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Advances in Applications of Industrial Biomaterials

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Preface

This book presents reviews of the latest research and practical applications in the field of novel industrial biomaterials. State-of-the-art research into the development of industrial biomaterials, their properties and practical applications in specific fields, including results already established, indicate great possible benefits. Biomaterials gained initial attention in medical applications, but their unique properties have provoked wider utilization in industry, especially in regard to aspects of environmental sustainability and protection. Industrial biomaterials can be classified by different aspects, but in general, they all pertain either to the substitution or complementation of existing materials in different industrial applications through consideration of the bioeconomy. Industrial biomaterials have been developed and studied within a wide swath of areas, ranging from the automotive and construction industries to the energy sector, food industry and waste recycling. Also, environmentally friendly synthesis, or green chemistry, of existing materials today is one of the foundations of the bioeconomy, imposed by the increased presence of numerous chemical pollutants. Many new methods have been studied for the purpose of decreasing pollution and providing added value simultaneously; using eco-friendly or degradable biomaterials in different products and consumer goods should be a cost-efficient way to achieve these goals.

Recent advances in the development of biomaterials for industrial applications are reviewed, along with possibilities for exchanging environmentally hazardous substances with environmentally friendly and degradable components in different sectors: the food industry, the automotive industry, energy production and renewable resources, environmental protection, etc. The authors are senior researchers in the various fields of material science, interlinked with different aspects of environmental preservation. Especially important is the incorporation of organic materials into different composites, to enable consumption of what would otherwise be waste material. Different materials, new production technologies and new application areas have all been reviewed. The food industry is an especially important sector for biopolymers, edible films and coatings in food production and biodegradable material classes. Construction industries are also very suitable for application of bio-based composites. One significant area of research in transportation is related to biofuels, such as biodiesel based on organic constituents or green composites in marine applications. The use of biomass in energy supply chains shows promising prospects. Environmental protection aspects related to new nanoparticles, such as nano zero valent iron, are also reviewed.

Bio-based chemicals and bio-based packaging are among the most sought-after products nowadays. Plastic pollution has reached dangerous limits and chemical pollutants pose a serious threat to sustainable natural ecosystems in general. The pollution within our water and soil further transmits itself into plants, animals and, ultimately, humans. On the one side, green chemistry and green products promise a significant decrease in waste through fully or partially biodegradable eco-friendly materials. On the other side, waste management is also one of the tasks in the circular economy today, and a decrease in waste or the incorporation of existing waste into usable products is also studied in the broader field of industrial biomaterials. Application of biomass in composites and plastic materials is one of the most important developmental directions of industrial biomaterials. The significant advantage of such materials is their considerably lower cost in comparison with traditional materials of the same material classes. For example, wood waste, waste from the food and beverage industries, organic waste such as agricultural fibres (straw or flax) and plastic waste can be used for fabrication of new composites in construction industries, the furniture sector and many other areas. Such cost-efficient materials not only decrease the final product's price, but also significantly contribute to waste management and recycling.

Renewables are the major drivers of change nowadays, representing the cutting edge of research from a number of different aspects. There is significant potential for biomaterial application in the maritime shipping sector as well, from production of ship parts to its application as marine fuel. The shipping sector faces challenges related to reducing pollutant emissions and greenhouse gases. International regulatory bodies and national environmental agencies have issued rules and regulations that drastically limit these emissions. As a renewable source of energy, biodiesel is one option in reducing the emission of pollutants and Green House Gases (GHG), as well as achieving lower carbon intensity in the maritime shipping sector. Although practical experience in the use of biodiesel as a marine fuel is very scarce, some advantages over marine diesel fuels have already been noted, such as reduction of particulate emissions and a lack of adverse effects on marine diesel engines with blends up to 20%. Drawbacks, in general, include limited raw materials, higher production costs, which cannot compete with low quality heavy fuels for marine application, and, in particular, potential problems involving bacterial formations in tanks during the storage and degradation of certain rubber and elastomer compounds, since biodiesel acts as a solvent.

The food industry is perhaps the most interesting sector for industrial biomaterials. Biopolymers and edible films are important constituents in food packaging that aims to provide extended food preservation, as well as protection from decay and harmful external influences, such as antibacterial and antimicrobial effects.

Novel active packaging has been studied, and the future will provide various forms of both environmentally sustainable and human friendly packaging of food and beverages. Natural polymers can be biopolymers of marine origin or can be obtained from agricultural by-products. Edible and biodegradable biopolymers are mainly made of polysaccharides, lipids, and proteins. The main advantage of the biopolymers is that they are eco-friendly materials. Degradation of disposed conventional synthetic plastic materials derived from petroleum requires very long periods of time and is harmful to ecosystems.

The selection of edible/biodegradable materials in a food industry depends on the final product and can be used in various forms: edible films and coatings, packaging, antimicrobial and antioxidative protection, and others. Edible films and coatings are used to protect the freshness of meat, seafood, fruit, vegetables, grains, confectionery products and food mixtures that can be canned, deep frozen or kept in some other form of storage. Nowadays, nanoscale research pertaining to the detection of pathogens, active packaging, antimicrobial packaging, and the formation of different protective barriers has already started to improve food packaging. It may be possible, very soon, to use particles that are not organic to introduce diverse components such as colours and odours. Or they could be used as carriers for the controlled release of drugs or fungicides. New nanomaterials will also be used to improve mechanical properties and oxidation stability, to increase protection against gases, and possibly to increase the biodegradability of common biomaterials. Multi-functional intelligent packaging will be used as a substitute for traditional packing. Another very hot topic in food-related research is the possibility promised by the novel nanoparticles, nanocomposites and biopolymers for the design and creation of foods with new microscopic structures. The building blocks can be combined in various ways (e.g., microemulsions and nanofibers), thus enabling a wide range of new food structures.

Potential applications are great, and the products commercially realized to date strongly indicate that the field of industrial biomaterial development has already significantly contributed to both the circular economy and the bioeconomy, at the same time enabling the preservation and protection of natural resources. Innovations that have been established fall within a wide range of different important products, such as new composites made of recycled materials, biofuels, nanoparticles for the cleansing of ecosystems, and many others. A range of different industries can benefit from these novel bio-based materials, from the construction sector to wood processing industries, from different elements of our transportation industries up to green energy production. We believe that this book will provide young researchers and professionals alike with valuable insights into opportunities offered by these new materials and technologies, from the point of view of different professional disciplines—chemical engineering, marine engineering, fields of material science, and engineering in general—while emphasizing safety as an important input, motivating people to pursue further research and practical applications in this broad and multifaceted field of science.

This work is the result of the joint efforts of different companies and academic and research institutions, participating in the large international project, WIMB Tempus, 543898-TEMPUS-1-2013-1-ES-TEMPUS-JPHES, “Development of Sustainable Interrelations between Education, Research and Innovation at WBC Universities in Nanotechnologies and Advanced Materials where Innovation Means Business”, co-funded by the Tempus Programme of the European Union.

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Contents

Some Applications of Biomaterials in Automotive Industry

Saša Prodanović and Miroslav Milutinović

Abstract Environmentally responsible behaviour should be promoted in all spheres of life. This issue applies to the automotive industry as much as it does elsewhere. This is one of the most important reasons for the expansion of the use of biomaterials in car manufacturing. They have numerous advantages in terms of eco-friendly production technologies, reduction in the exploitation of fossil resources and waste minimization due to their features of biodegradability and recyclability. The paper shows an overview of the basic definitions of and methods for obtaining certain biomaterials. Here, the emphasis is placed on bio-based plastics, rubber and composites, because of their overwhelming presence in newly oriented industries. Due to the various applications and characteristics of bio-plastics, an overview of the tensile strength of each variation is given, with an emphasis that similar tests were conducted for all of them. Furthermore, knowing that the mechanical, chemical, thermal and other characteristics of biomaterials are all considered to be satisfactory, there has been a reasonable attempt to use them instead of conventional materials whenever possible. Consequently, the work contains an overview of the application of biomaterials in making different parts in the automotive industry and descriptions of their incorporation into branded vehicles, as a tool for increasing human consciousness of the fact that making a profit and preserving nature can result from the same activity. The paper also involves analysis of the conditions that biomaterials have to satisfy in order to expand their usage in the production of parts for the automotive industry.

Keywords Automotive industry · Bioplastics · Biorubber · Biocomposites

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1 Introduction

Researches in the automotive industry have greatly contributed to expansion of the application of biomaterials in the industry in general. The new approach to design called ‘eco-design’ is the most suitable field for emphasizing the advantages of biomaterials. Emphasis is placed on the closed cycle, starting from the development and use of natural, less environmentally harmful materials, which also enable greater comfort, safety, and suitability for control, right up to their recycling at the end of the product’s lifecycle. Cars are composed of many different parts made of various materials, which is why there has been such considerable effort made towards greater participation of biomaterials in their production. The goal is to design as many car parts as possible with an approximately equal life cycle, while respecting the technical, economic and functional characteristics of the product, as well as its impact on the environment. However, this is often not feasible, because it is not easy to choose a material that satisfies several criteria, such as technical requirements, requirements of the environment and recycling, all at once. In recent years, this kind of multicriteria optimization has been supported by software. Teamwork by experts in various fields has been put into service for designing vehicles for the future (De Medina 2006). Biomaterials are becoming more competitive with conventional materials in terms of their technical characteristics, which is why their use has recently come to be seen as an important advantage in the technology race among car manufacturers.

Therefore, the aim is to use natural materials for the production of components without endangering quality and safety. Also, attention is increasingly devoted to the production of fuels from biomaterials. The eco-design of cars that includes biomaterials is fully consistent with the principles of the sustainable development of society.

After an introduction in the first part, the second part gives some definitions of biomaterials and displays their characteristics as feedstocks. The third one contains some brief historical insight, with examples from the very earliest biomaterial use. The fourth part is divided into three subchapters: plastics, rubber and composites, as the most common biomaterials in the automotive industry. Each contains a brief description and examples of breakthroughs in the production and application of the considered biomaterials in the automotive industry.

2 About Biomaterials

There are several definitions of what constitutes a biomaterial, some of which are based on the materials’ origin or their usage. One of them states that biomaterials are materials that are completely, or in a certain proportion, produced from raw agricultural materials or wood. Raw agricultural materials include starch, sugar, vegetable oil and cellulose from wood, natural fibers, straw, etc. Special biomolecules, such as lignin and natural rubber, are also important (Carus 2007). Putting the emphasis on their wide use in medicine, many definitions can be derived. One of them is that biomaterials are intended for support or replacement of parts or entire human organs. Using this type of definition in the context of the automotive industry, it would follow that biomaterials are intended for the replacement of conventional materials in producing parts, entire components or fuel for cars (Migonney 2014). Also, within themselves, older versions, such as plywood and particleboard, are increasingly being replaced with plastic materials through the use of different technological methods. In biomaterials, as in most biological systems, a wide range of properties is required, such as mechanical strength, biological activity, chemical durability, etc. This fact emphasizes the multidisciplinarity of biomaterials and, therefore, the process of designing new biomaterials requires cross-disciplinary approaches that include material science, biological science, chemical science, medical science and mechanical science (Basu et al. 2009). Using renewable feedstocks (biomass), bioplastics can be produced in various ways. There are three groups of procedures given in the following text. First, the growth and direct extraction of polymers from plants, which are then modified or formulated for use in plastic processes. These include polysaccharides, such as starches (obtained from potato, corn, wheat, etc.), celluloses (obtained from wood), oils and proteins. Second, the polymerization of bio-based intermediates (monomers that are bio-derived via direct extraction, thermo-chemical modification, or the fermentation of biomass materials, often starches). The main representatives of these are biopolyesters such as polylactic acids, polysuccinates and other polyesters obtained from sugars, bioethanol/butanol, lactic acid, etc. Third, the extraction of bio-based polymers that were made using microorganisms and biomass/waste feedstocks, for example, polyhydroxyalkanoate (Pilla 2011).

The advantages of biomaterials compared to conventional materials are reflected in:

- Protection of the environment due to reduced carbon dioxide (CO_2) emission,
- Specific characteristics, such as biodegradability, reduced weight, etc.,
- The saving of resources and development of rural areas through an increase in the number of workplaces.

Selecting the right material largely depends on the purpose of the product to be made from it, and therefore it is necessary to understand its mechanical properties. Use of biomaterials in the automotive industry involves the introduction of lightweight materials, improvement of their strength, improvement of the material in terms of sound insulation, vibration control, reduction in fuel consumption and application of a manufacturing process that is not harmful to the environment (Ontario's Bio Advantage Sector Pro-file 2011).

Biocompatibility, which represents the degree of acceptability of artificial implants produced from biomaterials to human tissues and the body as a whole,

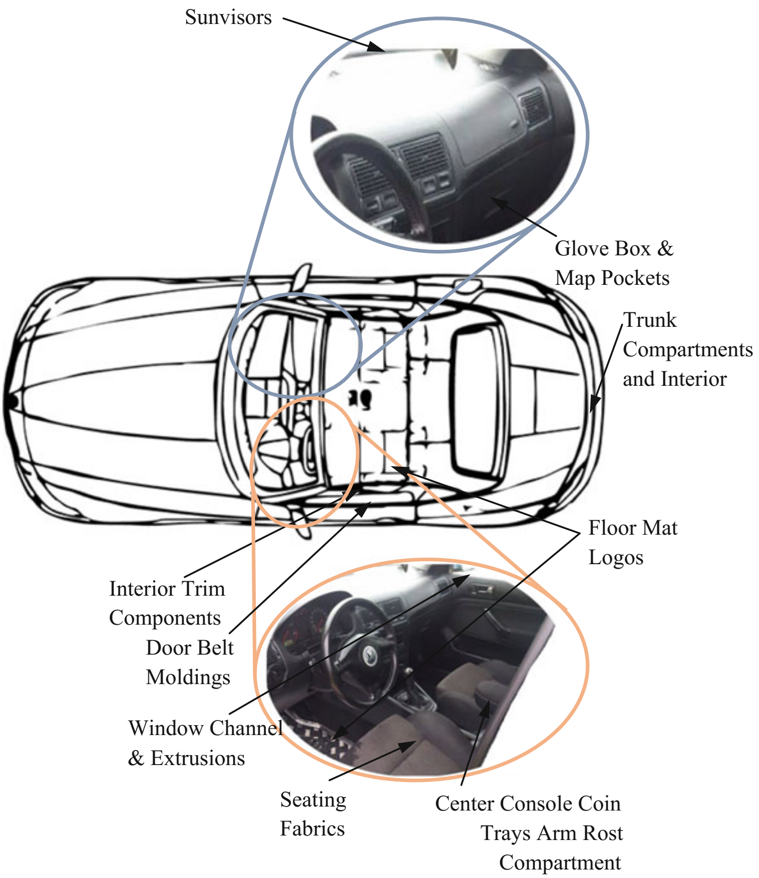

Fig. 1 Display of some biomaterials in a car

isn't a relevant requirement in the automotive industry. Of course, it is necessary that the materials be non-toxic. Great momentum in the application of and hope for a bright future for biomaterials have been supported by researches into bioplastics, biopolymers, biocomposites, natural fibers, nanocomposites based on biomaterials, lignin reinforced thermoplastics and biomass. Emphasis has also been put on wood and the composite materials of natural fibers, through the use of fibers from agricultural crops for the production of composites and advanced biocomposites based on wood (Ontario's Bio Advantage Sector Pro-file 2011). Figure 1 shows an overview of certain automotive parts that can be made from biomaterials, showing their diversity in size, performing function and place of embedding.

3 Short Historical Overview

Looking back at the timeline, the application of biomaterials follows almost all human breakthroughs in work as a meaningful activity. Simply by trying to compensate for some of their handicaps, people have been selecting and harvesting materials from nature with respect to their advantages in terms of adapting to the human body. In the particular moment, it was important for solving the problem at hand, and of course, there was no feel for the potential of biomaterials in the future regarding the advantages that are well-known today. So, at that time, the increase in their application was happening accidentally and spontaneously.

According to Migonney (2014), there are four generations of biomaterial:

The first was related to the simple maintenance and support of human organs and was limited to materials that were available to people in their immediate environment.

The second, dating from the mid-twentieth century, was built on the wings of scientific achievement and the industrial revolution.

The third is also a result of scientific work and was created with the appearance of polymers as the material of the future. This generation is now on the scene.

The fourth is in its infancy. Biomaterials from this generation have yet to become a reality.

In regards to the automotive industry, Henry Ford made one of the first steps toward the planned use of biomaterials. In 1937, this manufacturer produced soybean oil, which was used in the production of paints for automobiles. They also used plant-based plastics for production of the interior trim, steering wheels, timing gears, glove box doors, gear shift knobs, horn buttons, accelerator pedals, distributor heads, dashboards and body panels. Ford made a large breakthrough in the application of fibers from cotton, hemp, wood pulp, flax and ramie as plastic fillers and reinforcement materials (Rosato 2014). This technology progressed, and 1941, the so-called “Soybean Car” was presented. Ford models from that period contain wheat straw as a raw material for steering wheel production (Mielewski 2011).

The first attempts at usage of composite materials in this area were registered in the 1950s. Encouraged by their good characteristics, such as light weight, resistance to fatigue and suitability for molding, manufacturers initially hoped that these materials would significantly begin to replace metals as raw material. However, this did not happen, in large part because of their insufficient investigation into the character of the materials in regard to production and joining (Mangino et al. 2007).

4 Today’s Applications

The car, as a product with a huge number of components (more than 20,000), represents a whole piece whose manufacturing can involve different types of biomaterial (De Medina 2006). Therefore, it is not surprising that various new biomaterials, in both early times and more recently, have found their place in the automotive industry. This is confirmed by the fact that biomaterials are increasingly satisfying today's rigorous requirements for higher strength and reduced weight and cost. Their flexibility only increases with the number of different types, such as finished biomaterials like metals, plastics, rubber, ceramic, and composite biomaterials, as well as their raw materials, including wood, grain, hemp, cotton, etc. This chapter contains an overview of the participation of the most dominant types of biomaterial as raw materials in the production of car parts.

4.1 Plastics

Plastic, as a comparatively new material, has already taken on an important position in a wide range of car components in recent decades. Low cost and low weight are common features of the majority of plastic materials, and so, up until now, the choice of appropriate type was reflected in ensuring the features that the specific component should satisfy, such as strength, hardness, thermal stability, chemical resistance, etc. However, today's concept of biodegradable material usage directs manufacturers of plastics to apply methods that take into account the possibility of its recycling. Therefore, the aim is not only to increase the proportion of plastics as raw materials in the car as a final product, but also within the part that relates to plastics in general, increasing the percentage of biodegradable plastics, i.e., plastic materials that satisfy the closed recycling cycle shown in Fig. 2.

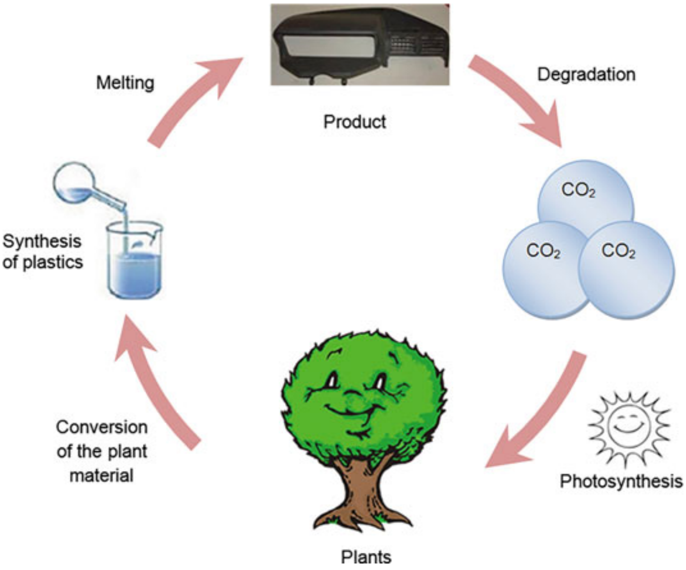

Fig. 2 Closed cycle of biodegradable plastics

This cycle starts with such renewable resources as land-efficient annual crops, including corn and sugar beets, castor (oil), switch-grass, and perennial cultures such as cassava, sugar cane and cellulose. Conversion of the plants into bioplastics takes CO_2, and thus changes its manner in relation to the process of its burning. The melting of bioplastics enables its modeling into different product shapes. Degradation involves the release of CO_2, which, through the process of photosynthesis, again supports the growth of plants, and thus closes the cycle shown in Fig. 2. This approach increases resource efficiency.

Bioplastics include a range of materials with different properties, and therefore they have large possibilities for application in the production of various parts in vehicles.

There are three groups of this kind of material (European bioplastics 2015):

1. Bio-based or partially bio-based, non-biodegradable plastics, such as mass commodity plastics, e.g., bio-based polyethylene (PE) and polyethylene terephthalate (PET), and bio-based technical performance polymers, e.g., polytrimethylene terephthalate (PTT), thermoplastic copolyester elastomers (TPC-ET) and bio-based polyamides.
2. Plastics that are both bio-based and biodegradable, such as polylactic acid (PLA), polyhydroxyalkanoates (PHA) and polybutylenes succinate (PBS).
3. Biodegradable plastics based on fossil resources, including polybutylene adipate-co-terephthalate (PBAT).

Based on comprehensive analysis, the tensile strength for the above-mentioned materials is given in Table 1, in which dispersion of the results is obvious. This dispersion depends on the basic material, and consequently on the ways of making certain types of bioplastic. These results show that for the same kind of basic material, it is possible to get different values of tensile strength.

When we talk about the properties of bioplastic, it is important to mention that it has no effect on cost, it is applicable with only minimal changes in production, and it has better characteristics in comparison with synthetic foams.

The other significant improvements that have been achieved using bio-based plastics are a reduction in emissions of greenhouse gases and less dependence on fossil resources. Bioplastic has found application in seats, headrests, armrests, bumpers and parcel trays.

It is important to mention that several different bioplastics play a primary role in the automotive industry, from bio-based polyamides, PTT and bio-based polyolefines to starch-blends and PLA-blends (Europaen bioplastics 2015).

Nowadays, there are numerous examples of the production and use of plastics as raw materials by car manufacturers and other companies. Some of these are as follows:

- Ford (USA) introduced foamed plastics with 40% soy proportion for headrests, armrests and seats in 2006 (Carus 2007). This manufacturer has assumed a key position in introducing plant-based materials into its products. Some that are already in use are: rice hull-filled electrical cowl brackets, cellulose

Table 1 Tensile strength of the different materials which were subjected to related tests

Material		Study	Tensile strength in MPa
PLA		Clarizio and Tatara (2012)	59.6
		DiOrio et al. (2012)	61.3
		Li and Sun (2011)	77.1
		Finkenstadt et al. (2008)	72
		Shumigin et al. (2011)	55
		Martin and Averous (2001)	68.4
		Huneault and Li (2007)	60
PE	HDPE	MakeltFrom (2009)	24–80
		Pan et al. (2009)	24
		Barbosa et al. (2012)	22.17
		Ebewele (2000)	17.2–39.2
		Askeland (2010)	37.93
		Muhammadi et al. (2015)	29
	LDPE	MakeItFrom (2009)	7
		The Crop Site (2017)	10
		Askeland 2010	20.6
		Muhammadi et al. (2015)	10
		Ebewele (2000)	10.3–17.2
		Kalpakjian and Schmid (2007)	7–40
PET		The Crop Site (2017)	55
		Ebewele (2000)	58.6–72.4
		Askeland (2010)	72.4
		May-Pat et al. (2012)	33.9 ± 7.06
		Scheirs (2003)	48.86
		Muhammadi et al. (2015)	56
PTT		Al-Omairi (2010)	58.05 ± 0.2
		Padeea et al. (2013)	57
		Reddy et al. (2012)	57
TPC-ET		British Plastics Federation (2017)	0.5–2.4
		The Crop Site (2007)	29–62
PHA		Bugnicourt et al. (2014)	15–40
		Snoei de Castro et al. (2014)	32
PBAT		Hongdilokkul et al. (2015)	14.1
PBS		Jamaluddin et al. (2016)	55
		Qiu et al. (2016)	35–45
		Zhanga et al. (2012)	31

fiber-reinforced console components, recycled cotton material for seat fabrics, soy foam seat cushions and head restraints and carpeting (Richardson 2014). Ford intensively researches bio-based resin with the idea that as many more parts of its vehicles as possible will be made from renewable and recyclable materials, taking into account strict quality standards. They have three current goals here. First, overcoming the performance and durability issues of neat PLA with nucleating agents, impact modifiers and moisture inhibitors. Second, evaluating the processability and performance of renewably sourced nylons—high-performance grades derived from castor oil. Third, exploring polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), and polybutylene terephthalate (PBT), made from renewable resources.

Their investigation into rice hull material involves testing its functionality and flammability. It has a very significant advantage because its hull isn't the main product in the cultivation process of its agricultural crop (Rosato 2014).

- Fiat (Italy) widely utilizes castor oil-derived long chain polyamides instead of the fossil-based version. They also intend to expand the share of bio-fillers used for reinforcement of certain kinds of plastic and elastomer in their components (Europaen bioplastics 2015). A bio-based polyurethane foam called BioFoam, consisting of 5 to 25% material of plant origin, is used in the Fiat models Uno, Punto, Strada, Siena, Idea and Palio in armrests, headrests and seats (Immonen 2015). Beside other famous European manufacturers, such as Volkswagen, Renault, Volvo, Opel, Porsche and Daimler, Fiat was involved in investigating the manufacture of Resin Transfer Molded (RTM) carbon/epoxy floor pans and carbon-glass/epoxy hybrid parts (Pilla 2011).
- Mitsubishi (Japan) uses PTT (Polytrimethylene terephthalate) floor mats in its test electric vehicle called the "i-MiEV" (Carus 2007).
- Toyota (Japan), in 1998, began to use PLA (Polylactic acid) for the manufacturing of dashboards in some its models. Nowadays, it is one of the companies most successful in producing bioplastics for application in their models of automobile. There are numerous other examples of bioplastic application by this car manufacturer. They use bio-based polyesters, bio-based PET and PLA-blends in significant amounts in the manufacturing of their components. Bio-based polyesters are characterized by good stiffness, electrical properties, workability, thermal resistance, surface gloss, dimensional stability and low deformation. They strove towards the goal of replacing 20% (by weight) of all oil-based plastics with bioplastics by 2015. Many Toyota vehicles contain soy-based seat cushions, such as the Prius, Corolla, Matrix, RAV4, and Lexus RX 350. Also, for example, their Toyota SAI and Toyota Prius models contain headliners, sun visors and floor mats made from bioplastic (Carus 2007; Europaen bioplastics 2015). Furthermore, they are trying to introduce door trim ornamentation that uses 100% plant-derived base material consisting of kenaf and polylactic acid (PLA), seat cushions that use polyol derived from non-edible castor oil, and, in general, as many more interior parts that use PLA as possible. They support the efforts of research companies, such as Toyota Boshoku, to improve the quality of bioplastics, especially in terms of heat resistance, sunlight resistance and abrasion resistance, which are characteristics required of automotive parts and their mass production (Toyota Boshoku 2015).

- The Japanese manufacturer Mazda has improved the mechanical and thermal characteristics of PLA using 88% crop and 12% crude oil, a mixture they have used since 2006 as a raw material in the fabrication of parts for their automobiles' interior (Carus 2007). A biofront stereocomplex PLA was developed by Teijin and Mazda with characteristics such as a higher crystallinity than PLA, heat-resistance, hydrolytic and hydrothermal resistance, a satisfactory level of strength, and resistance to abrasion and sunlight damage; it can be used for many applications in the automotive industry, for example, for car seat fabric (made out of 100% of this material) and door trim in the Mazda Premacy Hydrogen RE Hybrid model. Said model also contains an instrument panel and other interior parts (needing thermal and shock resistance and a nice finish) produced from the above-described PLA-based bioplastic with over 80% plant-derived content. Mazda has investigated the possibility of obtaining various polypropylene (PP) and ethylene-propylene copolymers from cellulosic biomass. These materials should be used as raw material for car bumpers and bumper spoilers, wheel arch liners, body panels, dashboards and dashboard carriers, door pockets, various consoles, heating ventilation air conditioning, reservoirs, pillar claddings and seats, battery covers, electronic housing and air ducts.
- Honda (Japan) produced textile for their automotive interiors by utilizing PPT (Polypropylene Terephthalate) based on corn and petrochemical components (Carus 2007). They also introduced a PTT (Polytrimethylene Terephthalate) seat in their "FCX" model car. Because of the breakthrough of flexible and semi-flexible polyurethane (PUR) foams, many manufacturers, and therefore Honda, use them as raw material for making interior parts. Specifically, Honda applies Agrol®-based PUR foams (flexible foams) produced by Bio-foam Insulation Systems for head and armrests.
- Polytec-Automotive (Germany) produced a prototype of a trunkliner for Audi A4 that consisted of sugarcane, resin/furan and jute, and was therefore entirely renewable. This company, in cooperation with BMW, has produced and tested door panels using bio-based thermosetting resins for BMW car models (Carus 2007).
- Daimler-Benz (Germany) has introduced bio-based polypropylene (PP) for producing engine/transmission covers in the Mercedes-Benz Travego Coach and bio-based polyamides (PA) for air filter housing, cogwheels for the steering angle sensor, accelerator pedal modules and cooling fans (Pilla 2011).
- Volkswagen (Germany) has introduced a lightweight multi-functional crankshaft cover into their new generation of diesel engine, produced with EcoPaXX® bio-based polyamide 410, developed by DSM (Dutch State Mines). The main advantages of this kind of bioplastic are very good mechanical properties at elevated temperatures, excellent toughness, 70% renewable content and a reduced weight due to low density, for example, 45% less than aluminum (De Guzman 2013).
- The Sorona-Biopolymer, which is injection moulding compatible and whose production is less energy-consuming, was launched onto the market in 2007 by

DuPont (USA), a multinational chemical company, and its new products offered to a wide range of customers (including automotive manufacturers). The big advantages of this type of plastic are its renewability in a proportion of 37% and a shiny surface that eliminates the need for various types of paint (Carus 2007). This biopolymer is also available in the form of a stain-resistant fiber and can be used for the production of automotive carpets. The process of Sorona production is based on sugar extraction from feed corn. DuPont also utilizes castor beans as one of the feedstocks for nylon that can be applied in vehicles (Pilla 2011). It can be clearly ascertained from the above-mentioned facts that this company is paying close attention to improvements in nature-friendly production, a notion proven by the fact that they were one of the first companies to publicly establish environmental goals 20 years ago (Davies 2015).

- The Lubrizol Corporation, a Berkshire Hathaway company (USA), deals with various materials, taking into consideration their environmental impact. In that direction, they have developed a new type of polymer, called Lubrizol Engineered Polymers, discovered after detailed investigations into the present scientific knowledge. These polymers are thermoplastic polyurethanes (TPUs) that are highly versatile and suitable for different modes of processing, such as extrusion, injection-molding, blow-molding, overmolding, calendaring and solution-coating. These polymers include the Estane® Engineered Polymers, which are generally characterized by their wide hardness diapason, from 60 Shore A to 85 Shore D. Ranges of their other properties vary from one to the other, and that fact increases their applicability, because it enables satisfying the different demands of manufacturers, carried out post-processing. In regard to the focus of this review, it is very important to note that the polymers mentioned are bio-based and recyclable. Their additional characteristics are abrasion resistance, optical clarity, moisture vapor transmission, low compression set, chemical resistance to fuels, oils, solvents and hydrolysis, flexibility at low temperatures (down to −45 °C), UV resistance, flame-retardancy (halogen and halogen-free), low gloss, fiber-reinforcement, water-repellence, static-dissipativeness, and conductive and nonconductive mattes, all of which should be emphasized in regard to the corresponding product to satisfy its defined requirements. There are tremendous possibilities for the application of Lubrizol's Engineered Polymers in the automotive industry, for example, for the adhesive film for automotive interior door panels, headliners and seat covers, high-performance seals for hydraulic cylinders, high-pressure hoses, jackets for various kinds of cable, etc. (Lubrizol 2013).
- When we talk about balanced thermal-mechanical properties, a very important place needs to be occupied by bio-based PBS made of bio-succinic acid and 1,4-butanediol. According to the survey by Faurecia (USA) and Mitsubishi Chemical (Japan), this kind of bioplastic is going to be a major raw material in the mass-production of automotive interior parts, for example, door panels, trim, strip, air ducts and instrument panels and console inserts (European bioplastics 2015).

- As previously mentioned, PLA (Poly Lactic Acid) is a very important type of bioplastic, and it is becoming the material of choice for both visible and invisible automotive parts. PLA products have a reduced carbon emission and high bio content, and therefore they have a nature-friendly orientation. They satisfy high functional requirements that are reflected in high heat resistance (up to 140 °C), impact resistance, UV resistance, high gloss and excellent colorability, dimensional stability and the ability to withstand the other demanding conditions that exist within engines. As an example, using Plantura, which is a family of high heat PLA compounds that are 95% bio-based, Röchling Automotive (Germany) has developed interior trim parts and an air filter box. It also provides resistance to low temperatures down to −30 °C. This filter box was mounted in a vehicle and proved as good as hoped with no changes, in a test that was carried out during a 150,000 km trip. For interior trim parts, Plantura demonstrates good resistance to scratching, as well as excellent hydrolytic resistance, which was tested at 100% humidity at 70 °C (Corbion 2015).

4.2 Rubber

Nowadays, there is a human attempt to form the history of rubber into a cyclic process. At the very beginning, only natural rubber, taken from a specific kind of tree, was produced. The most utilized plant for this purpose was Hevea brasiliensis. Afterwards, with the development of industry, synthetic rubber based on petroleum resources appeared and became widespread. The development of social consciousness and the intensification of activities for protecting the environment produced the idea of using biomass as a source for rubber products instead of petroleum. The actual strategy would be to produce, as much as possible, natural rubber and synthetic rubbers derived from biomass-based monomers, an idea that would tend to close the afore-mentioned cycle (Kunioka et al. 2014).

Different types of rubber and its other additional ingredients, as well as their numerous combinations, enable a wide range of products for which rubber can be utilized. In the automotive industry, rubber is used for the production of tires, various hoses, door seals (weather-strips), floor mats, etc.

The tire has to provide easy control of the vehicle, braking and stability in cornering, and therefore comfortable and safe driving. It needs to be durable too. There are two main ingredients in a rubber compound, rubber itself and the filler. Depending on the target characteristics of the tire, the objectives may be various. Only precise selection of one or more types of rubber and the type and amount of filler for blending with said rubber can provide for reaching such specified aims as optimized performance, maximized traction under both wet and dry conditions, and superior rolling resistance (Maxxis 2014).

