

RENEWABLE FIBERS AND BIO-BASED MATERIALS FOR PACKAGING APPLICATIONS – A REVIEW OF RECENT DEVELOPMENTS

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This review describes the state-of-the-art of material derived from the forest sector with respect to its potential for use in the packaging industry. Some innovative approaches are highlighted. The aim is to cover recent developments and key challenges for successful introduction of renewable materials in the packaging market. The covered subjects are renewable fibers and bio-based polymers for use in bioplastics or as coatings for paper-based packaging materials. Current market sizes and forecasts are also presented. Competitive mechanical, thermal, and barrier properties along with material availability and ease of processing are identified as fundamental issues for sustainable utilization of renewable materials.

Keywords: Bio-materials; Fibers; Bioplastics; Composites; Packaging; Paper; Coating

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INTRODUCTION

The packaging industry nowadays relies strongly on the use of petroleum-derived plastic materials, which raises some concerns from both economical and environmental perspectives. The continuing use of finite oil resources implies a likely eventual decrease in availability and thereby increasing costs of raw materials. Furthermore, because of their lack of biodegradability, petroleum-based products can pose significant waste disposal problems in some areas (Franz and Welle 2003; de Vlieger 2003; Robertson 2008). Packaging is a substantial part of our everyday life, and the consumer use of packaging materials has shown a continuous increase over time. The European packaging industry has a market value of about 80 billion EUR (Global Packaging Alliance 2011) and accounts for about 40% of the global packaging market. The future trend will be towards growing markets on a global scale. Packaging products manufactured from

renewable materials currently only represent about 2% of the market, traditional fiber-based (*i.e.* paper) packaging excluded.

The development of high-performance renewable materials is one important factor for sustainable growth of the packaging industry. Studies carried out by independent research institutes (*e.g.* the German ifeu, Institute for Energy and Environmental Research Heidelberg, and the Swedish IVL, Swedish Environmental Research Institute) have shown that packaging materials from forest-based resources can provide advantages from a carbon footprint perspective when compared to alternatives such as conventional plastics or glass packages. Two recent studies showed for example that paperboard is advantageous over glass or plastic bottles for packaging of liquids, owing to its renewable materials origin (Jelse *et al.* 2011; Wellenreuther *et al.* 2010). In addition, fiber-based packaging has the advantage of lower weight, which is favourable from a transportation perspective, and the final products can generally be recycled (Hohenthal and Veuro 2011). Other studies show that consumers prefer fiber-based packaging material because it is seen to be environmentally friendly.

Bio-based polymers applied as dispersion coatings on paper and paperboard for packaging applications and bioplastics with the same intended use provide sufficient barrier properties with respect to fats, but are usually only moderate water vapor barriers. Other weaknesses can include inferior mechanical properties, insufficient heat tolerance, and high moisture sensitivity relative to petroleum-derived plastics. In addition, to be competitive it is important that new bio-based packaging solutions should be economically viable and should be easily incorporated in present industrial manufacturing processes.

Recent trends in European consumer markets are moving towards “greener” packaging, (*i.e.* packaging from recyclable materials, recycled materials and re-usable packaging, reduced material use (lightweighting) and bio-derived polymers). This development has been driven by consumers and retailers and, in combination with EU directives, the establishment of more eco-efficient packaging has been created in Europe (Parker 2008).

Several national and international research projects have been performed in Europe over the last decade, and others are still in progress, with a focus on the potential of bio-materials for replacement of petroleum-derived packaging materials. Examples are the Food Biopack project, SustainPack, SustainComp, SUNPAP, FlexPakRenew, and RenewFuncBarr.

The Food Biopack Project provided some very useful insights into the production and application of bio-based packaging materials for the food industry, covering the whole perspective from properties of a variety of bio-derived materials (starch, cellulose, chitosan, proteins and polymers produced from bio-based monomers), to food packaging considerations, environmental impacts, life cycle analysis, and market issues (Weber 2000a,b).

SustainPack, the biggest research project on packaging undertaken to date, addressed improvements in a wide variety of packaging functionalities. An intriguing aspect was the development of self-healing coatings in order to maintain the barrier properties of packages when exposed to external stress (Andersson *et al.* 2009). Other issues that were successfully addressed included nano-sized thin top layers for improved

barrier performance (Amberg-Schwab and Kleebauer 2007), printed electronics for communication purposes (Robertsson 2008), and cellulose fibers for reinforcement (Aucejo 2005).

FlexPakRenew aimed to design and develop innovative and eco-efficient flexible paper packaging from renewable resources. The target was to replace petroleum-derived barrier films and to develop a multilayer packaging structure that would be ultimately biodegradable and in which the separate layers would each contribute to the performance of the packaging as a whole. Research efforts were directed to improvement of the flexible base paper by wet-end processing, to reinforced bio-based coatings for barriers against oxygen, grease and water vapor, to the application of thin nanocoatings for further improvement of barrier performance, and to the incorporation of novel, renewable materials with antimicrobial functionalities for prolonged shelf life of food products. Life cycle analyses were undertaken to assess the sustainability of the final structure with detailed studies of each component.

The aim of the Swedish national research project RenewFuncBarr is to develop cost-efficient, sustainable large-scale production of renewable materials intended for food packaging. The focus is directed towards starch, proteins, and waste products from the forest- and agricultural-based industries. In the project, conventional application techniques such as coating with water-based dispersions and extrusion are being used in combination with sophisticated techniques such as plasma deposition and electrospinning aimed at enhanced barrier functionality.

Sustainable composite materials are addressed in the SustainComp project, whereas the SUNPAP project aims to scale up production of nanoparticles for development of new, renewable fiber-based packaging products. Finally, Agrobar is a project concentrating on molecules derived from agricultural sources for use in barrier coatings. The Enzycoat and Enzycoat II projects aimed to develop active packaging using oxygen scavengers incorporated in barrier coating matrices comprised of bio-based materials.

This review contains an overview of the state-of-the-art of materials derived from the forest sector with the potential for use in the packaging industry. Examples are taken from both completed and ongoing research projects as well as from literature sources. The aim is to cover recent developments and key challenges for successful introduction of renewable fibers and bio-based materials in the packaging market.

BIO-MATERIALS

Renewable Fibers

Around 32 million tonnes of natural fibers are extracted each year from a wide range of plants and animals, according to FAO, the Food and Agriculture Organization of the United Nations (FAOSTAT 2009). These fibers are used to form fabrics, ropes, and twines that have played a fundamental role in human societies since the dawn of civilization. Natural fibers also play an important role in dressing the world's population and by allowing communication between people through paper (books, documents, etc.). Natural fibers also form the basis for various packaging materials used in our everyday life. With the objective of focusing the world's attention on the role of such raw

materials, the FAO declared the year 2009 as the International Year of Natural Fibers (FAOSTAT 2009).

The term “natural fibers” is used to designate numerous kinds of fibers that are naturally produced by plants and animals and are also derived from some minerals (Bledzki and Gassan 1999). To avoid any possible misunderstanding, it is important to clarify that in packaging ‘natural fibers’ usually refers to ‘plant fibers’, which can also be called ‘vegetable fibers’, ‘lignocellulosic fibers’, or ‘cellulosic fibers’. More specifically, two families of natural fibers can be distinguished (Bledzki and Gassan 1999), namely fibers extracted from

- i) different tree species
- ii) ‘annual plants’, which in this case includes hairs (cotton, kapok), fiber-sheafs of dicotylic plants or vessel-sheafs of monocotylic plants (*i.e.* bast (flax, hemp, jute, ramie), and hard fibers (sisal, henequen, coir))

The first family has already been strongly industrialized over the past century with different processes developed to fractionate the fibers such as kraft pulping, sulfite pulping, and mechanical pulping. About 300 million tonnes of pulp are produced every year from wood coming mainly from Scandinavia or North America in the form of softwood and in the form of hardwood from Asia, South America and other tropical or sub-tropical regions. The Russian Federation is also a large producer of softwoods and hardwoods (Mutanen *et al.* 2005). According to estimates, more than 1.7 million tonnes of pulp and papermaking fiber residues are generated globally each year, and these residues may also be available for upgrading (Millett *et al.* 1973). Table 1 shows an overview of world production and the production costs of the most important natural fibers included in the second agrofiber family, over the period ranging from 2003 to 2005 (FAOSTAT 2009; Moir *et al.* 2009).

Cotton and jute are the most important agrofibers in terms of volume worldwide. All other cellulosic natural fiber sources in the second family have lower and generally rather similar production volumes. The tonnages and geographical differences in production also vary. Asia and South America are the most important producing areas for agrofibers. For example, around 200 kilo-tonnes of sisal are produced each year in Brazil. This is in contrast to some other natural fibers such as jute, ramie, curauá, and rice fibers, for which the production is more transient, as detailed in a recent review (Satyanarayna 2007).

Natural fibers basically consist of cellulose, lignin, and hemicelluloses. Pectins, pigments, and extractives can be found in smaller quantities. Natural fibers are also referred to as cellulosic or lignocellulosic fibers. The chemical composition and cell structure of natural fibers is quite complicated. Each fiber is essentially a composite in which rigid cellulose microfibrils are embedded in a softer matrix mainly composed of lignin and hemicellulose (Satyanarayana 1990). The structure is frequently depicted in the literature, and a schematic drawing can be found, for example, in Siqueira *et al.* (2010).

Table 1. Estimated Global Production Volumes and Costs of Natural Fibers

Natural fibers	Main producing countries	World production		Production costs	
		Million tonnes	%	Million USD	%
<i>Cellulosic</i>					
Cotton	China, USA, India, Pakistan, Uzbekistan, Brazil	25.00	78.8	31.20	85.8
Jute	India, Bangladesh	2.70	8.5	0.48	1.3
Flax	China, France, Belgium, Belarus, Ukraine	0.08	0.2	0.43	1.2
Kenaf	Asian Countries	0.50	1.6	n.a.	n.a.
Coir	India, Sri Lanka, Thailand, Malaysia	0.45	1.4	n.a.	n.a.
Sisal, Henequen and other Agaves	Brazil, Tanzania, China, Kenya, Mexico	0.30	0.9	0.08	0.2
Ramie	China	0.15	0.5	0.17	0.5
Abaca	Philippines, Equator	0.08	0.3	0.03	0.1
Hemp	China, Spain, Korea, Russian Federation, Chile	0.09	0.3	0.03	0.1
<i>Proteins</i>					
Wool	Australia, China, New Zealand	2.20	6.9	2.96	8.1
Silk	China, India	0.14	0.4	0.98	2.7
Other animal fibers*		0.03	0.1	n.a.	n.a.
<i>Total</i>		<i>31.72</i>	<i>100</i>	<i>36.35</i>	<i>100</i>

*Including alpaca, cashmere, angora, mohair and camel. n.a.: data not available.

The properties of cellulosic fibers are strongly influenced by chemical composition as well as morphological factors such as internal fiber structure, microfibril angle, cell dimensions, and defects, which can vary according to location in the plant as well as between different plants (Dufresne 2008). The mechanical properties of natural fibers also depend on their cellulose type, because each type has its own crystalline organization which determines the mechanical properties (Bledzki and Gassan 1999).

Renewable fibers – key challenges and targets

For the use of renewable materials in packaging to grow, there are key cost and performance obstacles that must be addressed. Effective, secure, and long-lasting supplies of raw materials are also essential. Several particular challenges can be identified:

- i) The production of raw materials by nature should be sustainable. The global forest industry has become aware of the importance of sustainable forestry and has, for example, introduced the FSC (Forest Stewardship Council®) labelling, to promote responsible management of the world's

forests. The FSC label certifies that the material meets environmental, social, and economic needs in the whole supply chain (FSC 2011). Such a quality insurance system is, however, not yet implemented for all types of natural fiber. Competition with the cultivation of land for production of crops for the food industry is also a challenging issue, not least from an ethical viewpoint.

- ii) The extraction/purification processes to isolate fibers should be environmentally friendly and uniform quality fibers should be produced for further refinement into packaging products.
- iii) New applications should be targeted (*e.g.* biocomposites), and new value should be given to the fiber. For example, chemical modification or development of nano-scaled materials to provide unique properties to natural fibers.

