating liquid, eliminating the need for drying and easing solvent recovery. This process may be used for the production of acetate, triacetate, acrylic, modacrylic, PBI, spandex, and vinyon.

Melt Spinning

In melt spinning, the fiber-forming substance is melted for extrusion through the spinneret and then directly solidified by cooling. Nylon, olefin, polyester, saran and sulfar are produced in this manner. Melt spun fibers can be extruded from the spinneret in different cross-sectional shapes (round, trilobal, pentagonal, octagonal, and others). Trilobal-shaped fibers reflect more light and give an attractive sparkle to textiles. Pentagonal-shaped and hollow fibers, when used in carpet, show less soil and dirt. Octagonal-shaped fibers offer glitter-free effects. Hollow fibers trap air, creating insulation and provide loft characteristics equal to, or better than, down.

Gel Spinning

Gel spinning is a special process used to obtain high strength or other special fiber properties. The polymer is not in a true liquid state during extrusion. Not completely separated, as they would be in a true solution, the polymer chains are bound together at various points in liquid crystal form. This produces strong inter-chain forces in the resulting filaments that can significantly increase the tensile strength of the fibers. In addition, the liquid crystals are aligned along the fiber axis by the shear forces during extrusion. The filaments emerge with an unusually high degree of orientation relative to each other, further enhancing strength. The process can also

be described as dry-wet spinning, since the filaments first pass through air and then are cooled further in a liquid bath. Some high-strength polyethylene and aramid fibers are produced by gel spinning.

Stretching and Orientation

While extruded fibers are solidifying, or in some cases even after they have hardened, the filaments may be drawn to impart strength. Drawing pulls the molecular chains together and orients them along the fiber axis, creating a considerably stronger yarn.

5.3. Foaming

Polymer foams were first made in the 1930's and -40's, with foamed polystyrene being the first polymer foam in 1931. Polyurethane was invented by Dr. Otto Bayer at the start of the Second World War It was first used as a replacement for rubber and also used as a coating to protect other common materials at the time such as metals and wood.

The two decades following made polymer foams more widely used as new technologies developed, introducing methods such as injection molding, twin screw for foam and several extrusion techniques.

It is hard to go a day without coming across some sort of polymer foam. Polymer foams are found virtually everywhere in our modern world and are used in a wide variety of applications such as disposable packaging of fast-food, the cushioning of your furniture and insulation material.

Polymer foams are made up of a solid and gas phase mixed together to form a foam. This generally happens by combining the two phases too fast for the system to respond in a smooth fashion. The resulting foam has a polymer matrix with either air bubbles or air tunnels incorporated in it, which is known as either closed-cell or open-cell structure. Closed-cell foams are generally more rigid, while open-cell foams are usually flexible.

The gas that is used in the foam is termed a blowing agent, and can be either chemical or physical. Chemical blowing agents are chemicals that take part in a reaction or decompose, giving off chemicals in the process. Physical blowing agents are gases that do not react chemically in the foaming process and are therefore inert to the polymer forming the matrix.

Polymer foams are produced in a number of different ways. Examples are through slab-stock by pouring, extrusion and different forms of molding.

Polymer foams can be divided into either thermoplastics or thermosets, which are further divided into rigid or flexible foams. The thermoplastics can usually be broken down and recycled, while thermosets are harder to recycle because they are usually heavily crosslinked.

Issues facing the polymer foam industry are that of waste disposal, recyclability, flammability and the effect of blowing agents on the environment. The restriction on the use of CFC's (chloro-fluoro-carbons) has become very important in making polymer foams more environmentally friendly. Advances in biodegradable foam materials are also helping to improve the recyclability and waste disposal.

The reason polymer foams are so widely used is that they have a lot of advantageous properties. The density is low, and so the weight reduction compared to other options is significant. Some polymer foams have very low heat transfer, making them optimal insulators. Many are flexible and soft, meaning they provide more comfort when used for furniture and bedding.
In recent years, the application of foamed plastics have significantly expanded and diversified. Along with the growing market, there has been a growing interest in the development of environmentally-safe blowing agents. This note gives an overview of the most common production processes and specifically describes applications for the eco-friendly blowing agent's carbon dioxide (CO_2) and nitrogen (N_2) as well as appropriate supply systems, including pressurization and metering systems.

The advantages of foamed products are undeniable and have led to their widespread and still growing popularity. Their essential characteristics are, apart from a low consumption of raw materials, positive product qualities such as low density, outstanding heat and sound insulation,

mechanical damping, low water vapor permeability and reduced absorption of humidity. Different processes produce open-cellular, closed cellular, or integral foams, have numerous uses and applications. Some of the most important applications for foamed products can be found, in the fields of packaging, insulation, sound insulation and upholstery material.

The cellular structure of synthetic foams is created by blowing agents. Moreover, additives are often necessary, especially nucleation agents and stabilizers. From an economical point of view, extrusion foaming, injection-molded foaming, polyurethane foaming and EPS foaming are especially significant production processes.

5.3.1. Chemical foaming – physical foaming

A blowing agent is necessary to induce the foaming process. Depending on process and density, either chemical or physical blowing agents are applied.