This part of production also involves tendencies towards introduction of environmentally-friendly materials from both aspects: pollution within the manufacturing process (reducing the carbon footprint) and biodegradability. According to what was stated above, it is clear that bio-based rubber should satisfy the same requirements as conventionally produced rubber in order to be concurrent in the market. Large and continuous researches into this area are being financed and carried out by the world's leading companies. In the following review, some examples will be described:

- Goodyear and DuPont Industrial Biosciences (USA) are collaborating to develop BioIsoprene™, a new bio-based alternative to petroleum-derived isoprene. In fact, Isoprene is 2-methyl-1,3-butadiene, a colorless, volatile liquid hydrocarbon, traditionally obtained when processing petroleum or coal tar and taken as a raw chemical material. Although its pollution impact is obvious due to its ingredients, taking that content into account, there is a good possibility for obtaining advantages, because it can be produced from many different plants, such as corn stalks, sugarcane and waste from food (EMBL-EBI 2014; The Crop Site 2010). That leads to obtaining the already-mentioned bio version of this material. The BioIsoprene™ monomer can be used for the production of synthetic rubber, which is, from the other side, an alternative to natural rubber, because it demands the previously-listed cheaper sources. The development of BioIsoprene™ as a new bio-based raw material will reduce dependence on oil-derived products. This benefit should be significantly exploited by manufacturers of rubber and tires (Goodyear 2012).
- Goodyear (USA) has produced a tire called the BioTRED using nano-droplets of a complex starch. In addition to reducing rolling resistance and fuel consumption by 5%, another improvement is the lower energy amount required for their manufacture (Carus 2007).
- In 2012, the Goodyear Tire & Rubber Company tested the use of soybean oil in tires, because it can potentially increase tread-life by 10% and greatly reduce usage of petroleum-based oil by producers of tires (Business Sector Media LLC 2013).
- Bridgestone Americas (USA) researched, and subsequently discovered, another natural rubber source. That was shrub guayule, a perennial plant native to the southwestern US and a renewable source of natural rubber latex. The investigation was greatly supported by one of the world's leaders in tire and rubber production, the Bridgestone Corporation. Yulex (USA), a company that deals with agricultural-based biomaterials, was involved in this survey too. Guayule rubber has properties almost identical to those of the natural rubber harvested from hevea rubber trees, and its source (shrub guayule) doesn't represent a competitor to food or fiber crops, because it needs little water and doesn't require agrotechnical treatments (Bridgestone 2014; Business Sector Media LLC 2013).
- LANXESS Keltan® Elastomers (India), a world famous manufacturer of synthetic rubber and one of the bigger suppliers to the automotive and tire industries, has launched Keltan® Eco, a bio-based high-performance rubber. It is excellent as sealant material and is manufactured from rubber derived from

bio-based ethylene. Keltan® Eco is utilized for producing weather stripping, belts and hoses for the automotive industry. This material satisfies the high requirements defined for weatherstrips by car manufacturers, such as outdoor weather resistance, ozone resistance and noise sealing properties. Furthermore, it has very good coolant resistant properties and high temperature resistance up to 150 °C, and therefore long durability with good functionality at the same time, ensuring that these elastomers can be used for various types of hose (Instituto Technologico del Plastico n.d.).

4.3 Composites

Bio-based materials, due to their uncountable variations, are becoming even more widely and permanently spread beyond their already huge area of application thanks to the occurrence of bio-based composites, considering the enormous number of potential combinations of their ingredients. They enable a good compromise between performance and environmentally-friendly properties. Composites are blends of two or more components. One component has long stiff fibers, while the other is a binder or matrix that holds the fibers together. The fibers are notably stronger and stiffer than the matrix material. Their joining is necessary to form the composite. Both of them keep their individual features and both directly influence the properties of the produced composite. Also, due to the structure of composites as described, changes in one feature don't have to influence the other characteristics.

To determine fiber type, diameter (or cross-sectional width) and length should be taken into account. The preconditions for the material to be called fiber are: diameter or cross-sectional width is less than 0,0254 m and ratio length/diameter is greater than 10. If the microstructure of the fiber is mostly a single crystal, it is a whisker. Both fibers and whiskers can be continuous and discontinuous. Continuous fibers have an indefinite length, while discontinuous ones are continuously chopped. [AU: I can't determine what 'staple' means in this context.] Analogously, a continuous whisker is characterized by its indefinite length, while a discontinuous whisker has a definite length.

Bio-fibers can be made using wood from both deciduous and coniferous sources and various agricultural plants, such as straw from corn, wheat and rice crops. They are divided into three types. First are bast fibers, which include flax, hemp, jute and kenaf; these are fairly stiff when they are used as a composite reinforcement. Second are leaf fibers, which include sisal, henequen, banana and pineapple; these enhance composite toughness, while providing lower structural contribution. Third are seed or fruit fibers, including cotton, coir and kapok. The third group shows elastomeric-type toughness and very low structural capability.

The matrix should satisfy many demands regarding functionality and the quality of the composite, such as: keeping the fibers in the structure in place, preventing destruction of the filaments during fabrication, distributing or transferring loads, having satisfactory strength, modulus and elongation, increasing moisture resistance, influencing the electrical and chemical properties of the composite, wetting and bonding to fiber, necessarily penetrating into fiber bundles, eliminating voids and thus enabling a compact structure, having a low coefficient of thermal expansion, decreasing shrinkage and thus providing dimensional stability, having elastic properties in order to transfer the load to fibers, and having the ability to easily take the form of the final composite. Depending on the application, composites can be characterized by excellent chemical resistance and/or strength at elevated temperatures and/or low temperature capability.

Composites reinforced with natural fibers are coming into expanded use because of their light weight, low cost, high specific strength and other well-known and important features, like renewability and biodegradability. Bio-based composites are made from partially or fully eco-friendly materials. Partially eco-friendly materials consist of natural fibers mixed with petroleum-based plastics such as polyethylene, polypropylene, polyester, etc. Eco-friendly or green materials contain natural fibers mixed with natural plastics based on the renewable feedstocks mentioned in subsection 4.1 (Smitthipong et al. 2015; Brosius 2006).

Nowadays, they have a large number of applications in the automotive industry. Some of most famous are as follows:

- Many of the world’s leading automotive companies use Quadrant’s Natural Fiber Composite in their vehicle models. Some of these are the Audi A8, Mitsubishi Space Star minivan, BMW 7-series, Iveco heavy truck line, Porsche Cayenne, Volkswagen Touareg and Audi Q7 sport utility vehicle. The composite has a shorter alternative name, Quadrant’s Nafcoform material, and it consists of equal parts polypropylene and a natural fiber blend made up of equal quantities of kenaf, hemp and flax. Blending fibers prevents variability in any single fiber crop, and this ratio of fibers provides for relatively consistent performance in the final component. Their application is for the interior parts of a vehicle, such as load floors.
- The Ford Motor Co. (USA) in 2005 researched and rated as promising hemp mats and hemp twine (cut to one-inch lengths), as natural fibers, combined with various polyester and vinyl ester resins for underhood applications such as heat shields, engine covers and noise shields.
- In 2005, DaimlerChrysler AG (Germany) successfully introduced natural fiber composites for exterior application in the Mercedes A-Class two-door vehicle. Rieter Automotive Systems (Switzerland) has made a spare wheel pan cover using polypropylene resin and abaca fiber. Abaca is closely related to the banana plant and is better known as “Manila hemp.” It is a leaf fiber, consisting of long slim cells with 15% lignin. It is very suitable to applications in which great mechanical strength is required (Brosius 2006; FAO 2015).
- Mercedes uses jute-based composites for the door panels in their E-class model, banana-fiber reinforced composites in the A-class, and a number of other different bio-composites in the S-class. Some manufacturers have gone a step

further, such as the Araco Corporation (Japan), who, in 2003, produced a fully electric car whose body was totally made out of composites based mostly on kenaf called Grasshopper. After numerous surveys, Fiat presented the prototype of the Fiat Ecobasic, which has external panels produced from natural fiber composites (Fan et al. 2011; Karus et al. 2006; Njuguna et al. 2011).
- Mitsubishi, in 2006, introduced PBS (Plastic Building Supplies), which were produced through the fermentation of sugar and strengthened with bamboo fibers. These too have good rigidity. Mitsubishi's Green Plastic biocomposite was introduced into the Mitsubishi Concept cX car as a raw material for seat back panels, door trim and tailgate trim. That approach enables exploitation of the benefits of bamboo composites, such as dimensional stability, weather resistance, high impact resistance, long product lifetime, low maintenance, non-toxicity and low flame spread. (Abdul Khalil et al. 2012; Pilla 2011).
- Porcher Industries has developed a Greenlite® renewable reinforcement that, in combination with banana fiber and resin derived from pine wood, creates bio-composites utilized in the body frame of the BioMobile.ch. Porcher Industries is an international company that deals with the development and production of innovative products for various industrial branches. BioMobile.ch is an energy-efficient vehicle developed by the University of Applied Sciences Western Switzerland, Geneva—Technology, architecture and landscape, for international competition (Reinforced plastics 2012).
- The VTT (Valtion Teknillinen Tutkimuskeskus) Technical Research Centre (Finland) has developed procedures and product innovations for processing the most rapidly renewable surface layer of peat, which was used for energy production until now. The advantages of products containing peat fiber are their low cost, water resistance, impact strength, bio-origin and excellent fire endurance characteristics. Procedures for the manufacturing of materials containing peat fiber don't deviate from normal plastic processing methods such as compounding, extrusion and injection moulding. Peat can also be milled and then used as peat fiber, because it contains several peat fractions and the sort of long fibers that are preferable, being suitable as filling material and for reinforcing material in composite structures (Immonen 2015).

5 Conclusions

The flexibility of biomaterials, as a consequence of their various characteristics, greatly enlarges their applicability in all industrial areas, including the automotive industry. It is a permanently exploitable fact that with the increase in these possibilities, it is perfectly reasonable from the perspective of environmental protection to increase demands for car manufacturers to use them. Biomaterials act in this regard by enabling the formation of lightweight construction (in most cases), thus further reducing car weight, and consequently decreasing fuel consumption.

Another significant contribution is the environmentally-friendly technologies utilized for their production in relation to CO_2 emission. One more improvement in the observed domain is the utilization of biofuels as a kind of biomaterial as well. It is important that plants used to produce biomaterials do not come into competition with the plants or parts of plants that produce food. Therefore, it would be suitable to use plant waste or non-edible plants, which are less demanding in regard to climatic conditions and agrotechnical measures.

Very significant efforts are being concentrated on research into the technological properties of biomaterials, because simplifying technologies leads to lower production costs, thereby making these materials more attractive for car manufacturers. This paper presents an overview and analysis of the application of basic biomaterials used in the automotive industry. According to the results of numerous investigations, a portion of which have been detailed in this review, there is no doubt that biomaterials are the materials of the future, because they can contribute considerably to pointing the development of society down the right path, especially through big industries such as the automotive industry. Analysis of the conditions that biomaterials need to satisfy in order to develop different parts for the automotive industry, including comparison of their mechanical characteristics with those of related materials, should be the basis for further consideration in regard to the possible broadening of their application.

The authors declare that they have no conflict of interest.

For this type of study, formal consent is not required.

This article does not contain any studies involving human participants or animals performed by any of the authors.

References

Abdul Khalil HPS, Bhat IUH, Jawaid M et al (2012) Bamboo fibre reinforced biocomposites: a review. Mater Des 42:353–368

Al-Omairi ML (2010) Crystallization, Mechanical, Rheological and Degradation Behavior of Polytrimethylene terephthalate, Polybutylene terephthalate and Polycarbonate blend, Thesis submitted for the degree of doctor of philosophy, http://researchbank.rmit.edu.au/eserv/rmit:10756/Lafi.pdf&gathStatIcon=true. Accessed 2 Jan 2017

Askeland RD, Fulay PP, Wright JW (2010) The science and engineering of materials, Cengage Learning, Boston

Barbosa R, Morais SDD, Nóbrega CK, Araújo ME, Mélo AJT (2012) Influence of processing variables on the mechanical behavior of HDPE/clay nanocomposites. Materials Research 15(3):477–482. doi:10.1590/S1516-14392012005000054

Basu B, Katti D, Kumar A (eds) (2009) Advanced biomaterials, fundamentals processing and applications. Wiley, Hoboken

Bridgestone (2014) Bridgestone Begins Producing Natural Rubber in Mesa, Arizona. http://www.bridgestoneamericas.com/corporate/news/140922a.html?ref=rss. Accessed 23 Mar 2015

British Plastics Federation (2017) Thermoplastic Elastomers TPE, TPR. Accessed 2 Jan 2017

Brosius D (2006) Natural Fiber Composites Slowly Take Root. Composites World. http://www.compositesworld.com/articles/natural-fiber-composites-slowly-take-root. Accessed 29 Mar 2015

Bugnicourt E, Cinelli P, Lazzeri A, Alvarez V (2014) Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging, eXPRESS Polymer Letters, 791–808, doi:10.3144/expresspolymlett.2014.82

Business Sector Media LLC (2013) Bridgestone, Yulex Launch Separate Biorubber Projects. http://www.environmentalleader.com/2013/05/10/bridgestone-yulex-launch-separate-biorubber-projects/. Accessed 23 Mar 2015

Carus M (2007) Innovative biomaterials in Europe—Status and outlook bioplastics. NFRP & WPC and other innovative wood materials, Nova-Institut GmbH

Clarizio S, Tatara R (2012) Tensile Strength, elongation, hardness, and tensile and flexural moduli of PLA filled with glycerol-plasticized DDGS. J Polym Environ 638–646. doi:10.1007/s10924-012-0452-3

Corbion (2015) PLA bioplastics: A driving force in automotive. http://www.corbion.com/bioplastics/markets/automotive. Accessed 9 Mar 2015

Davies C (2015) Bioplastics Reshaping an Industry. DuPont. http://www.dupont.com/industries/packaging-and-printing/media/press-releases/bioplastics-reshaping-an-industry.html. Accessed 18 Mar 2015

De Guzman D (2013) DSM's bio-polyamide in VW engines. Green Chemicals Blog. http://greenchemicalsblog.com/2013/09/04/dsms-bio-polyamide-in-vw-engines/. Accessed 21 Mar 2015

De Medina HV (2006) Eco-design for Materials selection in automobile industry. Paper presented at the 13th CIRP international conference on life cycle engineering, LCE2006, Katholieke Universiteit, Leuven, 31 May–2 June 2006

DiOrio NR, Tatara RA, Rosentrater KA, Otieno AW (2012) In: Liu K, Rosentrater KA (eds) Distillers grains: production, properties, and utilization. CRC Press, Boca Raton, FL, pp 429–448

Ebewele RO (2000) Polymer science and technology. CRC Press, Boca Raton, New York

EMBL-EBI (2014) Isoprene. http://www.ebi.ac.uk/chebi/searchId.do?chebiId=CHEBI:35194. Accessed 23 Mar 2015

Europaen bioplastics (2015) Bioplastics in the automotive market—clear benefits and strong performance, Overview of materials and market development. www.europaen-bioplastics.org. Accessed 12 Mar 2015

Fan J, Nassiopoulos E, Brighton J et al (2011) New Structural Bio composites for car applications. Paper presented at the Conference on society of plastics engineers—EUROTEC 2011, Society of Plastics Engineers, Barcelona, 14–15 Nov 2011

FAO, Food and Agriculture Organization of the United Nations (2015) Future Fibres. http://www.fao.org/economic/futurefibres/fibres/abaca0/en/. Accessed 30 Mar 2015

Finkenstadt VL, Liu C-K, Cooke PH, Liu LS, Willett JL (2008) Mechanical property characterization of plasticized sugar beet pulp and poly(lactic acid) green composites using acoustic emission and confocal microscopy. J Polym Environ 9–26

Goodyear (2012) Bio-based tires edge closer to reality/collaboration between the goodyear tire & rubber company and dupont industrial biosciences results in breakthrough technology for tires made with renewable raw materials. http://www.goodyear.com/cfmx/web/corporate/media/news/story.cfm?a_id=646. Accessed 23 Mar 2015

Hongdilokkul P, Keeratipinit K, Chawthai1S, Hararak B, Seadan M and Suttiruengwong S (2015) A study on properties of PLA/PBAT from blown film process, IOP Conf. Series: Materials Science and Engineering, 1–8, doi:10.1088/1757-899X/87/1/012112

Huneault MA, Li H (2007) Morphology and properties of compatibilized polylactide/thermoplastic starch blends. Polymer 48:270–280

Immonen K (2015) From peat fibre to biocomposite. VTT Technical Research Centre of Finland. http://www.vttresearch.com/impact/references/from-peat-fibre-to-biocomposite. Accessed 7 Apr 2015

Instituto Technologico del Plastico (n.d.) LANXESS Introduces Keltan® Eco, a Bio-based Sealing Elastomer for Hoses and more, http://www.observatorioplastico.com/detalle_noticia.php?no_id=294948&seccion=reciclado&id_categoria=802. Accessed 24 Mar 2015

Jamaluddin N, Razaina MT, Mohd Ishak ZA (2016) Mechanical and morphology behaviours of polybutylene (succinate)/thermoplastic polyurethaneblend, Procedia Chemistry, pp 426–432. doi:10.1016/j.proche.2016.03.034

Kalpakjian S, Schmid SR (2007) Manufacturing processes for engineering materials, 5th edn. Pearson, Cambridge

Karus M, Ortmann S, Gahle C, Pendarovski C (2006) Use of natural fibres in composites for the German automotive production from 1999 till 2005. Nova-Institute, Hürth

Kunioka M, Taguchi K, Ninomiya F et al (2014) Biobased contents of natural rubber model compound and its separated constituents. Polymers 6:423–442. doi:10.3390/polym6020423

Li Y, Sun S (2011) Mechanical and thermal properties of biocomposites from poly (lactic acid) and DDGS. J Appl Polym Sci 121:589–597

Lubrizol (2013) Estane® Engineered Polymers. https://www.lubrizol.com/Engineered-Polymers/Brochures/Estane-Engineered-Polymers.pdf. Accessed 24 Mar 2015

May-Pat A, Avilés F, Toro P, Yazdani-Pedram M, Cauich-Rodríguez JV (2012) Mechanical properties of PET composites using multiwalled carbon nanotubes functionalized by inorganic and itaconic acids. eXPRESS. Polym Lett 6(2):96–106. doi:10.3144/expresspolymlett.2012.11

Mangino E, Carruthers J, Pitarresi G (2007) The future use of structural composite materials in the automotive industry. http://inderscience.metapress.com/content/h6281v7771886044/. Accessed 30 Mar 2015

MakeItFrom (2009) http://www.makeitfrom.com/about, Accessed 31 Dec 2016

Martin O, Averous L (2001) Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. Polymer 42:6209–6219

Maxxis (2014) How a tire is made. http://www.maxxis.com/other-automotive-information/how-a-tire-is-made. Accessed 23 Mar 2015

Michel A, Huneault Hongbo L (2007) Morphology and properties of compatibilized polylactide/thermoplastic starch blends. Polymer 48(1):270–280

Mielewski D (2011) Greening the Blue Oval: Sustainable Materials for the Automotive Industry. Ford Plastics Research Group

Migonney V (ed) (2014) Biomaterials. ISTE Ltd. Wiley, London and Hoboken

Muhammadi, Shabina, Afzal M, Hameed S (2015) Bacterial polyhydroxyalkanoates-eco-friendly next generation plastic: production, biocompatibility, biodegradation, physical properties and applications. http://dx.doi.org/10.1080/17518253.2015.1109715. Accessed 2 Jan 2017

Njuguna J, Wambua P, Pielichowski K, Kayvantash K (2011) Natural fibre-reinforced polymer composites and nanocomposites for automotive applications. Cellulose Fibers: Bio Nano Polym Compos 661–700. doi:10.1007/978-3-642-17370-7_23

Ontario's Bio Advantage Sector Pro-file (2011). Spotlight on Biomaterials. http://www.omafra.gov.on.ca/english/research/ktt/spot-biomaterials.pdf. Accessed 30 Mar 2015

Padeea S, Thumsorna S, Onb WJ, Surinb P, Apawetb C, Chaichalermwonga T, Kaabbuathongc N, O-Charoena N, Srisawata N (2013) Preparation of Poly(lactic acid) and poly(trimethylene terephthalate) blend fibers for textile application, 10th Eco-Energy and Materials Science and Engineering, Energy Procedia 34, 534–541

Pan B, Ning N, Liu J, Bai L and Fu Q (2009) Mechanical properties of SMC whisker reinforced high density polyethylene composites. Chin J Polym Sci 267–274

Pilla S (ed) (2011) Handbook of bioplastics and biocomposites engineering applications. Wiley, Hoboken and Scrivener Publishing LLC, Salem

Qiu TY, Song M, Zhao LG (2016) Testing, characterization and modelling of mechanical behaviour of poly (lactic-acid) and poly (butylene succinate) blends. Mech Adv Mater Mod Process. doi:10.1186/s40759-016-0014-9

Reddy JP, Misra M, Mohanty A (2012) Renewable resources-based PTT [poly(trimethylene terephthalate)]/switchgrass fiber composites: the effect of compatibilization, Pure Appl Chem Sci J IUPAC 521–532. https://doi.org/, doi:10.1351/PAC-CON-12-04-05

Reinforced plastics (2012) BioMobile.ch features bio-composite body. http://www.reinforcedplastics.com/view/24634/biomobile-ch-features-bio-composite-body/. Accessed 31 Mar 2015

Richardson J (2014) 2 Million tons of tomatoes for bioplastics: Ford & Heinz Team Up. Clean Technica. http://cleantechnica.com/2014/06/16/2-million-tons-tomatoes-bioplastics-ford-heinz-team/. Accessed 13 Mar 2015

Rosato D (2014) Back to the future with ford bioplastics. Multibriefs. http://exclusive.multibriefs.com/content/back-to-the-future-with-ford-bioplastics. Accessed 13 Mar 2015

Scheirs J (2003) Additives for the modification of poly(ethylene terephthalate) to produce engineering-grade polymers. Chemistry and Technology of Polyesters and Copolyesters, Modern Polyesters

Shumigin D, Tarasova E, Krumme A, Meier P (2011) Rheological and mechanical properties of poly(lactic) acid/cellulose and LDPE/cellulose composites. Mater Sci (Medžiagotyra) 32–37

Snoei de Castro J, Nguyen LD and Seppala J (2014) Bioconversion of commercial and waste glycerol into value-added polyhydroxyalkanoates by bacterial strains. J Micro Biochem Technology. doi:10.4172/1948-5948.1000165, https://www.omicsonline.org/open-access/bioconversion-of-commercial-and-waste-glycerol-into-valueadded-polyhydroxyalkanoates-by-bacterial-strains-1948-5948.1000165.pdf. Accessed 2 Jan 2017

Smitthipong W, Chollakup R, Nardin M (eds) (2015) Bio-based composites for high-performance materials, from strategy to industrial application. Taylor & Francis Group CRC Press, Boca Raton

The Crop Site (2010) BioIsoprene—a Renewable Product with Biofuel Potential. http://www.thecropsite.com/articles/1798/bioisoprene-a-renewable-product-with-biofuel-potential/. Accessed 23 Mar 2015

The Crop Site (2017) Mechanical properties of polymers. http://www.smithersrapra.com/SmithersRapra/media/Sample-Chapters/Physical-Testing-of-Plastics.pdf. Accessed 2 Jan 2017

The Crop Site (2007) Thermoplastic elastomers http://file.seekpart.com/keywordpdf/2011/1/11/201111114737595.pdf. Accessed 2 Jan 2017

Toyota Boshoku (2015) Use of bioplastics. http://www.toyota-boshoku.com/global/about/development/eco/bioplastic/index.html. Accessed 19 Mar 2015

Zhanga Y, Yua C, Chub PK, Lva F, Zhangc C, Ji J, Zhanga R, Wang H (2012) Mechanical and thermal properties of basalt fiber reinforced poly(butylene succinate) composites. Mater Chem Phys 133:845–849

Marine Applications of Natural Fibre-Reinforced Composites: A Manufacturing Case Study

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Abstract The rising concern about environmental issues and the need to find a realistic alternative to glass or carbon-reinforced composites have led to an increased interest in polymer composites filled with natural-organic fibers, derived from renewable and biodegradable sources. The scope of this article is to raise awareness regarding the current scientific and technological knowledge on these so-called green composite materials in order to support their larger application in a number of industry sectors. The general state-of-the-art in terms of green composites is proposed, together with some experimental evidence on the mechanical properties of various ecological materials. As a practical demonstration of this sustainable technology, the adoption of green composites as a valid replacement for fiberglass in sailing applications is also described. This article will, in fact, illustrate, step by step and in great detail, the Wet Lay-up Hand Laminating process used, together with Vacuum Bagging, to realize a yacht deck hatch out of ecological composite materials.

Keywords Boatbuilding · Green composites · Hybrid reinforcements · Manual stratification · Yacht desk hatch

1 Introduction

1.1 Composite Materials

Composite materials consist of two or more materials combined in such a way that the individual materials are easily distinguishable. The new material may be preferred for many reasons: common examples include materials which are stronger, lighter or less expensive when compared to traditional materials. The individual

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materials that make up composites are usually called *constituents*. Most composites have two constituent materials: matrix and reinforcement. The reinforcement is usually much stronger and stiffer than the matrix, and gives the composite its superior properties. The matrix holds the reinforcement in an ordered pattern. Because the reinforcement is usually discontinuous, the matrix also helps to transfer the load among the reinforcements. Considering the presence and the importance of fibers, these materials are also called *fiber-reinforced* composite materials. Most fundamental requirements for composites are directly related to the specificity of reinforcement. Reinforcements basically come in three forms: *particulate*, *discontinuous fiber*, and *continuous fiber*. Reinforcements are referred to as fibers when one dimension is at least one order of magnitude larger compared to others. Even if a large variety of reinforcement is possible, the most common are glass, carbon and aramid (commercially known as Kevlar). Matrix materials are usually some type of plastic, and these composites are often called *reinforced plastics*. The most common plastic matrices are epoxy and polyester and vinyl-ester resins.

1.2 Composites and Ecology

Fiber-reinforced composite materials have gained popularity, despite their generally elevated cost, in high-performance products that need to be lightweight, yet strong enough to withstand harsh loading conditions. At the same time, traditional composites do not represent a valid solution for the environment. One of the main limitations of the use of this large family of composites consists in the simultaneous presence of two different components. This makes reuse and recycling at the end of life quite difficult. Consequently, it is often preferable to engage in direct disposal into a dump or to incinerate the composite products. At the same time, plastic production requires remarkable consumption of oil-based resources, which are notoriously non-renewable. Polymer composites represent a great opportunity for a large range of applications, but the impact on the environment and the distance of these materials from a sustainable industry limits their level of diffusion (Pickering 2006).

With the boom in the nautical sector having started in the 1960s–70s, and given the expected lifetime of over 30 years of a recreational boat (Moreau 2009), the nautical industry expects that a number of boats will come to the end of their useful lives in the coming years. Even if these “dead” boats are not polluting in the sense that they are not releasing any harmful substances into the land or water, there is a risk that they will occupy valuable space in marinas and boatyards, or will be abandoned and dumped illegally, not to mention the derelict look it gives to the surroundings (ECDG 2011). Facing the reality of such risks, the recreational marine industry has recently launched several studies and pilot projects in Europe. However, a totally new approach to both product and production has to be proposed, including such modern tools for environmental evaluation as Risk Assessment and Life Cycle Assessment (Barberio et al. 2010).

1.3 Composites and Boats

As reported by Moreau (2009), in boat construction, the resins used in *fibre reinforced plastic* (FRP) structures are mainly thermosetting (polyester, epoxy, vinylester, etc.). Thermoplastic resins (polyamide, polypropylene, PET, PBT, etc.) have only recently started being used for boat-building or fittings. Recently, the composition of resins has evolved in two ways: both low emission and low styrene content resins are now available on the market. More recently, bio-based resins have started to appear, but their use is still very limited in the nautical sector. The environmental benefits of bio-based resins and adhesives lie in the elimination of toxins in general, the focus on human health and the environment, the reduction of hazardous and toxic materials and waste, the reduction of polluting air emissions, and their recycling capacities. Regarding fibres, natural fibres are also beginning to enter the composite market, but their use in structural elements is limited due to their relatively poor physical properties. Currently, they are used predominantly for filling functions. Glass fibres represent 89% of the worldwide volume of fibres used in composites, while only 10% are natural fibres (Moreau 2009). At the same time, numerous R&D studies for the use of natural fibres are under way and should allow for greater industrial applications in the midterm future

2 Green Composites

2.1 Environmentally-Friendly Materials

The rising concern about environmental issues and, on the other hand, the need for more versatile polymer-based materials have both led to an increase in the general interest in ecological composites. This need is leading scientific research to look for new alternatives, capable of replacing traditional polymer composites with substitutes that have a lower environmental impact, and which are thus often referred to as "*ecocomposites*" or "*green composites.*" These composites can be considered environmentally-friendly when the polymer matrix is biodegradable (e.g., if filled with natural-organic fillers), but also if it comes from renewable sources. The production and characterization of polymer composites based on recyclable polymers (e.g., polyolefins), filled with natural-organic fillers (e.g., fibers and particles extracted from plants) is an extremely interesting field of scientific research and industrial development. At the same time, in a recent period, investigations have also been focused on fibers. Instead of technological fibers such as glass, carbon and aramid, which are already widely used in marine and offshore industries (Camargo et al. 2016), more sustainable ones have been taken into consideration, such as flax, hemp, and cotton. Even if their level of performance is generally much lower compared to traditional composites, especially as far as mechanical resistance is concerned, it is notable that several applications could accept this degradation in requirements in the name of higher eco-sustainability (Sahari and Sapuan 2011).

2.2 Eco-Based Matrices

The availability of bio-based polymer matrices is relatively poor on the market nowadays, but it has been rapidly growing as a result of a large number of ongoing research and industrial investigations on the benefits introduced by these materials and their practical applicability in real cases. Preliminary information on the fundamental properties of composites realized through eco-based matrices is provided in De Paola et al. (2013), Hyseni et al. (2013).

Different kinds of bio-based polymer matrix are available. In particular, inside the families of:

- Thermoset matrices: polyols are compounds with multiple hydroxyl functional groups available for organic reactions, and they react with a large number of chemical species, called curatives or hardeners, to produce cross-linked thermoset matrices. The most important oil used in polyol production is soy bean oil, but cashew nut oil could also give the same results. In order to decrease the impact of their activity on global warming, polyols can also be combined with petroleum-based chemicals.
- Thermoplastic matrices: cellulose represents the most common commercial thermoplastic matrix among bio-based matrices, being 100% eco-sustainable and capable of providing high mechanical properties to the material. Starch-based polymers and Poly (lactic acid) PLA are both available: employment of the former depends on the ability to reduce their moisture absorption, while the latter has similar properties to polystyrene. Summing up, employment of these bio-based polymers depends on the possibility of modifying their properties in order to obtain an easier processing and improve toughness in the final biocomposite.

In addition to their environmental advantages at the end of life, bio-based resins reduce dependency on oil resources. For instance, propylene glycol, which is derived from bio-glycerine, a byproduct of bio-diesel production, can be used as a standard raw material in polyester resins. Vegetable oils from soya beans, castor trees or linseed can also constitute a base material for polyester. Many resin producers have launched R&D programs to obtain 100% bio-based resins, and a similar trend is currently evident in the development of bio-based adhesives.

2.3 Natural Fibers

Natural fibers are compounds combining cellulose, hemicellulose and lignin; they can be derived from leaves (e.g., sisal), bast (e.g., flax, hemp), seeds (e.g., cotton) or fruit (e.g., coir). The most important advantages of natural fibers relate to environmental issues: they are biodegradable and carbon positive, since they absorb more carbon dioxide than they produce (Bogoeva-Gaceva et al. 2007). In addition,

Table 1 Properties of natural and technological dried fibers

Fibers	Density (g/cm^3)	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile strain (%)
Jute	1.3–1.45	342–672	43.8	1.7–1.8
Flax	1.50	300–900	24.0	2.7–3.2
Hemp	–	142–819	4.8–34.4	1.5–4.5
Basalt	2.80	4800	90	3.1
Sisal	1.45	444–552	9.4–22.0	2.0–2.5
E-glass	2.54	3200	70	4.0
Aramid	1.44	2400–3600	60–120	2.2–4.4
Carbon	1.81	5490	294	1.9

they are non-irritating and tend to be non-abrasive, with the latter property resulting in reduced wear on tooling and manufacturing equipment. Other important advantages are shown in terms of specific material properties: using natural fibers in place of synthetic ones, it is possible to reduce the weight of a composite material by up to 40%, and it is also possible to improve flexural strength, stiffness and ductility (De Paola et al. 2013). In addition, improved properties in the case of natural fiber thermoplastic composites can be provided by physical and chemical treatments (Zivkovic et al. 2016). However, in terms of overall properties of strength, synthetic fibers perform better than natural ones, even if there are some natural fibres that can approach the tensile modulus and tensile stress of glass (Table 1). These properties are reported in the technical datasheets of *Carbon Fibers America* and *Twaron* for, respectively, carbon (e.g., T800H) and aramid fibers, in Lopresto et al. (2011) for glass and basalt, in Sridhar et al. (1982) for sisal and flax, and in Duval et al. (2011) for jute.

2.4 Hybridization

According to Hall (2003), laminated composites can be classified as:

- composite laminates, obtained using a single type of fiber,
- hybrid composites, obtained from two types of fiber in the same array,

where this “hybridization” can offer a larger flexibility in searching for the proper material solution in respect to each specific application (Hardaker and Richardson 1980).

An interesting application of hybrid composites, including the use of natural fibers, for the fabrication of small boats can be observed, for instance, in Misri et al. (2010).

The hybrid system for improved material or structural performance is, in fact, a well-known concept in engineering design. Furthermore, it can be an extremely valid strategy in the specific case of green composites. Hybridization is a process of *incorporating* two or more types of fiber of varying properties, usually synthetic fibers with natural fibers, or exclusively natural (Bakkal and Savas 2013), or synthetic mixed (Mishra and Mohanty 2003), in order to yield better strength, better stiffness, a high strength-to-weight ratio and other mechanical properties Santulli (2007). According to this, hybridization of natural composites has been found to be an effective way to improve a composite's mechanical properties and dimensional stability (moisture, temperature, etc.). In particular, it permits solving the difficulties in the practical use of natural fibers related to their low stiffness, lower in respect to that of the synthetic ones. The stiffness of biocomposites can, thus, be improved through hybridization, with the aim of permitting the adoption of this class of composite for structural applications.