Nanocellulose – an innovative concept

An emerging field deals with renewable nanofillers from cellulose. Fillers in this context refer to a variety of nanosized structures whose function is not only to fill a matrix but also to provide enhancement in properties (*e.g.* strength). The nomenclature concerning these structures is not consistent (Siqueira *et al.* 2010; Chinga-Carrasco 2011) and a number of terms can be found in the literature. In order to use nanofillers in packaging applications, they will have to be produced in large amounts. A key challenge has been the need to reduce energy consumption in producing nanofibrillated cellulose. However, much progress has been made in this direction, with specific energy consumption comparable to that of thermomechanical pulp (TMP) production in some instances, and upscaling of nanocellulose production is now being pursued in a number of countries. Films prepared from nanocellulose, now frequently referred to as nanopapers, can have impressive mechanical properties as well as other useful characteristics (Goncalves *et al.* 2008; Sehaqui *et al.* 2010; Olsson *et al.* 2010).

Moreover, nanocellulosic materials can be tailored to have antimicrobial or other specialized properties. The large potential of nanocomposites based on renewable matrices and fillers for applications in packaging markets arises from the great variety of polymers that can be extracted and/or synthesized from bio-based sources (mainly plant biomass). In order to compete with traditional polymers based on oil, the combination of bio-based polymers and (nanosized) fillers should be synergistic (*i.e.* the blend of components, which each are rather expensive, should interact to provide a strong performance improvement at a reasonable overall cost). Some key issues in favor of bio-based nanocomposites are:

- i) The high aspect ratio of cellulose nanofillers (when compared to cellulose fibers on micro- or millimeter scale) leads to improved mechanical properties in composite materials
- ii) Cellulose nanofillers can be combined with several biomass-derived polymer matrices and active organic molecules to develop innovative green nanocomposites and tailor-made papers, so-called nanopapers,

with potentially superior properties for industrial use. Areas of application in advanced nanopaper-based composites include electrically conducting papers and paper-based components for lithium ion batteries (Nyström *et al.* 2010; Jabbour *et al.* 2010).

- iii) Hydrophilic biopolymers are easily compatible with hydrophilic nanosized fillers. However, obtaining good compatibility between hydrophobic fillers and hydrophilic matrices or vice versa is a challenge. Improvement of nanofiller dispersibility can be achieved by surface functionalization and/or by modification of compounding technologies. In this way, more competitive renewable materials can be developed. Specific inorganic functionalization on the cellulose surface can also aid in achieving useful properties for these materials in packaging applications.

Compounding of nanocellulosics with water-insoluble biopolymers, such as polylactides (PLAs) or polyhydroxyalkanoates (PHAs), which are further described below, raises a number of challenges in terms of dispersion, physicochemical compatibility, and phase separation procedures. Dispersability of nanofillers in the polymeric matrix will need altered processing steps to assure a faster adaptation to pilot/industrial scale equipment. Since most of the biomass-derived materials are naturally dispersed in water, it becomes necessary to understand and control the manifold and often competing interactions (charge, hydrogen-bonding, etc.) in the aqueous dispersion state in order to allow reliable processing into desired structures. The huge amount of hydroxyl groups present in cellulose nanofillers, however, provides a wide range of ways for surface functionalization (*e.g.* by chemical modification in order to achieve compatibilization with more hydrophobic polymers).

Nanoscaled cellulose fibers are promising as candidates for the preparation of bio-nanocomposites, owing to their high abundance, strength and stiffness, low weight, and biodegradability. There is a broad range of nanocellulose applications, the packaging sector being one area in which nanocellulose-reinforced polymeric films are of interest. Films can be produced with high transparency and with improved mechanical and barrier properties when compared with unfilled polymeric films (Ramires and Dufresne 2011).

Microfibrillated cellulose, now more commonly referred to as nanofibrillated cellulose or NFC, has also seen a renaissance over the past two decades. The initial work in the 1980s was not continued at the time because of very high energy costs; however, in the 1990s this research topic was picked up again at a number of laboratories, most notably STFI-Packforsk in Stockholm, now Innventia AB, where the use of enzyme-based pretreatments was shown to be an effective way of significantly reducing the costs of NFC production. NFC produced by high-shear homogenization of wood pulp typically has nanofibril diameters in the 5-60 nm range (Klemm *et al.* 2011). In addition to a recent review on the use of NFC in nanocomposite materials (Siro and Plackett 2010), the literature now highlights novel application of NFC and other forms of nanocellulose for use in coatings, films, barrier layers, composites, papermaking, painting, and release agents (Ragauskas 2011; Chinga Carrasco 2009).

Various procedures can be used for production of nanocellulose from wood and other forms of biomass. In general, methods that minimize the degradation of cellulose are preferred (*i.e.* minimal changes in morphology, molecular weight and degree of crystallinity). Various methods for the extraction of cellulose can be found, but most of them can be classified into three main groups: chemical methods (Sun *et al.* 2004), mechanical methods (Nakagaito and Yano 2005), and enzymatic methods (Bayer *et al.* 1998). These methods can be used alone or in combination and are schematically presented in Fig. 1. For detailed descriptions, see *e.g.* Siqueira *et al.* (2010) and Lavoine *et al.* (2012).

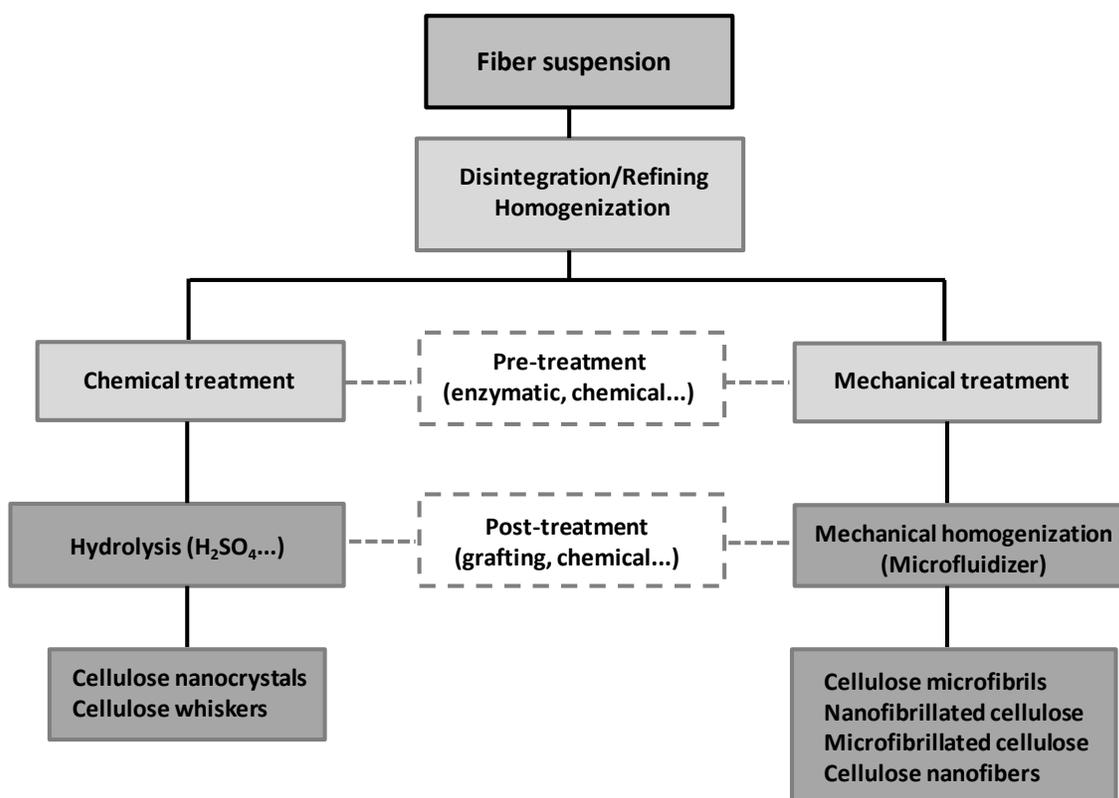


Fig. 1. Schematic overview of approaches to produce nanocellulosic materials from fibers.

Recent studies have demonstrated the potential of cellulose nanofibers (nanofibrillated and bacterially produced) as reinforcing elements in various bio-based polymers such as chitosan or poly(lactic acid) (Fernandes *et al.* 2010; Li *et al.* 2009; Nakagaito *et al.* 2009; Okubo *et al.* 2009) and also in specialized nanopapers. Both multi-functional bio-based composites and tailor-made nanopapers have shown improved mechanical properties and very promising functional properties, such as transparency, biodegradability, and specific surface properties to add new functionalities like gas barrier enhancement and heat sealability. Other applications may include incorporation of active molecules such as antimicrobial compounds, antioxidants, or aroma-active agents for controlled release, which may be useful in packaging as well as in other areas.

Nanocelluloses (nanofibers and whiskers) form a remarkable emerging class of naturally derived nanomaterials because of their extraordinary mechanical properties, combining high stiffness and strength with light-weight character. The use of nanocellulose potentially allows the inherent mechanical properties of cellulose to be more adequately exploited than in the case of cellulose fiber-based products (*e.g.* papers, macrocomposites). For example, cellulose I crystals can exhibit a Young's modulus of up to ca. 134 GPa, and their tensile strength is expected to be in the range of a few GPa (Nishino *et al.* 1995). These properties mean that nanocellulosics rank near the top of high-performance natural materials. Since cellulose nanofillers are derived from wood or plant sources, they are nearly inexhaustible, globally abundant and renewable, and represent one of the only resources which neither interfere with the food chain nor require direct petrochemical components for their functionality. In addition, such nanofillers are fully biodegradable or can be used as a fuel source.

Nanopaper produced from nanofibrillated cellulose, is a very interesting packaging material due to its high toughness and high effectiveness as an oxygen barrier (Henriksson *et al.* 2008; Nogi *et al.* 2009). However, so far, little effort has been dedicated towards further improvement of nanopapers and nanocomposites of low and high cellulose content taking into account the high specific surface area of cellulose nanofillers. In order to fully capitalize on the potential of nanocellulose, the goal should be to achieve tailored interactions with polymers by use of chemical modification and also by polymer adsorption to the nanofibers.

Innovative approaches for chemical modification of cellulosic fibers aimed at compatibilization with polymeric matrices have been presented by Neto and Bras (2008). Surface grafting by copolymerization, with the use of various coupling agents, was proven to significantly increase the storage modulus of extruded composites over that of the polymer alone or polymer compounded with ungrafted fibers. The composites showed a high biodegradation rate. A new technique called co-continuous grafting applying a "click" reaction between esterified cellulose and chemically modified polycaprolactone (PCL) was demonstrated to give polymer-fiber composites with highly increased Young's modulus (Neto and Bras 2008). Adhesion and surface issues relating to the use of cellulose and nanocellulose in combination with various polymers have been covered in a recent review (Gardner *et al.* 2008).

Scaled-up nanocellulose production facilities are now established or are under construction in various parts of the world (*e.g.* Canada, Sweden, Norway, Finland and Japan) and the availability of much larger quantities of such bio-material should further stimulate research and development as well as commercial interest.

Biopolymers

The prefix "bio" comes from the Greek "bios" meaning "human life". However, in the polymer, packaging and composite areas, several definitions are used, and misunderstandings are very common. Sometimes "bio" is used to designate a biodegradable material, but it is also used to designate materials from renewable resources. The European Bioplastics Association has a broader definition which refers to three types of bioplastics: 1) bio-derived and biodegradable/compostable (*e.g.* polylactides, polyhydroxyalkanoates), 2) fossil fuel-derived and biodegradable (*e.g.*

polycaprolactone) and 3) bio-derived and non-biodegradable (*e.g.* bio-polyethylene or BIO-PE and bio-polyethylene terephthalate or BIO-PET). A bio-derived polymer such as BIO-PE is chemically identical to PE derived from oil and therefore has the same chemical and physical characteristics. Whether or not the production of PE from biomass-derived ethanol can be considered sustainable is a question requiring detailed analysis and is beyond the scope of this review.

In the present paper, the term “biopolymers” is used to classify polymers derived from renewable resources and “bio” is here defined as bio-based. Biopolymers can be sorted according to their chemical composition, the method of synthesis, the method of processing, their economic importance, application areas, etc. Each classification provides different and useful information.

According to their origin, biopolymers can be grouped into three main categories (Petersen *et al.* 1999). Figure 2 schematically summarizes the classification of biopolymers (van Tuil *et al.* 2000).

- i) Polymers directly extracted from natural materials such as polysaccharides (*e.g.* cellulose, starch, chitin), lignins, proteins, and lipids.
- ii) Polymers produced by “classical” chemical synthesis from renewable bio-derived monomers (*e.g.* polylactide or PLA, which is polymerized from lactic acid obtained from dextrose). As noted above, BIO-PE is also an example in this category.
- iii) Polymers produced by microorganisms or genetically transformed by bacteria. This category includes polyhydroxyalkanoates or PHAs. Commercially, these principally consist of polyhydroxybutyrate (PHB) and copolymers of hydroxybutyrate and hydroxyvalerate (PHBV); however, other copolymers such as the Nodax® series from Procter & Gamble (now licensed to Meredian) have also been developed.