Chemical blowing agents are mixed into the plastic pellets in the form of powder or pellets and dissolve at higher temperatures. Above a certain temperature specific for blowing agent dissolution, a gaseous reaction product – usually nitrogen or CO_2 – is separated and acts as a blowing agent. Due to the generation of undesired by-products and higher costs, chemical blowing agents are primarily applied for high-density materials.

Physical blowing agents are metered into the plastic melt during foam extrusion or injection molded foaming or supplied to one of the initial products during polyurethane foaming. Physical blowing agents are used to create the often-requested low densities. Other advantages include a more homogenous foam structure, better process stability and significantly lower blowing agent costs.

Types of polymer foam

Polyurethane-Polyurethanes are any type of polymer containing a urethane linkage. The urethane linkage is -NH-CO-O-. The way to form polyurethanes is done by reacting isocyanates with compounds that have active hydrogen, such as diols, that contain hydroxyl-groups, in the

presence of a catalyst. Since there are many compounds containing active hydrogens and many different diisocyanates, the number of polyurethanes that can be synthesized is also large. The specific properties of the polyurethane can be tailored to a specific need by combining the appropriate compounds.

Polyurethanes can exist as both rigid and flexible foams, and as a coating or adhesive material. Since polyurethanes come in so many forms and can have a wide variety of properties, it is also used in many different applications. Rigid polyurethanes are used as insulation and flotation, while flexible ones are used for cushioning and packaging. In addition, they are used as adhesives in construction and transportation. Rhinoskin is an example of polyurethane used for coating and protection. It is sprayed onto a surface and then sets to protect the underlying layer.

Polyurethanes are mostly thermosets, which means they are hard to melt and reprocess and can therefore have the disadvantage of being non-recyclable.

Biodegradable foams-Biodegradable polymer foams are investigated not only because of the increasing waste and environmental problems for traditional polymer foams, but also because of the increasing price of petroleum products that are used in manufacturing the polymer foams.

Biodegradable foams are water soluble and sensitive to humidity, while traditional petroleum-based foams are more inert to water. Biodegradable foams are also limited in making foams that have microcellular structure, which means they will be hard to make into thin sheets. However, they are important in reducing the amount of CO_2 emission. There is also a wide range of different candidates of biomaterials that can be used for biodegradable foams, including ethylene vinyl alcohol, polyvinyl alcohol, polycaprolactone, polylactic acid and starch.

Starch-Starch foam was made already in 1989 as biodegradablepackaging, and is an alternative material to the traditional polystyrene foams. Starch is a polysaccharide made up of glucose units linked by glycoside linkages, and its length is generally between 500-2000 repeat units. Starch is made up of amylose and amylopectin Amylose is more linear and gives the foam flexibility and keeps the density low, while amylopectin is highly branced and makes the product more foamable. Starch can be extracted from for example corn or potatoes.

Starch foams are produced by extrusion where the starch is melted and mixed with a blowing agent. The blowing agent for starch is often water or methanol, which is turned into steam when the system is heated and forms air bubbles within the starch matrix. The extrusion process is a continuous, low-cost method that is easy to use. It is still hard to make the foam smooth and have a high number of closed cells. The use of thermoplastic polymer additives can help even out the surfaces, but can also decrease the degradability of the foam by incorporating slowly degrading or non-degradable polymers.

Synthesis

Polyurethane-As mentioned earlier polyurethanes are made by the addition reaction of polyisocyanates and polyols. When there are two functional groups it's termed a diisocyanate and diol as seen below.
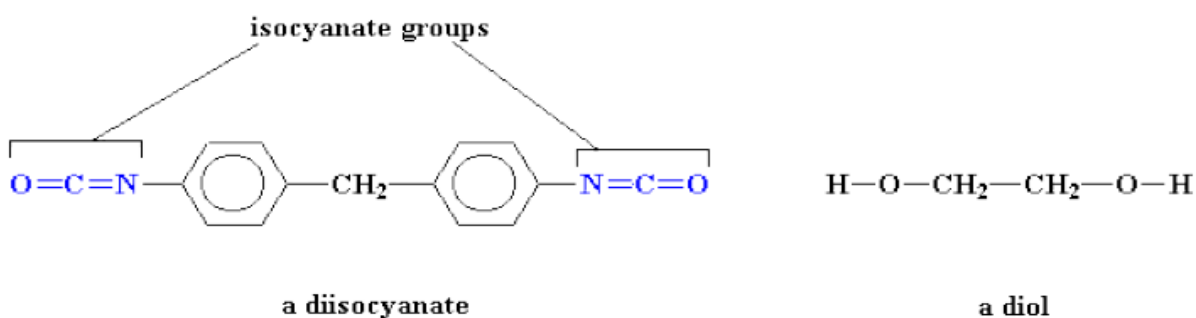

Figure 1: Reactants used for polyurethane

Along with a nucleophile like diazobicyclo[2.2.2]octane (DABCO), the mixing of these two monomers will form a dimer, which again will continue to react with other monomers, dimers and oligomers and form long polyurethane chains.