3 A Technology for Green Composite Production

3.1 Stratification

Composite materials are realized by adding layers, also called *plies* or *lamina*. A single ply consists of fibers oriented in a single direction (*unidirectional*) or in two directions (*bidirectional*, such as, e.g., a woven fabric). The thickness of the layers largely varies, depending on the characteristic of the fibers, resins, properties required, applications, etc. Thicknesses between 0.1 and 0.5 mm are frequently used in our researches on advanced composites, as in Ghelli and Minak (2011), Boria et al. (2016), Poodts et al. (2014), even if thicker layers are also common and may be especially used for low cost applications.

Composite properties are superior in the direction of the fibers, when oriented. If unidirectional, the composite materials have high strength and stiffness properties in the direction of the alignment of the fibers (Rohatgi 1988). Because most structures are not loaded in a single direction, even though one direction may dominate, it is convenient to orient fibers in multiple directions. This is accomplished by stacking multiple plies together, when each ply consists of unidirectional fabrics and fiber orientation may change from one layer to another, or using multidirectional fabrics. Such a stack is called a *laminate*, and the process is called *stratification*. The number of laminates depends on the properties of the layers so as to guarantee an adequate mechanical resistance and a reasonable weight. In general, these composites consist of 4–40 layers, even if there are well-known examples in naval ships of a larger number of layers being used (Mauritz et al. 2001).

Coming back to the characteristics of fibers, laminated composites can be obtained, in general, using long or short staple fibers. Short and discontinuous fiber composites, even if interesting and convenient in several aspects (such as cost, potentiality for process automation or material reuse), are characterized by mechanical properties significantly lower compared to materials with long and continuous fibers. However, in a large number of practical situations, short and discontinuous fibers are not totally randomly oriented. In this circumstance, the proper orientation of the different layers can lead to improvement of the mechanical properties of the composites, even in the case of short and discontinuous fibers.

3.2 Hand Lay-up Method

The Wet Lay-up Hand Laminating Method (also known as Hand Lay-up, for short) can be historically considered to be one of the earliest techniques used for the production of parts in composite materials. It can also be considered the simplest open moulding method of the composite fabrication processes. It consists in impregnating the fibers manually and then laying them on the mould. Nowadays, Hand Lay-up is still widely used in shipbuilding, especially with fiberglass. Since it is a low-volume, labour-intensive method, it is especially suited to large components, such as boat hulls. Glass or other reinforcing mat or woven fabric or roving is positioned manually in the open mould, and resin is poured, brushed, or sprayed over and into the glass plies. Entrapped air is removed manually with squeegees or rollers to complete the laminate structure. Room temperature-curing polyesters and epoxies are the most commonly used matrix resins. Curing is initiated by a catalyst in the resin system, which hardens the fiber-reinforced resin composite without external heat. For a high quality part surface, a pigmented gel coat is first applied to the mould surface.

This technique permits producing parts in composites of any size in a quite easy and inexpensive way, offering a practical answer to the limits encountered in other production technologies, such as in the case of woodworking (Fragassa 2017), even if attention has to be paid in respect to the environmental criteria on the emission of volatile compounds The technique can be used both for the realization of artefacts in "*solid laminate*," overlying layers of fiber up to the proper resistance, or in the "*sandwich*," consisting of external composite layers and a central core of a lightweight material. Inner and outer skins, beyond their primary function of sustaining loads, have additional purposes related to aesthetics and core protection.

3.3 Vacuum Bagging Method

Vacuum bagging is a technique used to create mechanical pressure on a laminate during its cure cycle. Pressurizing a composite lamination serves several functions. First, it removes air trapped between layers. Second, it compacts the fiber layers for efficient force transmission among fiber bundles and prevents shifting of fiber orientation during the cure. Third, it reduces humidity. Finally, and most importantly, the vacuum bagging technique optimizes the fiber-to-resin ratio in the composite part. These advantages maximize the physical properties of advanced composite materials.

It is noteworthy that in boatbuilding, production methods other than vacuum bagging are largely preferred, such as vacuum infusion. In Bank (2006), a complete overview of methods and processes is reported.

4 Materials and Hybrids

4.1 *Mechanical Characteristics*

As mentioned, in composites, the constituent materials, when combined, produce a material with characteristics different from those of the individual components. This is one of the reasons why composites offer a large range of chemical and physical properties. Furthermore, in the case of "green" constituents, there is an additional variability in properties intrinsically related to the high inconstancy of some parameters in the case of "living" elements (e.g., the percentage of water absorbed by flax).

A preliminary experimental testing of materials is necessary with the aim of reducing the high variability that used to distinguish green composites. The mechanical properties of several biocomposites, reinforced with natural fibers and moulded with a green matrix, have been tested in Pavlovic et al. (2013). All laminates have been realized through hand-up moulding. Three of them consist of natural fibers combined with an ecofriendly matrix (based on a specific vinylester). Two of them are hybrids, combined with two different fibers, both mixed up with a green thermoset resin (considering its low environmental impact). The first hybrid material is a compound of both synthetic and natural fibers (respectively, *carbon* and *flax*), and the second one is a compound with two different natural fibers (*basalt* and *flax*). The mechanical properties of these green materials have been compared with those of traditional fiberglass for nautical applications, obtained by combining fibers of glass with polyester resin.

4.2 *Experimental Tests*

In order to determine all mechanical properties of these laminates, four tests have been recently realized by the authors, according to the proper standards:

- A tensile test has been performed according to the ASTM D 3039 standard: a thin flat strip of material having a constant rectangular cross-section is mounted in the grips of a mechanical testing machine and monotonically loaded in tension while the load recorded. The ultimate strength of the material can be determined from the maximum load carried before failure.

- A flexural test has been performed according to the ASTM D 790 standard: a bar of rectangular cross-section rests on two supports and is loaded by means of a loading nose midway between the supports.
- A drop-weight impact test has been performed, according to the ASTM D-7136 standard, using a balanced, symmetric laminated plate. Damage is imparted through out-of-plane, concentrated impact (perpendicular to the plane of the laminated plate) using a drop weight with a hemispherical striker tip. The damage resistance is quantified in terms of the resulting size and type of damage in the specimen.
- An accelerated aging test uses aggravated conditions of heat and saline solution to speed up the normal aging processes of materials. It is used to determine the long term effects of expected levels of stress within a shorter time, usually in a laboratory according to controlled standard test methods.

Additional details on experiments and results are reported in Pavlovic et al. (2013), Hyseni et al. (2013), Fragassa (2016), or in the newest (Fragassa et al. 2017; Zivkovic et al. 2017). In particular, while the next-to-last (Fragassa et al. 2017), deals with the mechanical and impact characterisation of flax and basalt fibre vinylester composites, together with their hybrids, in the last one (Zivkovic et al. 2017), the influence of salt water absorption on these properties has also been investigated. These measures have now been considered in such a way as to enable selection of the proper combination of fibres and matrix, with the aim of providing an unconventional *green composite* to be used in the case study presented here.

4.3 Advantage of Hybridation

From these results, summarized in Table 2, it is already evident that green composites (e.g., basalt fiber and a vinylester green matrix) can represent a valid solution in terms of mechanical properties, at the level of other most common materials (e.g., fiberglass), but also adding the important property of eco-sustainability. They also confirm that the mechanical strength of basalt and hybrid laminates is greater than that of fiberglass. Adding their Young modulus, maximum strain becomes higher, as expected. Combining basalt with flax fibers proves to be a good method to reduce the stiffness and brittleness of basalt, demonstrated by plastic behaviour after yielding,

Table 2 Some mechanical properties of natural and hybrid composites (Fragassa et al. 2017)

Laminates	Tensile properties					Flexural properties		
	Σ (MPa)	ε (%)	E (MPa)	G (MPa)	ν (–)	σ (MPa)	ε (%)	E (MPa)
Flax	49.3	0.93	4854	2001	0.21	118.3	1.66	6930
Basalt	160.1	1.47	11,042	5368	0.03	265	1.84	14,481
Flax/basalt	86.5	1.12	8151	3879	0.13	144.8	1.69	8275

which provides greater flexibility to the material. The advantages of having a ductile material are multiple, as, for example, it can ensure greater security, because such a material shows, in general, large displacements before failure, when loaded statically. Thus, a ductile material is a good choice for structural elements, as we desire considerable warning to be provided before they fail. Similar behavior can be shown by multidirectional laminates subjected to progressive failure after the failure of the first ply.

5 Manufacturing

5.1 Case Study

In the case of the yacht desk hatch, this access door was realized as a sandwich, coupling two skins in green composite around a central core in light PVC. Each skin was realized by coupling four plies from two different green composites in an ecological hybrid composite. In particular, two plies of basalt fiber (Basaltex BAS 350 g/m^2, woven fabric) were used as an upper shell, creating a hard black surface. Two layers of flax (Lineo FlaxPly, 300 g/m^2, balanced fabric) were chosen to be the lower part, creating a brown and smooth internal surface. In both cases, green fibres were filled using a vinyl ester resin (Distitron VEef 220 STZ), obtained from bisphenol epoxy resin with low styrene content. All these constituents exhibit a high degree of environmental sustainability, particularly evident in comparison with the elevated impact of traditional materials such as fiberglass. As previously detailed, environmental sustainability is not only offered by the high fraction of natural elements used in the artefact (e.g., flax instead of glass; epoxy with low styrene), but also by the technological processes adopted for working the raw materials and made available on the market in the form of resins and fibers. At the same time, especially considering the substantial equivalence in terms of mechanical characteristics between basalt fibers and carbon fibers, both with a tensile strength higher than 4.000 MPa (Table 1), the hybrid material described here has been able to offer a level of resistance and lightness appropriate to the real application.

5.2 Mould Preparation

The manufacturing process started with the preparation of the mould (provided by the manufacturer), which had to be covered with a chemical agent to facilitate the release of the part when the lamination was finished and to avoid damage to the mould during the forming operation due to friction. In this case, a paste wax was used, specific for moulds in composite materials, as a release agent treatment. A *gel coat* was also laid out on the mould. The gel coat consisted of a resin filler which makes the mould smoother, allowing for a better surface as its finish.

5.3 “Skin Coat” Stratification

One of the most delicate phases was then ready to begin: the deposition of the first layer. Considering that this layer is the most external, and thus most in view, it is able to define the main properties of the artefact, including aesthetics and surface resistance. This so-called *skin coat* was realized by overlapping two plies of basalt and flax, rolled manually for the purpose of exalting the final finish of the product. With the aim of accurately cutting the fabric, a model in cardboard was realized, trimmed according to the geometry of the desk hatch (Fig. 1). Two basalt fabrics and two flax fabrics were trimmed to a size abundant enough to reach the edges of the template, so that the fabric would be sufficiently large and would fit easily onto the mould, covering it fully and comfortably in all its parts. The edges of the fabrics were trimmed from the wires coming out (Fig. 2). The preparation of the skin coat began with the impregnation by resin of the first fabric in basalt. The resin was prepared by mixing it with 2% (in weight) of catalyst, mixed well, for a total of 800 g of vinyl ester resin with low styrene content formulated (Fig. 3). The dry fabric (lying on the mould) was impregnated by pouring the resin on top and distributing it along the entire surface, using a spatula to carefully spread it to all its parts, from the centre to the edges (Fig. 4). The flax fabric was placed on top of that (Fig. 5), following which it was flattened, resin was poured on it, and that resin was spread until complete impregnation (Fig. 6).

The stratification of these two fabrics on the mould was particularly effortless thanks to their low weight, which permitted easy manipulation. In the cases of complex geometries, extreme care should be paid to the fastening of fabric that, once stretched, must be effectively retained in position to prevent shifting or folds (Fig. 7).

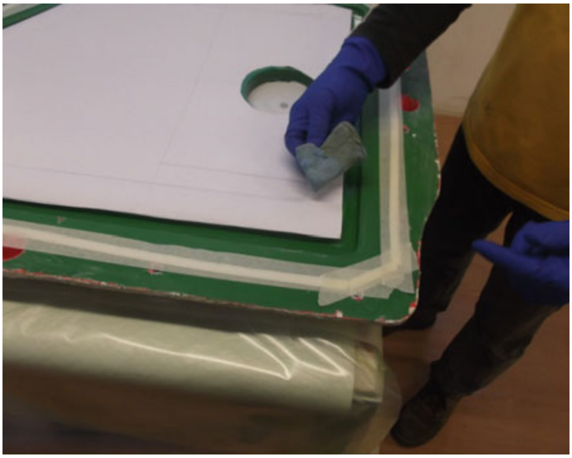


Fig. 1 A model in cardboard has been realized, and trimmed according to the geometry

Fig. 2 The edges of the fabrics have been trimmed from the wires coming out

Fig. 3 The resin has been prepared by mixing it with catalys in exact proportions

Fig. 4 The dry fabric has been impregnated by pouring the resin on top and distributing it along the entire surface, using a spatula

Fig. 5 The fabric made of flax has been placed on the previous one, flattening it

Fig. 6 The other resin has been poured and spread until complete impregnation

Fig. 7 Extreme care has been paid to the fastening of the fabric that, once stretched, has to be retained in position to prevent shifting or folds

5.4 Surface Finishing

After completing deposition of the skin coat, with a ply of basalt facing the mould cavity (as the first layer on the surface), all edges were trimmed with the aim of creating a precise overlapping between the mould and the vacuum bag. Additionally, a hole was drilled, creating an empty space where the handle would be allocated (Fig. 8), reinforcing the whole area with the remaining fabric scraps (Fig. 9).

As the next step, a micro-perforated film, which allows the excess resin and gaseous substances to escape from the laminate in a controlled manner, was stretched (Fig. 10), together with a fabric aerator (*bleeder*), which has the task of allowing the passage of air into the bag when it is subjected to depression, as well as sucking out the gases produced during polymerization (Fig. 11).

Fig. 8 A hole has been drilled, creating an empty space where the handle will be allocated

Fig. 9 The hole has been reinforced with the remaining fabric scraps

Fig. 10 A micro-perforated film, which allows the excess resin and gaseous substances to escape from the laminate in a controlled manner, has been stretched

Fig. 11 A fabric aerator (*bleeder*), which has the task of allowing the passage of air into the bag when it is subjected to depression, as well as to suck out the gases produced during polymerization, has been stretched

5.5 *Vacuum Bag Preparation*

Afterwards, it was necessary to prepare the vacuum bag that had been fixed to the mould (Fig. 12), all along its perimeter, by means of a double-sided high thickness tape, commonly called "tacky tape" (Fig. 13). This tape is adhesive on both sides and is protected by two layers that must be removed at the time of installation. The contact surface between the mould and the vacuum bag must be in good condition and perfectly clean. In this area, in fact, the vacuum bag must adhere perfectly to the mould, avoiding the passage of air from the outside. The vacuum bag is effectively fixed onto the mould, along the whole perimeter: one side of the tape adheres to the mould and the other to the vacuum bag, the high thickness of the tacky tape and its workability allowing for the creation of a barrier against the ingress of air from outside. The vacuum bag should also be applied with extreme care to avoid damage

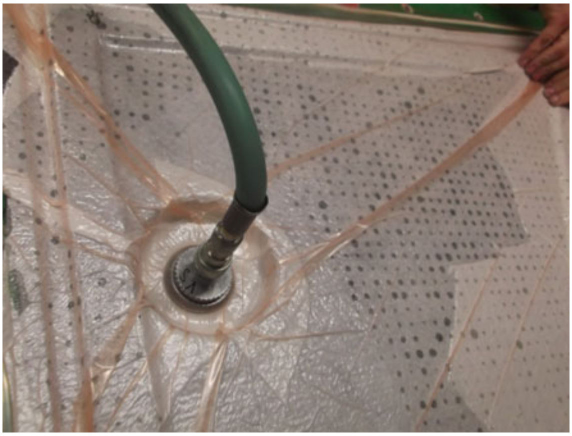
Fig. 12 The vacuum bag has been applied with extreme care to avoid damage in positioning

Fig. 13 The vacuum bag has been fixed to the mould, all along its perimeter, by means of a double-sided high thickness tape

in positioning (Fig. 12). It is all too easy to create tiny holes that, while hardly visible, can frustrate the attempt to create the right depression. It is also recommended, if possible, to use a vacuum bag made from a single piece, avoiding the necessity of assembling multiple parties. The drafting of the vacuum bag must obviously encompass the mould perfectly, considering that, once the depression is created, the bag adheres strongly (Fig. 14). It is therefore necessary to provide a sheet large enough to allow for full adhesion without creating tensions that might tear it, defeating the process. In general, the surface of the vacuum bag must be slightly higher than the developed surface of the mould.

Fig. 14 The drafting of the vacuum bag obviously has to encompass the mould perfectly, considering that, once the depression is created, the bag will adhere strongly

Fig. 15 When the vacuum pump is in operation, the air between the vacuum bag and the mould flows to the outside and the bag is pressed onto the mould



5.6 *Vacuum Sealing*

When the positioning operation of the vacuum bag is finished, it is possible to turn on the vacuum pump by connecting it to the intake valve, properly inserted. When the vacuum pump is in operation, the air between the vacuum bag and the mould flows to the outside and the bag is pressed onto the mould (Fig. 15). A depression is created in a very short time (a couple of minutes) and kept constant for a curing time of 12 h. Referring to the pressure of the pump, it is not possible to specify a value that will assure the validity of the process in all cases, but in this specific case, a value of 0.7 bar was preferred. At this stage, the first part of the process appears to be complete. However, it is important to remember that the resin is not fully cured, even if it is already in the solid state. An extra period of 24 h needs to be reserved before the vacuum bag is removed together with a micro-perforated film and the fabric aerator. The object, thus realized, has a perfectly glossy and reflective upper surface, corresponding to its side that is in contact with the mould (basalt fabric), while the opposite face is opaque and rough, because it was in contact with the peel-ply (flax).

5.7 Core Inclusion

The following day, after having consolidated the skin coat and removed the plastic bag (Fig. 16), the core in PVC was located, together with the last two plies as a final cover: a sandwich type construction was thus obtained (Fig. 17). The panel, which constitutes the core, was formed by a light material (PVC foam), squared, flexible,

Fig. 16 After having consolidated the skin coat, the plastic bag has been removed

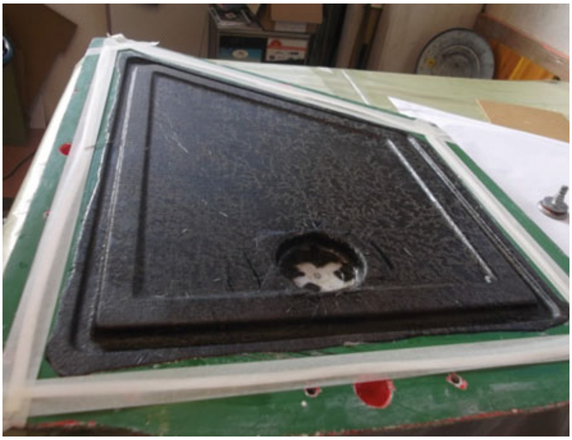
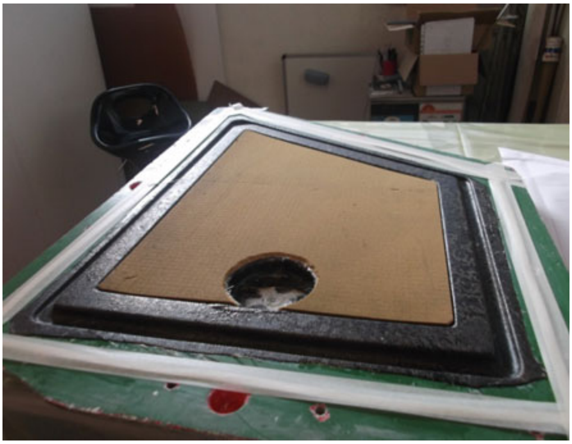


Fig. 17 The core in PVC has been located, just before the positioning of the last plies as a final cover



5 mm thick and generally serving to create space between the inner layers and the outer, increasing the stiffness of the artefact with respect to its weight. The panel was carefully contoured to avoid leaving empty spaces along the edges that would give rise to the accumulation of resin. The core had to be superficially impregnated with resin in such a way as to permit better skin adhesion. For this scope, a slight layer of resin was laid on the surface of the two stratifications (Fig. 18) and, after that, on the core (Fig. 19). A bioresin with 2% by weight of catalyst was also used in this phase.

Fig. 18 Resin has been laid on the surface of the stratifications

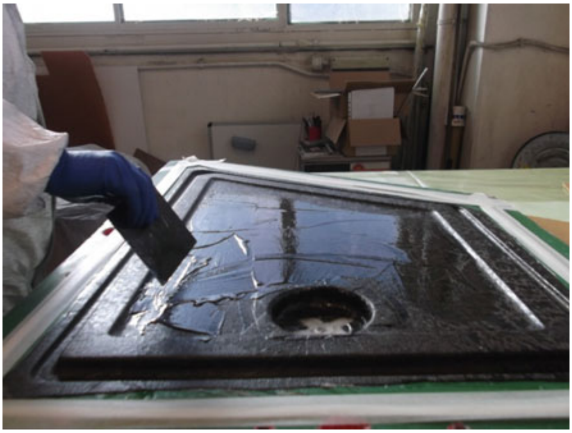
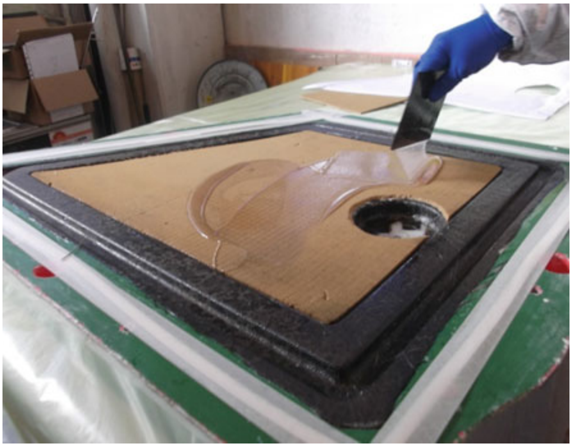


Fig. 19 The core has to be perfectly impregnated with resin through its entire thickness



5.8 Lower Surface

The second cover, used as lower part of the door, was manufactured through a similar procedure. It too was realized by overlapping plies of basalt and flax with resin stratification. But in this case, the basalt faced inward (with respect to the door) and the flax outside. In detail, the procedure included the following steps: impregnation by resin of two plies of basalt, deposition of two foils of flax, distribution of resin with a spatula, always with the foresight to perfectly distribute the resin and eliminate local excess (Fig. 20), provision of the laminate on the mould, edge finishing with a cutter, manual compaction of the layers so as to fit the shapes of the mould, deposition of the micro-perforated film, deposition of the fabric aerator, deposition of the plastic bag, connection of the valve to the vacuum pump, creation of the vacuum (Fig. 21).

Fig. 20 Excesses of resin have been eliminated

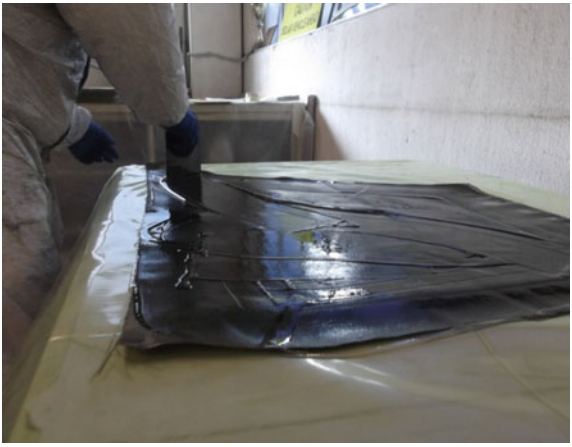
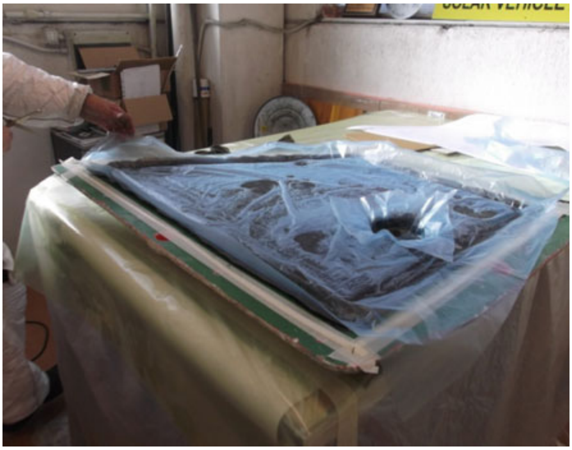


Fig. 21 Vacuum has been created



5.9 Final Finishing

After waiting 24 h, during which time the resin was allowed to cure at an ambient temperature, the artefact was released from the vacuum bag and removed from the mould. As usual, the extraction of the object from the mould was not trouble-free: specific attention had to be paid so as not to damage both factors (object and mould), also ascertaining that the resin had been completely cured. In this case, a plastic spatula, instead of a metal one, was used for the separation, minimizing the risk of scratches on the surfaces of the mould and the work piece.

5.10 An Ecofriendly Artefact

After sanding of the surfaces and finishing of the edges, the piece was ready for use. The access door, thus completed, presented a hard, intensely black, glossy and reflective upper surface, corresponding to the basalt skin coat (Fig. 22). It was considered to represent a valid solution as part of the upper deck on a luxury boat. The opposite face of the sandwich, made of flax, was opaque, naturally brown, smooth to the touch, and suitable as an internal part of the roof in compartments or cabins (Fig. 23). From a functional point of view, this door is characterized by its minimal thickness, lightness (only 1.8 kg) and, at the same time, high mechanical resistance, comparable to that of carbon fiber-reinforced components (Fragassa


Fig. 22 Upper surface in basalt (before finishing)

Fig. 23 Lower surface in flax (before finishing)

et al. 2017), even after prolonged immersion in salt water (Zivkovic et al. 2017). It is thereby evident that hybrid composites, such as the basalt-flax fiber-reinforced composite investigated here, could represent a valid material solution in boat-building, especially when eco-friendliness justifies an increase in cost.

6 Discussion and Conclusion

6.1 General Considerations

Recreational boating is sometimes considered a major source of pollution of the marine environment, due to its high visibility on lakes and along the coast. Even if this is far from the case, with boating actually accounting for less than 1% of overall pollution affecting the marine environment (Moreau 2009), the worldwide community has a different perception. This attention toward sustainability in processes and products can act to foster the adoption of uncommon materials, including, in the case of composites, the use of natural fibers and ecological resins.

The new ecological door is certainly more expensive than the original one. This is largely related to the adoption of more valuable raw materials such as fibers, flex and basalt instead of the cheap glass, able to redouble the material cost

(Santulli 2007). Even in the case of much wider utilization of green composites, as is quite reasonable to expect in the near future (Khalil et al. 2012), it is unlikely that the costs for these materials and their products will ever decrease in such a way as to be economically competitive with fiberglass. Thus, green composites will probably never represent a suitable material solution in the case of large-mass products, aimed at low-end markets (Bismark et al. 2006). Besides, eco-composites already appear to be a valid strategy for increased eco-sustainability, especially in respect to their mechanical properties. In Fiore et al. (2011), a direct comparison between the respective effects of glass and basalt, used as reinforcements in epoxy, is proposed and specifically addressed in regard to marine applications.

According to Artemenko (2003), for instance, basalt plastics have better physicomechanical properties than fibreglass plastics and are much less expensive than carbon-fibre-reinforced plastics. They also satisfy safety standards and environmental requirements. And even if other green reinforcements, such as flax, hemp, jute, etc., which offer lower performance than even basalt fibers (Table 1), are not able to provide the highest sort of performance offered by carbon fibers in the most exclusive applications, green hybrid composites can nevertheless demonstrate a specific resistance, acceptable in a large number of practical cases (Castegnaro 2017). Moreover, at least in anticipation, their final cost will soon be comparable with that of the carbon fiber-reinforced polymers. And in addition, they will guarantee a "*Thinking Green*" approach that several markets are already taking more and more into consideration, even renewing the level of competitiveness of composite products.

6.2 New Functionalities

Furthermore, fascinating evidence has been noted during the realization of the yacht deck hatch of the great potential interest in the case of other industrial applications. Ecological composites can offer products with a new aesthetic and a number of extremely refined functionalities. Basalt, for instance, is deeply black and intense in colour, much more homogeneous and aggressive than carbon, and often disrupted by the presence of fibers in evidence. Flax, its colour varying in shades of walnut and oak, looks warm and natural, perfect for enhancing its use for "human purposes." This is even more relevant in regards to contact. For example, it is impossible to handle fiberglass without adopting surface stabilization treatments that prevent glass fibers from escaping, polluting the environment or slipping into the skin. And it requires only minimum harm on surface, such as micro impacts or corrosion, to start this process. Contrastingly, with flax, it is immediately evident that this is, after all, simply another normal tissue, hardly different from the traditional garments and carpets that accompany us in life.

6.3 Green Composites and Environmental Sustainability

Currently, numerous research groups are dedicated to minimizing the environmental impact of polymer composite production, in which the polymer matrices are derived from renewable resources such as polylactide (PLA), thermoplastic starch (TPS) or thermoset matrices. Their high renewable content derives from vegetable oils and, combined with natural reinforced fibers (NF) to form environmentally-friendly and fully degradable composite laminates, they represent a potential substitute for petroleum-based resins. The complete characterization of the mechanical properties of ecological composites is an essential step for their common and widespread use. Several families of ecocomposite, consisting of a "green" matrix reinforced with natural fibers, have been produced and experimentally tested. These results have been compared with experimental data from "traditional" composites. The characterization of these materials' mechanical properties is an important factor for their application in real cases. In fact, mechanical properties such as flexural and tensile resistance can largely limit the use of green composites in industrial applications. The use of hybrid laminates, together with sandwich solutions, can offer an interesting practical solution. In this investigation, use of fibers of mineral (basalt) and plant (flax) origin as the reinforcing fibers are assembled in a *green* thermoset matrix in sailing applications, offering low environmental impact. It can be concluded that natural fiber-reinforced biodegradable polymer composites can offer a valid response to the desire for sustainability over a wide range of applications, including sailing applications.

Acknowledgements The artefact was built at in Metal Tig Srl of Castel San Pietro Terme, Italy. The hatch was designed by Ferretti Yachts, and has already been produced and installed on several luxury yachts. This research is part of a larger international investigation regarding the use of natural materials, including wood and cellulose-based reinforcements, in market-oriented applications (as detailed in Savoia et al. 2016).