Biodegradability

The renewable origin of biopolymers is certainly an important concern in modern societies where sustainable solutions to our future needs for energy and materials are increasingly in focus. However, for some material applications, the biodegradability or compostability of particular polymers will be important, and although most but not all bio-derived polymers are biodegradable, all biodegradable polymers are not necessarily bio-based.

A growing interest in developing environmentally friendly and biodegradable polymer systems has arisen over the last decade due to increasing environmental concerns and studies of end-of-life of materials currently used in packaging and other sectors (Oksman *et al.* 2006; Pandey *et al.* 2005). Biodegradable polymers offer a possible solution to waste-disposal problems associated with traditional petroleum-derived plastics (Mohanty *et al.* 2000). Although a total replacement of conventional plastics by biodegradable materials is not realistic in the current and foreseeable perspective, there are some specific applications for which such a replacement seems both obvious and useful.

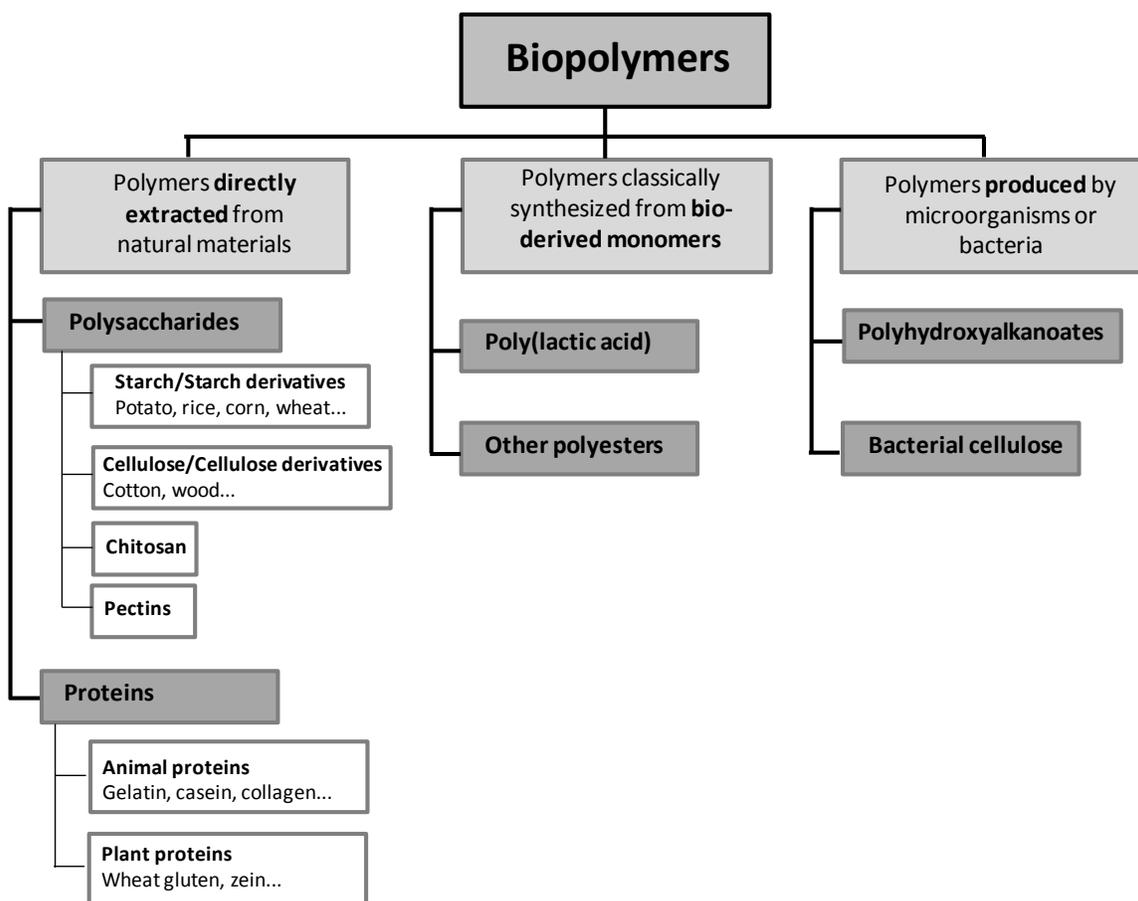


Fig. 2. Schematic overview of biopolymers

According to van der Zee (2005) the term biodegradation has not been consistently applied. For environmentally degradable plastics, biodegradation may mean fragmentation, loss of mechanical properties, or sometimes degradation through the action of living organisms (bacteria, fungi, etc.). Many groups and international organizations, such as the American Society for Testing and Materials (ASTM), the European Standardization Committee (CEN), the International Organization for Standardization (ISO), and the German Institute for Standardization (DIN) have all been actively involved in developing definitions and tests for biodegradability and compostability in different environments (Mohanty *et al.* 2000). There are several reasons why the establishment of a single definition among the international community has not been straightforward (van der Zee 2005), some of which are listed below:

- i) The variability of the definitions due to differences related to the environment in which the material is introduced;
- ii) Different opinions related to the scientific approach to or the concept of biodegradability;
- iii) Different opinions on the policy implications of the various definitions;

- iv) Challenges posed by language differences around the world.

Considering the ASTM definition (ASTM–D883-00), biodegradable polymers may be defined as polymers that undergo a significant change in their chemical structure under specific environmental conditions. These changes result in a loss of physical and mechanical properties as measured by standard methods. Biodegradable polymers can degrade through enzymatic activity or by attack of naturally occurring microorganisms such as bacteria, fungi, and algae. It seems important to understand that there are two steps to assure that a material is biodegradable: 1) physicochemical degradation of the material and, 2) bioassimilation by fungi and microorganisms to obtain water and oxygen, carbon dioxide, or methane. Since the year 2000, the European standard EN 13432 on composting and biodegradation is well accepted in Europe as a way of testing packaging for biodegradability. This standard is based on the following specifications:

- i) Low levels of heavy metals (below given maximum values);
- ii) Disintegration (*i.e.* fragmentation of the material so that after 12 weeks in a compost less than 10% of the initial mass should have dimensions larger than two mm when the final compost is screened through a sieve of two mm);
- iii) 90% of the initial weight should be bioassimilated in less than six months according to criteria defined in specific test methods (ISO 14851, ISO 14852, ISO 14855);
- iv) The quality of the final compost as determined by ecotoxicology tests including plant germination.

Polymers may also be designated as photobiodegradable, oxidatively degradable, hydrolytically degradable, or compostable (van der Zee 2005; Kolybaba *et al.* 2003). All these terms can contribute to confusion amongst scientists and consumers. To avoid this problem, more and more companies and researchers are focusing their communication on life cycle assessment (LCA) and carbon footprint evaluations to determine the total environmental impact of packaging materials. While LCA covers a wide range of environmental aspects, the carbon footprint concept focuses on the global warming potential, which covers most of the environmental impact from packaging and has been shown to be useful with respect to biopolymers (Parker 2008). It should be noted that use of so-called oxo-degradable polyolefins, which have entered some markets (*e.g.* shopping bags) in recent years, is now in question because a hazard may be posed by the many small plastic fragments left behind when these products are disposed of in the environment. Degradable and biodegradable polyolefins have recently been reviewed by Ammala *et al.* (2011).

Biopolymers – key challenges and targets

As outlined above, biopolymers can be broadly divided into three categories depending upon how they are sourced. Of these various biopolymers it is largely the polylactides (PLAs) which have so far made the greatest impact in the marketplace for packaging materials. A considerable amount of research has however been devoted to

potential packaging applications for other biopolymers such as starch, PHAs, chitosan, and proteins such as corn zein and gluten.

From a practical point of view, biopolymers offer two main advantages when compared with synthetic plastics: i) biodegradability and/or compostability, and ii) availability from renewable resources. The latter seems to be generally the more important when it comes to commercial interests; however, this viewpoint is now complicated by the availability of non-degradable BIO-PE derived sustainably from, for example, sugar cane.

There are some common challenges in terms of using biopolymers in packaging, related either to processability or to final properties. For example, satisfactory melt processing of PLA requires very low moisture levels but, as demonstrated by the products already in the market, this is achievable. From a property perspective, the gas barrier and water vapor barrier properties of PLA are insufficient for some of the more demanding food packaging uses and improvement in these properties has been a continuing research target. In this context, there have been many studies on the formation and properties of biopolymer nanocomposites, particularly involving use of layered silicate (*i.e.* nanoclay) additives. The improvement of barrier properties in PLA using this approach has been proven; however, the literature indicates that although oxygen permeability reductions of 50-60% at 23°C and 50% RH are to be expected using this approach, this is not sufficient to allow wider use of PLA in food packaging (*e.g.* for high moisture content foods) (Katiyar *et al.* 2011), and the additives may also make PLA films even more brittle than in their unmodified form. Ways of achieving even better barrier properties using alternative techniques (*e.g.*, layer-by-layer coating) or other nano-additives (*e.g.*, nanocellulose) or combinations of such technologies are therefore of interest. The combination of biopolymers with nanofillers and their use in areas such as food packaging is also now raising questions concerning the migration of nanoparticles or their associated organomodifiers and their toxicological properties. These topics are now receiving increasing research attention (*e.g.* Schmidt *et al.* 2009; Sharma *et al.* 2010). At the same time, enhanced application of PLA in packaging could greatly benefit from cost-effective methods to introduce better mechanical properties (*e.g.* reduced brittleness) and higher thermal stability (*i.e.* higher glass transition temperature, T_g).

The wider introduction of biodegradable/compostable plastics in packaging would benefit from an improved understanding of these materials from a waste management perspective, as well as from research aimed at fully clarifying the impact of bioplastics in the environment. The latter implies an increased need for improved life cycle analyses applied either to existing commercial bioplastics such as PLA or to biopolymers under development.

Potential of biopolymers in packaging – some innovative examples

Xylan isolated from bleached birch kraft pulp in combination with reinforcing nanoclays has been shown to give promising barrier properties with respect to water vapor and aromatic compounds (isoamyl acetate, limonene, cis-3-hexenol, and carvone) when coated on a low-grammage paper (Talja and Poppius-Levlin 2011). This is a significant finding since, like other carbohydrates, the good oxygen barrier properties of hemicelluloses have been reported, but hygroscopicity and therefore high water vapor

permeability is generally expected. In other recent investigations on hemicellulose/clay composites, Ünlü *et al.* (2009) evaluated the fundamental properties of biocomposites formed from corn cob xylan and montmorillonite clay and suggested that, depending on concentration, some intercalation of xylan in the clay galleries could occur. The combination of xylyans with various forms of nanocellulose could also offer a promising route to totally renewable, biodegradable films, which may find future application in fields such as food packaging (Saxena and Ragauskas 2009; Saxena *et al.* 2009). References to hemicellulose applications, including the food and food packaging sector, were included in a recent review of hemicellulose synthesis, chemistry, and properties (Albertsson *et al.* 2011).

Starch and proteins can be used as edible and biodegradable films and coatings for packaging applications (Pan and Caballero 2011). For example, these films and coatings may be used to protect export fruits and nuts from physical damage, to reduce shrivelling of the fruits, and to reduce rancidity of the nuts. Kafirin, a protein found in sorghum and available in large amounts as a by-product from the processing of sorghum, appears to be one of the renewable materials which may be highly suitable for such films and coatings (Stading 2003). Cast films from kafirin were found to provide water vapor barrier properties superior to those of whey protein-based films (Stading 2003) but water vapor- and oxygen barrier properties similar to those of zein (Gillgren and Stading 2008). Kafirin films also showed sufficient mechanical strength in the presence of a plasticizer (Gillgren and Stading 2008).

Novel acrylic hybrid latexes based on vegetable oil macromonomers (VOMMs) exhibited greater hydrophobicity and reduced surfactant migration as compared to commercial carboxylated styrene-acrylic latexes when used in paper coating formulations (Rawlins *et al.* 2009). Other novel approaches are latexes based on corn starch, for which a wide range of potential applications have been identified (Klass 2007a).

Composite films of a gelatin-based bio-coating (lipid protein coating) were shown to present improved barrier properties against oxygen and UV radiation (Farris *et al.* 2009). In another recent study, Bae *et al.* (2009) reported the potential uses for fish gelatin films reinforced with montmorillonite clay and the effect of such parameters as homogenization speed, pH, and ultrasonication on film properties.