The positive charge due to oxygen's electronegativityon the hydrogen at the end of the diol attracts the nucleophile, which wants to bind to a nucleus (nucleophile=nucleus loving). The oxygen then becomes more negative and reacts with a carbon on an isocyanate group. This leaves the nitrogen on the isocyanate group to be negative, which is highly unfavorable. The nitrogen will give off its negative charge to the hydrogen atom on the alcohol group, finally forming a urethane bond between the two monomer units, resulting in a urethane dimer. The dimer will have one end group that is isocyanate, while the other is an alcohol group. Each end can now react with other monomers and oligomers until polyurethane is formed. This is called a

step-growth reaction. Step-growth reactions are characterized by longer chains being able to react and add to a growing chain just like monomers can, unlike chain-growth polymerization where only monomers can add to the growing chain. It is also an addition reaction since no small compounds are given off during the reaction.
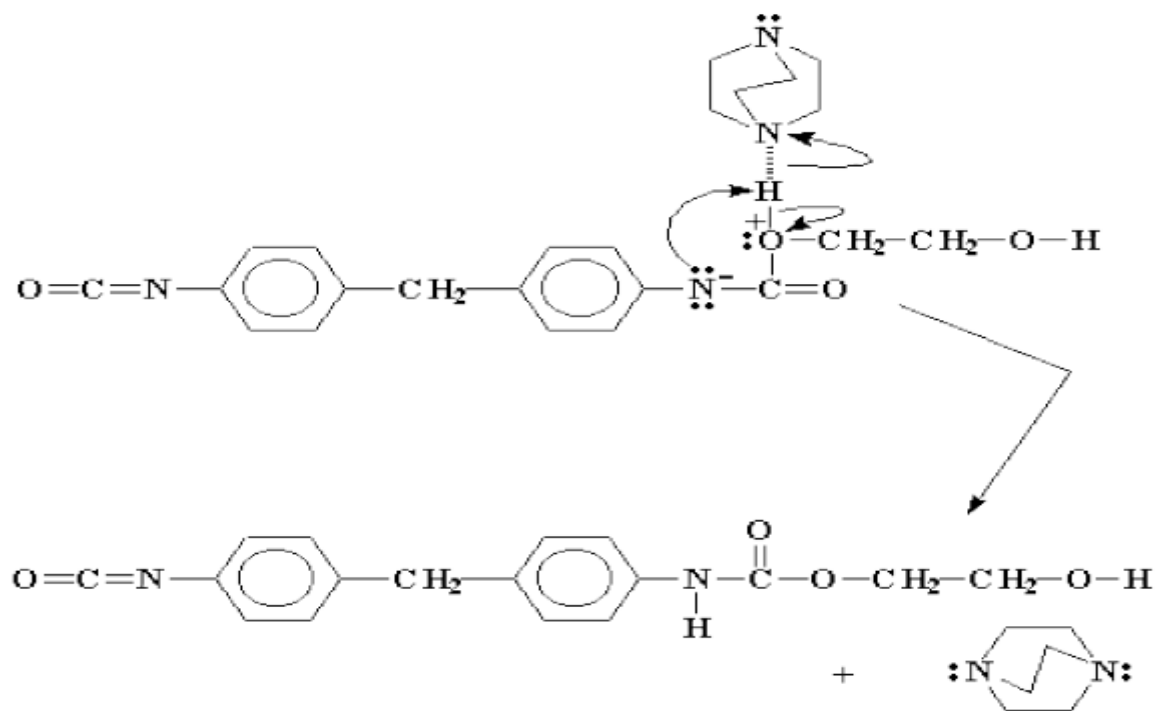

Figure 2: the DABCO attaches to the hydrogen of the alcohol group. The negative oxygen then reacts with the carbon on the isocyanate group, leading to a negative nitrogen. The nitrogen gives off its charge to the hydrogen and the two monomers become bound together to a dimer by a urethane linkage.

If instead of a diol, a macrodiol is used in the reaction, the polyurethane gets alternating soft and rigid segments, where the macrodiol makes up the soft segments in between the rigid blocks from the diisocyanate monomers.

The difference between making polyurethane and polyurethane foam is that a gas has to be incorporated in the final product. To achieve this the isocyanate group is reacted with water forming an amine and CO2 gas. Because the isocyanate group turns into an amine, the reaction with other diisocyanates will result in some urea-linkages in the polyurethane foam, but this doesn't affect the properties of the polymer foam much, and is necessary to get the gas to be produced and expand the polymer into a foam.
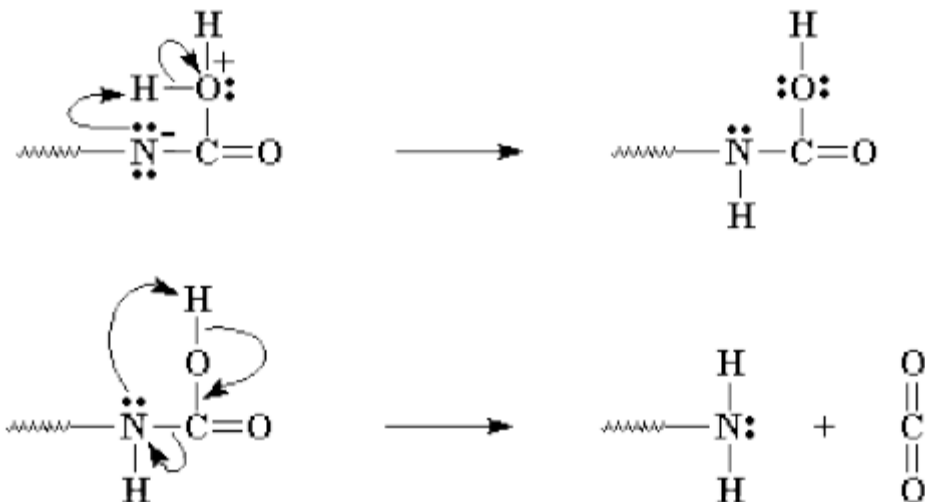
Figure 3. The reaction of water with isocyanate group forms and amine group and expels carbon dioxide gas.