References

Artemenko SE (2003) Polymer composite materials made from carbon, basalt, and glass fibres structure and properties. Fibre Chem 35(3):226–229

Bakkal M, Savas M (2013) Development of natural fiber reinforced laminated hybrid composites. Adv Mater Res 628:15–20

Bank LC (2006) Composites for construction: structural design with FRP materials. Wiley, London

Barberio G, Buttol P, Righi S, Andretta M (2010) Combined approach of Risk Assessment and Life Cycle Assessment for the environmental evaluations: an overview. In: Maggioli (ed) Proceeding of Ecomondo Congress, pp 1262–8, 3–6 November Rimini

Bismarck A, Baltazar-Y-Jimenez A, Sarikakis K (2006) Green composites as panacea? Socio-economic aspects of green materials. Environ Dev Sustain 8(3):445–463

Bogoeva-Gaceva G, Avella M, Errico M (2007) Natural fiber eco-composites. Polym Compos 28:98–107

Boria S, Pavlovic A, Fragassa C, Santulli C (2016) Modeling of falling weight impact behavior of hybrid basalt/flax vinylester composites. Procedia Engineering 167:223–230. doi:10.1016/j.proeng.2016.11.691

Camargo FV, Guilherme CEM, Fragassa C, Pavlovic A (2016) Cyclic stress analysis of polyester, aramid, polyethylene and liquid crystal polymer yarns. Acta Polytech 56(5):402–408. doi:10.14311/AP.2016.56.0402

Castegnaro S, Gomiero C, Battisti C, Poli M, Basile M et al (2017) A bio-composite racing sailboat: Materials selection, design, manufacturing and sailing. Ocean Eng 133:142–150

De Paola S, Minak G, Fragassa C, Pavlovic A (2013) Green Composites: A Review of State of Art. In: Proceedings of 30th Danubia Adria symposium on advanced mechanics. Croatian Society of Mechanics (ed). Primosten, Croatia, pp 77–78, 25–28 September 2013

Duval A, Bourmaud A, Augier L, Baley C (2011) Influence of the sampling area of the stem on the mechanical properties of hemp fibers. Mater Lett 65:797–800

European Commission DG Environment (2011) Recovery of obsolete vessels not used in the fishing trade, COWI A/S, Denmark

Fiore V, Di Bella G, Valenza A (2011) Glass-basalt/epoxy hybrid composites for marine applications. Mater Des 32(4):2091–2099

Fragassa C (2016) Effect of natural fibers and bio-resins on mechanical properties in hybrid and non-hybrid composites. In: Proceedings of the 8th conference on times of polymers & composites: from aerospace to nanotechnology. American Institute of Physics (AIP). 19–23th June 2016, Ischia (Italy). AIP Conference Proceedings, vol 1736, No. 4949693. doi:10.1063/1.4949693

Fragassa C (2017) From Design to Production: an integrated advanced methodology to speed up the industrialization of wooden boats. J Ship Prod Des 33(2):1–10

Fragassa C, Pavlovic A, Santulli C (2017) Mechanical and impact characterisation of flax and basalt fibre vinylester composites and their hybrids. Compos Part B. doi:10.1016/j.compositesb.2017.01.004

Ghelli D, Minak G (2011) Low velocity impact and compression after impact tests on thin carbon/epoxy laminates. Compos Part B Eng 42(7):2067–2079

Hall, BJ, Schaffer, GB, Ning, et al (2003) Al/AlN layered composites by direct nitridation of aluminium. J Mater Sci Lett 22:1627–1630

Hardaker KM, Richardson MOW (1980) Trends in hybrid composite technology. Polym Plast Technol Eng 15(2):169–182

Hyseni A, De Paola S, Minak G, Fragassa C (2013) Mechanical characterization of ecocomposites. In: Proceedings of 30th Danubia Adria Symposium on advanced mechanics. Croatian Society of Mechanics (ed), Primosten, Croatia, pp 175–176, 25–28 Sept 2013

Khalil HA, Bhat AH, Yusra AI (2012) Green composites from sustainable cellulose nanofibrils: a review. Carbohydr Polym 87(2):963–979

Lopresto V, Leone C, De Iorio I (2011) Mechanical characterisation of basalt fibre reinforced plastic. Compos Part B 42:717–723

Mishra S, Mohanty AK (2003) Studies on mechanical performance of biofibre/glass reinforced polyester hybrid composites. Compos Sci Technol 63(10):1377–1385

Misri S, Leman Z, Sapuan SM, Ishak MR (2010) Mechanical properties and fabrication of small boat using woven glass/sugar palm fibres reinforced unsaturated polyester hybrid composite. IOP Conf Ser Mater Sci Eng 11(1):012015

Moreau R (2009) Nautical activities: what impact on the environment? A life cycle approach for clear blue. Ed. European Confederation of Nautical Industries. 2th Ed. Brussels

Mouritz AP, Gellert E, Burchill P, Challis K (2001) Review of advanced composite structures for naval ships and submarines. Compos Struct 53(1):21–42

Pavlovic A, De Paola S, Fragassa C, Minak G (2013) Mechanical characterization of green composites: earliest experimental evidences by flexural tests. In: Proceedings of the ICCE 21 composite/nano engineering conference, Tenerife, Spain

Pickering SJ (2006) Recycling technologies for thermoset composite materials—current status, Elsevier Composites: part A 37

Poodts E, Minak G, Mazzocchetti L, Giorgini L (2014) Fabrication, process simulation and testing of a thick CFRP component using the RTM process. Compos Part B Eng 56:673–680

Rohatgi P (1988) Cast metal matrix/composites. Metals handbook. Cast ASM Int 15:840–854

Sahari J, Sapuan SM (2011) Natural fiber reinforced biodegradable polymer composites. Rev Adv Mater Sci 30:166–174

Santulli C (2007) Impact properties of glass/plant fibre hybrid laminates. J Mater Sci 42(11):3699–3707

Savoia M, Stefanovic M, Fragassa C (2016) Merging technical competences and human resources with the aim at contributing to transform the Adriatic area in a stable hub for a sustainable technological development. Int J Q Res 10(1):1–16

Sridhar MK, Basavarajappa G, Kasturi SG, Balasubramanian N (1982) Evaluation of jute as a reinforcement in composites. Indian J Fibre Text Res 7:87–92

T800H Technical Data Sheet CFA-007, Carbon Fibers America Inc

Twaron Technical Data Sheet, Teijin Ltd

Zivkovic I, Pavlovic A, Fragassa C (2016) Improvements in wood thermoplastic composite materials properties by physical and chemical treatments. Int J Q Res 10(1):205–218

Zivkovic I, Pavlovic A, Fragassa C, Brugo T (2017) Influence of moisture absorption on the impact properties of flax, basalt and hybrid flax/ basalt fiber reinforced green composites. Compos Part B 111:148–164. doi:10.1016/j.compositesb.2016.12.018

Influence of Biodiesel Blends on Characteristics of Gaseous Emissions from Two Stroke, Low Speed Marine Diesel Engines

Danilo Nikolic, Sead Cvrk, Nada Marstijepovic, Radmila Gagic and Ivan Filipovic

Abstract As a renewable source of energy, biofuels have a favourable impact on the environment and can replace fossil fuels to some extent. Biodiesel is one option for reducing the emission of pollutants and GHG in the shipping sector. By 2030, Lloyd Register predicts a global demand for about 100 million tons of biofuel in shipping, mostly biodiesel. This study investigates the influence of biodiesel blends on the characteristics of gaseous emissions from a two-stroke, low speed marine diesel engine. For this research, a reversible low-speed two-stroke marine diesel engine was used, without any after-treatment devices installed or engine control technology for reducing pollutant emission. Tests were carried out on three regimes of engine speed, 150, 180 and 210 rpm under heavy propeller condition, while the ship was berthed in the harbour. The engine was fuelled with low sulfur diesel fuel and blends containing 7 and 25% v/v of three types of second-generation biodiesel made from cast-off sunflower and palm oil waste from frying. For biodiesel production, a base-catalyzed transesterification was implemented. Biodiesel blends show better emission performance in regard to NOx, SO_2, CO, and CO_2 than pure low sulfur diesel fuel.

Keywords Used frying oils · Biodiesel · Low sulfur diesel fuel · Two-stroke low speed marine diesel engine · Gaseous emission

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1 Introduction

The continuous increase in international maritime traffic has correspondingly increased marine fuel consumption from about 250 million to 325 million tons over the period from 2007 to 2012 (IMO 2014). As a consequence, ships were responsible for 13, 15 and 2.2 (on an average annual basis) of global sulfur oxide (SOx), nitrogen oxide (NOx) and carbon dioxide (CO_2) emissions, respectively (IMO 2014). A ship's exhaust emission can be transported hundreds of kilometres inland. The median transport velocity of SOx and NOx is around 400 kilometres per day, while mean residence time is 1–3 days, indicating mean transport distances of 400–1200 km (Lamas and Rodriguez 2012).

The International Maritime Organization (IMO) recognizes the importance and need to limit the emission of pollutants and greenhouse gases originating from marine diesel engines. An International Convention for the Prevention of Pollution from Ships—MARPOL 73/78—was adopted by the IMO's Marine Environment Protection Committee (MEPC). The MARPOL Convention was amended in September 1997 to add the Protocol, which includes Annex VI, "Regulations for the Prevention of Air Pollution from Ships." Annex VI sets limits on SOx and NOx emissions, prohibits deliberate emissions of ozone-depleting substances, and also regulates emissions of VOC from tankers along with shipboard incineration. This Protocol entered into force on May 19th, 2005, and applies to all engines with over 130 kW of power. The MEPC revised MARPOL Annex VI with the aim of further strengthening emission limits and requirements pertaining to the sulfur levels in marine fuels. The amendments entered into force on July 1st, 2010. A new chapter "Review of Synthetic Fuels and New Materials Production Based on Pyrolysis Technologies" of Annex VI, entitled "Regulations on energy efficiency for ships," is aimed towards reduction of greenhouse gas (GHG) emissions from ships. Chapter "Review of Synthetic Fuels and New Materials Production Based on Pyrolysis Technologies" includes a set of technical and operational measures, in order to improve the energy efficiency of ships. This chapter entered into force in January 2013 and applies to all ships of over 400 gross tonnage. The IMO believes that these measures could help in reducing CO_2 emissions by between 45 to 50 million tons on an annual basis by 2020 (IMO 2015).

Biofuels could be an option for low carbon intensity in shipping. They are renewable and can be produced locally. The main drawbacks of biofuels are the limitation of raw materials and production costs. In general, the first generation of biofuels has been produced from grains, oil crops and sugar crops. These resources for the production of biofuels are limited. There is a threshold beyond which the production of sufficient biofuel would jeopardize food supplies and biodiversity. Since the first generation of biofuels has certain limitations, the second and third generations of biofuels are already under development worldwide. The basic raw material for production of the second generation of biofuels is biomass, which consists of the remains of the inedible portions of crops, other crops that are not used for food purposes, and industrial waste such as wood chips, bark and pulp from the processing of fruit and many other items. The third generation of biofuels includes production from microalgae. The price of biofuels is another key factor limiting their widespread use, mainly because of their higher cost of production compared to fossil fuels.

There is little practical experience with the use of biofuels in shipping. Several companies have tested biofuels, mostly in cargo and passenger ship engines. Most of these experiments have been carried out by shipping companies, sometimes in cooperation with classification societies. Tests were mostly conducted using FAME (fatty acid methyl esters—biodiesel), vegetable oils and BioLNG (Florentinus et al. 2011). The implementation of biodiesel as a marine fuel was tested in several research programs (RCCL Project Royal Caribbean—Cruises testing on biodiesel, MAERSK/LR Project, BV energy Project, Earthrace), in which certain advantages of biodiesel over fossil fuels were noted: blending can be made up to 100% of biodiesel, there was a reduction in particulate emissions, no adverse effects were detected in marine engines, and no bacterial formations were detected in tanks of biofuels during storage for more than 6 months. The potential problems when using biodiesel are: it acts as a solvent and tends to soften and degrade certain rubber and elastomer compounds that are often used in older engines, and it can easily remove deposits that remain after diesel fuel has been in the system, and thus clog filters (Florentinus et al. 2011). The IMO study (IMO 2007) concluded that low blends of biodiesel up to 20% (B20) could be used without any fuel system degradation. The application of smaller biodiesel blends at marine fuels distillates could be introduced relatively easily. This compound could be prepared at the time of bunkering. These studies were conducted on medium speed 4-stroke marine diesel engines.

The used frying oils, generated from fried food, could be a candidate for biodiesel production in regions with negligible vegetable oil production. Wastes containing oils are products of decomposition that impair the oil's quality, causing a reduction in productivity in the trans-esterification reaction and also possibly generating undesirable by-products that can spoil the final product. Therefore, it is of great importance to refine used frying oils for biodiesel production, using filtration, de-acidification or neutralization and whitening processes.

The influence of biodiesel (FAME) blends with low sulfur diesel fuel on the characteristics of gaseous emissions from marine diesel engine was investigated. A reversible, two-stroke, low speed, cross-flow scavenging, 4-cylinder marine diesel engine was used for the experiment. The engine was fuelled with low sulfur diesel fuel and blends containing 7 and 25% of two types of biodiesel. The two types of biodiesel were produced under lab conditions, using cast-off sunflower and palm oil waste from frying. Base-catalysed trans-esterification was used in this research.

2 Experimental Procedure

For this study, a marine diesel engine was employed. It was a reversible 4—cylinder, 2-stroke engine with cross-flow scavenging, model "ALPHA 494 R" produced by LITOSTROJ Ljubljana (Slovenia) under a Burmeister licence,

Table 1 Marine diesel engine specifications

Engine producer	Engine model	Working principle	Max power	Cyl. No.	Stroke/bore
Burmeister	Alpha 494-R	2-stroke	390 kW @ 320 rpm	4	490 mm/290 mm

Table 1. The engine can be regarded as low speed because the maximum engine speed is 320 min^{-1}, making a maximum power of 390 kW. Since it is an old type of marine diesel engine, there are no aftertreatment devices installed, nor any engine control technology for reducing pollutant emission. This is the preferable situation for an investigation of the direct influence of biodiesel on exhaust emissions from marine diesel engines.

The direct propulsion system of the ship is comprised of the engine, the propeller shaft that is connected to the output coupling, and the fixed pitch propeller. Measurements were made when the ship was berthed in the harbour. Running the engine when the ship is berthed is called a heavy propeller condition. For this reason, the measurements were carried out only on three regimes of engine speeds, 150, 180 and 210 min^{-1}.

During operation of the engine, power is constantly changing depending on the connected consumer. Under the conditions of operation of the vessel, the engine power that is transmitted to the fixed pitch propeller depends on the number of revolutions, pitch and propeller diameter. The resistance provided by the fixed pitch propeller is proportional to the square of the propeller speed:

$$M = k \cdot n^2 \tag{1}$$

Effective power, delivered to the propeller, can be expressed through the torque that is transmitted from the engine crankshaft via coupling to the propeller shaft and propeller, where it reverses the angular velocity ω. The recorded average torque and shaft speed data are used for effective engine power estimation in accordance with the formula (Borkowski et al. 2011)

$$P_e = M \cdot \omega = M \frac{\pi \cdot n}{30} [kW], \tag{2}$$

where:

M means the measured torque [kNm],
and n means the engine-propeller rotational speed [rpm].

For the set of different engine speeds of 150, 180 and 210 min^{-1} and the fuels, measurements of propeller shaft torque and power were conducted by means of strain gauges. This method established a functional connection between the elastic angular deformation of the propeller shaft and engine torque/power. Experimental measurements of propeller shaft torque and power are set as two pairs of type

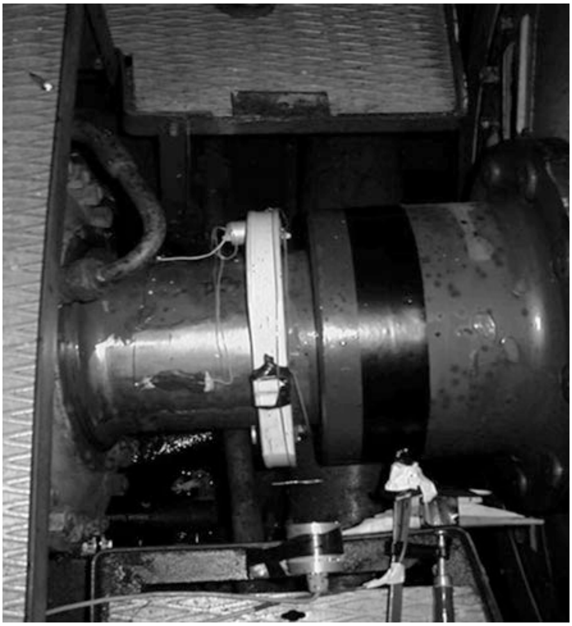

Fig. 1 Strain gauges mounted on the propeller shaft

XY21-6/350 strain gauges, connected in the Wheatstone bridge and powered with an AC voltage of 9 V, are installed onto the propeller shaft. The strain gauges are mounted at an angle of 180° relative to one another. From the Wheatstone bridge, a measuring signal is delivered to the radio transmitter, allowing a transfer of data to the receiver. A power source, transmitter and antenna are mounted on a ringed disc made of plastic in order to eliminate noise, and this is placed on the propeller shaft. Next to the shaft, a signal receiver and speed sensor are placed (Fig. 1). The signal receiver and speed sensor are connected to an electronic measuring device, the "Spider 8." The "Spider 8" is connected to a personal computer with "Catman 3.0" data processing software. Equipment was produced by Hottinger Baldwin MESSTEHNIK (HBM).

Hourly fuel consumption was measured for each engine speed and fuel type. For the fuel mass flow estimation, the volumetric method of fuel consumption measurement was employed according to the formula (Borkowski et al. 2011)

$$B = \frac{V_p \cdot \rho_p}{t} \, [\text{kg/h}], \tag{3}$$

where

B is the fuel mass flow [kg/h]
V_p is the fuel volume consumed during the measurement time [m^3]
ρ_p is the fuel gravity [kg/m^3]
and t is the time of measurement [h].

Table 2 Specification of exhaust emission analyser Testo, model 350-MARITIME

Parameter	Measuring range	Accuracy
°C, flue gas	−40 up to 1000 °C	max ±5 K
O_2	0 … 25 vol.%	
CO	0 … 3000 ppm	
NO	0 … 3000 ppm	
NO_2	0 … 500 ppm	
SO_2	0 … 3000 ppm	
CO_2	0 … 40 vol.%	
Pabs	600 … 1150 hPa	±5 hPa at 22 °C ±10 hPa at −5 °C up to 45 °C

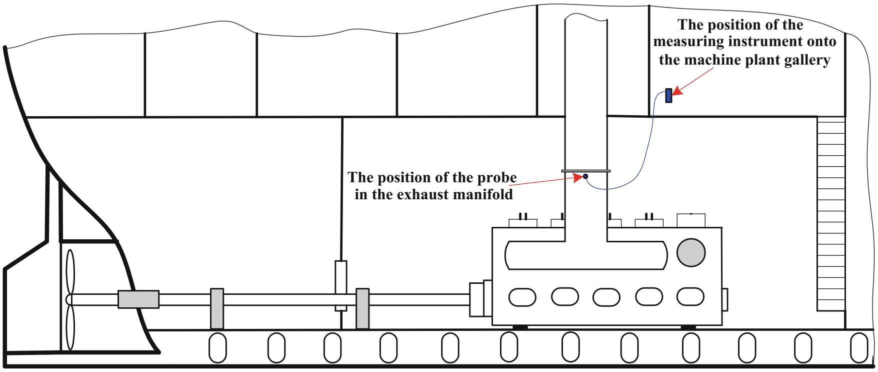

Fig. 2 Position of exhaust emission testing equipment

Exhaust emission analyser Testo, model 350-MARITIME, was used in the experiment for measuring SO_2, CO, NOx and CO_2 concentrations in the engine exhaust. Testo model 350-MARITIME has type approval by Germanisher Lloyd. The specification of the emission analyser is given in Table 2. The analyser was set on the gallery about two meters above the engine. The probe was positioned inside an opening of the exhaust gas collector. A lower part of the exhaust gas collector from the engine exhaust to the point of probe insertion was not cooled. Between each regime of engine speed, exhaust gas tests were conducted after the parameters of the engine, such as coolant and oil temperature, were stabilized. Figure 2 shows the schematic of the emission tests.

The marine diesel engine was fuelled with pure diesel fuel and blends containing 7 and 25% of two types of biodiesel (FAME), so there was no need for engine modifications. The diesel fuel was a representative fuel used by the fleet of Montenegrin vessel boats in territorial waters with a flashpoint above 60 °C. Biodiesel was produced under lab conditions, using cast-off sunflower and palm oil

Table 3 Test fuels basic properties

Parameters	Units	Fuel 1 DF	Fuel 2 DP7%	Fuel 3 DP25%	Fuel 4 DS7%	Fuel 5 DS25%
Density @ 15 °C	kg/m^3	833.4	836.37	844.8	837.2	846.6
Viscosity @ 40 °C	mm^2/s	2.92	3.00	3.21	2.95	3.23
Cetane number		51.3	52.5	53.9	53.5	54.2
Distillation % (v/v) recovered @ 250 °C % (v/v) recovered @ 350 °C 95% (v/v)	% (v/v) % (v/v) °C	29 91 354	26 92 356	20 92 360	28 91 357	19 89 361
Sulfur content	mg/kg	8.57	7.91	5.68	7.79	5.64
Water content	mg/kg	40.94	71.93	153.65	79.99	177.42
Total aromatics	% m/m	22.8	22.5	20.5	22.3	19.8
FAME content	v/v	0	7	25	7	25

waste from frying. This frying oil waste was collected from hotel restaurants. Base-catalysed trans-esterification was used for biodiesel production. The basic properties of the test fuel are given in Table 3, where DF stands for pure diesel fuel, DS stands for blends of diesel fuel and biodiesel made of sunflower oil waste from frying, and DP stands for blends of diesel fuel and biodiesel made of palm oil waste from frying. For blended fuels, to the initial letters, a percentage of biodiesel is added to it. The poor low-temperature properties of biodiesel were avoided by performing tests during the summer period. Also, the biodiesel was used in an experiment a couple days after it was produced in the laboratory, so the poor stability properties of biodiesel were avoided.

Tests were conducted under identical conditions. Fuel was supplied to the engine by an outside tank. For each fuel change, the fuel lines were purged, and the engine was left to run for a minimum 20 min in order to be stabilized under new conditions. Fuel samples were poured into separate tanks connected to the suction side of the engine fuel pump. Excess fuel was returned into the same tank. The tank was located on the gallery in the engine room about two meters above the engine, so that the fuel came to the fuel pump by force of gravity. A glass burette of known volume was used for fuel consumption measurements. It was attached in parallel to the tank.

The engine ran for 8600 h after the last overhaul, and there were no adjustments of the engine for this experiment. The purpose of the performed measurements was to determine trends of gaseous emissions in relation to different types and content of the second-generation biodiesel in the blends for the marine diesel engine in service.

Table 4 Dependence of engine speed on torque, effective power and fuel consumption

Engine speed, rpm	Torque, Nm	Effective power (propeller), kW	Fuel consumption, kg/h				
			Fuel 1 DF	Fuel 2 DP7%	Fuel 3 DP25%	Fuel 4 DS7%	Fuel 5 DS25%
150	4267	67	15.30	15.30	15.90	16.00	16.35
180	5609	105	23.20	23.35	24.25	24.45	24.95
210	7643	168	36.20	36.35	37.80	38.10	38.85

3 Results and Discussion

3.1 *Engine/Propeller Parameters*

With an increase in engine speed, the torque and effective shaft power increase as well (Table 4). Fuel consumption increases with an increase in the biodiesel share of the fuel (Table 4), which is due to the lower calorific value of biodiesel compared to diesel fuel.

3.2 *Exhaust Emission*

3.2.1 Oxides of Nitrogen, NOx

Different types of oxide of nitrogen (NOx) are produced when oxygen reacts with nitrogen in air and fuel at high temperatures (Heywood 1988). This means that the formation of NOx inside an engine cylinder is temperature dependent.

It can be observed from Figs. 3 and 4 that the amount of NOx increases with an increase in engine speed. The reason is very simple, i.e., the engine combustion temperature increases due to the increase in engine speed. The trend for the increase in NOx is smooth.

Emission of NOx from a biodiesel blend-fueled engine is significantly lower than the NOx emission from a diesel-fueled engine, at all engine speeds. This reduction ranges from 26 to 60%, and increases with increased biodiesel content in fuels and engine speed. Considering only blended fuels, with an increase in biodiesel content from 7 to 25%, there is evident NOx emission reduction regardless of engine speed. Possible reasons for the decrease in NOx are higher cetane numbers and a lower aromatic content of the biodiesel blends compared to the diesel fuel.

A higher cetane number in the biodiesel is usually associated with lower NOx emissions (Kalligeros et al. 2003; Monyem and Gerpen 2001). A higher cetane number reduces the ignition delay due to the reduced size of the premixed combustion. Reduced ignition delay results in lower NOx rates, since the combustion pressure rises more slowly, thus giving more time for cooling through heat transfer

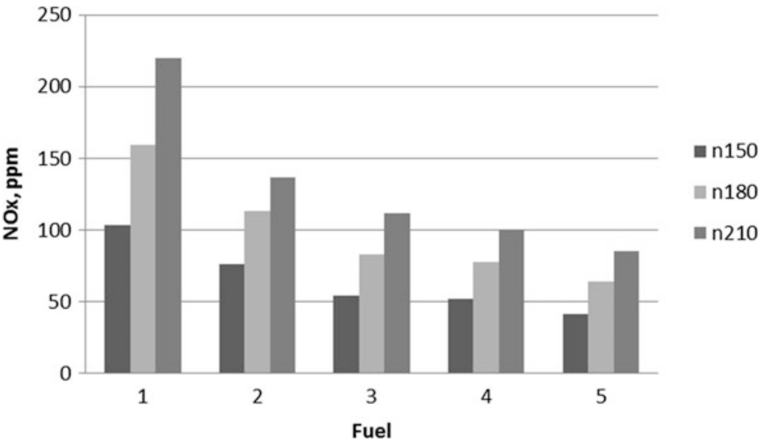

Fig. 3 Exhaust emission of NOx for different fuels, %

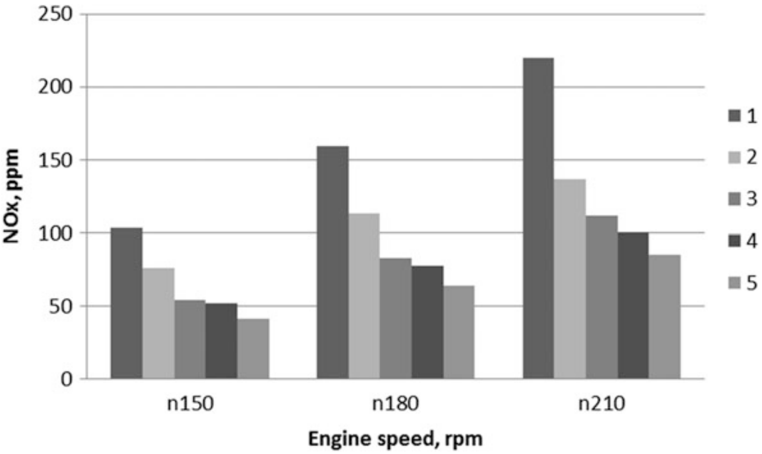

Fig. 4 Exhaust emission of NOx for different engine speeds, %

and dilution, and leading to the lower local gas temperatures (Kalligeros et al. 2003; Lee et al. 1998).

Furthermore, aromatic and poly-aromatic hydrocarbons are responsible for higher NOx emissions (Kalligeros et al. 2003; Takahashi et al. 2001; Spreen et al. 1995; Martin et al. 1997). This could be due to the higher flame temperatures associated with aromatic compounds. In reducing the aromatic and poly-aromatic content of the fuel, the flame temperature will be reduced as well, leading to a lower NOx production rate. Since biodiesel does not contain the above classes of compounds, its addition will reduce NOx emissions from the engines. The aromatics have high carbon–hydrogen ratios, and thus fuels with lower aromatics will lead to a smaller amount of CO_2 and a larger amount of H_2O being formed compared to high aromatic fuels. Since H_2O has a lower tendency to dissociate at high temperatures, this will lead to low aromatic fuels having lower concentrations of $O^\bullet$ radicals, which will further reduce the kinetic production of NOx (Kalligeros et al. 2003). This trend was also reported by Kalligeros et al. (2003), Dincer (2008) and Dorado et al. (2003). Others reported an increase in NOx emission with an increase in the biodiesel proportion in blended fuels, mostly due to the increased oxygen content of biodiesel fuels (Gumus and Kasifoglu 2010; Godiganur et al. 2010).

3.2.2 Sulfur Dioxide, SO_2

Exhaust emission of SO_2 is strongly dependent on fuel sulfur content. Since biodiesel has almost no sulfur content, the blending of diesel fuel with biodiesel can reduce the sulfur content, and thus reduce the emission of SO_2. The diesel fuel used in this experiment was the standard low sulfur diesel fuel used for naval vessels in Montenegro (Table 3).

It can be observed from Figs. 5 and 6 that SO_2 emission increases with an increase in engine speed. The reason for this increase is that more fuel is consumed, and therefore the greater amount of sulfur in the fuel is combusted. Also, emission of SO_2 decreases with a decreasing sulfur level in fuels for the same engine speed, and it is lowest for blends with 25% biodiesel (Fig. 5).

Sulfur in fuels lubricates the moving parts of the engine as well. Hence, the reduction in fuel sulfur content in diesel fuels, which is accompanied by a reduction in aromatic hydrocarbons, decreases its lubricity (Muñoz et al. 2011). According to (NREL and DoE 2009), the addition of as little as 2% biodiesel into marine diesel fuel significantly improves the lubricity of the moving parts of an engine.

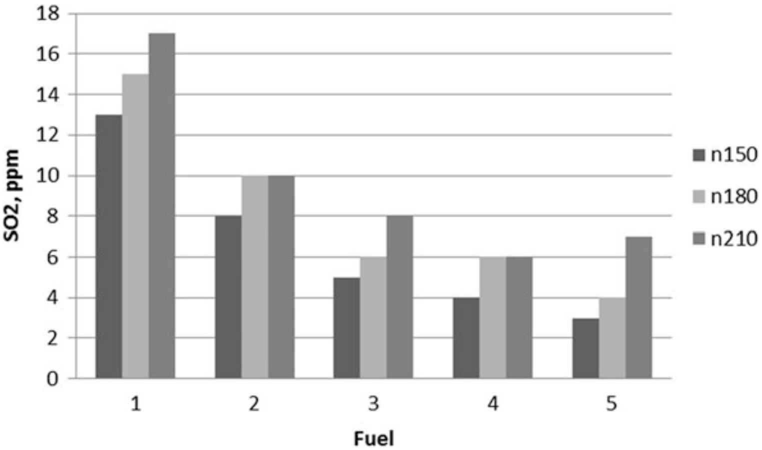

Fig. 5 Exhaust emission of SO_2 for different fuels, %

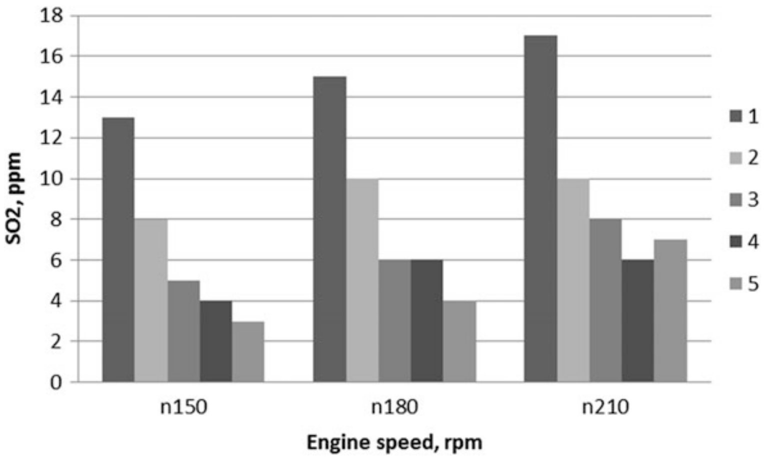

Fig. 6 Exhaust emission of SO_2 for different engine speeds, %

Therefore, adding biofuels into diesel fuel improves both SO_2 emission and fuel lubricity, the latter being very important for older two-stroke slow speed engines using low sulfur fuels, such as the engine used in this experiment.

3.2.3 Carbon Monoxide, CO

In an engine, CO emissions are controlled primarily by the air/fuel ratio. For fuel rich mixtures, CO emission increases steadily with a decrease in the air/fuel ratio, as the amount of fuel increases. For fuel lean mixtures, CO emission varies little with the air/fuel ratio. However, diesel engines always operate on the leaner side of the stoichiometric (Bhardwaj and Abraham 2008).

It can be observed from Figs. 7 and 8 that CO emission increases with an increase in engine speed. The reason for this increase is air/fuel ratio reduction with an increase in the load. Similar trends were reported by Gumus and Kasifoglu (2010), Usta et al. (2005) and Lertsathapornsuka et al. (2008).

Furthermore, emission of CO from a biodiesel-fueled engine is lower by more than 50% than that of a diesel-fueled engine at low and medium engine speeds. Considering only biodiesel blends, with an increase in biodiesel content from 7% to 25%, there is a reduction in CO emission regardless of engine speed, being most evident at maximum engine speed. This might be possible because of the oxygenated nature of biodiesel fuel. With biodiesel, owing to the inbuilt oxygen, the local air/fuel ratio during the combustion process becomes leaner, which results in the reduction in CO. This trend was also reported by Gumus and Kasifoglu (2010), Ramadhas et al. (2005). However, when applying maximum engine speed, there is notable increase in emitted CO when using biodiesel blends. At this high engine speed, poor combustion and other fuel characteristics annul the influence of

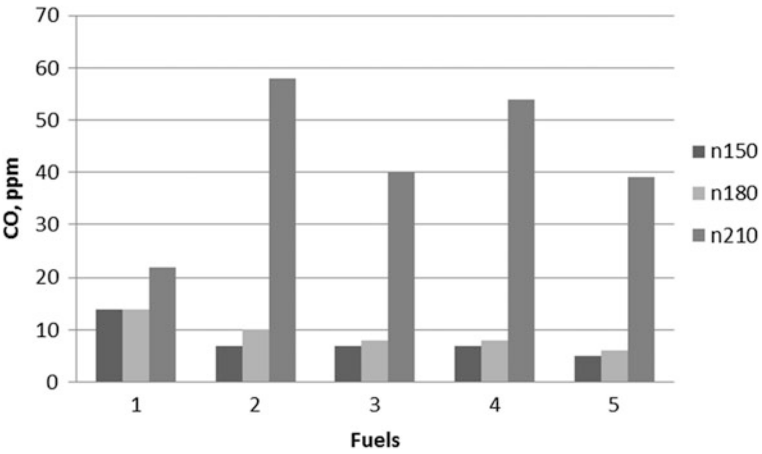

Fig. 7 Exhaust emission of CO for different fuels, %

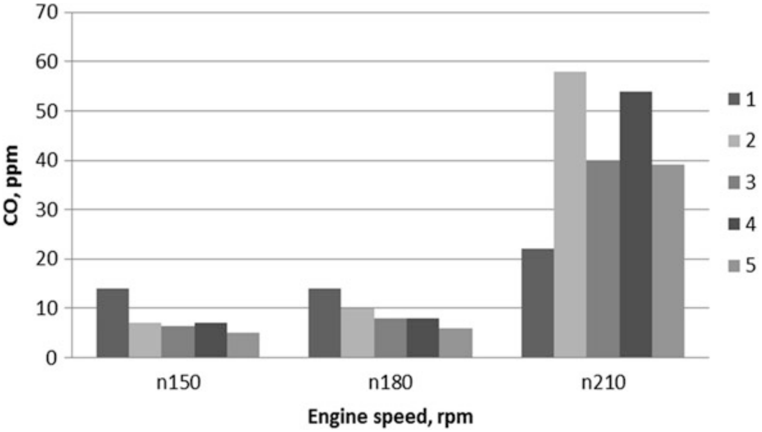

Fig. 8 Exhaust emission of CO for different engine speeds, %

biodiesel's higher oxygen content. This trend was also reported by Lujan et al. (2009), Fontaras et al. (2009).

3.2.4 Carbon Dioxide, CO_2

It can be observed from Figs. 9 and 10 that CO_2 emission increases with an increase in engine speed. The reason for this increase is that more fuel is consumed for higher power.

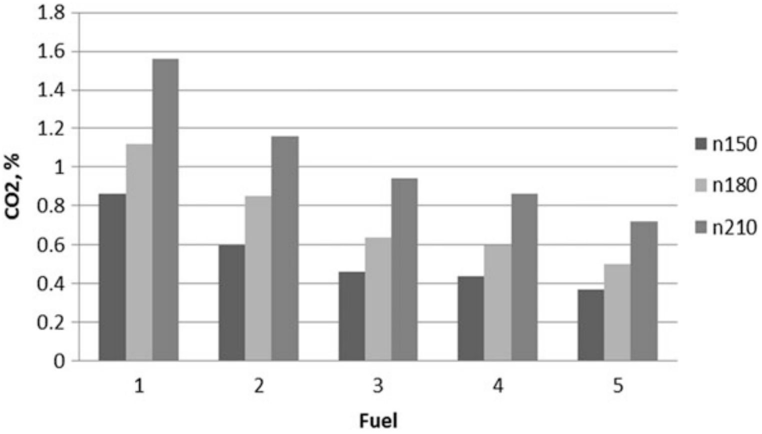

Fig. 9 Exhaust emission of CO_2 for different fuels, %

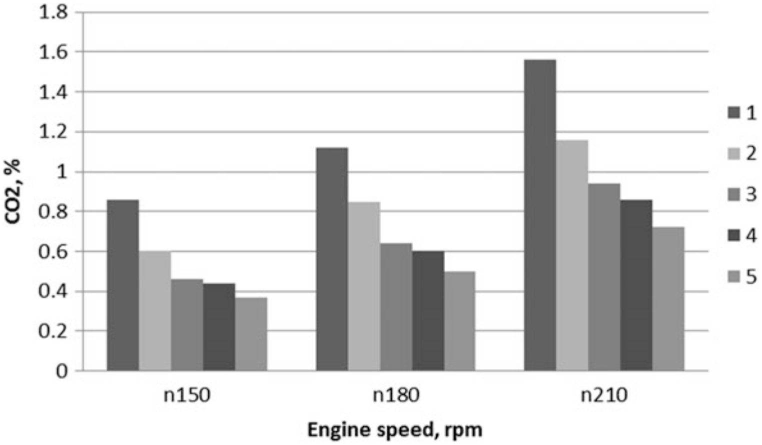

Fig. 10 Exhaust emission of CO_2 for different engine speeds, %

Emission of CO_2 from a biodiesel-fueled engine is lower than that from a diesel-fueled engine for a range of engine speeds, and this reduction is larger with biodiesel content in blends. The reason is that biodiesel blends have a lower carbon-to-hydrogen ratio than diesel fuel, and hence the combustion of these fuels produces less CO_2. This trend was also reported in Ozsezen et al. (2009), Utlu and Kocak (2008).