BIOPLASTICS AND BIOCOMPOSITES

Bioplastics

PLA is now manufactured in both commodity and specialty grades (*e.g.* medical) worldwide. The largest share of world production is held by NatureWorks Inc., a company wholly owned by Cargill and located in the US mid-west, which has PLA manufacturing and sales as its main business activity. Although a significant percentage of PLA production may be directed towards spun fibers (*e.g.* for textiles), there is no doubt that packaging has been a prime target and, in the case of food packaging, PLA films have been thermoformed into trays for packaging of salads, ready-to-eat meals, and delicatessen items. Such products are now available and in use in some European countries and in North America. PLA has also been used in blow-moulding processes to

manufacture such new items as non-carbonated beverage bottles (*e.g.* water). As reflected by news articles in such publications as *Bioplastics* magazine, produced by European Bioplastics, improvements in PLA-based products are continuing, whether through the use of additives (*e.g.* plasticizers, impact modifiers) or through new formulations that, for example, allow use of this bioplastic in, or as a coating on, disposable cups for hot drinks. A heat-resistant PLA formulation for use in, for example, ready-to-eat meals trays, is also now available. However, despite these commercial advances, there is still a considerable need for cost-effective methods to enhance PLA properties, especially in terms of higher gas and water vapor barrier properties, reduced brittleness, increased thermal stability (higher T_g) and, in the context of natural fiber-reinforced biocomposites, improved fiber/matrix surface compatibility.

Another family of biopolyesters, the PHAs, can be produced by controlled growth of certain bacteria under nutrient-limited conditions. The PHAs were first visualized in the laboratory of the French microbiologist Maurice Lemoigne in the 1920s, although their true nature was not then understood, as their discovery pre-dated the concept of macromolecules. Commercialisation of PHAs started as long ago as the 1960s with the introduction of the Biopol® product by ICI. This technology for manufacturing PHAs was subsequently handed down through several companies and is now in the hands of the US company Metabolix, which is currently establishing a large-scale PHA production facility in the US in a joint venture with the Archer Daniels Midland (ADM) company, known as Telles. Products are to be marketed by Telles under the trade name Mirel®. Although this venture is very significant in terms of PHA production overall, it should be mentioned that a recent survey indicates as many as 20 companies worldwide are now pursuing PHA commercialization. These companies are in operation either at pilot plant scale or are able to produce PHAs at levels of up to 10,000 tonnes/annum. An example of one of these companies is Meredian Inc., which has licenced the Nodax™ PHA copolymer technology previously developed by Procter & Gamble. Although many of the companies under development or already in operation are aiming to operate as raw material suppliers, packaging end-uses are seen as a key future application for PHAs as well as lower volume/higher value uses in medicine (*e.g.*, drug delivery, implants).

In addition to PLA and PHAs, thermoplastic starch-based polymers or polymer blends are now commercially available, and the Italian company Novamont is a leader in this field with its line of Mater-Bi® products. Starch is not a true thermoplastic polymer, but in the presence of plasticizers such as water or glycerol and at higher temperatures (90-180°C) under shear it readily melts and flows. The relative disadvantages of starch-based plastics are their water sensitivity and inferior mechanical properties; however, technical solutions are available through blending or through various forms of chemical derivatization or graft copolymerization. Commercially, starch-based packaging has been previously adopted by companies such as McDonald's and at high-profile international events such as the 2000 Olympic Games in Sydney, Australia. As well, other outdoor sporting events, festivals, and concerts often feature 'green' disposable cups, plates, cutlery and other utensils made from starch-based plastics. The use of such biodegradable and compostable (B & C) tableware, which is usually contaminated with food residues after use, allows a large amount of waste material to be composted rather than being disposed of by other means.

Complementing PLAs, PHAs, and starch, other biopolymers such as zein and gluten (proteins) as well as chitosan or forms of cellulose or cellulose derivatives have been investigated for their potential in various packaging-related products. Although water sensitivity can be an issue, these biopolymers have particularly interesting oxygen barrier characteristics that have attracted attention. Zein and its use, as an example, has been comprehensively covered in a review article (Lawton 2002). Moreover, as noted earlier, the generation of nano-forms of cellulose (*e.g.* cellulose whiskers or nanofibrillated cellulose) from wood, agricultural crops, or marine biomass continues to be an exciting research field with significant implications for the use of nanocellulose in packaging (*e.g.* as a biopolymer reinforcement or as a paper coating).

A number of other bio-based plastics have been developed and are either in use or have potential packaging uses. The first thermoplastic ever produced was cellulose nitrate, shortly followed by the acetate homologue. Cellulose-derived plastics are available to this day and are represented in the current market by, for example, Innovia Films with their Cellophane™ and Natureflex™ brands. Cellophane™, developed over 80 years ago, is widely used in specialty markets such as breathable packaging for baked goods and in Cellotherm™ ovenable and microwaveable packaging.

In addition to BIO-PE from Braskem, Dow, or Solvay and bio-polyurethane from Cargill, Dow or DuPont, there are other bio-derived or partly bio-derived plastics now making an impact in the food and beverage markets. One of the best-known examples is the Coca Cola Plantbottle™ which is based on PET and in which 20% of the carbon content derives from ethylene glycol obtained from bioresources.

Biodegradable plastics based on chemical synthesis (*i.e.* poly(glycolic acid), poly(lactic acid), polycaprolactone (PCL), poly(vinyl alcohol) (PVOH); products of microbial fermentation (*i.e.* polyesters and neutral polysaccharides) and compounds obtained from chemically modified natural products (*e.g.* starch, cellulose, chitin or soy protein) have also been covered in the literature (Flieger *et al.* 2003).

Thermal Stability of Polymers used in Bioplastics

During conversion by melt processing, polymers are subjected to elevated temperatures where the access of oxygen is prevented or very limited. This section deals with the thermal stability of biopolymers of highest relevance for the packaging industry (*i.e.* PLA, PHAs, nanocellulose, and starch).

PLA

The basic building block for PLA is lactic acid (2-hydroxypropionic acid), which is a three-carbon chiral acid naturally occurring mostly in the L(-) form. Hence, the abbreviation PLLA is often used, resulting in the polymer name poly(L-lactide). Although the terms polylactide and poly(lactic acid) seem to be used interchangeably in the literature, the use of the term polylactide is normally more appropriate, since this refers to the polymer synthesized from the lactide dimer by the more commonly used ring-opening polymerization (Fig. 3). In contrast, poly(lactic acid) would normally be used to describe the polymers synthesized by other methods, for example, polycondensation (Henton *et al.* 2005; Söndergaard and Inkinen 2011).

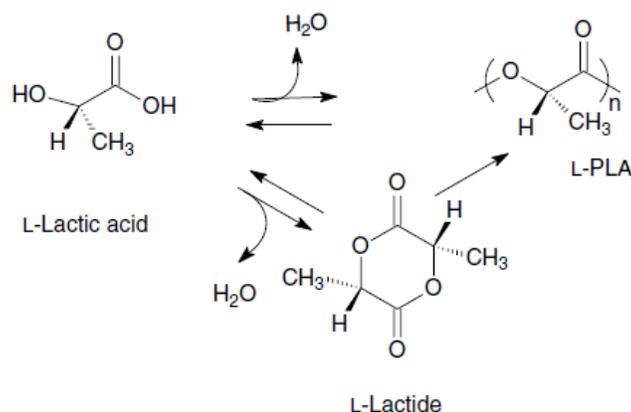


Fig. 3. Formation of PLA from lactic acid or lactide dimer

Although PLA can be processed on standard converting equipment with minimal modification, its unique material properties must be taken into consideration in order to optimize the conversion of PLA to molded parts, films, foams, and fibers (Lima *et al.* 2008). Although interest in wider use of PLA to produce packaging materials for food products is high, apart from technical challenges and relatively high cost, recycling also presents some challenges. PLA can be separated from PET by using infra-red scanning technology; however, the required infrastructure does not yet exist, and similarly, industrial scale composting facilities are still far from common. Given that the so-called skeleton waste from tray thermoforming can represent 50% of the incoming film, there is a clear need for cost-effective PLA waste utilization. This challenge is complicated by the molecular weight reduction that inevitably occurs when melt processing PLA. A technology for recovering monomers from PLA to be used for later PLA synthesis (LOOPLA) has been developed by the Belgian company Galactic and could be more extensively implemented if PLA volumes for recycling were sufficient.

One of the drawbacks of processing PLA in the molten state is its tendency to undergo thermal degradation, which is related both to the process temperature and the residence time in the extruder (Lima *et al.* 2008). The thermal degradation of PLA can be attributed to: a) hydrolysis of the ester linkages by trace amounts of water, which occurs more or less randomly along the backbone of the polymer, b) zipper-like depolymerization, c) oxidative, random main-chain scission, d) intermolecular transesterification to monomer and oligomeric esters, and e) intramolecular transesterification resulting in formation of monomer and oligomer lactides of low molecular weight. Above 200°C, PLA can degrade through intra- and inter-molecular ester exchange, cis-elimination, and radical and concerted non-radical reactions, resulting in the formation of CO, CO₂, acetaldehyde, and methylketene. It has also been proposed that thermal degradation of PLA can occur by way of a non-radical, “backbiting” ester interchange reaction involving the -OH chain ends. Depending on the point in the backbone at which the reaction occurs, the product can be a lactide, an oligomeric ring structure, or acetaldehyde plus carbon monoxide. At temperatures above 270°C, homolysis of the polymer backbone can occur. The formation of acetaldehyde is expected to increase with increasing process temperature, with the highest proportion formed at 230°C. Although acetaldehyde is

considered to be non-toxic and is naturally present in many foods, the acetaldehyde generated during melt processing of PLA must be minimized, especially if the converted PLA (*e.g.* container, bottle, and films) is to be used for food packaging. The migration of acetaldehyde into the contained food can result in off-flavors which will impact the organoleptic properties and consumer acceptance of the product (Lima *et al.* 2008).

Strategies to improve the melt stability of PLA can be found in various patents as reviewed by Lima *et al.* (2008). Polycarbodiimide (CDI) was observed to improve the thermal stability of PLA during processing. The results showed that addition of CDI at 0.1 to 0.7 wt% led to stabilization of PLA at 210°C for up to 30 min. Considering the mechanism, CDI could react with the residual or newly formed moisture and lactic acid, or carboxyl and hydroxyl end groups in PLA, and thus hamper thermal degradation and hydrolysis of this polymer (Yang *et al.* 2008). The melt stability of PLA may vary from supplier to supplier as a result of the different processes and technologies used (Lima *et al.* 2008).

PHA

The simplest of the PHAs (PHB and PHBV) are similar to PLA in terms of sensitivity to trace amounts of water, exposure to which can bring about hydrolysis of the ester linkages more or less randomly along the polymer backbone. Besides this, PHB in particular shows poor thermal stability at temperatures above the melting point, which is typically at or near 175°C (Hablott *et al.* 2008). Studies dedicated to thermal degradation of PHB and PHBV have revealed that thermal degradation occurs rapidly near the melting point, mainly due to a random chain scission process as depicted in Fig. 4 (Hablott *et al.* 2008).

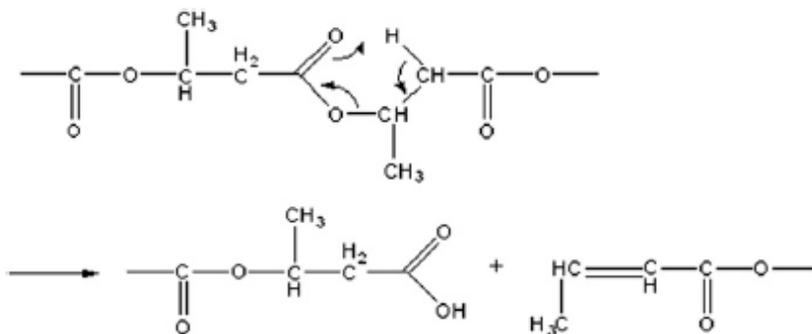


Fig. 4. Degradation of PHB by chain scission

It is interesting to note that, despite the structural similarities, the thermal degradation mechanism outlined above is not applicable to the degradation of PLA. The reason is that PHAs contain a labile hydrogen atom in the vicinity of the ester carbonyl (C=O) group. This labile hydrogen is not present in the structure of PLA, the result of which is that PLA is more thermally stable than the PHAs (Šimon 2011).