Blowing agents-As seen in the last paragraph, water was used as a blowing agent to produce CO2. Because the water needed to be part of a reaction, it's a chemical blowing agent. Physical blowing agents don't take part in a chemical reaction, but are volatile liquids that evaporate and make the foam expand. First generation physical blowing agents are mostly outruled because of their negative environmental impact on the ozone layer. This is especially the case for chlorofluorocarbons.

CFC's and HCFC's

CFC's are ideal blowing agents besides the tremendous environmental concerns associated with them. They are not flammable, have fitting boiling points and are non-toxic. They also have good thermal insulation properties.This is why it has been hard to find a replacement for these blowing agent that has equivalent properties.

Hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC) are blowing agents with a lot smaller impact on the ozone layer and with similar properties. HCFC's are being phased out since they still have ozone depletion problems. Although HFC's have no impact on the ozone depletion, it has high global warming potential. However, they have a lower shelf life and can sometimes be flammable, which creates concern because this decreases the safety of polyurethane foams.

CO$_2$-Liquid CO_2 is used as a blowing agent because it does not have the same environmental issues as CFC's and HCFC's. It has a low global warming potential and is inexpensive. It is also easier to obtain low density foams using CO_2.

Manufacturing methods

Slabstock-Slabstock processing has its name from the way that the foam is cut into large slabs after being processed, instead of formed into specific geometric shapes. The materials are spread onto a conveyor through a mixing head, and the foam forms on the conveyor constrained by walls so the foam forms a large slab of material. The foam is then cut into suitable size slabs.

Molding-Molding processes can be divided into either cold-molded or hot-molded processes, differing by their molding temperatures. The process injects foam into separate formed molds and shapes the foams into individual pieces with the same shapes. This process is more complicated than slabstock and more costly.

Properties of polymer foams

Structure-As mentioned earlier foams can be divided into open-cell and closed-cell structures. However, the term cell in this context is somewhat different than what it is usually considered as. In all foams the cell or pore structure is not a specific uniform unit, there is instead a wide range of different sized cells and pores and a certain amount that are closed-cell and open-cell although one will be the dominating structure.

Since the size and shape of the cells or pores are very disperse the best approach to describe foam structures is through statistical models, since there is never a regular packing of spherical cells in a foam. The models used range from cells being modeled as spheres, polygons and dodecahedrons.In addition the cells are usually elongated in a certain direction as the polymer is foamed, making it harder to model the foam as any ideal model. It is not only the polymer itself that contributes to the properties of the foam, but the gas-filled space between them. In comparison to other non-polymeric foams where the voids or gas-filled spaces do not interact with the surrounding matrix, in polymer foams the intercellular gas interacts with the matrix and affects its properties and behaviors and can change them over time.

5.4. Reinforced polymer

Fibre-reinforced polymer (FRP), also *Fibre-reinforced plastic*, is a composite material made of a polymer matrix reinforced with fibres. The fibres are usually glass, carbon, or aramid, although other fibres such as paper or wood or asbestos have been sometimes used. The polymer is usually an epoxy, vinylester or polyester thermosetting plastic, and phenol formaldehyde resins are still in use. FRPs are commonly used in the aerospace, automotive, marine, and construction industries.

Composite materials are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct within the finished structure. Most composites have strong, stiff fibres in a matrix which is weaker and less stiff. The objective is usually to make a component which is strong and stiff, often with a low density. Commercial material commonly has glass or carbon fibres in matrices based on thermosetting polymers, such as epoxy or polyester resins. Sometimes, thermoplastic polymers may be preferred, since they are moldable after initial production. There are further classes of composite in which the matrix is a metal or a ceramic. For the most part, these are still in a developmental stage, with problems of high manufacturing costs yet to be overcome. Furthermore, in these composites the reasons for adding the fibres (or, in some cases, particles) are often rather complex; for example, improvements may be sought in creep, wear, fracture toughness, thermal stability, etc.