4 Conclusion

In this study, the influence of biodiesel (FAME) blends with low sulfur diesel fuel on the characteristics of exhaust emissions from marine diesel engines was investigated. A reversible 4—cylinder, two-stroke, low speed with cross-flow scavenging, marine diesel engine was used. The engine was fuelled with pure low-sulfur diesel fuel and blends containing 7% and 25% of two types of biodiesel, made of cast-off sunflower and palm oil waste from frying. The experimental results may lead to the following conclusions:

- NOx emissions could be reduced using biodiesel, which is mostly attributable to its higher cetane number and lower aromatic content.
- SO_2 emissions could be reduced using biodiesel, which is attributable to its lower sulfur content.
- CO emissions could be reduced using biodiesel, which is mostly attributable to its oxygenated nature, which makes for leaner combustion.
- CO_2 emissions could be reduced using biodiesel, which is attributable to its lower carbon-to-hydrogen ratio compared to diesel fuel.

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References

Bhardwaj O, Abraham M (2008) A comparative study of performance and emission characteristics of a CRDe SUV fueled with Biodiesel blends & Diesel fuel. SAE Technical Paper 2008-28-0075, SAE, Warrendale, PA

Borkowski Tadeusz, Kasyk Lech, Kowalak Przemyslaw (2011) Assessment of ship's engine effective power fuel consumption and emission using the vessel speed. J KONES Powertrain Transp 18(2):31–39

Dincer K (2008) Lower emission from biodiesel combustion. Energy Source Part A 30:963–968

Dorado MP, Ballesteros E, Arnal JM, Gomez J, Lopez FJ (2003) Exhaust emissions form a diesel engine fueled with transesterified waste olive oil. Fuel 82:1311–1315

Florentinus A, Hamelinck C, van den Bos A, Winkel R, Cuijpers M (2011) Potential of biofuels for shipping—final report, Ecofys 2011 by order of: European Maritime Safety Agency (EMSA)

Fontaras G, Karavalakis G, Kousoulidou M, Tzamkiozis T, Ntziachristos L (2009) Bakeas E (2009) Effects of biodiesel on passenger car fuel consumption, regulated and non-regulated pollutant emissions over legislated and real-world driving cycles. Fuel 88:1608–1617

Godiganur S, Murthy CHS (2010) Reddy RP (2010) Performance and emission characteristics of a Kirloskar HA394 diesel engine operated on fish oil methyl esters. Renew Energy 35:355–359

Gumus M, Kasifoglu S (2010) Performance and emission evaluation of a compression ignition engine using a biodiesel (apricot seed kernel oil methyl ester) and its blends with diesel fuel. Biomass Bioenergy 34:134–139

Heywood BJ (1988) Internal combustion engine fundamentals. McGraw Hill. ISBN 0-07-100499-8

IMO International Maritime Organization (2007) Feasibility study into the use of biofuels in the Norwegian domestic fleet, Marine Environment Protection Committee, 57th session, Agenda item 4

IMO International Maritime Organization (2014) Third IMO GHG study 2014—final report, MEPC 67/INF.3

IMO International Maritime Organization (2015) Note by the International Maritime Organization to the forty-third session of the Subsidiary Body for Scientific and Technological Advice (SBSTA 43) Paris, France, 1 to 4 December 2015. Agenda item 10(c) Emissions from fuel used for international aviation and maritime transport. Update on IMO's work to address emissions from fuel used for international shipping

Kalligeros S, Zannikos F, Stournas S, Lois E, Anastopoulos G, Teas Ch, Sakellaropoulos F (2003) An investigation of using biodiesel/marine diesel blends on the performance of a stationary diesel engine. Biomass Bioenerg 24:141–149

Lamas MI, Rodriguez CG (2012) Emissions from marine engines and NOx reduction methods. J Marit Res IX(I):77–82

Lertsathapornsuka V, Pairintrab R, Aryusukb K (2008) Krisnangkura K (2008) Microwave assisted in continuous biodiesel production from waste frying palm oil and its performance in a 100 kW diesel generator. Fuel Process Technol 89:1330–1336

Lee R, Pedley J, Hobbs Ch. (1998) Fuel quality impact on heavy duty diesel emissions—a literature review. SAE Paper No. 982649, SAE, Warrendale, PA

Lujan JM, Bermudez V, Tormos B, Pla B (2009) Comparative analysis of a DI diesel engine fuelled with biodiesel blends during the European MVEG-A cycle: Performance and emissions (II). Biomass Bioenerg 2009(33):948–956

Martin B, Beckman D, Aakko P, De Giacomo N, Giavazzi F (1997) Influence of future fuel formulations on diesel engine emissions—a joint European study. SAE Paper No. 972966, SAE, Warrendale, PA

Monyem A, Gerpen JH (2001) The effect of biodiesel oxidation on engine performance and emissions. Biomass Bioenerg 20:317–325

Muñoz M, Moreno F, Monné C, Morea J, Terradillos J (2011) Biodiesel improves lubricity of new low sulphur diesel fuels. Renew Energy 36:2918–2924

National Renewable Energy Laboratory (NREL) and U.S. Department of Energy (2009) Biodiesel Handling and Use Guide, 4th ed.; Report Number NREL/TP-540-43672; Office of Scientific and Technical Information: Oak Ridge, TN, USA

Ozsezen AN, Canakci M, Turkcan A (2009) Sayin C (2009) Performance and combustion characteristics of a DI diesel engine fueled with waste palm oil and canola oil methyl esters. Fuel 88:629–636

Ramadhas AS, Muraleedharan C, Jayaraj S (2005) Performance and emission evaluation of a diesel engine fueled with methyl esters of rubber seed oil. Renew Energy 2005(30):1789–1800

Spreen KB, Ulman TL, Mason RL (1995) Effects of cetane number, aromatics and oxygenates on emissions from a 1994 heavy duty diesel engine with exhaust catalyst. SAE Paper No. 950250, SAE, Warrendale, PA

Takahashi S, Nikolic D, Wakimoto K, Iida N (2001) Effects of Aromatics Contents and 90% Distillation Temperature of Diesel Fuels on Flame Temperature and Soot Formation, SAE Paper No. 2001-01-1940, SAE, Warrendale, PA

Usta N, Ozturk E, Can O, Conkur ES, Nas S (2005) Combustion of biodiesel fuel produced from hazelnut soapstock/waste sunflower oil mixture in a diesel engine. Energy Convers Manag 2005(46):741–755

Utlu Z, Kocak MS (2008) The effect of biodiesel fuel obtained from waste frying oil on direct injection diesel engine performance and exhaust emissions. Renew Energy 33:1936–1941

Review of Synthetic Fuels and New Materials Production Based on Pyrolysis Technologies

Petar Gvero, Indir Mujanić, Saša Papuga, Srđan Vasković and Ranko Anatunović

Abstract The production of synthetic fuels and new materials from biomass is a wide subject, and because of that, the author has decided to focus on thermochemical conversion processes, particularly pyrolysis, which is a widely used technology and one of the most promising for synthetic fuel production. The technology of pyrolysis is explained, as well as the differences between slow and fast pyrolysis. Fast pyrolysis technology is particularly promising for liquid fuel production and is specially processed, as are the types of pyrolysis reactors commonly used in practice, such as fluidized beds and ablative, vacuum and microwave reactors. According to the demand of certain technologies for the use of pyrolysis products for energy, some requirements in regard to the quality of the products are very strict, and technologies related to the use of catalysts and catalytic processes in pyrolysis have been analyzed. Liquid products of the pyrolysis process were analyzed from the perspective of content and use in the energy sector, as well as in the chemical industry. Analysis related to the gaseous products of pyrolysis and their use for energy purposes is also presented.

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1 Introduction to the Biomass Pyrolysis Process

Pyrolysis is a thermochemical process that involves the heating of material in the absence of oxygen, which leads to thermal degradation into gaseous, liquid and solid products. This process thermally decomposes biomass into gas, liquid and solid by rapidly heating it to above 300–400 °C, usually going up to 700 °C. The result of the thermal decomposition process of biomass is the production of char and non-condensable gas (the primary slow pyrolysis products), as well as condensable vapours (the liquid product obtained from fast pyrolysis) (Goyal et al. 2008; Venderbosch and Prins 2011).

Pyrolysis processing of biomass is developed through primary and secondary mechanisms. The primary mechanism involves the breaking of chemical bonds within the polymers, resulting in a release of volatile compounds and a solid residue that are still able to react. After that, the volatile compounds react through secondary mechanisms, such as the cracking and recombination of the molecules (Collard and Blin 2014). During pyrolysis, the heavier hydrocarbon molecules of the biomass are broken down into smaller hydrocarbon molecules, non-condensable gases like CO, CO_2, and solid carbons such as char:

$$C_nH_mO_p + heat \rightarrow \sum_{liquid} C_aH_bO_c + \sum_{gas} C_xH_yO_z + \sum_{solid} C.$$

Unlike combustion, the pyrolysis process is not exothermic; however, this statement should be taken conditionally, because questions relating to the heat of the pyrolysis reactions are complex. In this context, some authors have identified that biomass pyrolysis proceeds in two reactive steps, the first being the primary pyrolysis process and the second being related to the further reactions of the primary char. The heat of reaction in the second step is exothermic and almost independent of experimental conditions and char yield. On the other hand, the literature shows a wide variation in the reaction heat of the primary pyrolysis process dependent on the initial biomass particle weight and on the type of retort used in the measurements (Rath et al. 2003).

Pyrolysis is one of the potential routes to harnessing energy and useful chemicals from biomass. It is a process that has been used for centuries, representing, as it does, the basis for wooden charcoal production. In the last decade, pyrolysis processes have become more attractive, because they present the basis for production of the second generation of synthetic fuels, as well as new materials and chemicals. The structural constituents of biomass, cellulose, hemicelluloses, lignin and extractives, pass through the pyrolysis process at different rates and by different pathways and reaction mechanisms (Vamvuka 2011). The process of thermal decomposition of biomass is very complex, because it depends on the type of material, temperature, pressure, heating rate, reaction time, etc. The process parameters are responsible for the determination of the relationship between the pyrolysis product components and their characteristics. From a chemical kinetics perspective, the kinetics of the thermal decomposition of biomass materials is complicated, as it involves a large number of reactions in parallel and in series. Several studies indicate the existence of slight interactions between cellulose, hemicelluloses and lignin components in biomass particles during the thermal decomposition process (Vamvuka 2011).

The focus of this text is to present the status of the technologies and the solid, liquid and gaseous products yielded from different types of technology developed on the basis of the biomass pyrolysis process, mainly related to their use in the energy and environmental sectors.

Table 1 indicates the product distribution obtained from different modes of the pyrolysis process (Bridgwater 2004).

Pyrolysis processes can be "slow" or "fast," depending on the operation conditions in the reactor. The terms "slow" and "fast" in regard to pyrolysis are not precise from the perspective of heating rates and time. Some of the main characteristics of slow and fast pyrolysis are as follows:

- Slow pyrolysis is an irreversible process of thermal decomposition of the organic components of a biomass material, in which biomass particles are heated up to 500 °C. Residence time varies from 5 min to 30 min (Mohan et al. 2006). During conventional pyrolysis, the process of biomass devolatilization is slow, and as a result of this, tar and char are the main products of the process. In a case of biomass carbonization (charcoal production), the process characteristics are slower heating rates and longer residence times for the particles, which can vary from hours to days, depending on the particle size and type, as well as reactor type and outside conditions. Under these circumstances, gaseous products do not escape from the particle as rapidly as they do in fast pyrolysis. Heating rates in conventional pyrolysis are typically much slower than those in fast pyrolysis (5–7 K/s) (Goyal et al. 2008). But depending on the reactor system and fuel particle characteristics, heating rates can be higher, from 0.1 to 2 K/s per second, and characteristic process temperatures are around 500 °C. Gas residence time may be greater than 5 s. Torrefaction is a process of thermochemical treatment of a biomass in a temperature range of about

Table 1 Typical yields (dry wood basis) produced by different modes of wood pyrolysis (Bridgwater 2004, adapted with the permission of Thermal Science)

Process	Conditions	Liquid (%)	Char (%)	Gas (%)
Fast pyrolysis	Moderate temperature, short residence time particularly vapour	75	12	13
Carbonization	Low temperature, very long residence time	30	35	35
Gasification	High temperature, long residence time	5	10	85

200–320 °C, with the aim of improving the properties of solid biomass fuels; it can be treated as a slow pyrolysis process.

- Fast pyrolysis can also be called short residence timed pyrolysis, because residence time is a few seconds to a fraction of a second and heating rates reach 300 K/s (Goyal et al. 2008). Fast pyrolysis is usually a high-temperature process (400–650 °C, although it can go up to 1250 °C, depending on the purpose of the process), in which biomass is rapidly heated in the absence of oxygen (Mohan et al. 2006; Vamvuka 2011; Tripathi et al. 2016). The intermediate pyrolysis of a biomass is a process that results in bio-oil with low tar yields and viscosity, which stands as the true distinction between the intermediate pyrolysis and fast pyrolysis processes. Depending on the heating rate, fast pyrolysis can be a "flash" pyrolysis, in which temperature can range between 777 and 1027 °C or up to 1200 °C, depending on the purpose of the process (Panwar et al. 2012; Tripathi et al. 2016). Generally, flash pyrolysis refers to heating rates greater than around 1000 °C/s (Radlein and Quignard 2013; Tripathi et al. 2016). The yield of fast pyrolysis processes is 60–75% wt. of liquid bio-oil, 15–25% wt. of solid char, and 10–20% wt. of non-condensable gases, depending on the feedstock material (Panwar et al. 2012). The most important characteristics of the fast pyrolysis process can be divided into four groups (Panwar et al. 2012): (1) very high heating and heat transfer rates in the process, which requires adequate preparation of the raw material, principally a fine grinding of the biomass feed, (2) a carefully controlled pyrolysis reaction temperature, usually within the range of 450–600 °C, (3) typical residence times for the vapours of <2 s, and (4) rapidly cooled pyrolysis products (vapours and aerosols) so as to have bio oils as the final products.

Pyrolysis plays a key role in the reaction kinetics of all thermo chemical conversion processes (such as combustion, gasification and pyrolysis), and due to that fact, the reactor design is crucial, as is determination of the distribution, composition and properties of the process's products. (Panwar et al. 2012). At least four parallel reactions leading to char, liquids and gases have to be mastered to optimize the process. The biomass pyrolysis pathways are shown in Fig. 1 (Bridgwater 2012).

The products spectrum related to the different pyrolysis pathways is given in Fig. 2.

As presented in the text above, it can be summarized that a lower process temperature, longer vapour residence time, and slow pyrolysis with large wood particles favours the production of charcoal. This is especially true for a slow thermal treatment under pressure. Higher process temperatures and longer residence times lead to biomass conversion into gaseous products, while moderate temperatures and shorter vapour residence times make for optimal conditions for liquids as process products, particularly the fast pyrolysis of small biomass particles (Meier and Faix 1999; Bridgwater 2004). The technical and economic limitations of the pyrolysis process are obvious, and due to that, it is possible to find different concepts for pyrolysis reactors, targeting certain specific products. The most widely used concepts will be briefly explained in the following text.

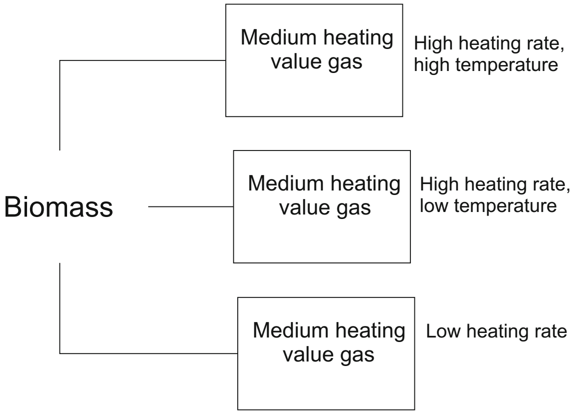

Fig. 1 Biomass pyrolysis pathway (adapted from Bridgwater 2004, with reprint permission from Thermal Science)

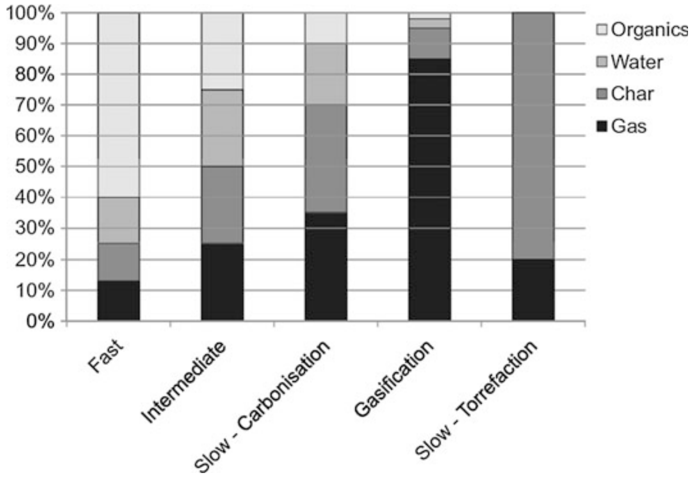

Fig. 2 Products spectrum from pyrolysis (Bridgwater 2012, with reprint permission from Elsevier)

2 Fast Biomass Pyrolysis Reactor Types

There are different kinds of reactor, depending on the purpose of the process.

In commercial biomass pyrolysis reactors, the following can be used as heat carriers: the wall of the reactor (vacuum reactors), gas (fixed bed reactors), solid particles (fluidized bed reactors) or a combination of the above-mentioned carriers.

The technical requirements for pyrolysis reactors with the aim of obtaining a high yield of good quality oils are (Meier and Faix 1999):

(1) The achievement of rapid heat transfer from the heating medium to the fuel particle, (the heating medium can be a gas and/or a solid material), and high heating rates (low temperature gradient) inside the particle in which pyrolysis takes place;
(2) Rapid mass transfer from the inside of the particles to the surface, and further rapid mass transfer from the hot reactor to the cold trap (rapid quenching) are both necessary.
(3) The residence time of the pyrolysis vapours in the hot zone of the reactor should be no longer than a few hundred milliseconds (in the case of the production of chemicals) or 2–3 s (in the case of low viscosity fuel production). Consequently, secondary reaction cannot be completely avoided under technical conditions.

2.1 Fluidized Bed Reactors

The bubbling (BFB) and circulating fluidized bed (CFB) reactors are well known, representing a proven technology that has been in practical use in the chemical industry and energy sector for a long time. Both reactor types (BFB and CFB) have a long operating history, providing good temperature control in the reactor and very efficient heat transfer from the bed to the biomass particles. As reactor designs, they are characterized as providing high heat transfer rates in conjunction with uniform bed temperatures, both being necessary attributes for fast pyrolysis. The heat transfer limitation lies within the particle, thus requiring very small particles of typically no more than 3 mm to obtain good liquid yields (Bridgwater et al. 1999). A substantial carrier gas is needed for fluidization or transport. By selecting the appropriate size for the bed fluidizing media, as well as the flow rate of the carrier gas, it is possible to adjust the pyrolysis gas/vapour residence time in the freeboard area of the reactor (the area above the fluidized bed), which means that the residence time can be set to a desired value, generally between 0.5 and 2.0 s (Wan Isahak et al. 2012). In some optimistic scenarios, at least 10–20 m^2 of the bed surface area is required per ton/hour of biomass fed material in this kind of reactor (Venderbosch and Prins 2011). Generally, in the bubbling fluidized bed reactors, an operating temperature of 500–550 °C in the bed usually results in the highest liquid yields, at about 0.5 s residence time, however, the larger reactors can operate at a somewhat lower temperature, with longer residence times (Wan Isahak et al. 2012). It is important to know that for this type of reactor, the sand-to-biomass (fluidized bed to fuel particle) heat transfer is efficient, over 500 W/m^2K, while the heat transfer from the heating coils to the fluidized bed is relatively low, the gas-to-coil wall heat transfer being estimated as 100–200 W/m^2K, due to the thermal resistance inside the coils (Venderbosch and Prins 2011).

In a circulating fluidized bed reactor (CFB), the feed biomass particles, due to the nature of the process, have to be smaller than those used in bubbling bed reactors (BFB); the typical size of the particles is in the range of 1–2 mm

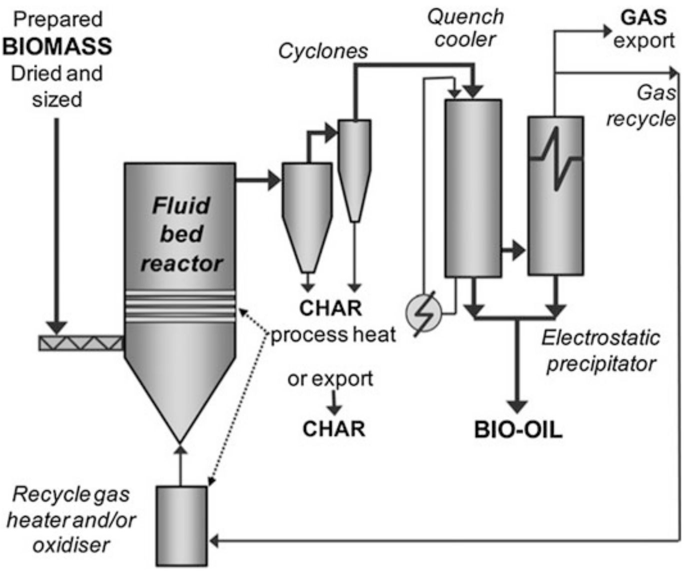

Fig. 3 Bubbling fluidized bed reactor with an electrostatic precipitator (Bridgwater 2012, with reprint permission from Elsevier)

(Wan Isahak et al. 2012). In CFB reactors, the residence times for the particles is in the range of 0.5–1.0 s in the high heat transfer pyrolysis zone, before it is entrained over to the char combustion section or the main reaction zone (Wan Isahak et al. 2012) (Fig. 3).

2.2 *Ablative Pyrolysis Reactors*

Ablative pyrolysis or surface pyrolysis takes place at 550–600 °C and higher rates, essentially independent of the feedstock particle size. It seems to be very promising for an industrial application, because it fulfils the requirements of flash pyrolysis with regard to high heating and mass transfer rates regardless of the use of large wood chips (Meier and Faix 1999; Vamvuka 2011). The key advantage is the ability to process much larger particles, as the mechanism of heat transfer in the reactor is different, and the absence of a fluidizing or transport gas, both of which contribute to a more compact and intensive reaction system (Vamvuka 2011). The process in this type of reactor depends on the way in which the wood particles are pressed against a heated surface and rapidly moved. During this process, wood particles melt at the heated surface and leave an oil film behind, after which the oil evaporates. This process uses larger particles of wood and is typically limited by the rate of heat supply to the reactor. This concept allows for the design of compact and intensive reactors that do not require a carrier gas, although the weak points of this concept are the ablative surface area and its control, as well as the moving parts at a high temperature (Bridgwater et al. 1999).

The most famous ablative pyrolysis reactor is the rotating cone reactor. In this high intensity reactor, biomass of an ambient temperature is mixed with hot sand. Upon being mixed with hot sand of 550 °C, the biomass decomposes into 70% wt condensable vapours, 15% wt non-condensable gases and 15% wt char. An important characteristic of this reactor type is the absence of a carrier gas, as it is the rotating action of the cone that propels the solids from the reactor's entrance to its exit. Because of the absence of a carrier gas, the vapour products are not diluted and their flow is minimal. An undiluted and concentrated product flow from the reactor leads to small downstream equipment with related minimal investment costs (Vamvuka 2011).

In general, ablative pyrolysis has two major limitations. First is the difficulty of getting sufficient heat transfer from hot gases to the ablative surface. The temperature difference between the hot flue gas (around 800 °C) and the pyrolysis reactor (500 °C), and the value of the heat transfer coefficient, are relatively small. Second are the difficulties in the contact between feedstock of diverse morphologies (particle shape, structure, and density) and the ablative surface. In practice, relatively few feedstocks would be suitable for ablative pyrolysis (Venderbosch and Prins 2011).

A technique related to ablative pyrolysis is screw and "auger pyrolysis," in which the biomass is transported along a hot tube by mechanical displacement using twin augers. These are particularly suitable for feed materials that are difficult to handle or feed, or are heterogeneous. This is essentially a type of transported bed reactor, as the twin auger is effectively a series of sealed pockets that advance the feed to the discharge port. Heat may be supplied by heating the walls of the auger tube barrel or by circulating pre-heated sand that is mixed with the biomass (Radlein and Quignard 2013). The nature of mechanically driven reactors is that very short residence times are difficult to achieve compared to BFB and CFB reactors, and hot vapour residence times usually vary within the range of 5–30 s, depending on the design and size of the reactor (Bridgwater 2012) (Fig. 4).

2.3 Vacuum Pyrolysis

Vacuum pyrolysis is a process characterized by heating rates comparable to those of slow pyrolysis, but it removes pyrolysis products as rapidly as in the previous methods, thereby simulating fast pyrolysis. Vacuum pyrolysis of biomass is generally conducted at a temperature of 450–600 °C and at a total pressure of 0.05–0.20 MPa (Tripathi et al. 2016; Vamvuka 2011). The advantages of the vacuum pyrolysis process are: (1) the technology allows for the processing of larger biomass particles than most fast pyrolysis reactors, (2) heating rates in vacuum pyrolysis are very low, compared with the other systems described above, (3) the use of vacuum pyrolysis leads to larger equipment and higher costs. Liquid product yield and

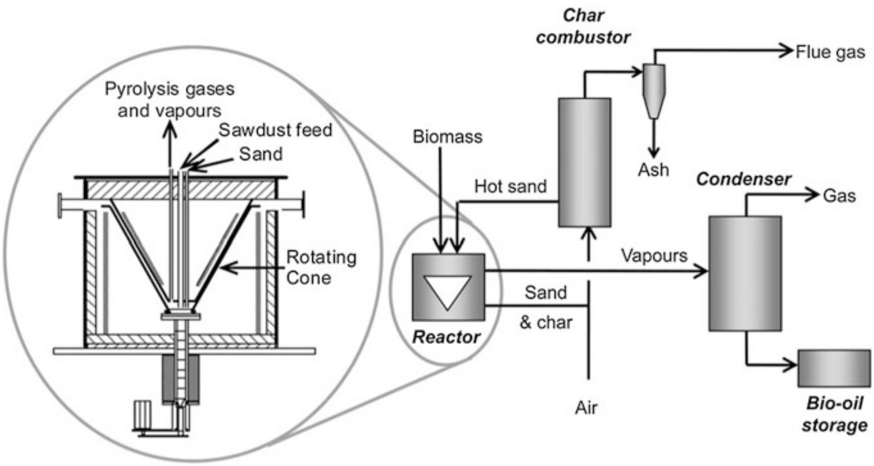

Fig. 4 Rotating cone pyrolysis reactor and integrated process (Bridgwater 2012, with reprint permission from Elsevier)

quality of vacuum pyrolysis are achieved through the removal of the vapours as soon as they are formed, by operating under a low pressure (Tripathi et al. 2016). Total liquid yields are typically lower by up to 60–65% compared to 75–80% wt from the previous two methods, but the liquid products of vacuum pyrolysis are significantly different compared to the other fast pyrolysis processes, and include water content, a higher heating value and other physical properties (Vamvuka 2011; Bridgwater et al. 1999; Bridgwater 2012). This is due to the fact that a vacuum allows for decomposition of the organic components under the lower temperatures (Tripathi et al. 2016).

2.4 Microwave Pyrolysis

By comparing microwave pyrolysis with the other conventional pyrolysis technologies, it can be seen that microwave heating is fundamentally different from all other pyrolysis techniques. Microwave pyrolysis includes the transfer of energy to the biomass particle through the interaction of the molecules within the particle. The advantage of microwave heating is non-contact, volumetric and selective heating, and that the heat is generated within the material rather than from an external source (which means heating goes from the interior of the fuel particle), resulting in rapid heating of the biomass particle and high heating efficiency (Wu et al. 2014; Huang et al. 2016). It is also important to emphasize that microwave pyrolysis is a technology that offers a way to recover the energetic and chemical value of the waste materials, through the production of potentially useful pyrolysis products, appropriate for future reuse (Lam and Chase 2012).

From the other side, this approach, compared to the other pyrolysis technologies, generates an enlargement of the production rates. Microwave heating requires a material with a high dielectric constant or loss factor, such as water, and due to that, water is rapidly driven off, after which the particle heats up and begins forming char. Another problem related to microwave pyrolysis is the phenomenon of hot spot formation, which has an influence on the inhomogeneity of the microwave field, and therefore can have significant influence on the yield and characteristics of the pyrolysis products (Huang et al. 2016).

In general, the technology of microwave pyrolysis can produce more solid and gas products (primary component content is H_2 = 39%, CH_4 = 9%, CO = 33% and CO_2 = 23%) but less liquid product than conventional pyrolysis (Huang et al. 2016).

Besides the above-mentioned pyrolysis technologies, many variations and modifications exist with the aim of obtaining products with the most appropriate content and characteristics adequate for the end use. Some of the technologies and approaches will be described briefly in the following text.

2.5 Catalytic Pyrolysis

Catalytic biomass pyrolysis is a promising thermochemical conversion route for biomass treatment, introduced with the aim of improving the quality of the products, chemicals and bio-oils with existing achievement levels in petrochemical products and the industry. The introduction of the catalysts into the pyrolysis process enhances chemical reactions, including cracking, decarbonylation, decarboxylation, hydrocracking, hydrodeoxygenation, and hydrogenation, and it could be applied at different phases and positions of the process (Dickerson and Soria 2013).

Depending on the position of the catalyst in the reactor, catalytic pyrolysis is usually divided into two different processes: (1) in situ and (2) in-bed processes (Shun et al. 2013). In the in situ process, catalysts are applied during pyrolysis, and the biomass is cracked to produce pyrolytic vapours that pass through catalyst beds, where they are converted into bio-oil, as well as gaseous and solid by-products. During the in-bed process, catalytic pyrolysis occurs in a reactor where biomass feedstock and catalysts are mixed together, which allows for direct contact between them, but in processes with a separate char combustor, the catalyst can be regenerated continuously (Venderbosch and Prins 2010; Shun et al. 2013). It is important to emphasize some negative effects related to catalytic upgrading: during this process, concentration of the aromatic and polycyclic aromatic species, particularly PAH (Polycyclic Aromatic Hydrocarbons), increases, the effect being more intensive with an increase in the catalysis temperature (Yaman 2004).

Using condensation of pyrolysis vapour to obtain bio-oil and the evaporation of bio-oil for upgrading purposes is not thermally efficient. Therefore, the introduction of catalysts into the pyrolysis process before the condensation of vapour in order to induce vapour-phase catalytic reactions is a worthwhile and promising route. There are a lot of materials used as catalysts among zeolites, HZSM-5, HY, ZSM-5, etc., and they can be divided into primary and secondary catalysts (Wan Isahak et al. 2012; Tripathi et al. 2016). Primary catalysts are the ones that are mixed into the biomass material before pyrolysis, and secondary catalysts are not mixed with biomass, but rather are kept in a separate reactor located in back of the main pyrolysis reactor (Tripathi et al. 2016). Regarding the availability of catalysts, for example, zeolites with different porous structures, such as ZSM-5, are already a commercial product and widely used as a catalyst for biomass pyrolysis in fluidized beds (decreasing the concentration of liquid products and increasing the yield of gaseous products), while HZSM-5 and HY are very efficient in the conversion of highly oxygenated crude bio-oils or pyrolysis vapours to hydrocarbons, in which light aromatic hydrocarbons (benzene, toluene, xylene and naphthalene) are dominant (Bulushev and Ross 2011; Wan Isahak et al. 2012). According to some reports, the Al-MCM-41 catalyst effectively removed acids from the bio-oil, but in comparison with ZSM-5, it had low hydrothermal stability (leading to delamination) (Bulushev and Ross 2011). For the hydrodeoxygenation process or hydro treating processes, hydrogen rich solvents are usually used and their activation takes place through the use of a catalyst. In this case, catalysts usually take the form of metal oxides, which lead in the direction of the removal of oxygen, water and carbon dioxide. Catalytic cracking of pyrolysis vapours is another method by which bio-oils containing oxygen are catalytically decomposed into hydrocarbons (Titiloye 2014). There are some natural catalysts in biomass that have influence on pyrolysis products, such as metallic minerals that can change the final product's yield (Sharma et al. 2015).

2.6 *Hydropyrolysis*

Hydropyrolysis represents an attempt in the development of pyrolysis technology to reduce certain problems that are related to the products of fast pyrolysis, such as acidity, high water content, and viscosity (Balagurumurthy et al. 2013). The main goal of the hydrolysis process is to reduce oxygen content in bio-oil products by using a single step process, and attempts have been made to integrate fast pyrolysis with the hydrocracking process by adding hydrogen under high pressure into the reactor (Bridgwater 2012; Balagurumurthy et al. 2013). The presence of hydrogen in the reactor prevents the formation of free radicals and olefins, which are responsible for the instability of bio-oils produced through the fast pyrolysis process (Balagurumurthy et al. 2013).