The influence of quaternary ammonium compounds (QACs) on the thermal and thermo-mechanical degradation of PHB has been studied. This is of interest because such surfactants are commonly used as organomodifiers in commercial nanoclays. Research

findings suggest that QACs can have a catalytic effect on the thermal degradation of PHB, as reflected by a dramatic decrease in PHB molecular weight (Hablott *et al.* 2008). In another study, the thermal degradation of poly(3-hydroxybutyrate) in the presence of two plasticizers (glycerol, glycerol triacetate) was investigated as a function of the annealing time, temperature, and cooling rate after thermal treatment. The presence of glycerol leads to a significant prodegradative effect on PHB, presumably due to an alcoholysis reaction, while glycerol triacetate (triacetin) behaved as an almost inert additive in this respect (Janigová *et al.* 2002).

Some additives can increase the thermal stability of PHAs. For example, addition of 1 wt% of carboxyl-terminated butadiene acrylonitrile rubber (CTBN) or polyvinylpyrrolidone (PVP) modified the crystallization rate, crystallinity, melting temperature, and thermal stability of PHB (Hong *et al.* 2011). The degradation kinetics of PHB were changed due to the steric hindrance effects of the added PVP. The best improvement in thermal stability was obtained in the case of the PVP-modified PHB. The method of using CTBN or PVP to improve the thermal stability of PHB could be useful industrially because it does not depend on a requirement for high purity PHB.

Nanocellulose

Nanocellulose, either in the form of NFC or chemically extracted cellulose whiskers, will thermally degrade at higher temperatures than PLA or PHAs. However, nanocellulose can contain considerable amounts of tightly bound water, which would bring about accelerated polymer degradation when using nanocellulose as filler in PLA or PHAs. For this reason, there has been much attention paid to processes for drying the nanocellulose raw material while retaining its nano-scale characteristics, a challenge that is inherently difficult with cellulose because of the agglomeration phenomena associated with capillary effects during drying.

In thermal degradation studies, cellulose nanowhiskers showed two well separated pyrolysis processes and degradation occurring over a temperature range from 220 to 280°C and also between 330 and 500°C, with initial moisture loss at 120°C. Untreated fiber exhibits a number of degradation steps at 110°C, with intermediate loss at 280°C and at 352°C. The degradation of hemicellulose is not observed for cellulose nanowhiskers due to the removal of hemicellulose during alkali treatment. Cellulose nanocrystals start to decompose at lower temperature than microcrystals due to the increasing number of free chain ends at the surface, which are liable to earlier decomposition. Thermal resistance can be increased by neutralizing the sulfate groups, which are a residue of the sulfuric acid treatment used in the nanowhisiker extraction process. The increase in the first degradation temperature, corresponding to moisture loss from the whiskers is attributable to the strong adhesion of water molecules in highly exposed nanowhiskers having large surface area (Pandey *et al.* 2008).

The thermal stability of dried NFC has been shown to decrease after homogenization and drying. Derivative thermogravimetric analysis (DTGA) showed a shoulder at around 250°C for dried NFC, corresponding to expected dehydration reactions in cellulose (Quiévy *et al.* 2010).

Starch

In a similar way to nanocellulose, starch can contain a large amount of strongly bound water, which is practically the only product evolved upon heating up to 200°C (Simon 2011). The chemical structure and thermal reaction pathway of four native and modified starch samples was studied after heating to 600°C. Chemical reactions started at around 300°C, generating ether and ethylene segments via thermal condensation and dehydration mechanisms. Heating at increased temperatures generated substituted phenol/benzene and furan structures with methylene or ether linkages between these aromatic rings. Varied thermal reactivity was observed for starch samples around 300°C due to differences in molecular weight, pH, or structural modification. However, the reaction pathways were thought to be similar. Above 400°C the starch structure was destroyed and the product appeared structurally similar to thermally cross-linked/decomposed phenolic/furfuryl alcohol resins; thereafter, the thermal reaction of the systems followed a similar pathway as these resins (Zhang *et al.* 2002). No significant differences in chemical structure were observed for the four samples after heating above 350°C, and identical carbon structures were generated at 600°C.

Mechanical Properties of Polymers used in Bioplastics

The application of biopolymers requires that the materials have sufficient stiffness and strength during their service life. Achieving that is difficult because of water sensitivity and relatively low strength, especially in moist environments. Polysaccharides (starch, cellulose) and hydrocolloids (pectin, alginate, carrageenan, protein) form strong films, but they have the ability to swell upon absorption of water, resulting in a considerable loss of mechanical properties (Rhim *et al.* 2007). Improvement of physical properties can be achieved by chemical modification (pH change, solvent change, salt addition, cross-linking etc.) or physical modification (*e.g.* by lamination, formation of composites, or addition of reinforcing particles).

The engineering properties of biobased plastics vary widely because of the wide range of biological starting materials. Most bioplastics have inferior mechanical properties at elevated temperatures when compared to petroleum-based plastics, but there are some exceptions (Smock 2011). The mechanical properties in terms of modulus are not very different than those of conventional polymers under ambient conditions. The modulus of bio-based polymers can range from 2500 to 3000 MPa, but is lower for thermoplastic starches and for rubbery materials like medium chain length PHAs. However, the modulus of most bio-based and petroleum-derived polymers can be tailored to meet required mechanical properties by means of plasticizing, blending with other polymers or fillers, by cross-linking or by the addition of reinforcing fibers (van Tuil *et al.* 2000).

In Table 2 the tensile properties of two commercial biopolyesters, polylactide (PLA) and polyesteramide (PEA), are compared to those of two petroleum-based polymers, polypropylene (PP), and polystyrene (PS) (Averous 2004; Auras *et al.* 2004; Vujković *et al.* 2007).

Table 2. Mechanical Properties of Biobased and Petroleum-Based Polymers

	PLA	PEA	PP	PS
Tensile strength (MPa)	44	17	35	49
Tensile modulus (GPa)	3.9	0.3	1.4	3.4
Strain at break (%)	5.4	420	100	10
Flexural strength (MPa)	88	-	49	80

Van de Velde and Kiekens (2002) have presented a review of the tensile properties of various biopolymers (Table 3). Specific tensile strength and specific tensile modulus were determined by dividing the mechanical properties by the polymer density. Specific properties become important as they determine the dimensions necessary for a certain mechanical strength or stiffness in a particular material use.

Table 3. Tensile Properties of Biopolymers: Polylactide (PLA), Polyglycolide (PGA), Polycaprolactone (PCL), and Polyhydroxybutyrate (PHB)

	PLA	PGA	PCL	PHB
Tensile strength (MPa)	21-60	60-99.7	20.7-42	40
Tensile modulus (GPa)	0.35-3.5	6-7	0.21-0.44	3.5-4
Strain at failure (%)	2.5-6	1.5-20	300-1000	5-8
Specific strength (Nm/g)	16.8-48	40-45.1	18.6-36.7	32-33.9
Specific modulus (kNm/g)	0.28-2.8	4-4.5	0.19-0.38	2.8-2.97

Among the polymers in Table 3, PGA has the highest density and also the highest tensile properties. PCL seems to be the weakest polymer with a high strain at failure. It is well known that the molecular weight of polymers can play an important role in determining the mechanical properties. An increase in molecular weight from 50,000 to 200,000 g/mol gives a tenfold increase in tensile strength for L-PLA (*i.e.* from 15.5 to 150 MPa) (Van de Velde and Kiekens 2002). Unfortunately, without modification the impact strength and thermal properties of PLA are not sufficient for some applications. Stereocomplex PLA produced from L-lactide and D-lactide is therefore being intensively investigated (Sudesh and Iwata 2008).

In order to lower the price and to enhance the biodegradation rate, PLA can be mixed with native starch. By adding 30 to 50wt% starch to PLA, the tensile strength decreases to about 60% and the strain at break to about 50% relative to that of pure PLA. Since PLA is a brittle polymer with low extensibility, decreasing its flexibility further reduces the usefulness of this polymer. The addition of coupling agents allows the adhesion between PLA and starch to be improved, thus resulting in strength properties near that of pure PLA (Kovach and Tabi 2011).

Many of the commercially important PHAs with properties resembling those of commodity thermoplastics are those that contain monomers ranging from 4 to 6 carbon atoms. The tensile modulus (3.5 GPa) and the tensile strength (ca. 40 MPa) of PHB are comparable to those of PP. However, the strain at failure is only 6%, whereas that of PP can be around 400%, reflecting the stiff and brittle character of PHB. The mechanical properties of PHBV are dependent on the molar ratio of 3-hydroxyvalerate (HV) to hydroxybutyrate. The value of the tensile modulus decreases with an increase of HV from 0 to 25 mol%, thus indicating that PHBV is more flexible than PHB. At the same time, PHBV is tougher, reflected by an increase in impact strength. With increasing content of

3HV over 30 mol% the tensile strength decreases and the copolymers become very soft (Sudesh and Iwata 2008).

The mechanical properties of biodegradable polymers can be tailored by blending or compounding with organic fillers. For example, wide application of unmodified starch plastics has been limited due to poor mechanical properties, such as film brittleness. However, by altering the amount of filler by weight percent in starch, the tensile strength and elongation or modulus of the resulting composition can be adjusted. For example, Wilhelm *et al.* (2003) found that the tensile modulus for starch/clay hybrids increased with the clay content, while strain at break decreased. The same effect (*i.e.* increase in modulus and tensile strength and decrease in strain), was obtained by de Cavalho *et al.* (2001) for starch plasticized with glycerol and various amounts of clay. Huang and Yu (2006) determined that at 8% filler content the tensile strength and modulus, and even the strain, increased for starch/MMT nanocomposites.

Biocomposites

Biocomposites have one or more of their phases derived from biological origins (*e.g.*, plant fibers from crops such as cotton, flax or hemp, or from recycled wood, waste paper, crop processing by-products, or regenerated cellulose fibers such as viscose/rayon). The matrix phase within a biocomposite may consist of a natural polymer, possibly derived from vegetable oils or starches. More commonly, however, synthetic fossil-derived polymers (virgin or recycled thermoplastics) act as matrices.

The majority of biocomposites are currently used in the automotive, construction, furniture, and packaging industries, where increasing environmental awareness and the depletion of fossil fuel resources are providing the drivers for development of new renewable products.

Over the last few years, many researchers have investigated the use of natural fibers as load-bearing constituents in composite materials. The use of such composites has increased due to their relative cheapness, the possibility of recycling or composting (depending upon the polymer used) without harming the environment, and because of their competitive specific strength properties (Bledzki and Gassan 1999; Saheb and Jog 1999; Mohanty *et al.* 2006; Avérous and Digabel 2006).

The use of lignocellulosic fibers potentially presents safer handling and working conditions when compared to the use of synthetic fibers. Bio-fibers are non-abrasive to mixing and molding equipment, which can also contribute to significant cost reductions.

The production of 100% bio-based composites as a substitute for petroleum-based products is still a challenge. Bio-resins (or bio-plastics) present some limitations. A viable solution would be to combine small amounts of petroleum-based resins with bio-based resins to develop a cost-effective product having higher performance and a wider range of applications. Agro-polymers (*e.g.* polysaccharides) obtained from biomass by fractionation, such as starch and cellulose, are the best known renewable resources available for making biodegradable plastics (Belgacem and Gandini 2011; Vazquez *et al.* 2011). Thermoplastic starch shows drawbacks such as a strong hydrophilic character (water-sensitive) and some post-processing variation of the properties. The mechanical properties of thermoplastic starch films depend strongly on the amylose/amylopectin ratio and the type and amount of plasticizer (Lourdin *et al.* 1995; Rindlav-Westling *et al.*

1998). However, starch composites with mechanical properties comparable to or even higher than those of conventional polymers have been reported (Krochta and De Mulder-Johnston 1997).

A large number of biodegradable polymers are commercially available. They show a wide range of properties and they can compete with non-biodegradable polymers in composite manufacturing. Vegetable oils from soybean, peanut, walnut, sesame, and sunflower have been exploited for this purpose (Xia and Larock 2010). Fish-oil based polymers (Li *et al.* 2000) have also attracted attention due to their high degree of unsaturation, good damping, and shape memory properties. Soy proteins have also been used in bio-plastics. Dried soy plastics display an extremely high modulus, 50% higher than that of currently used epoxy engineering plastics. So with a proper moisture barrier, soy protein is a potential starting material for engineering green composites, which show potential for rigid packaging as well as housing and transportation applications (Gällstedt *et al.* 2011).

Biocomposites – some innovative examples

The combination of natural fibers such as kenaf, hemp, flax, jute, henequen, pineapple leaf fiber, and sisal with polymer matrices from both finite and renewable resources to produce composite materials that are competitive with synthetic composites requires special attention (*i.e.* fiber–matrix interface and novel processing methods). By embedding natural fibers into bio-based polymers such as cellulose, polylactides, starch, PHAs, and soy-based plastics, so-called green bio-composites are routinely being produced (Mohanty *et al.* 2002).