Fibre reinforced polymer (FRP) are composites used in almost every type of advanced engineering structure, with their usage ranging from aircraft, helicopters and spacecraft through to boats, ships and offshore platforms and to automobiles, sports goods, chemical processing equipment and civil infrastructure such as bridges and buildings. The usage of FRP composites continues to grow at an impressive rate as these materials are used more in their existing markets and become established in relatively new markets such as biomedical devices and civil structures. A key factor driving the increased applications of composites over the recent years is the development of new advanced forms of FRP materials. This includes developments in high performance resin systems and new styles of reinforcement, such as carbon nanotubes and

nanoparticles. This book provides an up-to-date account of the fabrication, mechanical properties, delamination resistance, impact tolerance and applications of 3D FRP composites.

The fibre reinforced polymer composites (FRPs) are increasingly being considered as an enhancement to and/or substitute for infrastructure components or systems that are constructed of traditional civil engineering materials, namely concrete and steel. FRP composites are lightweight, no-corrosive, exhibit high specific strength and specific stiffness, are easily constructed, and can be tailored to satisfy performance requirements. Due to these advantageous characteristics, FRP composites have been included in new construction and rehabilitation of structures through its use as reinforcement in concrete, bridge decks, modular structures, formwork, and external reinforcement for strengthening and seismic upgrade.

The applicability of Fiber Reinforced Polymer (FRP) reinforcements to concrete structures as a substitute for steel bars or prestressing tendons has been actively studied in numerous research laboratories and professional organizations around the world. FRP reinforcements offer a number of advantages such as corrosion resistance, non-magnetic properties, high tensile strength, lightweight and ease of handling. However, they generally have a linear elastic response in tension up to failure (described as a brittle failure) and a relatively poor transverse or shear resistance. They also have poor resistance to fire and when exposed to high temperatures. They loose significant strength upon bending, and they are sensitive to stress-rupture effects. Moreover, their cost, whether considered per unit weight or on the basis of force carrying capacity, is high in comparison to conventional steel reinforcing bars or prestressing tendons. From a structural engineering viewpoint, the most serious problems with FRP reinforcements are the lack of plastic behavior and the very low shear strength in the transverse direction. Such characteristics may lead to premature tendon rupture, particularly when combined effects are present, such as at shear-cracking planes in reinforced concrete beams where dowel action exists. The dowel action reduces residual tensile and shear resistance in the tendon. Solutions and limitations of use have been offered and continuous improvements are expected in the future. The unit cost of FRP reinforcements is expected to decrease significantly with increased market share and demand. However, even today, there are applications where FRP reinforcements are cost effective and justifiable. Such cases include the use of bonded FRP sheets or plates in repair

and strengthening of concrete structures, and the use of FRP meshes or textiles or fabrics in thin cement products. The cost of repair and rehabilitation of a structure is always, in relative terms, substantially higher than the cost of the initial structure. Repair generally requires a relatively small volume of repair materials but a relatively high commitment in labor. Moreover the cost of labor in developed countries is so high that the cost of material becomes secondary. Thus the highest the performance and durability of the repair material is, the more cost-effective is the repair. This implies that material cost is not really an issue in repair and that the fact that FRP repair materials are costly is not a constraining drawback.

When considering only energy and material resources it appears, on the surface, the argument for FRP composites in a sustainable built environment is questionable. However, such a conclusion needs to be evaluated in terms of potential advantages present in use of FRP composites related to considerations such as:

- Higher strength
- Lighter weight
- Higher performance
- Longer lasting
- Rehabilitating existing structures and extending their life
- Seismic upgrades
- Defense systems
- Space systems
- Ocean environments

In the case of FRP composites, environmental concerns appear to be a barrier to its feasibility as a sustainable material especially when considering fossil fuel depletion, air pollution, smog, and acidification associated with its production. In addition, the ability to recycle FRP composites is limited and, unlike steel and timber, structural components cannot be reused to perform a similar function in another structure. However, evaluating the environmental impact of FRP composites in infrastructure applications, specifically through life cycle analysis, may reveal direct and indirect benefits that are more competitive than conventional materials.

Composite materials have developed greatly since they were first introduced. However, before composite materials can be used as an alternative to conventional materials as part of a sustainable environment a number of needs remain.

- Availability of standardized durability characterization data for FRP composite materials.
- Integration of durability data and methods for service life prediction of structural members utilizing FRP composites.
- Development of methods and techniques for materials selection based on life cycle assessments of structural components and systems.

Ultimately, in order for composites to truly be considered a viable alternative, they must be structurally and economically feasible. Numerous studies regarding the structural feasibility of composite materials are widely available in literature. However, limited studies are available on the economic and environmental feasibility of these materials from the perspective of a life cycle approach, since short term data is available or only economic costs are considered in the comparison. Additionally, the long term affects of using composite materials needs to be determined. The byproducts of the production, the sustainability of the constituent materials, and the potential to recycle composite materials needs to be assessed in order to determine of composite materials can be part of a sustainable environment. Therefore in this chapter describe the physicochemical properties of polymers and composites more used in Civil Engineering. The theme will be addressed in a simple and basic for better understanding.