3 Liquid Products from the Pyrolysis Process

Liquid products of the biomass pyrolysis process, so-called “bio-oils,” are a complex mixture of water and organic chemicals, and may consist of more than 300 organic compounds (Bulushev and Ross 2011). They were formed through the fast and simultaneous chemical reactions of depolymerization and fragmentation of the main biomass constituents: cellulose, hemicellulose, and lignin, with a rapid increase in the process temperature (Krutof and Hawboldt 2016). After this phase, rapid quenching then “freezes in” the intermediate products of the fast degradation of biomass constituents. Rapid quenching captures a lot of pyrolysis products that would otherwise continue to react (molecule degradation, cleaving or condensation) if the residence time at a high temperature was extended (Mohan et al. 2006). As already mentioned above, the yield and composition of biomass pyrolysis products depend on the characteristics of the biomass feedstock (type, geometry, etc.) and operating parameters of the reactor. Water content is typically in the range of 15–35% wt, although values outside this range have been reported. As already mentioned, chemically, pyrolysis bio-oil is a complex mixture of water and organic chemicals, which includes alcohols, aldehydes, ketones, esters, phenols, guaiacols, catecols, syringols, sugars, furans, alkenes, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, hydroxyaldehydes, hydroxyketones, other carboxylic acids, aromatics, nitrogen compounds and miscellaneous oxygenates (Mohan et al. 2006; Vamvuka 2011; Radlein and Quignard 2013). Their average molecular weight varies within the range of 300–1000 g mol^{-1}. The compound with the highest concentration is hydroxyacetaldehyde (up to 10% wt), followed by acetic and formic acids (5 and 3% wt, respectively) (Vamvuka 2011; Radlein and Quignard 2013). Bio-oils also have a low pH value (2-3,7) due to the presence of carboxylic acids, as well as having more nitrogen and chlorine than petroleum, which are unsuitable characteristics, but generally contain less sulphur than petroleum (Bulusheva and Rossa 2011; Kan et al. 2016).

Liquid fuel production from the pyrolysis process is interesting because liquid fuels are easier to transport, store and can be an alternative energy source. The disadvantages of biomass as a raw material in pyrolysis processes for the purpose of producing liquid fuels are the variations in the characteristics (which can strongly depend on the location), the low energy density and the necessity of careful organization of the supply logistics in order to avoid or reduce unnecessary production costs. Water content in bio-oil pyrolysis products is another important issue, as high water content is one of the major barriers to bio-oil’s utilization as a fuel, which is also the case with the oxygen content, especially in regard to its use in IC engines or certain other sophisticated devices. In medium and low speed engines, bio oils can be used directly, while high speed engines require blends of bio oil with methanol and cetane-improving additives (Krutof and Hawboldt 2016; Wan Isahak et al. 2012). Biomass pyrolysis oils can be used directly as a liquid fuel for boilers, or as a fuel for diesel engines and gas turbines, for the purpose of heat and electricity generation, or it can be catalytically upgraded in order to achieve standards of transport grade fuels (Panwar et al. 2012). The lower heating value (LHV) of bio-oils is only 40–45% of that exhibited by hydrocarbon fuels. On a volume basis, it is 60% of the heating value of hydrocarbon oils, because of the high oxygen content, the presence of water and the higher density. A typical higher heating value of bio-oil is 15–20 MJ/kg, due to its considerable oxygen content, which is in the area of 30–40% wt (Kan et al. 2016; Vamvuka 2011).

Some recent research has shown that fast pyrolysis products can be used to generate electricity. Bio-oil combustion tests have shown that pyrolysis bio-oils can replace heavy and light fuel oils in industrial boiler applications. It was shown that pyrolysis bio-oils are more similar to light fuel oil, although there are significant differences in ignition, viscosity, energy content, stability, pH, and emission levels (Venderbosch and Prins 2011). For their use in furnaces and boilers, some modifications to the systems are necessary, said systems usually requiring some supplementary fuel for the start and sometimes for the regulation of the combustion process due to variation in the quality of the bio oils (Krutof and Hawboldt 2016). The recent analyses have shown that the high feasibility and cost efficiency of electricity generation through the use of pyrolysis bio-products as a fuel are more beneficial than those of any other biomass conversion method in the long term (Malik and Sangwan 2012).

Bio-oil can also provide fuel for transportation. Initially, it was thought that bio-oil could be directly fired in diesel engines, but the acidity, viscosity, and presence of particulate matter make it unsuitable even for stationary diesel engines. Thus, bio-oil must be upgraded to a fuel suitable for transportation. In general, bio-oils are upgraded in FCC reactors at atmospheric pressure or in high-pressure hydrotreating reactors in order to reduce their oxygen content, as well as through the use of a supercritical water method in order to produce fuel with a higher heating value (Venderbosch and Prins 2011; Wan Isahak et al. 2012).

Pyrolysis is expected to play an important role in future biorefineries, either as a central unit or as a peripheral unit for valorizing biorefinery side-streams for enhanced economic viability (De Wild and Reith 2011).

The different thermal characteristics, particularly the thermal stability of hemicellulose, cellulose and lignin, provide an opportunity to use pyrolysis as a technology for the thermal fractionation of biomass into products, which can then serve as substitutes for conventional petrochemical products (De Wild and Reith 2011). The main phase of cellulose conversion occurs from 300 to 390 °C, with the highest decomposition rate generally appearing at reaction temperatures of 330 to 370 °C (Collard and Blin 2014). Products that can be yielded from cellulose pyrolysis at reaction temperatures in the range of 200–400 °C, are: levoglucosan, hydroxyacetaldehyde, 1,6-anhydro-β-D-glucofuranose, furfural, hydroxymethylfurfural, furan, and other C1-C4 oxygenates (e.g., methanol, formaldehyde, formic acid, acetone, acetol, lactones, etc.). It can also be used as glucose, polymers, antibiotics and a food browning agent in ‘liquid smoke’ (De Wild and Reith 2011). For reaction temperatures higher than 400 °C, the process’s residue becomes more aromatic (Collard and Blin 2014). The main phase of hemicelluloses conversion occurs from 150 to 350 °C, and can yield: acetic acid, furfural, furan, furanone, methanol, other C1-C4 oxygenates (e.g., formaldehyde, hydroxyacetaldehyde, acetone, acetol, lactones, etc.), C5 and C6-anhydrosugars, and humic substances. It can also be used on the market as a bulk-chemical, a vinegar (food), a cleansing agent, vinyl acetate, acetic anhydride, esters, a solvent, a road de-icer (as calcium acetate), an intermediate commodity chemical, a resin, an adhesive, a food flavouring agent and a precursor to speciality chemicals (Collard and Blin 2014; De Wild and Reith 2011).

Perhaps the most promising biomass component is lignin, the main conversion step of which occurs in the temperature range of 200–450 °C, with the highest decomposition rate generally occurring in the range between 360 and 400 °C. Hundreds of compounds have been identified in GC analysis as fragments from lignin (amongst others, phenols, eugenols, and guaiacols) and holocellulose (sugars, acetaldehyde, and formic acids). Large fractions of acetic acid, acetol, and hydroxyacetaldehyde have been identified; (poly) phenols are also present, sometimes in rather high concentrations (Collard and Blin 2014; Venderbosch and Prins 2011). The market applications for chemicals produced through the lignin pyrolysis process can be in fine chemicals, pharmaceuticals, food flavouring agents such as ‘liquid smoke,’ the fragrance industry, bulk-chemicals, wood-adhesives, resins, plastics, fuel additives, solvents, fuel, antifreeze, ethanol denaturant, 2nd energy carrier for H_2 and bio-diesel (De Wild and Reith 2011).

4 Gaseous Products

Similarly to char, about 10–35% of gaseous components (syngas) are produced through slow pyrolysis processes; a higher syngas yield is possible in flash pyrolysis at high reaction temperatures (Jarihul et al. 2012). The gaseous pyrolysis products contain: carbon dioxide, carbon monoxide, methane, hydrogen, ethane, ethylene, minor amounts of higher gaseous organics and water vapour on a mass basis, but generally, pyrolysis gas consists mainly of CO and CO_2, with smaller percentages of C_xH_y, (mainly CH_4) and H_2 (Vamvuka 2011; Neves et al. 2011). The primary gases of the fast pyrolysis process (less than 5% wt of the dry feed) contain about 53% wt CO_2, 39% CO, 6.7% hydrocarbons (including methane) and 0.8% H_2. In practice, a portion of the organic vapours and tars undergo secondary reactions, and are cracked to secondary gases, containing 9% wt CO_2, 63% CO, 27% HC and 1.4% H_2. The LHV of these primary gases is 11 MJm^{-3}, and that of pyrolysis gases formed after a severe secondary cracking of the organic vapours is 20 MJm^{-3} (Vamvuka 2011; Kan et al. 2016). Based on the collected data, the heating rate seems to have little effect in determining the composition of the pyrolysis gas (Neves et al. 2011). Reactor temperature has a significant influence on pyrolysis processes and the resulting product distribution. Studies have also shown that an increase in reactor temperature correspondingly increased the syngas flow rate, which lasted for a shorter period of time and then reduced dramatically. High moisture content in raw biomass particles creates unfavourable effects on syngas production, by contributing to the extraction of water-soluble components from the gaseous phase, consequently causing a significant decrease in yields of gaseous products (Jarihul et al. 2012). The yields of CO, CH_4 and H_2 show a similar pattern of change as a function of the pyrolysis reaction temperature, but the observed trend of CO_2 is different; the yield of CH_4 (where, C_xH_y mainly accounts for C2 hydrocarbons) appears to have linear dependency on the yield of CH_4 (Neves et al. 2011).

Syngas from the biomass pyrolysis process can be used as a renewable alternative fuel for internal combustion (IC) engines and industrial combustion processes. Some studies have shown that internal combustion engines using syngas as fuel produced about 30% less engine power output compared to petrol, due to the difference in quality (Jarihul et al. 2012). One of the pathways for the upgrading of the gaseous components produced and its use in IC engines is so-called bio-methane production through the synthesis process of the pyrolysis vapours (Gorling et al. 2013).

5 Solid Products

The thermal decomposition of biomass that occurs in the absence of oxygen, along with slow heating rates, creates solid products with the generic name of charcoal or biochar. These products can be, depending on the process parameters, further divided into fuel charcoal, activated charcoal and bio-coke, which also have some fine differences regarding their application.

Biochar is primarily carbon (~85%), but it can also contain mineral fractions, oxygen and hydrogen. The advantage of biomass, unlike fossil fuels, is low ash content; in the case of wood, it is 0.5 to 1%, and biochar ash has a low inorganic ash content. Due to the high carbon content and low water content, the lower heating value (LHV) of biochar is about 32 MJ/kg, which is substantially higher than the raw biomass material, and its liquid product (Basu 2013).

The yield and characteristics of biochar produced through pyrolysis processes depends on the design of the reactor, the physical and chemical characteristics of the biomass particles, and the operating parameters, such as heating rate, temperature and residence time in the reaction zone. During biomass pyrolysis, depending on the reactor type, type of biomass and process parameters, between 10–35% of biochar is produced, while slow pyrolysis at temperatures from 300 to 800 °C favours biochar yield (35%) (Jahirul et al. 2012). Lower process temperatures and longer vapour residence time favor the production of charcoal (Bridgwater 2012; Demirbas 2004). Due to that, charcoal production from biomass requires slow heating and a long duration pyrolysis process, at relatively low temperatures, around 400 °C, but as has already mentioned, the process parameters depend on the particular kind of pyrolysis technology. For example, comparing the microwave and conventional pyrolysis technologies in biochar production, it can be recognized that some of the conventional technologies require reaction temperatures higher than 600 °C and that their products can be low grade, with PAH and CO_2 formation, while microwave pyrolysis requires less energy consumption in the process and, as a result, produces a high quality biochar (Li et al. 2016).

Torrefaction has been developed as a possible option for improving the fuel characteristics of biomass, so that it can be used more efficiently as a clean and adequate fuel for the processes of combustion and gasification, with higher energy density (HHV = 20–25 MJ/kg) (Collard and Blin 2014). In this process, which actually represents slow (<50 °C/min) low-temperature pyrolysis, biomass is treated at temperatures in the range of 200–300 °C. Treatment at these temperatures results in the loosing of the fiber structure of the biomass particles and improves the grindability characteristics of the fuel. The most unstable oxygenated fractions, originated from hemicelluloses, are converted, with the result being a change (reduction) in the O/C (to around 0.5) and H/C ratios and improvement of the uniformity in properties among different biomass feedstocks, due to which they can be used as substitutes for coal (Bridgeman et al. 2010; Collard and Blin 2014; Basu et al. 2014).

During the pyrolysis (carbonization) process, volatiles (gaseous components) react with the char layer when flowing out of the particle to form char. A longer residence time of volatiles leads to greater char formation, due to these secondary reactions; at the same time, this has the consequence of decreasing the char reactivity by covering the active sites and the inorganic matter, which could play the role of a catalyst in the process. The time during which the char particle remains at final temperature, e.g., soaking time, also influences the char's reactivity. In this case, the decrease in reactivity is a result of the rearrangement of the char structure to a better alignment of the plane layers of carbon. The mineral matter and ash content, and its presence in the biomass pyrolysis (and carbonization) process, favors an increase in char and gas yield and its reactivity (Venderbosch and Prins 2011).

Hence, agricultural residues, with their high sodium and potassium content, and generally higher ash content than wood, provide more char with higher reactivity than wood. Ammonium salts containing phosphorus can also promote char formation during pyrolysis, reducing oil yields (Venderbosch and Prins 2011). It was found that hot biochar acts as a catalyst and favours the cracking of vapours during the fast pyrolysis process (Sharma et al. 2015). When it comes to the dependence of char yield on the type of biomass, lignin is often considered to be the component of wood that produces the most char, but hemicellulose has also been reported as giving relatively high char yields (Jahirul et al. 2012). Cellulose forms char through secondary reactions with the char layer that are very dependent on the size and geometry of the biomass particle, the char yield increasing with increasing particle size (Demirbas 2004; Bellais 2007). At the same time, the differences in char yields become less important between small and large particles in the case of pyrolysis at high reaction temperatures; this is explained by the heating rate, and the residential time of the volatiles (Bellais 2007).

Biochar is generally characterized by its physical properties, such as particle size, particle size distribution, internal surface area, moisture content, porosity, volatile matter content and pH, and its chemical composition, represented through elemental analysis and the carbon yield in char, the cation exchange capacity and the heating value. Taking into consideration the variety of feedstock biomass materials and pyrolysis operating conditions in different reactor types, it is expected that it would be difficult to predict biochar behaviour (Marshall 2013).

The implementation of pyrolysis systems in the context of biochar production has numerous benefits and applications, such as agriculture, active carbon production, waste management, renewable energy and climate change mitigation.

Potential agricultural applications include soil improvement, fertilization in organic food production, which can be used in the production of greenhouse growth media, nutrient-enriched soil supplementation and carbon sequestration. The use of biochar as a component for fertilization in agriculture may enhance crop yield through increased nutrient and moisture retention, improvement of soil structure, absorption of pollutants, reduction of use of artificial fertilizers, etc. Biochar in combination with water, ammonia and carbon dioxide in soil makes ammonium bicarbonate (NH_4HCO_3), which stays in the soil and doesn't cause damage to adjacent water and ecosystems. The application of biochar in the fertilization process may also reduce the release of nitrous oxides from agricultural land, with the additional benefit of reducing both GHG and N_2O emissions. It is also used in the sequestration of carbon in soil, which results in a reduction of carbon dioxide levels in the atmosphere through the uptake by plants (Dutta 2010; Brownsort 2009).

The volatile components of biochar (in this context, biochar is a material used in agriculture) have been identified as key properties for its suitability in soil amendment applications. As a result, volatile matter content has been specifically measured and is being correlated to the existence of toxic polycyclic aromatics (PAHs), whose level is strictly regulated, biochar with lower levels of PAH being considered to be quality (Brownsort 2009; Dutta 2010; Marshall 2013). Biochar pyrolysis systems (for agricultural purposes) use low cost technology and low grade biomass raw materials, which allow for the sustainable use of existing local resources, such as agricultural residues and fresh biomass (waste from the cultivation of fruit, viticulture, etc.), to deliver benefits as soil fertilisers while still providing energy products.

Biochar can potentially play an important role in sequestration processes, for the long term storage of carbon. After production and incorporation into soils, under certain conditions, biochar can remain stable over a long period of time (Brownsort 2009). Carbon from agricultural and forest residues, when left on the ground, is released over time into the atmosphere as CO_2 or CH_4, however, if biomass is converted into biochar, as much as 50% of the carbon contained in the biomass stays in the soil as a stable biochar residue (Basu 2013).

Charcoal produced through pyrolysis (carbonization) was one of the earliest fuels used in human civilization. It has high fixed carbon content and a modest amount of volatile matter, and can be used as a renewable fuel. Charcoal can also be used directly for clean heat and power generation or co-fired with other solid fuels in conventional generating plants. At the same time, the use of biochar can mitigate problems with direct biomass combustion, such as non-homogenous combustion, low bulk density, high water affinity, low energy content, and rotting characteristics. In its traditional form as charcoal, it is used extensively for cooking. The use of pyrolysis technology in appropriate scales in developing countries may be a way to improve otherwise inefficient traditional charcoal-making processes, reducing the biomass requirement for the same charcoal output and allowing for the use of agricultural wastes as an alternative feedstock to wood, with the potential for co-products to provide electrical power as well (Brownsort 2009).

The potential for the alleviation of climate change through the use of pyrolysis biochar systems lies in the combination of the two above-mentioned benefits of their application—the reduction of greenhouse gas emissions by avoiding their release from agriculture, waste disposal and the combustion of fossil fuel, and the sequestration of atmospheric carbon dioxide in a stable form of carbon.

Another important feature of biochar is that it can be used as a bio-adsorbent, either by treating the biochar itself as an adsorbing agent or by using the biochar as a precursor for activated carbon. Bio-adsorbents can be used for land reclamation, water remediation or air emission control. This is accomplished through adsorption of heavy metals, pollutants and other contaminants.

Biochar can be used as a raw material in active carbon production if its pores' structure and surface area are appropriate for this purpose. The biochar obtained from the biomass pyrolysis process has a direct influence on the subsequent char oxidation step, since the amount and type of pores in the char particle determines accessibility of gas to the active surface sites, and biochar produced through slower pyrolysis processes has higher surface area properties (Chhiti and Kemiha 2013; Marshall 2013).

Activated carbon has a very high adsorption capacity, due to its large pore surface area, and its use is mainly related to water purification systems, as well as air and gas cleaning. The principle of production of active carbon is the removal of the tarry products from conventional fuel charcoal, by thermal (usually by using steam), chemical (treatment by acids) and mechanical means. This so-called activation process makes the pores in charcoal particles more accessible for absorption (by increasing its absorption characteristics) and increases the pore surface area by orders of magnitude (Demirbas 2004; Basu 2013).

Biochar produced in pyrolysis processes can have surface area values ranging from 0.5 to 450 m^2/g, which are significantly lower than those of commercially activated carbons produced from coal and petroleum sources (500–1200 m^2/g).

Other potential applications of solid pyrolysis products include the manufacturing of metallurgical (redefined as bio-coke) and advanced materials (nanotubes, fibres, composites, etc.) (Marshall 2013). Bio-coke is produced specifically for metal extraction as a substitute for conventional coke, which is produced from coking coal. It needs certain specific properties for its use in blast furnaces in regard to adequate compressive strength and good fracture resistance. Using bio-coke in blast furnaces has a great potential to reduce net CO_2 emissions from the iron and steel industries by replacing fossil coal (Basu 2013).

6 Conclusion

This paper has shown the importance of understanding the biomass pyrolysis process and its mechanisms as a key for the technologies that produce various types of products from biomass raw material. Pyrolysis is primarily interesting as a method for production of solid, liquid and/or gaseous fuels, but also products of interest to other industries and branches of the economy. For that reason, slow and fast pyrolysis were both explained, as well as the different types of reactor that are already in use at different stages, from the experimental to the fully commercial, from the very simple to the high-tech processes supported by catalysts. A short review of the catalysts and catalytic processes was presented. The authors have tried to give some details about solid, liquid and gaseous pyrolysis products, their characteristics and use, primarily as fuels, but also as materials that can be used in agriculture and other industries. Pyrolysis products can be used directly or must be upgraded, depending on the technology requirements, but it is important to emphasize that pyrolysis products can be competitive with fossil fuels and oil-derived products, particularly from the aspect of sustainability and the environment. All of this was mentioned in this paper in an attempt to shed more light on pyrolysis-based technologies, giving added value to biomass as a valuable and renewable resource that can obviously play a more important role in the economy of the countries and areas which are rich in this resource.

References

Balagurumurthy B, T. S. Oza TS et al (2013) Renewable hydrocarbons through biomass hydropyrolysis process: challenges and opportunities, J Mater Cycles Waste Manage 15:9–15

Basu P (2013) Biomass Gasification, Pyrolysis and Torrefaction (Second Edition), 147–176

Basu et al (2014) An experimental and theoretical investigation on torrefaction of a large wet wood particle. Biores Technol 159:215–222

Bellais M (2007) Modelling of the pyrolysis of large wood particles, Doctoral Thesis, KTH—Royal Institute of Technology, Stockholm

Bridgeman et al (2010) Overview of solid fuels, characteristics and origin, In: Lackner M, Winter F et al (eds) Handbook of combustion A. K., Willey-VCH

Bridgwater A (2004) Biomass fast pyrolysis. In Gvero P (ed) Special issue of Thermal Science 8 (2):21–49

Bridgwater AV (2012) Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenerg 38:68–94

Bridgwater A, Meier D Radlein D (1999) An overview of fast pyrolysis of biomass. Org Geochem 30:1479–1493

Brownsort PA (2009) Biomass pyrolysis processes: performance parameters and their influence on biochar system benefits, Master thesis, University of Edinburgh

Bulusheva DA, Rossa JRH (2011) Catalysis for conversion of biomass to fuels via pyrolysis and gasification: a review. Catal Today 171:1–13

Chhiti Y, Kemiha M (2013) Thermal conversion of biomass, pyrolysis and gasification: a review. Int J Eng Sci (IJES) 2(3):75–85

Collard F, Blin J (2014) A review on pyrolysis of biomass constituents: mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. Renew Sustain Energy Rev 38:594–608

Demirbas A (2004) Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. J Anal Appl Pyrol 72:243–248

De Wild P, Reith H (2011) Biomass pyrolysis for chemicals. Biofuels 2(2):185–208

Dickerson T, Soria J (2013) Catalytic fast pyrolysis: a review. Energies 6:514–538

Dutta B (2010) Assessment of pyrolysis techniques of lignocellulosic biomass for biochar production, Master thesis, Department of Bioresource Engineering, Faculty of Agricultural & Environmental Sciences, McGill University, Ste-Anne-de-Bellevue, Quebec

Gorling M, Larsson M et al (2013) Bio-methane via fast pyrolysis of biomass. Appl Energy 112: 440–447

Goyal HB, Seal D et al (2008) Bio-fuels from thermochemical conversion of renewable resources: a review. Renew Sustain Energy Rev 12:504–517

Huang YF, Chiueh PT et al (2016) A review on microwave pyrolysis of lignocellulosic biomass. Sustainable Environment Research 26:103–109

Jahirul MI, Rasul GR et al (2012) Biofuels production through biomass pyrolysis—a technological review. Energies 5:4952–5001

Jing L, Jianjun D et al (2016) Biochar from microwave pyrolysis of biomass: a review. Biomass Bioenergy 94:228–244

Kan T, Strezov V et al (2016) Lignocellulosic biomass pyrolysis: a review of product properties and effects of pyrolysis parameters. Renew Sustain Energy Rev 57:1126–1140

Krutof A, Hawboldt K (2016) Blends of pyrolysis oil, petroleum, and other bio-based fuels: a review. Renew Sustain Energy Rev 59:406–419

Lam SS, Chase HA (2012) A review on waste to energy processes using microwave pyrolysis. Energies 5:4209–4232

Malik P, Sangwan A (2012) Nanotechnology: a tool for improving efficiency of bio-energy. J Eng Comput Appl Sci (JEC&AS):37–49

Marshall AJ (2013) Commercial application of pyrolysis technology in agriculture. Report Ontario Federation of Agriculture, Ontario

Meier D, Faix O (1999) State of the art of applied fast pyrolysis of lignocellulosic materials—a review. Bioresour Technol 68:71–77

Mohan D, Pittman CU Jr Steele PH (2006) Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 20(3):848–549

Neves D, Thunman H et al (2011) Characterization and prediction of biomass pyrolysis products. Prog Energy Combust Sci 37:611–630

Panwar NL, Kothari R et al (2012) Thermo chemical conversion of biomass—eco friendly energy routes. Renew Sustain Energy Rev 16:1801–1816

Radlein D, Quignard A (2013) A short historical review of fast pyrolysis of biomass. Oil and Gas Science and Technology, Institut Francais du Petrole, 2013, 68 (4): 765–783

Rath J, Wolfinger MG et al (2003) Heat of wood pyrolysis. Fuel 82:81–91

Sharma A, Pareek V et al (2015) Biomass pyrolysis—a review of modelling process parameters and catalytic studies. Renew Sustain Energy Rev 50:1081–1096

Shun T, Zhijun Z et al (2013) Recent progress of catalytic pyrolysis of biomass by HZSM-5. Chin J Catal 34:641–650

Titiloye J (2014) Catalysis in Biomass Transformation. In Hornung A (ed) Transformation of biomass: theory to practice. Willey, London, pp 113–120

Tripathi M, Sahu JN et al (2016) Effect of process parameters on production of biochar from biomass waste through pyrolysis: a review. Renew Sustain Energy Rev 55:467–481

Vamvuka D (2011) Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes—an overview. Int J Energy Res 35:835–962

Venderbosch RH, Prins W (2010) Fast pyrolysis technology development. Biofuels Bioprod Bioref 4:178–208

Venderbosch RH, Prins W (2011) Fast Pyrolysis. In: Brown RC (ed) Themochemical processing of biomass: conversion into fuels. Chemicals and Power, Wiley, pp 124–156

Wan Isahak WNR, Hisham MWM et al (2012) A review on bio-oil production from biomass by using pyrolysis method. Renew Sustain Energy Rev 16:5910–5923

Wu C, Budarin VL et al (2014) Conventional and microwave-assisted pyrolysis of biomass under different heating rates. J Anal App Pyrol 107:276–283

Yaman S (2004) Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy Convers Manag 45:651–671

Biodegradable Polymers Based on Proteins and Carbohydrates

Ljubica Vasiljevic and Stefan Pavlović

Abstract Biodegradable polymers have become an import focus of interest in recent years. They include polymers manufactured from feedstocks originating either from non-renewable petroleum resources or from renewable biological resources. This review presents a general overview of biodegradable polymers, with a special emphasis on the polymers based on proteins and carbohydrates. Most biodegradable polymers (e.g., starch, chitin, cellulose, collagen and other polypeptides) have been synthesised or are formed in the natural environment during the growth cycles of organisms. These complex forms of carbohydrate consisting of glycosidic bonds are usually one of the major constituents of animal and vegetable exoskeletons (cellulose, carrageenan, chitin). Scientists have already identified certain microorganisms and enzymes that can degrade such polymers. Certain polymers draw attention to their biodegradability property. Bacteria, plants and animals produce this type of polymer, which presents the possibility for very momentous renewable resources. Some of the main plant proteins that can be used as potential sources are soy protein, corn protein (zein) and wheat proteins (gluten). Casein, collagen protein or gelatin, and keratin are important animal proteins. Environmental effects and chemical structure are the main factors upon which biodegradability depends. Another feature that depends on these factors is mechanical behaviour. Some other factors that impact mechanical behaviour are: processing parameters, storage, etc.

Keywords Biodegradable polymers · Carbohydrates · Proteins

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1 Introduction

The use of plastic materials derived from oil leads to certain general problems, especially when it comes to environmental pollution and human health. This is the reason why biodegradable biopolymers have become a topic of such great interest for study (Ghanbarzadeh and Almasi 2013).

The process of biodegradation takes places as a result of the effect of enzymes and other chemical agents that are directly related to living organisms. The first segment of this process presents the fragmentation that involves reduction of the molecular weight of the starting polymers by way of either abiotic reactions, i.e., photodegradation, oxidation, and hydrolysis, or biotic reactions, that is, degradation by microorganisms (Barlow and Morgan 2013). This is followed by bioassimilation of the polymer fragments by microorganisms and their mineralisation (Dawes 2012).

The basic factors that make some materials biodegradable are chemical structure and environmental influences. Mechanisms and estimation techniques of polymer biodegradation have been reviewed (Lucas et al. 2008).

Biodegradable materials can be produced from natural polymers (e.g., cellulose, starch and proteins). Those are the two major renewable sources of biopolymers.

1.1 Polysaccharides (Carbohydrates)

For the purpose of material applications, the most important polysaccharides are cellulose and starch, but more complex carbohydrate polymers are produced by fungi and bacteria. In contemporary studies, special attention is paid to polysaccharides such as curdlan, xanthan, hyaluronic acid, and pullulan. Due to this distinguishing quality (primarily due to the structures of these polymers, which can be normally arranged and branched), enzymes that catalyse hydrolysis reactions during the biodegradation of each kind of polysaccharide differ from each other (Prajapati et al. 2014).

1.1.1 Thermoplastic Starch

One of the representatives of the polysaccharide group is starch, which is a reserve material of photosynthetic tissues from plant storage organs and seeds (Ebnesajjad 2012). The two main constituents of starch are amylopectin and amylose. The lesser represented components in starch are proteins and lipids. Amylose is essentially a linear molecule of (1 → 4)-linked a-D-glucopyranosyl units with some slight branches by (1 → 6)-a-linkages (Fig. 1). The molecules of amylose typically have molecular weights from 105 to 106 g mol^{-1} (Huang et al. 2014). Amylopectin is a highly branched molecule composed of chains of α-D-glucopyranosyl residues

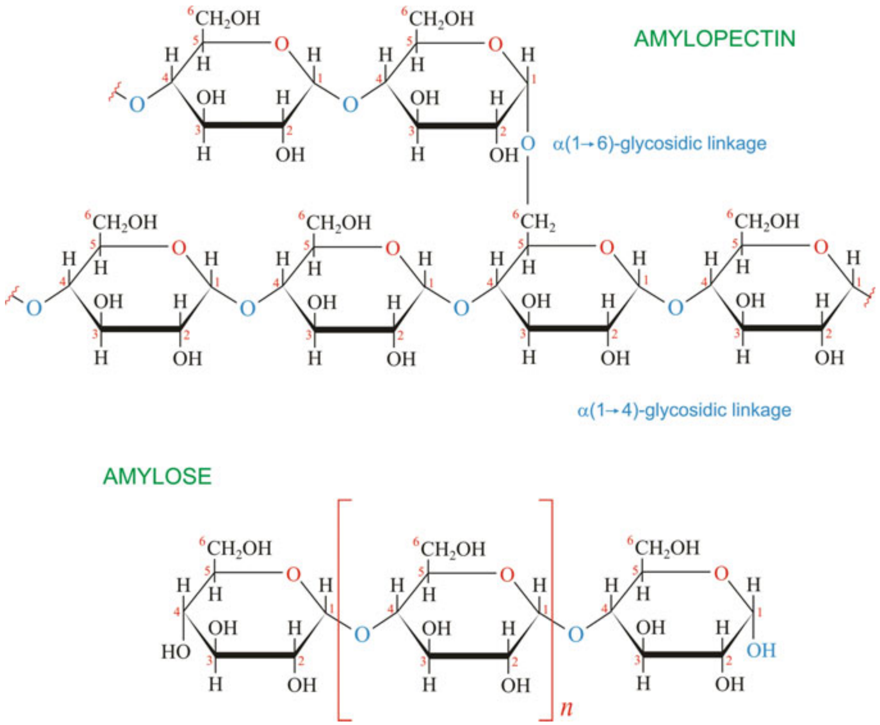

Fig. 1 Chemical structure of starch (amylose and amylopectin) E. Generalic, http://glossary.periodni.com/glossary.php?en=starch

linked together mainly by (1 → 4)-linkages but with (1 → 6) linkages at the branch points. Amylopectin consist of hundreds of short chains of (1 → 4)-linked α-D-glucopyranosyl interlinked by (1 → 6)-a-linkages (Fig. 1). This molecule is extremely large and highly branched (molecular weights range from 106 to 108 g mol^{-1}).

A, B and C represent three types of crystallinity in starch. Type ‘A’ mainly refers to cereal starches such as maize, wheat, and rice; type ‘B’ is associated with tuber starches (potato, sago); and type ‘C’ crystallinity falls between A and B (e.g., bean and root starches). In the case of the amylose-fatty acids-monoglycerides complex, another Vh-type of crystallinity was introduced. Layers in the starch granules are of a size between 120 and 400 nm, and the size of the crystalline and amorphous lamella are between 9 and 10 nm. One of the representatives, the main builder of the semi-crystalline layers in the starch granule, is amylopectin. The short chains with polymerization degrees from 15 and 18 form a double helical conformation (Huang et al. 2014) and are associated with clusters.

Thermoplastic starch is a form of processed plasticized starch (typically treated with heat and pressure in order to completely destroy the crystalline structure). Starch in the form of gelatin represents the disruption of molecular organisation within the starch granules, a process affected by interactions between starch and water (Almasi et al. 2010). Figure 2 focuses on the gelatinization process diagrammatically (Huang et al. 2014).