Biocomposites based on regenerated cellulose fiber, pure cellulose fibers, pulp fibers or MFC (microfibrillated cellulose) incorporated in polymer matrices like PVOH or PLA have been described by Cheng *et al.* (2007).

The layer by layer technique (LBL), first described by Decher and colleagues in the 1990s (Decher *et al.* 1992), can be used to create composite materials based on cellulose whiskers, and a polar polymeric matrix (such as chitosan) allows the formation of a dense and homogeneous structure. Similar structures (green composites) can be obtained from cellulose nanocrystal/xyloglucan multilayers. More recently, biodegradable nanocomposites were obtained via the LBL technique using highly deacetylated chitosan and cellulose whiskers (de Mesquita *et al.* 2010; Jean *et al.* 2008) or by using chitosan and montmorillonite clay overlaid on PLA film (Svagan *et al.* 2012). Application of the LBL method to coating of paper has also been described (Zheng *et al.* 2006).

Cellulose nanoparticles prepared by drop-wise addition of ethanol/HCl aqueous solution into an aqueous NaOH/urea solution prepared from MCC (microcrystalline cellulose) have been shown to improve the thermal stability, tensile strength, and the water vapor barrier properties in composite glycerol-plasticized starch films (Chang *et al.* 2010).

Compatibility between filler and matrix in biocomposites

Although the use of natural fibers to reinforce plastics has many advantages, the composite properties do not always meet the material requirements of the desired applications. One reason for this is weak adhesion between hydrophilic fibers and

hydrophobic matrix materials. One of the most common solutions to the problem is the use of maleic anhydride (MAH) as a compatibilizer, to improve the adhesion between fibers and the polymer matrix. In a project funded by Tekes (the Finnish Funding Agency for Technology and Innovation) entitled ‘Biocomposites as constructive materials-BIKO’, MAH was grafted onto PLA using peroxide as an initiator. Samples were extruded using a Brabender single-screw extruder. Composites with 30 wt% fibers were reported to have a tensile strength of 78 MPa and an elastic modulus of 8 GPa.

The use of lignin as a coupling agent in natural fiber composites has also been studied. Lignin can act as a compatibilizer between the hydrophilic fibers and hydrophobic matrix polymer, thus strengthening the fiber-matrix interface. Lignin treatment of flax fibers (Peltola 2010; Thielemans *et al.* 2002) has been shown to improve compatibility between fibers and a thermoset matrix, thus also improving the mechanical properties of the composites.

In one study, flax fibers were treated with pine kraft lignin and/or lignosulfonate solutions. Alkaline aqueous solutions of 1% or 3% pine kraft lignin were prepared. Addition of NaOH to pH >11 was required to dissolve the water-insoluble kraft lignin. Water solutions with 1% lignosulfonate were prepared by mixing. Flax fibers were immersed in the solutions for 10 minutes and the excess water was then extracted by spin-drying, followed by drying in a hot air dryer (Peltola 2010; Thielemans *et al.* 2002). For composite production, Ingeo™ 3001D grade PLA (NatureWorks, USA) was used as a matrix polymer. Composites containing 30 wt% fibers were produced using a co-rotating twin-screw extruder (Berstoff ZE 25x33D). The compounds were then processed through an injection moulding machine (Engel ES 200/50 HL) into tensile test specimens, followed by normal mechanical testing of the specimens (ISO-527, ISO-179). NaOH treatment of flax fibers improved the impact strength of the PLA composites, probably due to the roughening of the surface of the fibers. The addition of small amounts of kraft lignin (1% solution) maintained the impact strength values and clearly improved the tensile strength and strain at break of the composites, thus compatibilizing the material. When more kraft lignin was added, a decrease in mechanical properties was seen, so the optimum lignin content in the solution was less than 3%. The influence of different coupling agents on the mechanical properties of composites, expressed as percentage differences compared to untreated composites, is presented in Table 4. The results demonstrate the potential of some reinforcement strategies for biocomposites, which may be useful for future packaging development.

Table 4. The Influence of Coupling Agents on the Mechanical Properties of PLA/flax Composites (30 wt% fibers). Data from Peltola (2010).

Coupling agent	Tensile strength (%)	Elastic modulus (%)	Strain at break (%)	Impact strength (%)
0.25% MAH 0.25% peroxide	23	4	65	28
1% Kraft lignin (pine)	14	4	28	62
1% Lignosulfonate	7	-5	52	59

PAPER-BASED PACKAGING

Coating renewable polymers onto a paper or paperboard supporting substrate is generally advantageous when compared to self-supporting bioplastic materials, because sufficient mechanical strength is easily achieved through the paperboard, which itself is bio-based, recyclable, and biodegradable. Paper and board comprises the largest market share (42%) for primary and secondary packaging material in Europe, according to the Global Packaging Alliance (2011), followed by plastics (36%), metal (14%), and glass (8%). However, key challenges include improving the strength of the paper material, enhancing its resistance to moisture, reducing the weight of material (less raw material use), maintaining functionality, and imparting barrier properties or other functionalities. Up-scaling novel solutions developed in the laboratory to industrially feasible and economically viable applications is a key requirement, covering all steps from material supply to converting machinery.

Fiber-based packaging has a variety of uses and applications, providing an essential element throughout all supply chains. The fibers in paper and board provide strength and structure to packaging materials. Chemical additives to the fiber suspension combined with coating applications provide the opportunity for high quality printing, grease/oil resistance and a variety of additional barrier properties that enhance the final package quality.

Paper and Paperboard – Challenges, Opportunities and Targets

At present, there are more than 40 packaging products based on nanotechnology on the market, compared to the 400 traditional products currently used. Forecasts of the market for packaging materials containing nanostructured compounds are quite promising (from 360 million USD in 2008 to approx. 20 billion USD in 2020). Among them, paper and paperboard packaging is an important growing area as a result of the high degree of recyclability and biodegradability compared to metal and plastic packaging (Kerry and Butler 2008). The market value of paper and paperboard in Western Europe was forecast to grow by about 8% from 2009 to 2014 (Datamonitor 2010a). The market value for wrapping and paper packaging in Europe is about 33 billion USD (2009) and is forecast to grow by about 23% until 2014 (Datamonitor 2010b). The largest market segment is food and beverage packaging, which accounts for almost 60% of the market's total value.

A number of factors have combined to create renewed interest in recyclable barrier coatings as an alternative to waxed packaging. A recyclable barrier coating must provide equivalent functionality at competitive cost. At present, for environmental and economic reasons, demands for smaller, lightweight packaging built up from a “monomaterial” structure, as opposed to extrusion-coated and waxed products, has evolved. A new generation of recyclable barrier-coated products must also address environmental concerns about recovery and recycling. These products must be repulpable, biodegradable, reprocessible, result in lower energy consumption, and treatment chemicals should be recoverable. Recyclable barrier coatings will be of greatest value in the manufacture of a number of important products, especially for packaging.

When making media for use in recyclable wax barrier replacements, special size press treatments are used (*e.g.* by lignosulfonate or starch cross-linked with glyoxal that provide adequate performance for recyclable barrier-coated packaging) (Klass 2007b).

For the alternatives to be more cost-effective than wax and to find wide industrial acceptance, it would be desirable to reduce the required amount of coating weight. Opportunities may lie in linerboard surface treatments such as calendering, low impact coating applications, and the pre-treatment of linerboard surfaces through more economical pre-coatings. Such coatings may incorporate the use of plate-like mineral pigments (Popil and Schaepe 2005). Hyper-plate-like clays with the potential to partially replace latex in base coat formulations have proven to be effective in terms of water resistance and are thus interesting as a recyclable alternative to wax-impregnated board, which typically goes to landfill after use (McLain and Walround 2010). Substitution of fibers in the substrate and potential reduction of basis weight is another application of such plate-like kaolin clays, which requires less energy for drying and thus results in a lower total carbon footprint in the products (McLain and Walround 2010).

Barrier Properties of Paper and Paperboard

Barrier properties are a fundamental requirement for fiber-based packaging materials, to protect the packaged goods, to prolong the shelf life of packaged food, and to prevent product loss during the lifetime of the packaging. Improvement of the barrier properties of paper and paperboard is usually related to the use of specific coatings, additives, or sizing agents that can act as barriers to characteristic compounds such as water, oxygen, grease, or aromas. In this way it is possible to reach barrier properties that cannot be obtained just through changes in or refinement of paper processing protocols.

Typically, barrier coatings are based on oil-derived polymers, which inevitably increase the carbon footprint of the final packaging and endanger its biodegradability. New bio-materials with adequate barrier properties are therefore needed to obtain paper-based renewable packaging that can compete with the oil-derived materials that are used today. In this regard, the sustainable improvement of the barrier properties of paper is closely related to research focused on the development of new biopolymers with high barrier properties, since this represents a highly appealing application for most of these materials. The state-of-the-art in this field of biopolymer applications has been reviewed in a recent book chapter (Aulin and Lindström 2011).

It is well known that the association of biopolymers to paper provides interesting functionalities while also maintaining the environmentally friendly characteristics of the material. Renewable biopolymer coatings can surely act as gas and solute barriers and complement paper, as well as other types of packaging, by minimizing food quality deterioration and extending the shelf life of degradable products (Andersson 2008; Debeaufort *et al.* 1998; Khwaldia and Arab-Tehrany 2010; Butinkaree *et al.* 2008; Miller and Krochta 1997).

Among the continuously increasing number of studies related to new barriers from biodegradable and sustainable materials, only a limited number are already focused on paper coating applications and have reported results for the barrier properties of paper-based composite materials for packaging applications. The attention in research reports is often focused mainly on the properties of self-standing films, with the idea that coatings

with similar properties can be easily obtained on paper or different substrates. As a consequence, relatively few publications describe the direct characterization of paper coatings, even if bio-materials such as whey proteins (Han and Krochta 1999; Han and Krochta 2001; Lin and Krochta 2003; Gällstedt *et al.* 2005) isolated soy proteins (Park *et al.* 2000; Rhim *et al.* 2006), caseinates (Khwaldia *et al.* 2004, Khwaldia *et al.* 2005; Khwaldia 2010), wheat gluten (Gällstedt *et al.* 2005; Guillaume *et al.* 2010), corn zein (Parris *et al.* 2000; Trezza *et al.* 1998; Trezza and Vergano 1994), chitosan (Gällstedt *et al.* 2005; Kjellgren and Engström 2008; Kjellgren *et al.* 2006), alginate (Rhim *et al.* 2006), starch (Laratonda *et al.* 2003; Matsui 2004), and cellulose derivatives (Havimo *et al.* 2011; Aulin *et al.* 2010; Hult *et al.* 2010) have already been investigated as barrier coatings for paper packaging.

In the present section a brief report on these studies will be presented, focusing attention on those bio-materials that have explicitly been tested for the improvement of paper barrier properties. Some general conclusions are, however, valid for biopolymers used in films and bioplastics as well.

The barrier properties of interest for paper and paperboard packaging are usually focused on oxygen, water vapor, and aroma permeability, which are essential to extend the shelf life of fresh foods as well as for other biodegradable or water-sensitive products. For a similar reason, grease resistance and hydrophobicity are of importance for many applications of paper and paperboard packaging and are commonly measured to define the general characteristics and potentialities of new materials. For all these properties, standardized measurement protocols exist that allow definition of the barrier properties of the different materials and comparison on a common basis.

In the case of oxygen permeability the oxygen transmission rate (OTR) is defined as the amount of oxygen that permeates through the material per unit time and unit area and is usually measured at various relative humidities, following methods such as those outlined in ASTM D3985-05 or ASTM F1927-07.

The water vapor transmission rate (WVTR) is defined as the amount of water vapor that is transmitted through a material per unit time and unit area. Different standards exist for its measurement, such as ASTM E 96, ISO 2528, TAPPI T 448, and T 464. Since the permeability of hydrophilic materials such as paper and bio-based polymers is strongly affected by temperature and humidity, WVTR and OTR values should always be accompanied by a note about the test conditions (*i.e.* temperature and relative humidity).

Concerning water absorption, the Cobb test (ISO 535) is usually considered, which gives a measure of the mass of water absorbed on a test area over a specified time (typically 60 s). Grease resistance methods are usually related to the observation of stain on the surface of the paper after contact with an oil or greasy substance (TAPPI T 454, T 507 and UM 557). Other methods exist for those materials for which the grease or oil resistance is given by means of a coating or internal treatment (ISO 16532-1 and 2).