5.4.1. Manufactured process and basic concepts

The synthetic polymers are generally manufactured by polycondensation, polymerization or polyaddition. The polymers combined with various agents to enhance or in any way alter the material properties of polymers the result is referred to as a plastic. The Composite plastics can be of homogeneous or heterogeneous mix. Composite plastics refer to those types of plastics that result from bonding two or more homogeneous materials with different material properties to derive a final product with certain desired material and mechanical properties. The Fibre reinforced plastics (or fiber reinforced polymers) are a category of composite plastics that specifically use fibre materials (not mix with polymer) to mechanically enhance the strength and

elasticity of plastics. The original plastic material without fibre reinforcement is known as the matrix. The matrix is a tough but relatively weak plastic that is reinforced by stronger stiffer reinforcing filaments or fibres. The extent that strength and elasticity are enhanced in a fibre reinforced plastic depends on the mechanical properties of the fibre and matrix, their volume relative to one another, and the fibre length and orientation within the matrix. Reinforcement of the matrix occurs by definition when the FRP material exhibits increased strength or elasticity relative to the strength and elasticity of the matrix alone.

Polymers are different from other construction materials like ceramics and metals, because of their macromolecular nature. The covalently bonded, long chain structure makes them macromolecules and determines, via the weight averaged molecular weight, Mw, their processability, like spin-, blow-, deep draw-, generally melt-formability. The number averaged molecular weight, Mn, determines the mechanical strength, and high molecular weights are beneficial for properties like strain-to-break, impact resistance, wear, etc. Thus, natural limits are met, since too high molecular weights yield too high shear and elongational viscosities that make polymers inprocessable. Prime examples are the very useful poly-tetra-fluor-ethylenes, PTFE's, and ultrahigh-molecular-weight-poly-ethylenes, UHMWPE's, and not only garbage bags are made of polyethylene, PE, but also high-performance fibers that are even used for bullet proof vests (alternatively made from, also inprocessable in the melt, rigid aromatic polyamides). The resulting mechanical properties of these high performance fibers, with moduli of 150 GPa and strengths of up to 4 GPa, represent the optimal use of what the potential of the molecular structure of polymers yields, combined with their low density. Thinking about polymers, it becomes clear why living nature used the polymeric concept to build its structures, and not only in high strength applications like wood, silk or spider-webs.

5.4.2. Mechanism of Reinforcement

The reinforcement of a low modulus polymer with a high modulus, high strength fibre uses the plastic flow of the polymeric material under stress to transfer the load to the fibre; this results in a high strength, high modulus composite. The aim of the combination is to produce a two-phase material in which the primary phase (i.e. the fibres) is well dispersed and bonded by a weak secondary phase (i.e. the polymer matrix). The principal constituents influencing the strength and

stiffness of composites are the reinforcing fibres, the matrix and the interface between the fibres and the matrix.

5.5. Polymer surface coating

Coatings of polymeric materials can be applied on a variety of substrates using a number of different techniques such as extrusion, dispersion coating and solution appli cation. These converting techniques, which in general are off-line processes, give vast possibilities to form coated, multilayer and laminated structures. The end-use areas include liquid packaging, flexible packaging, packaging boards and different wraps and sacks with composite structures based e.g. on paper, board, plastic films and metallic foils in order to give the package material the required protective properties and appearance. In general, the package should protect against mechanical impact, chemical attack and UV-light, possess adequate flexibility or stiffness, transparency or opacity, printability and sealability. This requires among other things that the adhesion of the facing materials, the mechanical properties of each material and the surface friction of the product are adjustable factors. Simultaneously, the performance of the converting product must meet the requirements on cost-effectiveness during the manufacture and use, and more often, also during recycling and disposal. Therefore, often a compromise between the costs and the desired characteristics of the materials must be found. Towards more compact, flexible and cost-effective converting techniques, the development of the dry surface treatment (DST) has been targeted to overcome several limitations related to the conventional processes. Some of them are discussed below. With DST, the coating and su rface smoothening are accomplished in a combined process, which employs the electrostatic deposition of dry coating particles onto the substrate, followed by a thermo mechanical fusing and fixing phase in a heated roll nip. It is assumed that a wide selection of materials is manageable with the DST, which in addition provides a variety of possibilities to adjust the surface properties of the products.

Dispersion and solvent-based coating methods enable production of low coat weights and the use of materials that are not extrudable. The drawbacks in these methods include an energy-intensive evaporation and drying stage after application as well as handling of media in liquid and gaseous forms. One restriction in using liquid media may be a chemically or physically sensitive base substrate. The DST process may gain in being more or less solvent-free, i.e. no drying is required

after application of the coating. In extrusion coating, the material-related factors limiting the coating speed and efficiency include e.g. the draw strength, the neck-in and the adhesion properties of the melt. Therefore, the extrusion coating and lamination lines usually require specifically manufactured machinery when processing of different materials and operation at specified tension levels, as the base materials may vary from 10 μm thick films to 500 g/m2board, coat weights from 7 to 100 g/m2, line widths from 300 to 3000 mm and machine speeds between 20 and 600 m/min. In the dry surface treatment, the non-contact application directly to the desired coat weight might be advantageous in reducing the web stress and minimising the need for collection and circulation of materials. In the fixation phase of the DST-process, the fusing and homogenisation of the coating layer is done in a nip at low tension (low elongational shear rate compared to the stretching of the melt in extrusion coating). Taken all together, it is expected that the DST could provide a less material-dependent converting process than extrusion. Temperature-sensitive materials, that may suffer from the changes e.g. in density or composition during the melt processing in extrusion, may become available due to lower temperatures and shorter melt processing times applied in the DST-process. The nip dwell time may be as short as a few milliseconds, and high temperatures are compensated for by the applied compression pressure in the nip. In comparison, during melt processingin extrusion coating, chemical changes of the polymers may cause degradation of the performance of the product, but also spreading of volatile decomposition products into the surrounding air. Offensive odours and tastes remaining in the products primarily relate to volatile organic compounds (VOC) (2).