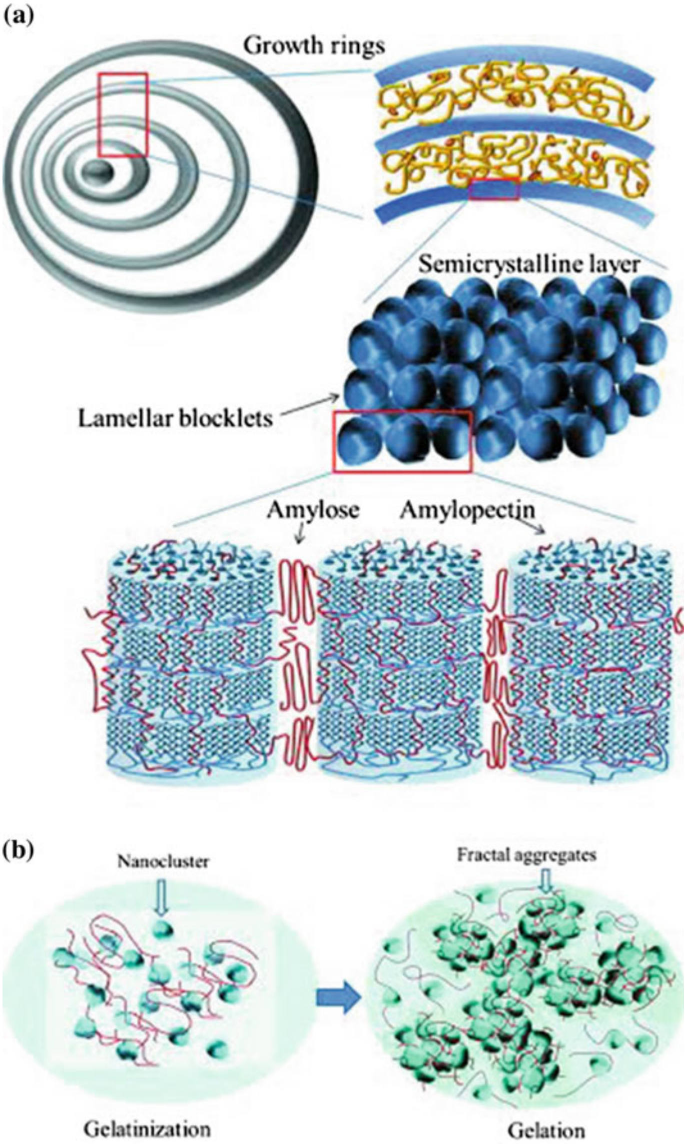

Fig. 2 Representation of a *hierarchical* structure model (tapioca starch granule) (**a**). **b** Process of gelatinization of linear amylose chains and nanoclusters of amylopectin, (*left*); gelation for loosely fractal-structured networks on a micrometer scale (*right*). Copyright © Hsien-Kai Huang et al. (2014), Published under CC BY 3.0 license. Available from: http://dx.doi.org/10.1107/S2052252514019137

In this figure, we can observe different starch granules (composed of linear amylose) and amylopectin. In Fig. 2, it can be observed how the addition of water and heat leads to the amylose diffusing out and to swelling. Granules, which mostly contain amylopectin, collapse and are held in a matrix of amylose (Fig. 2b).

In the paper (Fang and Fowler 2003), it is observed that there are different ways of obtaining thermoplastic starch (one of them involves obtaining it from native starch through various agents). In this paper, a variety of methods have been described (e.g., an extrusion process which includes three differents phenomena: fragmentation of granules, hydrogen bond cleavage and partial depolymerization). In addition, the process of extrusion enables a very intimate mixing of the polymers and any additives. Utilizing a temperature range of 120–220 °C, mechanical energy and heat cause crystal starch to be homogenised and melted in an extrusion process involving a plasticiser. In molecules such as polyglycols (e.g., glycerol, sorbitol, etc.), amines and amides are used as non-volatile plasticisers for starch (Rajeswari et al. 2013).

These starch films could be used in the production of food packaging, disposable food service ware, composting bags, loose fill products, and purchase bags (Xiong et al. 2008).

1.1.2 Cellulose and Its Derivatives

Cellulose is composed of polymer chains consisting of unbranched β(1 → 4) linked D-glucopyranosyl units (anhydrofructose unit) (Fig. 3). The source of the cellulose determines the length of this β(1 → 4) glucan chain.

It is important to note that bundles of cellulose are grouped into microfibrils (due to the formation of hydrogen bonds), and then microfibrils are grouped into cellulose fibers (Hamad 2006).

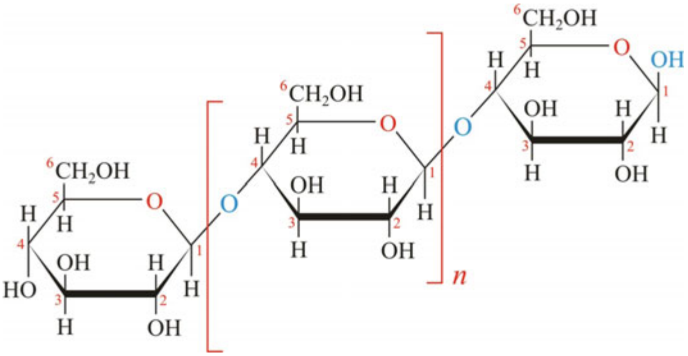

Fig. 3 Chemical structure of cellulose E. Generalic, http://glossary.periodni.com/glossary.php?en=cellulose

Many useful characteristics originate from the unique functional properties associated with the chemical structure of cellulose. These structures have structural properties which indicate extended, planar chain conformation and oriented, parallel-chain packing in the crystalline state (Smith 2005).

The biodegradation of cellulose is complicated due to the fact that cellulose exists together with lignin; fortunately, pure cellulose decomposes readily (Ebnesajjad 2012). Research findings suggest that the fermentation of cellulose is a potential source of chemicals such as ethanol and acetic acid, but so far, this has not achieved any commercial importance.

Esterification of the cellulose backbone provides structural modifications that account for a greatly expanded range of applications unavailable to the parent polysaccharide. Carboxymethyl cellulose has application in the food industries and for pharmaceuticals, especially due to the fact that its film is an obstacle for some substances (e.g., lipid, oxygen, carbon dioxide, etc.). It is, however, poorly resistant to water vapour transmission (Ghanbarzadeh et al. 2010).

1.1.3 Fibers (Lignocellulosic Complex)

Natural fibres have a lignocellulosic nature and are composed of cellulose, hemicelluloses, lignin, pectin and waxy substances (Kabir et al. 2012). Lignocellulosic biomass is composed of 30–50% cellulose, 20–50% hemicellulose, and 15–35% lignin (Lee et al. 2014). Lignin and pectin are coupled with the cellulose-hemicellulose network, providing an adhesive quality to keep the molecules together. This adhesive quality determines the strength and stiffness of the fibre. The structure of the fiber cell wall is shown in Fig. 4.

Figure 5a depicts polysaccharides with 5 and 6 carbon atoms in a ring. Differences between the hemicellulose and cellulose are reflected in the following:

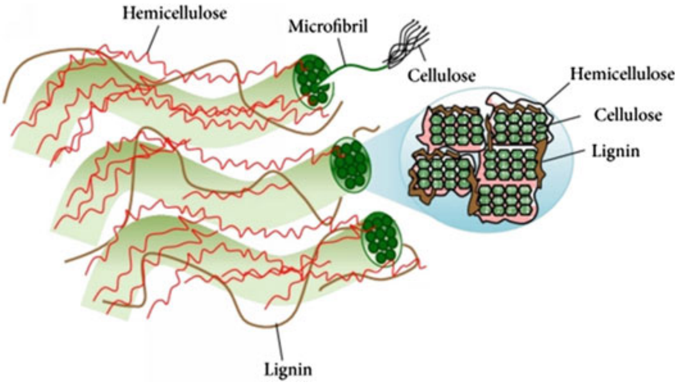

Fig. 4 Structure of the plant cell wall structure and microfibril cross-section. Copyright © 2014 H.V. Lee et al. Published under CC BY 3.0 license. Available from: http://dx.doi.org/10.1155/2014/631013

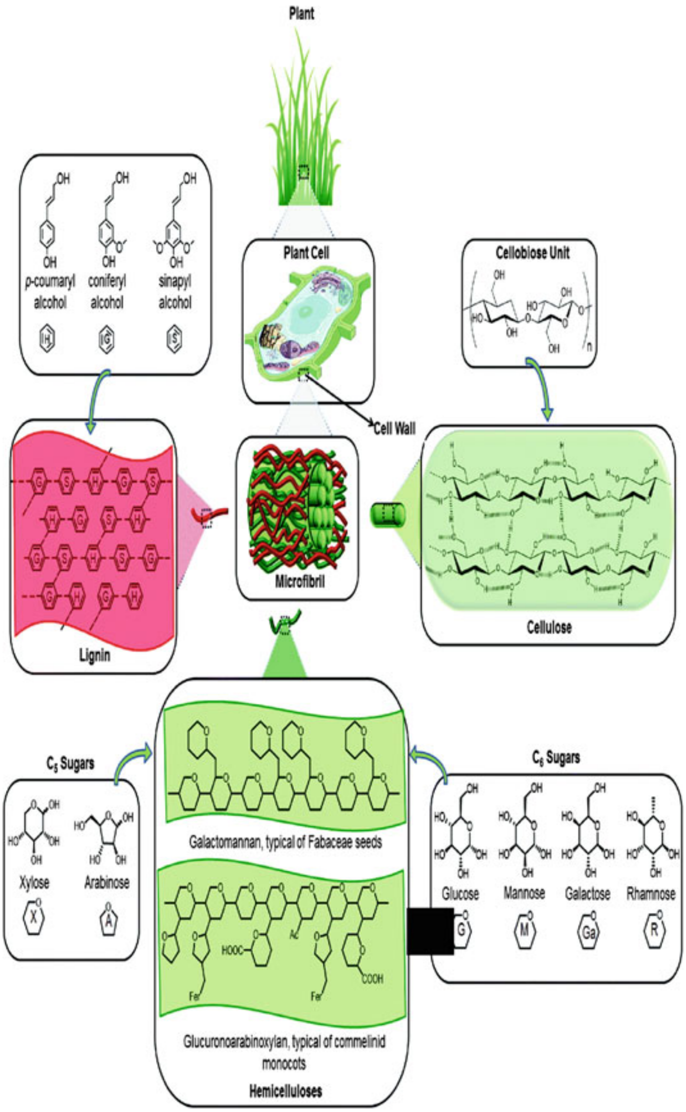

Fig. 5 The main components and structure of lignocellulose. Copyright © 2015 Isikgor, F.H., & Becer, C.R. Published under CC BY 3.0 license. Available from: doi:10.1039/C5PY00263J

hemicellulose contains several different sugar units, whereas cellulose contains only 1,4-β-D-glucopyranose, hemicellulose exhibits a considerable degree of chain branching, whereas cellulose is a linear, and finally, the degree of polymerization of cellulose is 10–100 times higher than that of hemicellulose.

Lignin is a complex hydrocarbon polymer, which has both aromatic and aliphatic constituents (Fig. 5b). These are completely insoluble in the majority of solvents and cannot be decomposed into monomeric units. Lignin is totally amorphous and has a hydrophobic nature. It is the compound responsible for giving rigidity to plants. It is considered to be a complex, three-dimensional copolymer whose molecular weight is very high. It cannot be hydrolyzed by acids, but it can be dissolved in hot alkali. It is readily oxidised and easily condensable with phenol.

Heteropolysaccharides are known collectively as pectins. They give plants flexibility. Pectin is a complex anionic polysaccharide composed of β-1,4-linked D-galacturonic acid residues, wherein the uronic acid carboxyls are either fully (HMP, high methoxy pectin) or partially (LMP, low methoxy pectin) methyl esterified (Tharanathan 2003) (Fig. 5c).

Various techniques for separating these components from the lignocellulosic complex have been proposed.

Lignin and hemicellulose are disrupted and solubilized in a solvent mixture composed of water, methyl-isobutyl-ketone (MIBK), ethanol, and sulfuric acid (H_2SO_4). Afterwards, they are subjected to a steam explosion treatment, which is catalysed by the acidic conditions created within the reactor owing to the added sulfuric acid and endogenous acetic acid. This process, apart from being environmentally friendly, separates lignin, hemicellulose and cellulose with a high degree of purity, a lower production cost, and quite significant energy savings (Kulesa 1999).

1.1.4 Chitin and Chitosan

Chitin is a polysaccharide present in various animal species that can also be formed by fermentation processes in fungi. Chitosan is a linear polysaccharide composed of randomly β(1 → 4) linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (deacetylated unit (Barikani et al. 2014). Figure 6 depicts the structure of chitin.

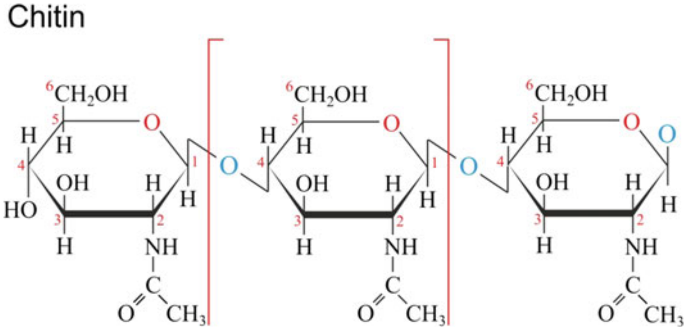

Fig. 6 Chemical structure of chitin E. Generalic, http://glossary.periodni.com/glossary.php?en=chitin

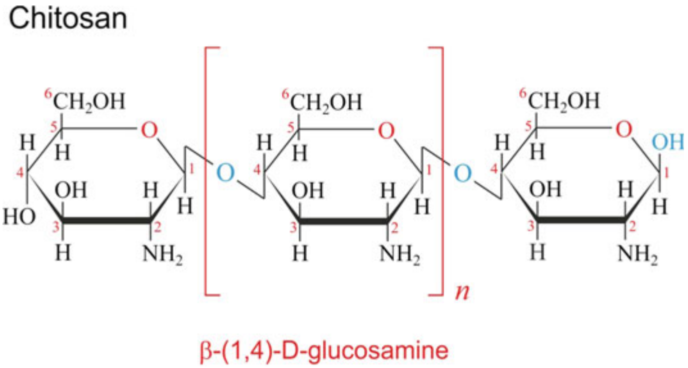

Fig. 7 Chemical structure of chitosan E. Generalic, http://glossary.periodni.com/glossary.php?en=chitosan

Chitin exhibits insolubility in its native form, but chitosan dissolves in water. Figure 7 depicts the structure of chitosan.

It has been discovered that chitosan is non-toxic after oral consumption by humans, and it has thus become a food additive approved by the FDA. The main factors on which the rate of chitosan degradation depends are crystallinity and degree of acetylation. The highly deacetylated form has the lowest degradation rates and may have a life span of several months in vivo. Chemically modified forms of chitosan produce materials with a variety of physical and mechanical properties (Lopez et al. 2014).

Potential applications of chitosan powders, gels, fibres, and films have been tested and found to be numerous: for example, membrane barriers, encapsulation, etc. The film-forming properties of chitosan are good; therefore, it can be utilised as a food packaging material (Lopez et al. 2014).

1.1.5 Gums

Gums are polysaccharides that have the ability to build gels in solutions. The degree of cross-linking depends on numerous factors, such as pH, type of counterion, and the functional charge density of these polymers (Ebnesajjad 2012). We shall discuss here the types of polysaccharide commonly used.

Alginic acid is an anionic polysaccharide. This acid is present in a special type of algae (brown algae). Alginate is a non-branched, binary copolymer of (1 → 4) glycosidically linked β-D-mannuronic acid and α-L-guluronic acid monomers. There have been extensive investigations of this polysaccharide, with special emphasis on its biodegradability. Alginate-based materials cannot be degraded due to the action of enzymes in mammals (Bouhadir et al. 2001).

1.2 Polypeptides (Proteins)

Proteins are natural polymers with the ability to form amorphous three-dimensional structures stabilised, mainly through noncovalent interactions. The functional properties of these materials are highly dependent on structural heterogeneity, thermal sensitivity, and the hydrophilic behaviour of proteins (Duro et al. 2014). Various vegetable and animal proteins are most often utilised as biodegradable polymers.

1.2.1 Corn Zein

Zein is representative of a group of prolamine proteins. This protein is found in maize. 50% or more of total endosperm protein is accounted for by it, and it is only known to play a role in nitrogen storage for the germinating embryo. It has the ability to be extracted with aqueous alcohol and dried to a granular powder (Ali et al. 2014). On the basis of differences in solubility, zein consists of three protein fractions, i.e., α-zein, β-zein, and γ-zein. α-Zein represents 75–85% of the total protein, and two groups of proteins, Z19 and Z22, dominate it, according to sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS PAGE) (Argos et al. 1982). Owing to the hydrophobic nature of zein, water absorption is extremely low in the low water activity (a w) range (Rogina 2014).

Zein plasticization increases polymer mobility, decreases glass transition temperature (Tg), and markedly changes rheological properties (Ghanbarzadeh et al. 2007). Common zein plasticisers include glyceryl monoesters, glycerol, fatty acids, and polyethylene glycol.

Zein has been used in the manufacture of a wide variety of commercial products, including coatings for paper cups, soda bottle cap linings, and clothing fabric (Eatemadi et al. 2016).

1.2.2 Wheat Gluten

Dry wheat flour comprises 9–13% protein and 75–80% starch, whereas wheat gluten consists principally of wheat storage protein (70–80%, dry matter basis). The albumins and globulins, as representatives of wheat proteins (15–22% of total protein), which present in, respectively, water- and salt-soluble forms, are isolated with starch granules in the processing of gluten. For cereal technologists, gliadin is responsible for the extensibility of wheat flour dough, acting as a filler which dilutes glutenin interactions. As seen from the commercial aspect, it is an industrial byproduct of wheat starch production through wet milling (Eatemadi et al. 2016).

There are numerous fields of application for wheat gluten (e.g., the bakery industry, surface coatings on paper, biodegradable plastic films, detergents, cosmetics, etc.) (El-Wakil et al. 2015).

1.2.3 Soy Protein

The soybean plays a most important role in the food industry, primarily in reference to the production of edible oils and other products of edible oil. The great majority of soy proteins (~90%) are globulins, capable of being fractionated into 2S, 7S, 11S and 15S based on their sedimentation coefficients. The 7S and 11S fractions, the principal fractions, accounting for, respectively, about 37 and 31% of the total extractable protein, are capable of polymerization (Liu 2012).

The functional properties that account for the usefulness of soy protein in foods are cohesiveness, adhesiveness, emulsification, dough and fibre formation, shippability, solubility, and foaming. Soy protein films exhibit a higher flexibility, smoothness, transparency, and clarity compared to other films from plant proteins. Biodegradable plastics also occur as a product of soy isolate and concentrate in the thermal-moulding process (Swain et al. 2004).

1.2.4 Collagen and Gelatin

Collagen is the protein that is present in the highest percentages in human and animal bodies. Similar to cellulose in plants, collagen molecules support mechanical stresses transferred to them by a low-modulus matrix (Zhang et al. 2014).

Collagen is a rod-type polymer nearly 300 nm in length. Its molecular weight is 300.000. The most common type of collagen is Type I. Type I collagen is the single most abundant protein in mammals. It is built up from three polypeptide subunits of similar amino acid compositions. Each polypeptide contains about 1050 amino acids, comprising approximately 33% glycine, 25% proline and 25% hydroxyproline, while lysine is relatively abundant (Hu et al. 2014).

Collagen is degraded within the body by enzymes, such as collagenases and metalloproteinases, yielding corresponding amino acids. Due to its enzymatic degradability, as well as its unique physico-chemical, mechanical and biological properties, extensive investigations have been carried out into its various applications. The solubility of collagen mostly refers to acidic aqueous solutions, and it can be processed into diverse forms such as tubes, sponges, foams, sheets, nanofibrous matrices and dispersions.

Research has also shown that the degradation rate of collagen in biomedicine can be significantly changed by enzymatic pre-treatment or cross-linking via various cross-linking agents. Bovine or porcine skin or bovine or equine Achilles tendons are currently the most important sources of industrial collagen. The two processes are mainly used for producing gelatin commercially: partial depolymerization of the collagen and demineralized bone through prolonged liming. The occurrent hydrolysis is accompanied by the extensive release of collagenous material, which solubilizes at near neutral pH at temperatures of 60–90 °C (Type B gelatin). In the acid process (Type A gelatin), skin or bone is soaked in a dilute acid, followed by extraction at acid pH. Collagen and gelatin properties are of particular interest for areas such as leather chemistry, surgery, pharmacy, and food science (Hanani et al. 2014).

1.2.5 Casein and Caseinates

Casein is the main protein of milk, representing 80% of the total milk proteins. It is a phos-photoprotein that may be separated into various electrophoretic fractions, αs1-casein, αs2-casein, β-casein and κ-casein, which differ in their primary, secondary and tertiary structure and molecular weight. The casein micelles remain stable during the majority of commonly used milk processes—heating, compacting, and homogenization. It is possible to preserve micellar integrity through extensive electrostatic and hydrogen bonding, as well as hydrophobic interactions (Sawale 2016).

The steps in the casein production process, all very important, are: acidification to about pH 5, adjustment of temperature to between 30 and 40 °C, pressing, washing or centrifuging the curd in order to remove the surplus of water, and finally, drying and grinding. Production of rennet casein differs essentially from acid casein production in the means of coagulation. A proteolytic enzyme, such as chymosin (rennin), cleaves the-casein fraction to release a glycomacropeptide, thus destabilising the casein micelles and promoting casein coagulation in the presence of calcium cations.

The end-uses of casein and caseinates have gradually shifted from industrial to food applications. Approximately 70–80% of the casein produced in the world is used as a food ingredient (Sawale 2016).

1.2.6 Whey Proteins

Whey proteins represent a type of protein which remains in milk serum upon pH/rennet coagulation of casein during the manufacture of cheese or casein (Sawale 2016). Whey protein, which represents approximately 20% of total milk proteins, is a mixture of proteins with diverse functional properties. The five main proteins are α-lactalbumins, β-lactoglobulins, bovine serum albumin, immunoglobulins, and protease peptones. α-lactalbumins, β-lactoglobulins and bovine serum albumin comprise, respectively, 57, 19 and 7% of the total whey protein. The immunoglobulins and protease-peptone fractions are remnants of the whey protein. Whey proteins are globular. They are soluble at pH 4.6 (Dybing and Smith 1991).

Ultrafiltration, reverse osmosis, gel filtration, electrodialysis, and ion exchange chromatography are the industrial processes by which whey protein is recovered. Classification of whey protein products is based on their composition. They are particularly categorised depending on their protein content. Whey protein concentrate (WPC) is composed of 25–80% protein. Whey protein isolate (WPI) consists mostly of >90% protein (Ferraro et al. 2016).

Whey protein, which occurs as a byproduct of the cheese industry, possesses excellent nutritional and functional properties and tremendous potential for human food and animal feed application (Cuq et al. 1998). Whey proteins used in the manufacture of edible film packaging material have multiple environmental benefits due to the film`s biodegradability and its capacity to control moisture, carbon dioxide, oxygen, lipid, flavour and aroma transfer (Gounga et al. 2007; Ozdemir and Floros 2008).

1.2.7 Other Proteins

Other proteins with the potential for use as biopolymeric materials in various applications exist. The most important are elastin (a major protein component of vascular and lung tissue), fish myofibrillar protein egg albumins, and wool keratin (Ferraro et al. 2016).

When the temperature exceeds 25 °C, elastin undergoes a folding process. Owing to the unique thermal transition properties of elastin, there have been extensive investigations regarding its potential as a smart, injectable drug delivery system (Mithieux et al. 2004). There are a number of papers that speak about areas of application of proteins (e.g., use of egg albumins to encapsulate organic hydrophobic compounds in pharmaceutical chemistry application of proteins in coating and film preparation, keratin-based preparation, etc.) (Shiku et al. 2004; Yamauchi et al. 1996). The large amount of cystine in keratin is favourable for the formation of many disulphide bonds that would have the ability to stabilise the proteic network. However, a major disadvantage is their unpleasant mouthfeel, so keratin-based edible coatings have not found many applications (Yamauchi and Khoda 1997). There have also been a variety of applications of other proteins, including proteins from rye, pea, barley, sorghum, rice, sunflower, pistachio and peanut (Ferraro et al. 2016).

2 Conclusions

There are only a few groups of the above-mentioned biopolymers that have market importance at present. The main reason is their price level, which is not yet competitive. The future of each biopolymer is dependent not only on its competitiveness but also on a society's ability to pay for it.

Biodegradable materials are gradually replacing synthetic polymers; this refers especially to those biodegradable materials derived from renewable natural resources.

Sustained multidisciplinary research efforts by chemists, polymer microbiologists, technologists, environmental scientists, and chemical engineers are necessary for the commercialization and implementation of biopolymer-based eco-friendly packaging materials. Biopolymers have already been used in the field of medicine.

Biopolymers are environmentally friendly, however, they show certain cost-associated limitations in terms of performance factors like thermal resistance, barrier and mechanical properties. It is necessary to conduct further researches on this kind of material with the aim of enhancing barrier properties, incorporating intelligent labelling, and informing the consumer about the possible applications of these materials.

References

Argos P, Pederson K, Marks MD, Larkins BA (1982) Structure model for maize zein proteins. J Biol Chem 257:9984–9990

Almasi H, Ghanbarzadeh B, Entezami AA (2010) Physicochemical properties of starch-CMC-nanoclay biodegradable films. Int J Biol Macromol 46:1–5

Ali S, Khatri Z, Oh KW, Kim IS, Kim SH (2014) Zein/cellulose acetate hybrid nanofibers: Electrospinning and characterization. Macromol Res 22(9):971–977

Barikani M, Oliaei E, Seddiqi H, Honarkar H (2014) Preparation and application of chitin and its derivatives: a review. Iran Polym J 23(4):307–326

Barlow CY, Morgan DC (2013) Polymer film packaging for food: An environmental assessment. Resour Conserv Recycl 78:74–80

Bouhadir KH, Lee KY, Alsberg E, Damm KL, Anderson KW, Mooney DJ (2001) Degradation of partially oxidized alginate and its potential application for tissue engineering. Biotechnol Prog 17:945–950

Cuq B, Gontard N, Guilbert S (1998) Proteins as agricultural polymers for packaging production. Cereal Chem 75(1):1–9

Dawes EA (ed) (2012) Novel biodegradable microbial polymers. Kluwer Academic Publishers, London

Dybing ST, Smith DE (1991) Relation of chemistry and processing procedures to whey protein functionality: a review. Cultured Dairy Prod J 26:4–12

Duro-Castano A, Conejos-Sánchez I, Vicent MJ (2014) Peptide-based polymer therapeutics. Polymers 6(2):515–551

Eatemadi A, Daraee H, Zarghami N, Melat Yar H, Akbarzadeh A (2016) Nanofiber: synthesis and biomedical applications. Artificial cells, nanomedicine, and biotechnology 44(1):111–121

Ebnesajjad S (ed) (2012) Handbook of biopolymers and biodegradable plastics: properties, processing and applications. William Andrew, Oxford

El-Wakil NA, Hassan EA, Abou-Zeid RE, Dufresne A (2015) Development of wheat gluten/nanocellulose/titanium dioxide nanocomposites for active food packaging. Carbohyd Polym 124:337–346

Fang J, Fowler P (2003) The use of starch and its derivatives as biopolymer sources for packaging materials. J Food Agric Environ 1:82–84

Ferraro V, Anton M, Santé-Lhoutellier V (2016) The “sisters” α-helices of collagen, elastin and keratin recovered from animal by-products: functionality, bioactivity and trends of application. Trends Food Sci Technol 51:65–75

Ghanbarzadeh B, Musavi M, Oromiehie AR, Rezayi K, Razmi Rad E, Milani J (2007) Effect of plasticizing sugars on water vapor permeability, surface energy and microstructure properties of zein films. LWT 40:1191–1197

Ghanbarzadeh B, Almasi H, Entezami AA (2010) Physical properties of edible modified starch/carboxymethyl cellulose films. Innovative Food Sci Emerg Technol 11:697–702

Ghanbarzadeh B, Almasi H (2013) Biodegradable polymers. In: Chamy R, Rosenkranz F (eds) Biodegradation-life of science, InTech, Rijeka, pp 141–186

Gounga ME, Xu S, Wang Z (2007) Whey protein isolate-based edible films as affected by protein concentration, glycerol ratio and pullulan addition in film formation. J Food Eng 83:521–530

Hamad W (2006) On the development and applications of cellulosic nanofibrillar and nanocrystalline materials. Can J Chem Eng 84:513–519

Hanani ZN, Roos YH, Kerry JP (2014) Use and application of gelatin as potential biodegradable packaging materials for food products. Int J Biol Macromol 71:94–102

Hu Y, Liu L, Gu Z, Dan W, Dan N, Yu X (2014) Modification of collagen with a natural derived cross-linker, alginate dialdehyde. Carbohyd Polym 102:324–332

Huang HK, Sheu HS, Chuang WT, Jeng US, Su AC, Wu WR, Lai HM (2014) Correlated changes in structure and viscosity during gelatinization and gelation of tapioca starch granules. IUCrJ 1 (6):418–428

Kabir MM, Wang HKT, Cardona F (2012) Chemical treatments on plant-based natural fibre reinforced polymer composites: an overview. Composites: Part B Engineering 43(7):2883–2892

Kulesa G (1999) Clean fractionation-inexpensive cellulose for plastics production. Chemical project fact sheet. http://infohouse.p 2ric.org/ref/08/07452.pdf (30 Mar 2017)

Lee HV, Hamid SBA, Zain SK (2014) Conversion of lignocellulosic biomass to nanocellulose: structure and chemical process. Sci World J 2014:1–20

Liu J, Qiaomei R, Yuting D, (2012) Glycation a promising method for food protein modification: physicochemical properties and structure, a review. Food Res Int 49(1):170–183

Lucas N, Bienaime C, Belloy C, Queneudec M, Silvestre F, Nava-Saucedo JE (2008) Polymerbiodegradation: mechanisms and estimation techniques. Chemosphere 73:429–442

Lopez O, Garcia MA, Villar MA, Gentili A, Rodriguez MS, Albertengo L (2014) Thermo-compression of biodegradable thermoplastic corn starch films containing chitin and chitosan. LWT-Food Sci Technol 57(1):106–115

Mithieux SM, Rasko JEJ, Weiss AS (2004) Synthetic elastin hydrogels derived from massive elastic assemblies of selforganized human protein monomers. Biomaterials 25:4921–4927

Ozdemir M, Floros JD (2008) Optimization of edible whey protein films containing preservatives for mechanical and optical properties. J Food Eng 84:116–123

Prajapati VD, Maheriya PM, Jani GK, Solanki HK (2014) Carrageenan: a natural seaweed polysaccharide and its applications. Carbohyd Polym 105:97–112

Rajeswari N, Selvasekarapandian S, Karthikeyan S, Sanjeeviraja C, Iwai Y, Kawamura J (2013) Structural, vibrational, thermal, and electrical properties of PVA/PVP biodegradable polymer blend electrolyte with CH_3COONH_4. Ionics 19(8):1105–1113

Rogina A (2014) Electrospinning process: versatile preparation method for biodegradable and natural polymers and biocomposite systems applied in tissue engineering and drug delivery. Appl Surf Sci 296:221–230

Sawale PD (2016) Casein and caseinate: methods of manufacture. Encycl Food Health 1:676–682

Smith R (ed) (2005) Biodegradable polymers for industrial applications. Woodhead Publishing, Sawston

Shiku Y, Hamaguchi PY, Benjakul S, Visessanguan W, Tanaka M (2004) Effect of surimi quality on properties of edible films based on Alaska Pollack. Food Chem 86:493–499

Swain SN, Biswal SM, Nanda PK, Nayak PL (2004) Biodegradable soy-based plastics: opportunities and challenges. J Polym Environ 12(1):35–42

Tharanathan RN (2003) Biodegradable films and composite coatings: past, present and future. Trends Food Sci Technol 14:71–78

Xiong HG, Tang SW, Tang HL, Zou P (2008) The structure and properties of a starch-based biodegradable film. Carbohyd Polym 71(2):263–268

Yamauchi K, Khoda A (1997) Novel proteinous microcapsules from wool keratins. Colloids Surf B 9:117–119

Yamauchi K, Yamauchi A, Kusunoki T, Khoda A, Konishi Y (1996) Preparation of stable aqueous solution of keratins, and physicochemical and biodegradational properties of films. J Biomed Mater Resour 31:439–444

Zhang Q, Lu H, Kawazoe N, Chen G (2014) Pore size effect of collagen scaffolds on cartilage regeneration. Acta Biomater 10(5):2005–2013

Application of Biopolymers in the Food Industry

Radoslav Grujic, Milan Vukic and Vesna Gojkovic

Abstract Plastic materials obtained from oil are used in the food industry. These polymers are cheap and available. They have good mechanical properties, good barriers for oxygen and vaporizable aromatic substances, and they can be hot welded. However, the main disadvantage is that biopolymers are not biodegradable, and certainly not environmentally friendly. That is the reason why the application of plastic materials must be limited and gradually replaced by materials that cause fewer ecological problems. Edible and biodegradable natural polymeric materials are one of the alternatives for food usage. These are made from polysaccharides, lipids, and proteins. Their application saves money that would otherwise need to be spent on environmental protection. Biodegradable natural polymeric materials can be used as edible films and coatings, packaging materials, carriers of antimicrobial and antioxidative materials, etc. Nanocomposites will be applied for food packaging in the future. Nanoscale research, including detection of a pathogen, active packaging, antimicrobial packaging, and the formation of barriers, will improve food packaging. It may be possible to use particles that are not organic to introduce diverse components such as colors and odors. They also may be used as tanks for the controlled release of drugs or fungicides.

Keywords Biodegradable natural materials · Edible films · And coatings · Packaging materials · Carrier of antimicrobial and antioxidative materials

1 Introduction

The polymers that we get from crops and the sea (plants and animals) are the ones most commonly used. Polysaccharides (cellulose, starch, and chitin) and proteins (casein, whey, collagen, and soy) are examples of the biopolymers that see the most

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frequent use. These natural polymers can be utilized in different ways in the food industry. Polysaccharides have been the subject of the most intensive research, being used as material for food packaging.

Scientists are currently testing various polysaccharides and their derivatives in order to produce biodegradable/edible films. Intensive study has been done on: alginate, pectin, carrageenan, konjac, chitosan, pullulan, cellulose and starch, along with their derivatives (Kristo and Biliaderis 2006; van Tuil et al. 2000; Chao Qiu et al. 2015; Espitia et al. 2014a; Gyawali and Ibrahim 2014). Proteins have recently begun to be used as edible films. Collagen and gelatin are materials that continue to be used, as they have been for years, for wrapping sausages and other products made of meat. Potential uses of certain other proteins have been studied in recent years: wheat gluten, corn zein, whey protein, casein and soy protein (van Tuil et al. 2000; Wang and Padua 2005). Lipid-based films have neither been studied nor used that much, due to their weak mechanical properties. The use of these materials is limited to the production of edible fruit coating. The most frequently used lipids are acetoglycerides, beeswax and surfactants (Kester and Fennema 1986).

Poly(hidroxyalkanoate)s (PHAs) are materials that consist of renewable, biologically degradable, biocompatible, optically active polyesters. They are produced by many bacterial species in the form of intracellular particles. PHAs represent spare energy and carbon reserve materials (Weber et al. 2002). Besides single materials, those consisting of two or more components are being used more and more (composite materials). In this way, it is possible to use the best of each of those materials, as well as obtaining materials with significantly improved features. Different materials are used in the food industry: Hydrocolloid/Lipid Composite Materials and Synthetic Polymer/Biopolymer Mixed Materials. Synthetic polymers are made biodegradable by incorporating biopolymers degraded by microorganisms. Starch derivatives are the most frequently used for this purpose. The possibility of using other biopolymers, such as cellulose/polyurethane mixtures, gluten/synthetic resin mixtures, vegetable protein/vinyl compound mixtures, and lipid/synthetic polymer mixtures, is being studied.