Improvement of the barrier properties of paper

Due to extreme variations in film/coating thickness, application techniques, measurement conditions etc., it is very difficult to provide comparable literature data on barrier properties for various materials. However, typical oxygen and water vapor

permeability values for a variety of polymers can be found in Weber (2000b) and Noller *et al.* (2011), whereas some data for barrier-coated paper is presented, for example, in a review by Andersson (2008). Bio-based polymers such as thermoplastic starch or PLA present water vapor permeability values higher than those of conventional polymers such as polyethylene (HDPE) or polypropylene (PP), and higher oxygen permeability values than polymers such as PVOH or ethylene vinyl alcohol (EVOH). Therefore, for wider adoption in the packaging industry a significant improvement in the barrier properties of bio-based polymers is needed. The main routes to improve the gas barrier properties of biopolymers are discussed in the sections below and can be divided as follows:

- i) Development of nanocomposites
- ii) Surface chemical modification of biodegradable polymers by grafting or other innovative techniques
- iii) Use of biodegradable coatings or multilayers on paper or other substrates

Many materials have been and are currently studied to improve the barrier properties of paper while avoiding detrimental environmental impacts from the resulting packaging. Some of these materials have been known for a long time and are already used in the packaging and paper industries, while others have become particularly attractive in the last few years due to their intrinsic sustainability and their relative abundance as by-products from other processes. These materials can generally be grouped in three different families (*i.e.* proteins such as whey, wheat gluten and zein, polysaccharides like chitosan, starch and cellulose, and polyesters such as PLA, PCL and PHAs).

Proteins have been of interest for a long time because of their film-forming ability and their potential for use in food packaging applications. Concerning barrier properties, protein-based films often have very low OTR but high WVTR due to their intrinsically hydrophilic nature. Studies on the application of proteins as barrier layers on paper and paperboard have been made with whey protein/sodium caseinate as well as with wheat gluten, soy proteins, and zein.

Whey protein (both isolated and concentrated) was studied as a paper coating by Krochta and coworkers (Han and Krochta 1999; Han and Krochta 2001; Lin and Krochta 2003; Chan and Krochta 2001). These researchers analyzed the influence of whey protein on the barrier properties and grease resistance of paper and paperboard. Whey protein coatings were found to consistently reduce the water vapor permeability and, when high enough coat weight was used ($>10 \text{ g/m}^2$), to act as an effective grease barrier. Low application levels (*e.g.* 2 g/m^2) were not sufficient to obtain a continuous coating on the paper surface, as observed by Gällstedt and others (2005). Among the different plasticizers considered in order to obtain smooth films on the paper surface, glycerol was found to cause long-term failure of the whey protein-isolated coatings, possibly because of its migration in the paperboard. The addition of other additives, such as sucrose, on the other hand, allowed good and stable grease resistance to be imparted to isolated and less expensive concentrated whey protein coatings (Lin and Krochta 2003).

Khwalidia *et al.* investigated the improvement of the barrier and mechanical properties of paper coated with sodium caseinate, a milk protein, with or without paraffin wax (Khwalidia *et al.* 2004) as well as in combination with other additives such as glycerol, mica, and carnauba wax (Khwalidia *et al.* 2005). The addition of sodium caseinate allowed the water vapor barrier to be improved, while the presence of wax brought about a further improvement only when coated as an independent layer. The addition of wax to caseinate in a composite coating led to a decrease of the barrier properties. In multi-component composite coatings on the other hand, a reduced WVTR was obtained by increasing the amount of wax and mica and by decreasing the percent of glycerol.

The use of wheat gluten as a barrier coating on paper-based materials has been considered by different authors (Gällstedt *et al.* 2003; Khwalidia 2010; Gastaldi *et al.* 2007; Chalier *et al.* 2007) who found interesting results in terms of aroma and water vapor barrier properties. For example, Guillaume *et al.* (2010) showed a decrease of up to 56% in WVTR and a 400-fold reduction in oil wettability for wheat gluten-coated paper when compared to uncoated paper. Gällstedt *et al.* (2005) found that the oxygen permeability of compression-molded wheat gluten films on laboratory paper sheets was in line with that of synthetic films such as oriented PET. Chalier *et al.* (2007) studied the permeation of aroma compounds in wheat gluten-coated paper and found a general increase in barrier properties of the coated paper, which were maintained at high relative humidities and at which the coated paper showed aroma barrier properties higher than those of low density polyethylene (LDPE) for all the compounds tested.

Soy protein-coated paper was tested by various researchers and found to be potentially suitable for use in commercial food packaging. In particular, Park *et al.* (2000) observed interesting improvements in the oil barrier characteristics of soy protein-coated paper, while a study by Rhim *et al.* (2006) showed that soy protein coatings have superior properties with respect to alginate films as far as water resistance and moisture barrier are concerned.

Corn zein is used as a basis for edible films to protect food from oxygen, moisture and grease, but has also been tested as a paper coating. Trezza and Vergano (1994) and Trezza *et al.* (1998) tested the grease resistance as well as the barrier properties of zein coatings and found that good grease resistance and a decreased WVTR could be obtained when adequate coat weight was used to obtain a continuous layer on the paper sheet. Oxygen permeability values, on the other hand, could not compete with those of other materials currently used in packaging applications. Similar results were also obtained by Parris *et al.* (2000), who measured WVTR and grease resistance of a Kraft paper spray- or brush coated with zein. A recent book chapter provides an overview of the state of development of protein-based films and coatings (Gällstedt *et al.* 2011).

Among the polysaccharides, chitosan has been studied extensively for application as a barrier coating (Gällstedt *et al.* 2003; Kjellgren and Engström 2006; Kjellgren *et al.* 2006; Bordenave *et al.* 2007; Bordenave *et al.* 2010; Gällstedt and Hedenqvist 2006; Ham-Pichavant *et al.* 2005). This biopolymer has good film-forming properties and high surface compatibility with paper, which together with its intrinsic barrier and anti-microbial properties make it highly attractive for coating applications. Among the different studies, various methods for coupling chitosan with paper, either through the

addition of this polysaccharide directly to the pulp or by use of techniques such as rod and curtain coating, have been investigated (Gällstedt and Hedenqvist 2006; Gällstedt *et al.* 2003; Kjellgren *et al.* 2006). In the first case, only cast films obtained from pulp/chitosan mixtures showed interesting barrier properties, since other approaches using a handsheet mould led to a general decrease in mechanical and barrier properties with respect to the original paper. It was found that a general increase of the barrier properties could be obtained with a chitosan coating weight higher than 5 g/m² when using rod coating techniques, while curtain coating on paperboard, even at low coat weights, led to oxygen permeability values similar to those of oriented PET. Grease resistance was also improved by chitosan coating, while Cobb₆₀ values were substantially unchanged or increased due to the hydrophilicity of the coating materials. The hydrophilicity and water vapor barrier properties of chitosan-coated paper were also investigated by Bordenave *et al.* (2007; 2010). These researchers noticed that, despite the hydrophilic character of chitosan, the WVTR decreased by up to 62.5% after the addition of a chitosan coating to the original paper. Coating with emulsions of chitosan and hydrophobic compounds such as palmitic acid was also considered as a way to increase water resistance. The presence of palmitic acid did not reduce the water vapor permeability of the chitosan coating, but it substantially improved the water resistance as measured by contact angle, which maintained the value observed in the original paper sheets.

Starch (Laratonda *et al.* 2003; Matsui 2004; Laratonda *et al.* 2005; Jonhed *et al.* 2008) is used in native or modified forms to improve paper properties, including physical strength, oil/grease resistance, and optical properties. Among different modifications, starch acetate is one of the most commonly used in order to decrease paper hygroscopicity. Paper impregnated with starch acetate has shown significant reduction in water absorption (Laratonda *et al.* 2003, 2005; Fringant *et al.* 1998). Improvements related to starch impregnation or coating have also been found in terms of water vapor permeability, which was related to reduction of both solubility (starch being less hygroscopic than paper) and diffusivity (since starch acetate seems to impregnate the paper substrate and partially fill both superficial and internal pores, thus decreasing the number of open pores available for water vapor transfer) (Laratonda *et al.* 2005). However, values of WVTR were still not comparable with those obtained using LDPE coatings (Fringant *et al.* 1998).

The mixture of starch and mineral pigments with high aspect ratio (highly plate-like) particles applied in thin layers on paper or board surfaces results in good water-, oil- and air barrier properties, thus keeping the freshness of packed products. For this purpose, Imerys (Paris, France) has developed two new barrier kaolins. These hyper-platy particles with nano-dimensional thickness create a tortuous path in the coating structure that inherently resists penetration of low molecular weight substances. Incorporating these kaolins in a formulation reduces cost while enhancing barrier performance (Ostle 2008). Water-based suspensions of polymer-clay nanocomposites are expected to provide the coating layer with excellent physical and barrier properties if the clay platelets with a high surface area are well dispersed (exfoliated) in the polymer matrix, thereby increasing the diffusion path tortuosity (Sun and Joseph 2007).

There are a few reports in the literature concerning the potential of alginate coatings to improve barrier properties to water, either used alone or in combination with

other bio-materials such as chitosan (Rhim *et al.* 2006; Ham-Pichavant 2005). Results show that this bio-material is not able to reduce the water resistance of paper, but has some synergistic effects when used in combination with chitosan, definitely increasing the fat resistance of the substrate with respect to the use of alginate or chitosan alone (Ham-Pichavant 2005).

Cellulose is the basic component of paper, and it can sound strange to use it as a coating on paper itself; however, a number of cellulose-based materials (hydroxypropyl cellulose and long chain cellulose esters) or cellulose derivatives (nanowhiskers or nano-fibrillated cellulose) have been produced lately which can be used to surface finish paper and to improve its properties (Havimo *et al.* 2011; Aulin *et al.* 2010; Hult *et al.* 2010; Belbekhouche *et al.* 2011; Minelli *et al.* 2010; Syverud and Stenius 2009; Sothornvit 2009). Among the different materials, nano-fibrillated cellulose (NFC), has shown very interesting barrier properties (Hult *et al.* 2010; Plackett *et al.* 2010, Syverud and Stenius 2009; Sothornvit 2009) and has been used in different studies related to paper coating (Aulin *et al.* 2011; Hult *et al.* 2010; Syverud and Stenius 2009). In particular, it was shown that carboxymethylated NFC can lead to very high barrier properties, provided that it completely covers the paper surface. Indeed, tested papers coated with a few grams of NFC per square meter showed a decrease of up to six orders of magnitude in air permeability and also showed increased grease resistance (Hult *et al.* 2010). In this regard it should be noted that carboxymethylation seems to play an important role in the definition of NFC barrier properties, since NFC obtained without such treatment gave discontinuous coatings even at higher coat weights, so that the final paper showed a decrease in air permeability of less than two orders of magnitude and OTR values were well above those measured for pure NFC films (Aulin *et al.* 2010; Syverud and Stenius 2009). However, not only the coat weight but also the interactions between the coating layer and the base paper determine the final barrier properties.

Biodegradable polyesters such as PLA and the PHAs have been widely studied for their possible application in the paper and packaging industries; however, there have been only a limited number of studies related to their properties when used as paper coatings. In the case of PLA, for which extensive literature reports are available, only a few studies concerning its use as a coating can be found. In one study on improved water resistance of PLA-coated paperboard (Rhim *et al.* 2007), the researchers found that PLA effectively reduced both water absorptivity and WVTR and that a coat weight of about 50 g/m² was needed to obtain optimal performance. On the other hand, Krook *et al.* (2000) studied the properties of paperboard coated by compression molding with different biodegradable polymers such as PCL, PHBV, and a liquid crystalline copolyester (LCP). The water vapor barrier was improved for all materials, with the LCP providing the best results. Blends of pulp fibers with PLA and PHB have been investigated, but the polymer fraction needed to obtain improvements in properties such as water absorbance is generally too high (70% wt) to be of practical interest.

In another interesting example, paper coated with PVOH reinforced with cellulose nanocrystals showed reduced WVTR (Paralihar *et al.* 2008; Choi and Simonsen 2006). Other examples of the nanocomposite approach to improvement of barrier properties include fillers of different chemical compositions and morphological structures, such as modified clays, natural fibers, cellulose whiskers, or microcrystalline cellulose in

different matrices such as PVOH (Kvien and Oksman 2007; Sriupayo *et al.* 2005), PLA (Bondeson and Oksman 2007; Tingaut *et al.* 2010), PHAs (Wang and Sain 2007), chitosan (Wian *et al.* 2009), or starch (Mathew and Dufresne 2002).