Multilayer coatings can be produced with the DST-process in stepped application stages, with or without an intermediate fixation. The degree of mixing or penetration of the polymers in the corresponding interphase region may be enhanced by applying the layers before the fusing or by adjusting the thermo mechanical treatment in order to increase the melt flow. In extrusion, the production of multilayers requires several successive extruders or coextrusion of the layers. Some experimental results point to that coextrusion of melts through channels with varying geometries can cause the layers or strands to rearrange, even when the polymers in the different layers have similar flow (viscoelastic) properties. This rearrangement of layers may be caused by secondary flows occurring in the changing flow channels, and naturally depends on the

viscoelastic character of the polymers.In general, the mixing of layers is not acceptable when aiming at optimum barrier properties of the structure.

THE DRY SURFACE TR EATMENT TECHNIQUE

Deposition and Attachment of the Dry Coating Particles onto the Substrate

The dry surface treatment employs the electrostatic deposition of dry, fine-sized particles and a thermomechanical surface treatment to fix the coating layer onto the substrate and to smoothen the coating surface. Previous studies with the DST-method have concentrated on pigment coated papers, but the same principles should hold for the production of thermoplastic polymer coatings. Figure 1 gives an outline of the two main steps in a one-sided DST-process. The characteristics of the simultaneous two-sided DST-process are discussed in.

The electrostatic deposition involves transfer of the fluidized and charged coating particles (typically with a negative charge) onto the paper surface by means of a strong electric field and an air stream. The electric field between several pointed electrodes (with a negative polarity) and a grounded counter-electrode causes a formation of free electrons and ions, which, affected by the field, accelerate towards the oppositely charged electrode.

The paper web passes through the electric field and is in contact with the grounded electrode. A fluidized stream of the coating particles is fed into the field area and the particles are charged through collisions with free ions. The effect of the aerodynamic forces and the electric field then directs the coating particles onto the moving web. The control of the coat weight is accomplished by adjusting the flow of the supply air and the mass flow of the particles and their charging, which can be affected e.g. by the voltage of the charging electrodes and the geometry of the electrode system. In order to obtain an optimum mass transfer and particle layering on the paper, the electric force exerted by the field on the particles should exceed gravitational and aerodynamic effects that may disturb the process. In addition to the field, the size, the surface area and the dielectric properties of the particles are important factors in determining the attainable charging of the particles and thereby their attachment onto the substrate. Attachment forces between the particles and the substrate include e.g. electrostatic image forces and

electrostatic contact potentials, van der Waals forces and, if the substrate is moist, capillaryattraction may also exist.

In general, a high charge density on the surface of the particleis advantageous in increasing the transfer efficiency of the field and the attraction force between the particle and the paper surface. It may to some extent be generalised that smaller particles (i.e. particles of a lower weight) may acquire a higher charge per unit mass and therefore may be more effectively transferred by the field. In the case of non-porous polymer particles, a suitable particle size is between 1 and 100 μm, but in order to obtain coatings of low thickness, the size distribution should be relatively narrow with a small average particle size. Although being light in weight, the charge density of the particles must be adequate in order for them to be attracted to the paper despite the small surface area available. Another material-related factor affecting the DST-process is the rate ofdecay of the particle charge. The low electrical conductivity of polymeric particles may reduce the dissipation of charge, reducing also the time-dependence of the process, which may become critical in the electrostatic attachment before the fixing phase when the substrate material is highly conductive.

Fusing and Fixing of the Coating Layer

With a sufficiently small particle size, a uniform coverage of the surface can be obtained with a thin coating layer. A small particle size is also advantageous in the fusing phase for reaching a stable rate of sintering and compaction of the coating layer. The thickness of the layer should be relatively uniform in order to achieve a uniform propagation of the sintering and melting front in the thickness direction of the coating. A very broad particle size distribution that contains large particles or particle aggregates may result in uneven sintering and in density variations or even voids in the layer. During the sintering process, the void content and contact areas between the particles change continuously, changing also the effective heat conduction. Efficient heat conduction and particle coalescence is not obtained until a compacted particulate bed has been formed. Polymers are effective thermal insulators, which can give rise to relatively steep temperature gradients in the sintering layer. There are experimental relations for estimating the sintering and compaction times within a powder-based polymeric layer, but a complete model describing the densification, the temperature profiles and the phase changes is still not at hand.

In order to obtain a homogeneous coating with sufficient mechanical strength and adequate sealing of the paper surface, the coating layer has to fuse thoroughly and anchor to the substrate.In the DST-process, the temperature and the heat transfer in the roll nip must be sufficientlyhigh to allow for the coalescence of polymer particles and the film formation. In the nip, the compaction of the layer is further enhanced by the applied pressure. The layer is assumed to homogenize through molecular diffusion across the interface between the contacting polymer particles. The diffusion is governed by the thermomechanical properties of the polymer in relation to the time scale of the fixation process. The molecular weight distribution, molecular architecture and crystallinity of the polymer are factors that here have significant effects on the thermomechanical fixation. Further, the conditions during fusing should allow for stress relaxation within the coating layer, since otherwise structural defects, such as weakening of the coating/substrate interface may appear. Furthermore, an effective heat-induced softening of the polymer must be combined with adequate mechanical properties at elevated temperatures in order to avoid polymer sticking to the hot roll surface.

The adhesion between different surfaces can, in principal, be divided into chemical and mechanical interactions, with the first type related e.g. to hydrogen bonds, dispersion forces and Lewis' acid-base interactions and the other to mechanical interlocking between the polymer and a rough substrate surface. The incorporation of functional groups into the polymer, either in the preparation phase or during the coating process (e.g. oxidation), can be used to promote the "chemically-related" adhesion to paper-based substrates. Additionally, copolymerisation and blending of different polymers may be used to improve the affinity between materials. In the case of polymer coatings, the flow into and the anchoring of the polymer melt to the rough and porous paper surface can contribute significantly to the attachment (12). In extrusion, oxidation of the polymer and treating or priming the substrate are frequently used methods to improve both chemical bonding and surface area available for mechanical interactions (14, 15). The ozone created in the application stage in the DST process may, to some extent, have a chemical priming effect on the substrate.

Polymer Coating Materials

There are a number of techniques for preparing thermoplastic polymeric particles; with some techniques the polymerisation product is directly in a powdery form and in others, some post-treatments are required. In preparation of materials for the extrusion processes, the base polymer is typically in a powder form, but is then mixed with additives and stabilisers in a subsequent melt mixing process, followed by granulation into a size of 2000 – 4000 μm pellets. Grinding of the thermoplastic granulates to powder often requires cryogenic conditions. On the other hand, suitable sized polymeric particles may be obtained directly from the polymerisation reactor, provided that the properties of the polymer fit the coating application. Grinding and screening of the powder may be required in any case. Precipitation and suspension polymerisation techniques may provide useful tools for obtaining particles of the desired size, but both processes require evaporation of the liquid suspending medium. For example, drying from a water-based suspension consumes extra energy and may require the use of dispersants, whose remains may impair the coating properties. Traces of solvents may also have negative effects. Some polymers, including polyolefins, are suitable for polymerisation in a gaseous medium, for example in supercritical carbon dioxide.The reactions in the supercritical medium can be carried out either in a homogeneous or in a heterogeneous (i.edispersion polymerisation) polymerisation system. The precipitation is controlled by the pressure and temperature conditions and the polymerisation product may be obtained in a powdery form. Additionally, the reaction medium is recyclable.

The processability of coating materials, in extrusion as well as in the DST-process, is affected by the solid feed properties, the specific thermodynamical and viscoelastic properties as well as the chemical nature of the polymer. In both coating processes, the compression and fusing of the polymeric materials depend on the friction and bulk density of the solid raw materials and the thermodynamical properties such as the specific heat, heat of fusion, melt density and thermal diffusivity of the polymers. Factors, such as the molecular weight distribution, chemical modification, thermal stability and additives, may be adjusted or used in order to control the rheological properties of the polymer melt. Several physical and chemical properties can be adjusted already in the preparation phase, but the powders can be further modified by suitable treatments and additives.

In the case of extrusion coating it is known that low molecular weight polymers may provide coatings with high pinhole resistance, high stress crack and abrasion resistance combined with high toughness, whereas polymers with a higher molecular weight may exhibit better adhesion through better wetting of the substrate, high stiffness and induces less curl. To a large extent, the same results are expected to apply also for coatings produced in the DST-process With regard to the permeability or the barrier properties of a coating layer (and the composite structure as a whole), three basic issues are of importance; i) the direct permeability or the mass transport ofa gas or liquid, ii) the absorption of specific flavours, which is encountered especially with food and beverage packaging, and iii) the migration or diffusion of small molecular residuals (waxes, polymerisation residuals or plasticisers) towards the surface, causing changes in odour and taste. Concentrating on the first issue, it may be generalised to some extent that polar polymers are good barriers against oxygen and other non-polar molecules, but they are not especially water-resistant. Correspondingly, non-polar polymers serve as good barriers against moisture, but are oxygen-permeable.

In this study, the aim is to compare some structural characteristics and performance of polyethylene-based coatings on papers, produced by the dry surface treatment and by extrusion coating. It should be stressed that the aim is to evaluate the feasibility of the DST-process with regard to polymer coating of paper products. The results should in a sense be regarded as being of a preliminary nature since there certainly is room for improvements. Furthermore, the comparison with extrusion-coated substrates is only valid for the material used here, it cannot be claimed to have a general validity.

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