The TEMPO oxidation technique aimed at using bio-based reinforcements with hydrophobic polymers is a new method that is displaying useful results. One example is the use of TEMPO-oxidized cellulose whiskers incorporated in PLA, which reduced the WVTR of the membranes (Paralika *et al.* 2008). In another study, TEMPO-modified NFC was coated on PLA films, leading to a reduction of OTR from 746 to 1 $\text{cm}^3/\text{m}^2 \cdot \text{d} \cdot \text{Pa}$ compared with a pure PLA film or a PLA film coated with unmodified NFC (Fukuzumi *et al.* 2009).

A recent study showed that the incorporation of sulfonated cellulose whiskers obtained from softwoods reduced the WVTR of xylan/sorbitol films (Saxena and Ragauskas 2009).

Starch and nanoclay – An innovative approach

It is now well established that the effective dispersion of swelling clays into polymer matrices can offer a unique property profile. The incorporation of this type of additive offers demonstrated enhancement of the mechanical, barrier, and fire-resistance properties of the host polymer (Utracki 2004). Previous studies aimed at combining starch, plasticizer, and clay have largely been directed towards the formation of self-supporting, thermoplastic starch films and the activity in this direction has recently been the subject of an informative review (Chivrac *et al.* 2009).

Recent activities within two EU-funded projects aimed at developing sustainable packaging, SustainPack and FlexPakRenew, have focused on the incorporation of swelling clays into starch-plasticizer formulations to improve their barrier properties when coated on paper and board. The successful results obtained from the work on this concept within SustainPack led to the submission of a joint patent application among the researchers involved. The outcome of this research effort has been the development of laboratory-scaled coatings which routinely offer WVTR values as low as 15 $\text{g}/\text{m}^2 \cdot \text{d}$ at 23°C and 50% RH. The coating formulations developed are composed of readily available materials with a guaranteed supply. Moreover, the formulations are in themselves robust in that similar WVTR values can be obtained using selected combinations of different starches, plasticizers, and clays.

This brief summary will illustrate how critical it is to identify the correct combinations of clay and plasticizer to be used with the chosen starch matrix. In some cases the clay acts as a compatibilizer and coerces particular pairings of starch and plasticizer to form coherent coatings, a feat that is not possible in the absence of clay.

The substrate used was a low basis weight paper (40 g/m^2) with a WVTR value of 870 $\text{g}/\text{m}^2 \cdot \text{d}$. These and all subsequent WVTR values were obtained at 23°C and 50% RH. When this paper was coated twice with one of two different starches, here denoted S1 or S2, the WVTR values were reduced to 320 and 256 $\text{g}/\text{m}^2 \cdot \text{d}$ respectively. The addition of a plasticizer denoted P1 to starch S1 almost destroyed the barrier properties, causing the WVTR to increase to 673 $\text{g}/\text{m}^2 \cdot \text{d}$. Plasticizer P1 also exerted a negative influence on starch S2, but the effect was considerably less dramatic, causing the WVTR to increase from 256 to 286 $\text{g}/\text{m}^2 \cdot \text{d}$.

Figure 5 presents indicative data, selected from an extensive range of samples, in which four different commercial bentonite clays, here denoted Ben 1-Ben 4, were incorporated into starches S1 and S2 before and after plasticization with P1. It is immediately evident that the incorporation of Ben 1 and Ben 2 significantly reduced the WVTR of starches S1 and S2, whereas Ben 3 and Ben 4 had the opposite effect. This was particularly noticeable in the absence of plasticizer but it is important to note that all combinations of starch, plasticizer and clay acted to reduce the WVTR. In fact, the effect of adding Ben 1 to a mixture of S1 and P1 was phenomenal – reducing the WVTR from 673 to ca. 15 g/m²·d.

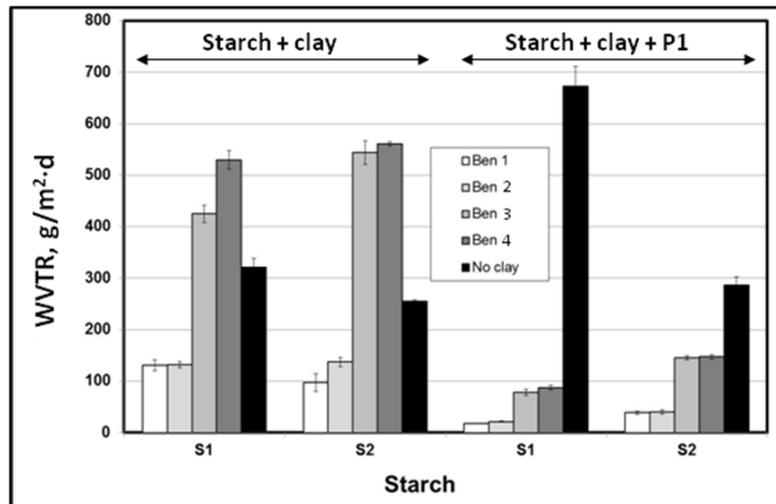


Fig. 5. WVTR values obtained at 23°C and 50% RH for selected combinations of starch, plasticizer and clay coated on low basis weight paper at a coat weight of 15-20 g/m²

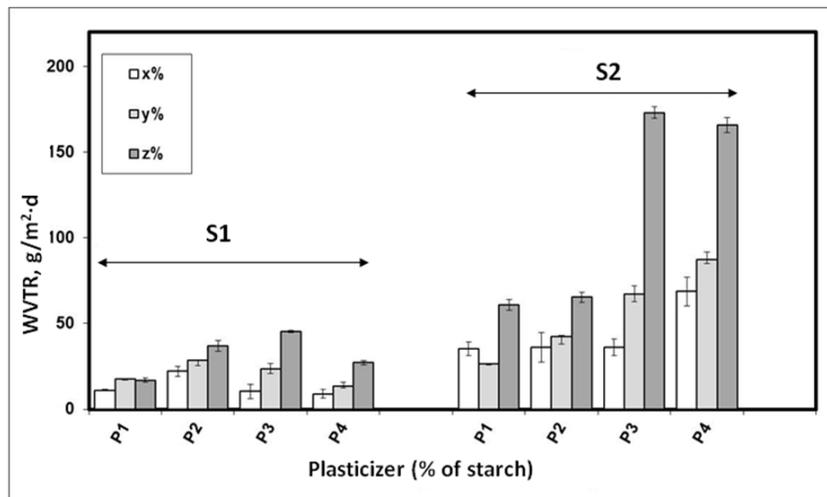


Fig. 6. The effect of different types and quantities of plasticizer on the WVTR values, obtained at 23°C and 50% RH, for starches S1 and S2 containing Ben 1

Figure 6 illustrates how important it is to select the correct combinations of starch, plasticizer, and clay. It is clear that coatings involving starch S1 provided the highest

barrier properties, with WVTR values between 45 and 10 $\text{g/m}^2\cdot\text{d}$. Combining S1 and P1 with Ben 1 provided the most robust formulation in that the different levels of plasticizer exerted relatively little influence on the final WVTR value. In contrast, starch S2 was considerably more sensitive to the nature and quantity of plasticizer with which it was combined, resulting in WVTR values which varied from 173 to 27 $\text{g/m}^2\cdot\text{d}$.

These laboratory-scaled coatings are undergoing trials at the pilot scale and the results are encouraging. Nonetheless, there are still issues to be addressed, including the resistance to creasing and bending together with challenges associated with heat sealability and printability.

Multilayer Coatings for Paper and Paperboard

To meet high demands for barrier properties with respect to water vapor, oxygen, and grease resistance, the formation of a multilayer structure is often necessary. Multilayered structures are well established in the packaging sector, one common example of which is the combination of PE with aluminum foil as an oxygen- and light protection layer. The development of new materials and new processes however requires new solutions. For example, biopolymer coatings with high oxygen barriers and fat resistance can be combined with a hydrophobic top coating to give the required water vapor barrier. Figure 7 shows a schematic sketch of a multilayer structure like the one investigated in the FlexPakRenew project (Guérin 2011). The functional layer can provide, for example, antimicrobial properties. Other structures are coatings containing a gas absorbing substance for active packaging (Eckl 2009).

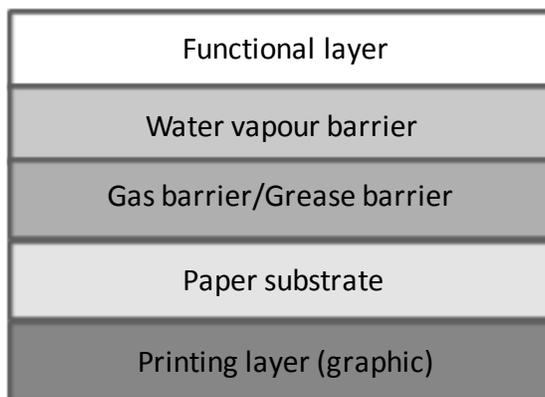


Fig. 7. Typical multilayer coating structure.

Schönweitz and Schmidt (2006) presented multilayer structures in which a starch coating was sandwiched between a styrene-butadiene/clay pre-coat and a barrier latex top coat. A substantial decrease in WVTR was obtained with each subsequent layer when applied onto a paperboard substrate. The final multilayer structure showed excellent fat resistance and water vapor barrier as well as oxygen barrier properties approaching the requirements for a variety of food types.

Santarella (2006) demonstrated the successful application of a gelatin coating on a low grammage base paper. Combined with a top coating of barrier latex, both low WVTR and high grease resistance were achieved. However, the OTR value was extremely high.

Multilayer coatings involving a bio-based, moisture-sensitive layer protected by an organic nanolayer applied by grafting alkyl chains to the surface -OH groups via a novel technique named chromatogeny has recently been demonstrated (Noller *et al.* 2011). The reaction renders the surface hydrophobic by the formation of fatty acid esters in a solvent-free process. A significant reduction in WVTR for coatings of various starch derivatives was found both at normal (23°C and 50% RH) and at tropical (38°C and 90% RH) conditions after grafting with a fatty acid containing 18 carbons.

Physical vapor deposition of inorganic nanolayers on polymer substrates has been shown to reduce the water vapor and oxygen transmission rates by a factor of 1000 (Noller *et al.* 2011). The surface roughness of the substrate and the evaporation of residual water during the vacuum process were found to be factors limiting the successful application of the technique. The second factor demonstrated the inherent brittleness of starch coatings (*i.e.* loss of plasticizing water caused cracks). This drawback could be overcome by further development of a pre-conditioning and re-moistening process.

A multilayer coating of NFC and shellac resin on paper substrates resulted in substantially decreased air permeance and oxygen transmission rate. Water vapor transmission rates corresponding to values considered in the high barrier category (*i.e.* close to 5 g/m²·d in food packaging) were reached (Hult *et al.* 2010).

A recent LCA approach to multilayered packaging structures showed that a bio-based, starch-clay composite coating combined with a thin inorganic nanolayer was favourable, in terms of greenhouse gas emissions (CO₂ equivalents), when compared to a PET/aluminum laminate applied on the same paper substrate (Hohenthal and Veuro 2011).

CONCLUDING REMARKS

Current trends in the packaging industry are towards lighter weight packaging materials for reduction of raw material use, transportation costs, and reduction of waste. Interest in renewable and recyclable materials combined with reinforcing fillers will continue to grow. With increased volumes the production costs are also likely to become more competitive. In terms of renewable materials, besides bioplastics and coatings for paper or paperboard, three-dimensional packaging structures based on biopolymers have also gained interest in recent research projects, and some products are already available on the market. This subject will be covered in a forthcoming review article.

A successful introduction of bio-based packaging in the market requires a safe and long-lasting supply of raw material. However, lower costs at equal or improved functionality or, alternatively, acceptance of higher priced materials, are today the major hindrances to wider adoption of bio-based packaging. Furthermore, LCA analyses should prove that the new materials and/or processes are favorable from a sustainability perspective. The total environmental impact of a package is a subtle balance between the amount of material used to form the packaging and its functional properties. Too much use of material directly leads to an over-use of resources, but too little use of packaging may on the other hand lead to unnecessary loss or damage of packaged goods, which in turn would lead to increased waste. As a rule of thumb, a food package is responsible

only for up to 10% of the total environmental impact of a food product (Hanssen 1998). Even though packaging waste only accounts for about 3% of the total amount of waste generated in Europe, it still represents over 60 million tons of waste per year (de Vlieger 2003).

Many exciting initiatives have been undertaken, and several research and network projects with the focus on bio-based materials for packaging purposes are in progress. We are looking forward to the outcome of these projects and are confident that they will positively contribute to sustainable development in the packaging sector.

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