Films made of edible and biodegradable natural polymeric materials are one of the alternatives for food packaging. Their application saves money that would otherwise need to be spent on environmental protection. Films made of polysaccharides, lipids, and proteins are the most frequently used in practice.

2 Biopolymers

Natural polymers (biopolymers) are obtained from raw materials in agricultural production or from the sea (van Tuil et al. 2000; Averous and Pollet 2012). Natural polymers are mostly hygroscopic, which limits their application in food packaging. On the other hand, the majority of polymers prevents gas leaking into or out of the product.

In order to produce edible/biodegradable wrappers, we need to use renewable raw materials such as polysaccharides, proteins, and lipids. It is possible to use only one or to combine two or more of those materials (Khwaldia et al. 2010; Jensen et al. 2015). Which materials will be used to produce packaging depends on the desired usage of the product. Different admixtures can be added to the films: plasticizers, regular paper pigments, antioxidants, or antimicrobial agents.

2.1 Polysaccharide-based Films

Polysaccharides are natural polymers the most intensive study of which over time as been for use as materials for food packaging. Polysaccharides are not toxic and are quite widely available. A lot of different polysaccharides and their derivatives have been tested to produce biodegradable/edible films: alginate, pectin, carrageenan, konjac, chitosan, cellulose, pullulan, and starch. Polysaccharide-based films are excellent barriers for preventing gas leakage, and they keep out aromatic materials and lipids, but they are not a good barrier against water vapor, which can pass through them easily (Kester and Fennema 1986; Guilbert 1986; Espitia et al. 2014a, b; Caio et al. 2014a).

2.1.1 Alginate, Pectin, Carrageenan

Sodium-alginate is derived from brown seaweed. Pectin is a complex of polysaccharides that builds lamellae plant cells (Caio et al. 2014b; Espitia et al. 2014a, b). Carrageenan is extracted from red seaweed (Paula et al. 2014). Alginate and pectin films can be formed by dipping the supporting plate into aqueous alginate, while low-methoxyl pectin solutions produce films followed by ionic crosslinking with a calcium salt and drying. Carrageenan films are formed when warm neutral or alkaline solutions are cooled. When the gel is formed, they are dried under specific conditions. Since they are dissolvable, these films have weak mechanical properties. They are not moisture-resistant. Carrageenan films are good barriers for oxygen and lipids; they prevent fat oxidation in products. Films from this group are used as an edible coating for fruit, vegetables, cheese and meat products (Kester and Fennema 1986). Alginates are used as natural binders in coating paper to produce surface consistency. Rhim et al. (2006) noticed that products coated in alginate films were losing less water.

2.1.2 Chitosan and Pullulan

Chitosan is a derivative of chitin, a polymer which is found in the exoskeleton of crustaceans, fungal cell walls and other animal sources (Srinivasa et al. 2002; Serrano and Banon 2012; Ali et al. 2015; Arancibia et al. 2015). Pullulan is a polysaccharide of micro-biological origin (Kristo and Biliaderis 2006). Films made of these materials have good mechanical properties; they are good barriers for oxygen transition (Coma et al. 2003; Gallstedt and Hedenqvist 2006). Chitosan has antimicrobial properties and can inhibit the growth of microorganisms on the surface of a product. Pullulan is used for food coating. Derivatives with significantly improved water stability but extremely decreased biodegradability can be created through chemical modification of these polysaccharides. Kjellgren et al. (2006), Bordenave et al. (2007) published their studies on the properties and usage of chitosan-based films which are used to produce paper, carton and cellophane packaging.

2.1.3 Starch, Cellulose and Their Derivatives

Starch is a polysaccharide which is found as an energy-stored substance in many vegetable products (grains, potato, legumes, etc.). Starch cannot be used to produce food coating films, but after certain mechanical modification, it is possible to get a product with solid mechanical properties (Gutierrez et al. 2015). If starch is mixed with cellulose and proteins, its physical characteristics can be improved (Peressini et al. 2004). Large amounts of starch are produced from corn, potato, wheat, and rice. Cellulose is the most widely spread natural polymer. It is one of the cheapest raw materials found on the market, and it is widely used for the production of wrappers and coatings. It is known that it is not well soluble in water, due to its high hydrophilicity and crystal structure, which also makes application of cellulose rather difficult. Cellophane films, suitable for food packaging, are made of cellulose. Cellophane is not moisture-resistant, but it has good mechanical properties. If cellophane film is covered with polyvinylidene chloride, the protective properties of cellophane are improved. These materials are successfully used for the packaging of meat products, confectionery products, and cheese. Cellulose has many derivatives, the most significant of which are cellulose acetate, carboxymethylcellulose, methylcellulose, ethyl cellulose, hydroxypropyl and hydroxyethyl cellulose. The derivate that is most frequently applied is cellulose acetate. Some of these derivatives have good properties, but they are not used much because of the expense required for their production (van Tuil et al. 2000).

2.2 Protein-based Films

Proteins have been successfully used to form films/coating (Krochta 2002; Sobral et al. 2005; Gounga et al. 2007; Chao et al. 2015). Collagen and gelatin have been used in the food industry for coating sausages and other meat products for years. Proteins are used to coat fruit and vegetables, meat, eggs and other kinds of food. Collagen and gelatin films are translucent, but they are permeable to moisture. The ways to make biodegradable films based on milk casein and vegetable proteins have been intensively studied.

2.2.1 Wheat Gluten and Corn Zein

Gluten consists of two storage proteins, gliadin and glutenin. Zein is a protein which is extracted from corn, through the use of alcohol. Films based on these two proteins are formed by adding alcohol soluble proteins to the product in a thin layer and letting it dry. Such films have the following properties: water solubility, opacity, and mechanical and barrier properties, the latter of which depend on the conditions during their processing (protein concentration, ethanol concentration, and pH) (Gennadios and Weller 1990). Films based on wheat gluten are shiny and water resistant under good conditions. They are not soluble in water, but they absorb water when they are drowned. Zein-based films are used to protect food with a short shelflife (Wang and Padua 2005).

2.2.2 Caseinate and Whey Protein

Casein is the most significant milk protein, representing as much as if not more than 80% of the total protein in milk. Up to 20% of the total protein in milk are whey proteins. Casein-based films are opaque and water insoluble, but they absorb water (the mass of the film can be increased up to 90% if they are immersed for 24 h) and have good mechanical properties (Khwaldia et al. 2004; Khwaldia 2010; Gallstedt et al. 2005; Sadek et al. 2015). Their main disadvantage is their cost. Whey is a by-product of cheese production. It is rich in proteins, especially β-lactoglobulin. Due to their availability and low cost, whey proteins are being intensively studied as raw materials for the manufacture of biodegradable films.

2.2.3 Soy Protein

Soy proteins are available on the market in various products that differ in their protein content (soy flour, soy concentrate, and soy isolate). The two basic elements of soy proteins are 7S (conglycinin, 35%) and 11S (glycinin, 52%). Soy protein-based film can be made in two ways: by heating of the dispersion of soy isolated proteins or by pouring and drying solutions which contain soy proteins. The main disadvantages of soy protein-based films are weak mechanical properties and moisture sensitivity. These films are very brittle. In order to improve their properties, various chemical, enzymatic and physical modifications of proteins are effected (van Tuil et al. 2000; Gonzalez and Alvarez 2013; Jensen et al. 2015). Rhim et al. (2006) claim that a carton wrapper is stronger when it is coated with soy protein than when covered with alginate coating. Soy protein polymers are used as glues, dyes, and paper coating.

2.3 Lipid-based Films

Lipid-based biopolymers are the least studied polymers, because of their weak mechanical properties and inability to form films. The usages of lipid-based polymeric films are limited to an edible coating for fruit and meat products. Acetoglycerides, beeswax and surfactants are the most frequently used lipids for producing an edible coating for fruit and meat products (Kester and Fennema 1986; Acevedo-Fani et al. 2015). Triglycerides, fatty acids, and waxes in edible coatings decrease water permeability and are good barriers against moisture migration. Sausages look nicer when they are packaged in this type of film. Composite materials that contain proteins or polysaccharides (enable film integrity) and lipids or wax (stop water permeability) have good mechanical properties, and they represent great barriers against moisture migration (Krochta 2002).

Poly(hidroxyalkanoate)s (PHAs) represent a family consisting of renewable, biodegradable, biocompatible, optically active polyesters. They are produced by different bacteria. The composition of a particular monomer can be controlled, appropriately enough, by using different bacteria, which is also the way to control the substrate structure used in biopolymer synthesis (Weber et al. 2002).

2.4 Hydrocolloid/Lipid Composite Films

Polysaccharide and protein films and coatings are good barriers against gasses and vaporizable aromatic substances. These types of film hinder the movement of water. Combining protein-based polymers or polysaccharides and lipid-based polymers affords one the advantages of all biopolymers. The lipid component in the film is a barrier against water vapour, while the hygroscopic components (proteins or polysaccharides) are a barrier against oxygen and carbon dioxide; all are used as a film's matrix (Krochta and de Mulder-Johnston 1997; Baldwin et al. 1997; Anker et al. 2002; Imran et al. 2012).

2.5 Synthetic Polymer/Biopolymer

The biodegradability of synthetic polymers can be made quicker through the incorporatation of biopolymers, which are degradable by microorganisms. Nowadays, the polymers that are most commonly used in the food packaging industry are starch-based polymers. Some other polymers (cellulose/polyurethane mixtures, gluten/synthetic resin mixtures, vegetable protein/vinyl compound mixtures, lipid/synthetic polymer mixtures) are being studied, but their application is not great in practice. There are two methods of starch application. In the first, starch granules, which are sensitive to enzymatic activity, are used to fill in the synthetic matrix. In this case, starch does not change the mechanical properties. In the second, after modification, starch derivatives are used as one of the ingredients in the polymer mixture. The mechanical properties of those materials subsequently get worse, due to the proportion of starch in the polymer mixture. Despite their low mechanical properties, there are benefits to their usage due to their biodegradability.

3 Potential Application of Biopolymers in Food Production

The selection of edible/biodegradable materials in food production depends on the specific features of a given product. Weber et al. (2002) reported that edible films and coatings are used to protect meat, seafood, fruit, vegetables, grains, confectionery products, and food mixtures which can be fresh, canned, frozen or processed in different ways. Food packaging materials must be chosen in accordance with food quality and its safety, and they must fulfill particular legal requirements. Films will increase the value of a product.

4 Packaging Materials

Plastic materials obtained from oil (such as polyolefins, polyesters, polyamides, polyethylene, polyvinyl alcohol, rubber latex, fluorocarbons, etc.) (Chan and Krochta 2001a, b; Schreiber et al. 2013) are used for food packaging. These polymers are cheap and available. They have good mechanical properties (such as tensile and tear strength), they are good barriers for oxygen and vaporizable aromatic substances, and they can be hot welded. Contrastingly, plastic materials are not permeable to water vapor, and they are not biodegradable, which means that they are not environmentally friendly (Gonzalez and Alvarez 2013). That is the reason why application of plastic materials must be limited and gradually replaced by other materials that cause fewer ecological problems. The shelf-life of food products can be widely extended if edible casings and coatings made of polysaccharides, proteins and lipids are applied. They are good barriers for the transfer of gasses and water vapor. Consumers want to purchase products that contain biodegradable materials. They want to purchase high-quality products too. They are concerned about environmental problems caused by the disposal of non-renewable food packaging materials. They are interested in the use of renewable raw materials for food packaging and they are willing to increase usage of agricultural by-products.

The application of edible films in food packaging has been studied by a great number of scientists around the world (Krochta 2002; Khwaldia et al. 2004). Application of these films enhances the quality and safety of food products, as well as extending their shelf-life (Lee 2010; Coma 2008). Films made from biopolymers work as barriers against the diffusion of moisture, gasses and vaporizable aromatic materials; they can carry a great number of additives (such as flavoring agents, antioxidants, vitamins, colorants, etc.) (Khwaldia et al. 2010). Biodegradable films can contain different antibacterial agents: nisin, lysozyme and organic acids (benzoic, sorbic, propionic, and lactic acid). They are used in the production of various food products (such as cheese and meat products) (Ozdemir and Floros 2001; Han and Gennadios 2005). This is the best way to preserve food and stop its deterioration.

4.1 Edible Films and Coatings

An edible film is a thin layer of material that can be eaten. It is found on the surface of certain food products, it covers the product, or it is put between food components. In other words, it is a material used for food protection (coating or films) that extends the shelf-life of a product and does not need to be removed before consuming. It is important that the product has the physical integrity to stand alone. An edible film is between 0.050 and 0.250 mm thick.

Edible coatings have multiple tasks:

- to stop the migration of substances in or out of a product (moisture, oxygen, carbon dioxide, flavors or other food ingredients),
- to stop the loss of food ingredients (e.g., antioxidants, antimicrobials, and flavor) and
- to improve the mechanical integrity or handling characteristics of the food.

Edible and biodegradable coatings are suitable for prolonging the shelf-life of food and increasing its quality of not causing pollution of the environment. Edible films must be strong and flexible enough to resist the forces exerted on them during food processing and handling (Jooyandeh 2011). Sometimes, edible coatings have good mechanical properties and can replace synthetic packaging films (Krochta and de Mulder-Johnston 1997). Edible coatings can be consumed together with food, providing additional nutrients and improving sensory characteristics and antibacterial properties. Natural polymers are applied for the production of edible films. Materials that are used as edible food coatings must comply with regulations related to food products (Guilbert et al. 1996).

The natural films that are renewable are polysaccharides and proteins. Cellulose, starch and their derivatives are the most frequently used polysaccharides, as are extracts isolated from algae (carrageenan and agents, pectin, and chitosan). Due to the great number of polysaccharides which can be used as raw material for making coatings, edible polysaccharide-based coatings represent products with various characteristics. Collagen from meat, gelatin, whey proteins, zein from corn, soy proteins, and gluten from wheat are used to produce protein films. Films made from protein and polysaccharide are permeable by moisture but not permeable by oxygen. High mechanical resistance, when humidity is high, is the main characteristic of these coatings.

Edible coatings are very thin layers directly formed on the surface of food or materials. They are usually thinner than edible films. Edible coatings can improve the physical properties and quality of food, but they are less firm and flexible than films. In order to make a product attractive to consumers, edible coatings, as well as color and gloss, can be used to improve the features of a product (Jooyandeh 2011).

Edible packaging is widely used in the food industry today. Coatings are used in food production to protect food and extend shelf-life. Traditional coating methods are used for application of edible films, such as spray fluidization, falling and pan coatings, spraying, dipping, or brushing. Humidy products must be dried after these processes, while lipid-based coatings must be cooled (Debeaufort et al. 1998). The greatest number of edible films is formed when the solvent used in the above-mentioned processes is removed. For example, the diluted solvent of biopolymers is applied to food in thin layers, and during its evaporation, a thin film is formed. Water and ethanol are safe solvents used in the food industry. The process of drying can be done in many different ways: it can be done under ambient conditions, hot air, infrared energy or microwave energy. During the drying process, there are two phases that influence film properties Kozempel et al.(2003). The physical properties of the film that is formed depend on the manner in which the drying process has been done. The morphological structure of the film can be changed under various conditions, which can be applied to appearance, mechanical properties and permeability by moisture and gasses (Perez-Gaga and Krochta 2000; Lopez-Castejon et al. 2015; Garcia-Tejeda et al. 2015).

Edible and biodegradable films must fulfil specific requirements, such as: moisture barrier, solute and/or gas barrier, water or lipid solubility, color and appearance, mechanical and rheological characteristics, non-toxicity, etc. (Larotonda 2007; Paula et al. 2014; Sadek et al. 2015). These properties depend on the type of material that is used to make films and coatings, as well as the way they are formed and applied. Plasticizers, crosslinking agents, antimicrobials, antioxidants, and texture agents can be used to improve their properties further.

The mechanical properties of polymeric packaging films and coatings depend on two sets of forces: between the films, polymer molecules are formed for all polymeric films or coatings (cohesion), and between the film and the substrate, they are formed for coatings only (adhesion). Some properties of the film, including resistance, flexibility and permeability, depend on the degree of cohesion. If cohesion is strong, then flexibility, gas and solute barrier properties will be decreased, while porosity will be increased (Gontard et al. 1993). Cohesion depends on the biopolymer structure, the type of parameter set during the process of their formation and the manner in which they are set (temperature, pressure, solvent used, application techniques, techniques of solvent evaporation, etc.), the presented plasticizer, additives' crosslinking, thickness of the film, etc. (Larotonda 2007).

There are numerous examples of their application in the literature: meat casings from collagen, waxes for fruits and vegetables, corn zein-based coatings for candies, etc. Research has been done on potential uses of proteins isolated from whey, corn, starch, wheat, soy protein, peanuts, cellulose and casein (Krochta 2002; Gennadios 2002; Zhang and Mittal 2010; Jooyandeh 2011; Caio et al. 2014a, b). The use of protein-based films is limited due to their hydrophilic property. The application of biopolymers is significant and useful. Edible films that are based on proteins and carbohydrates are usually more cohesive and flexible than films based on vax, and they show better gas-barrier properties under certain conditions. They show greater possibility than any other material for adjusting film properties during the process of application, even for specific applications (Jooyandeh 2011).

Nowadays, producers are replacing synthetic, plastic films with biodegradable and edible films and coatings in order to protect the environment. Han and Gennadios (2005) reported that edible packaging films are polymeric films made of edible materials, which can give mechanical protection to a product and create chemical, physical, and biological barriers between foods and their outside settings. Besides, edible films can improve their appearance, help them maintain their nutrients, carry biologically active substances, and be active in shelf-life extension (Arrieta et al. 2014).

Edible films can improve the quality of fresh, frozen and processed meat, poultry and fish in the way that they retard moisture and reduce lipid oxidation and discoloration. They improve the appearance of a product in retail packages. Their usage reduces the loss of mass and flavors while less oil is absorbed in battered and breaded food products during the process of frying. Antimicrobial and antioxidant agents are used for making edible films. Khan et al. (2013) reported that lipid-based, polysaccharide-based and protein-based edible wrappers and coatings, as well as composite materials based on these raw materials, have the best qualities to be used for food packaging.

4.2 Antimicrobial Films and Active Packaging

Food poisoning, particularly of the sort that has happened over the last few decades, has raised our awareness of the need to discover new procedures to inhibit the growth of microorganisms to protect food safety and quality. One of the latest ways to preserve food is to apply antimicrobial films to the surface of a product. Several studies show that antimicrobial films and coatings are very efficient in reducing the level of such pathogen microorganisms as Escherichia coli O157:H7, Listeria monocytogenes, Salmonella Typhi and Staphylococcus aureus (Pintado et al. 2009; Xiao et al. 2010; Gyawali and Ibrahim 2014; Caio et al. 2014a, b; Ali et al. 2015; Alboofetileh et al. 2014; Aldana et al. 2015; Arancibia et al. 2015). Different matrixes are used to incorporate antimicrobial agents (for example, proteins, lipids, polysaccharides or composites). Organic acids, enzymes, bacteriocins, peptides, polysaccharides and essential oils are incorporated into polymer coatings as antimicrobial agents. The great benefit of antimicrobial edible films is that they may be used as inhibitors. They affect potential polluters on the surface of a product, and prevent their penetration inside the product.

Polysaccharides, such as chitosan, for examples, create strong films that can carry high levels of antimicrobial agents. Chitosan films that are made of hydrochloric, formic and acetic acids are hard and brittle, while films that are made of lactic or citric acids are soft and elastic, which enables the production of multilayer coatings and wrappers.

Coma et al. (2002) discovered that chitosan wrappers which contain 1% of acid inhibit *L. monocytogenes* and *L. Innocua* if we apply them onto the surface of cheese. The existence of an *L. innocua* population on the surface of cheese was 10 times higher in chitosan-free samples than in chitosan-coated samples. Chen et al. (1996) developed antimicrobial methylcellulose, chitosan, and methylcellulose-chitosan films (3:2) containing 2, 4 or 5% sodium benzoate or potassium sorbate. Methylcellulose films containing 2% sorbate or benzoate yielded clear inhibition zones for *Rhodotorula rubra* and *P. notatum* on potato dextrose agar.

The use of antimicrobial films based on soy and corn proteins was developed by Dawson et al. (1997). When they were prepared containing nisin and lysozyme, these films were inhibitory to gram-positive bacteria in both solid and liquid media, and when EDTA was added, gram-negative organisms were inhibited as well. In their study, (Cerisuelo et al. 2013) introduced active biodegradable packaging. This is significant because it lengthens the shelf-life of fruit, avoiding additional processing.

Today, a great number of natural polymers (macromolecules) are used to form antimicrobial films: proteins such as whey protein, wheat gluten protein, soy protein, triticale protein, pea protein, fish protein, polysaccharides including chitosan, starch, hydroxypropylmethyl-cellulose, carboxymethyl-cellulose and blends of both (Pareda et al. 2011; Ramos et al. 2012; Sanchez-Gonzelez et al. 2013). In order to prepare antimicrobial films, at least one component that can form a suitable, continuous, cohesive and adhesive matrix must be included. Admixtures used to form antimicrobial films contain a film-forming agent (macromolecule), a solvent (water, ethanol and others), plasticizers (glycerol, sorbitol and others), a pH adjusting agent (acid, sodium hydroxide and others) and an antimicrobial agent (Zinoviadou et al. 2010).

It is important to have the exact information about the types of microorganism when antimicrobial agents are selected in order to be the most efficient. The fact that microorganisms are divided into groups can be very helpful. Microorganisms are divided into several groups: those depending on oxygen (aerobes and anaerobes), those forming cell walls (Gram-positive and Gram-negative), those depending on growth-stage (spores and vegetative cells) or ideal growth temperature (thermophilic, mesophilic and psychotropic), and those resistant to acid/osmosis (La Storia 2012). It is possible to use two or more antimicrobial agents instead of only one. Application of two or more agents that have weaker effects, but which are cheaper, can be extremely efficient in microorganism inhibition because of their complementary effects.

Application of antimicrobial films and coatings needs to provide microorganism action after subsequent contamination, independent of previous food preservation and production processes (for example, high temperatures or pressure). These films inhibit the action of the remaining microorganisms, no matter how small their number is. This is the way to lower the price of preserving food and still do it safely.

To what extent antimicrobial films will be accepted and used in the food industry depends on existing regulations and the ratio between their purchase price and their efficiency after application.

4.3 Nanomaterials and Food Packaging

Nanotechnology has the potential to impact many aspects of food systems. Today, food packaging is being improved thanks to nanoscale innovations. It makes it faster and easier to detect pathogens and to form barriers while active packaging and antimicrobial packaging are being developed. It may be possible to use particles that are not organic to get diverse components, such as colors and odors. They also may be used as reservoirs for the supervised release functions of drugs or fungicides.

Besides that, nanomaterials will be used to improve mechanical properties and oxidation stability, to increase barriers against gasses, and possibly to increase the biodegradability of common biomaterials.

Application of nanocomposites will have a significant effect on food packaging in the future (Jose Fabra et al. 2013; Liu et al. 2014; Gonzalez and Alvarez 2015; Villaman Dieguez et al. 2015). Modern, multi-functional intelligent packaging will be used as a substitute for traditional packaging. New materials that will be used for food packaging in the future will improve preservation of fruit, vegetables, drinks, wine and other types of food. It will be possible to produce packages with firmer mechanical, barrier and thermal properties by adding suitable nanoparticles. Nano-structured materials will be capable of inhibiting the entrance of bacteria and microorganisms, which will be very significant for food safety. Nano-sensors embedded in the packaging will warn the consumer whether the food in the package is spoiled. Nanomaterials will reduce packaging waste.

Weiss et al. (2006) suggest that nanotechnology will strengthen the food industry. The safety of food products will be increased thanks to the application of nanoparticles. Food products go through sensors and are subjected to pathogen and contaminant detection during processing and shipping. There are devices that follow a certain product and track shipments. There are systems, known as smart or intelligent systems, that enable the collection of data, localization, reporting, and remote control of food products. These systems can improve the effectiveness and safety of food processing and transportation. It is possible to express and display the most important facts of food products and to improve delivery systems that carry, protect, and deliver nutraceutical ingredients to a specific place where they become active.

5 The Influence of Biopolymeric Materials on the Environment

Interest in the production of biodegradable materials has been growing recently. The reason for this is increased awareness of the problems caused by the disposal of conventional synthetic plastic materials derived from petroleum. The greatest usage of plastic in the world today is in the packaging of food, owing to the combined fact that petroleum-derived plastic materials are available in large quantities at low cost and that they have favorable functional characteristics. But it takes a long time to degrade plastics and other types of food packaging products harmful to the environment. The food packaging industry is putting a lot of effort into reducing the amount of waste they produce, which is where biopolymeric materials come in, as it has been shown that they can have a positive effect on the environment.

Alves and Mano (2008), Imran et al. (2012), Prakash et al. (2014) have all reported that demand for environmentally-friendly materials as alternatives to synthetic and non-biodegradable films is great. Many countries have developed standards which define the quality and properties of biomaterials, first and foremost biodegradability. These standards initiate the reduction of waste, especially food packaging waste.

Application of biopolymers in food production, processing and preservation contributes to environmental protection: the use of raw fossil materials is reduced while the biodegradability of new raw materials is increased. Application of biomaterials reduces global warming. Application of biomaterials in food packaging has a social dimension that plays a significant role in preserving the quality of fresh products and extending the global food market. Thus, biomaterials and nanotechnology are becoming increasingly more accepted in the food industry and especially in the manufacture of packaging materials. Consumers constantly demand products with specific physical and chemical characteristics, as well as functional foods. Production of such food requires the implementation of food components with different bioactivity characteristics.

Use of classical technologies for the production of functional foods with the sort of characteristics being demanded is insufficient. Biomaterials, with their inherent bioactivity and nano size (1–10 μm), are easier to implement in food products. Nano-sized particles increase the solubility, stability and availability of components. Use of nanotechnology will only increase in the years to follow. However, having in mind all of the positive characteristics of biomaterials, one must also consider the potential health effects.

At the present, it is not sufficiently clear whether these materials do pose any health hazards for consumers. Clearly, the situation demands performance of risk analysis and hazard assessment in order to avoid any negative effects that may arise with these new materials.

References

Acevedo-Fani A, Salvia-Trujillo L, Rojas-Grau MA et al (2015) Edible films from essential-oil-loaded nanoemulsions: physicochemical characterization and antimicrobial properties. Food Hydrocolloid 47:168–177

Alboofetileh M, Rezaei M, Hosseini H et al (2014) Antimicrobial activity of alginate/clay nanocomposite films enriched with essential oils against three common foodborne pathogens. Food Control 36:1–7

Aldana DS, Andrade-Ochoa S, Aguilar CN et al (2015) Antibacterial activity of pectic-based edible films incorporated with Mexican lime essential oil. Food Control 50:907–912

Ali A, Noh NM, Maysoun AM (2015) Antimicrobial activity of chitosan enriched with lemongrass oil against anthracnose of bell pepper. Food Packag Shelf Life 3:56–61

Alves NM, Mano JF (2008) Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications. Int J Biol Macromol 43(5):401–414

Anker M, Berntsen J, Hermansson AM et al (2002) Improved water vapor barrier of whey protein films by addition of an acetylated monoglyceride. Innov Food Sci Emerg Technol 3:81–92

Arancibia MY, M. Lopez-Caballero E, Gomez-Guillen MC et al (2015) Antimicrobial and rheological properties of chitosan as affected by extracting conditions and humidity exposure. LWT Food Sci Technol 60(2):802–810

Arrieta MP, Peltzer MA, Lopez J et al (2014) Functional properties of sodium and calcium caseinate antimicrobial active films containing carvacrol. J Food Eng 121:94–101

Averous L, Pollet E (2012) Biodegradable Polymers. In: Averous L, Pollet E (eds) Environmental silicate nano-biocomposites. Springer, London, Heidelberg, New York, pp 13–39

Baldwin EA, Nisperos-Carriedo MO, Hagenmaier RD et al (1997) Use of lipids in coatings for food products. Food Technol 51:56–64

Bordenave N, Grelier S, Pichavant F et al (2007) Water and moisture susceptibility of chitosan and paper-based materials: structure-property relationships. J Agric Food Chem 55:9479–9488

Caio GO, de Moura MR, Aouada FA et al (2014a) Antimicrobial and physical-mechanical properties of pectin/papaya puree/cinnamaldehyde nanoemulsion edible composite films. Food Hydrocolloids 41:188–194

Caio GO, de Moura MR, Fauze AA et al (2014b) Antimicrobial and physical-mechanical properties of pectin/papaya puree/cinnamaldehyde nanoemulsion edible composite films. Food Hydrocolloid 41:188–194

Cerisuelo JP, Bermudez JM, Aucejo S et al (2013) Describing and modeling the release of an antimicrobial agent from an active PP/EVOH/PP package for salmon. J Food Eng 116:352–361

Chan MA, Krochta JM (2001a) Grease and oxygen barrier properties of whey-protein-isolate coated paperboard. Tappi J 84:57

Chan MA, Krochta JM (2001b) Color and gloss of whey-protein coated paperboard. Tappi J 84:58

Chao Q, Xiaojing L, Na J et al (2015) Rheological properties and microstructure characterization of normal and waxy corn starch dry heated with soy protein isolate. Food Hydrocolloid 48:1–7

Chen MX, Yeh GHC, Chiang BHC (1996) Antimicrobial and physicochemical properties of methylcellulose and chitosan films containing a preservative. J Food Process Preserv 20:379–390

Coma V (2008) Bioactive packaging technologies for extended shelf life of meat-based products. Meat Sci 78:90–103

Coma V, Martial-Gros A, Garreau S et al (2002) Edible antimicrobial films based on chitosan matrix. J Food Sci 67:1162–1169

Coma V, Deschamps A, Martial-Gros A (2003) Bioactive packaging materials from edible chitosan polymer. J Food Sci 68:2788–2792

Dawson PLI, Han Y, Padgett TR (1997) Effect of lauric acid nisin activity in edible protein packaging films. Poult Sci 76:74–75

Debeaufort F, Quezada-Gallo JA, Voilley A (1998) Edible films and coatings: tomorrow's packagings: a review. Crit Rev Food Sci Nutr 38(4):299–313

Espitia PJP, Wen-Xian Du, de Jesus Avena-Bustillos R et al (2014a) Edible films from pectin: physical-mechanical and antimicrobial properties—a review. Food Hydrocolloid 35:287–296

Espitia PJP, J. de Jesus Avena-Bustillos R, Wen-Xian Du et al (2014b) Optimal antimicrobial formulation and physical-mechanical properties of edible films based on pectin for food preservation. Food Packaging and Shelf Life 2:38–49

Gallstedt M, Hedenqvist MS (2006) Packaging-related mechanical and barrier properties of pulp-fiber-chitosan sheets. Carbohydr Polym 63:46–53

Gallstedt M, Brottman A, Hedenqvist MS (2005) Packaging related properties of protein and chitosan-coated paper. Packag Technol Sci 18:161–170

Garcia-Tejeda YV, Salinas-Moreno Y, Martinez-Bustos F (2015) Acetylation of normal and waxy maize starches as encapsulating agents for maize anthocyanins microencapsulation. Food Bioprod Process 94:717–726

Gennadios A (2002) Protein-based films and coatings. CRC Press, Boca Raton, pp 1–672

Gennadios A, Weller CL (1990) Edible films and coating from wheat and corn proteins. Food Technol 44:63–69

Gontard N, Guilbert S, Cuq JL (1993) Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten film. J Food Sci 58:206–211

Gonzalez A, Alvarez ICI (2013) Soy protein—poly (lactic acid) bilayer films as biodegradable material for active food packaging. Food Hydrocolloid 33(2):289–296

Gonzalez A, Alvarez ICI (2015) Nanocrystal-reinforced soy protein films and their application as active packaging. Food Hydrocolloid 43:777–784

Gounga ME, Xu SY, Wang Z (2007) Whey protein isolate-based edible films as affected by protein concentration, glycerol ratio and pullulan addition in film formation. J Food Eng 83:521–530

Guilbert S (1986) Technology and application of edible protective films. In: Mathlouthi M (ed) Food packaging and preservation. Elsevier Applied Science, London, pp 371–394

Guilbert S, Gontard N, Gorris LGM (1996) Prolongation of the shelflife of perishable food products using biodegradable films and coatings. LWT Food Sci Technol 29:10–17

Gutierrez TJ, Morales NJ, Perez E et al (2015) Physico-chemical properties of edible films derived from native and phosphated cush-cush yam and cassava starches. Food Packag Shelf Life 3:1–8

Gyawali R, Ibrahim SA (2014) Natural products as antimicrobial agents. Food Control 46:412–429

Han JH, Gennadios A (2005) Edible films and coatings: a review. In: Han JH (ed) Innovations in food packaging. Elsevier Academic Press, London, pp 239–262

Imran M, Revol-Junelles AM, Rene N et al (2012) Microstructure and physico-chemical evaluation of nanoemulsion-based antimicrobial peptides embedded in bioactive packaging films. Food Hydrocolloid 29:407–419

Jensen A, Lim LT, Barbut S et al (2015) Development and characterization of soy protein films incorporated with cellulose fibers using a hot surface casting technique. LWT-Food Sci Technol 60:162–170

Jooyandeh H (2011) Whey protein films and coatings: a review. Pak J Nutr 10(3):296–301

Jose Fabra M, Lopez-Rubio A, Lagaron JM (2013) High barrier polyhydroxyalcanoate food packaging film by means of nanostructured electro spun interlayers of zein. Food Hydrocolloid 32:106–114

Kester JJ, Fennema OR (1986) Edible films and coatings: a review. Food Technology 40:47–59

Khan MI, Adrees MN, Tariq MR et al (2013) Application of edible coating for improving meat quality: a review Pak. J Food Sci 23(2):71–79

Khwaldia K (2010) Water vapor barrier and mechanical properties of paper-sodium caseinate and paper-sodium caseinate-paraffin wax films. J Food Biochem 34:998–1013

Khwaldia K, Perez C, Banon S et al (2004) Milk proteins for edible films and coatings. Crit Rev Food Sci Nutr 44:239–251

Khwaldia K, Arab-Tehrany E, Desobry S (2010) Biopolymer coatings on paper packaging materials. Compr Rev Food Sci Food Saf 9:82–91

Kjellgren H, Gallstedt M, Engstrom G et al (2006) Barrier and surface properties of chitosan-coated greaseproof paper. Carbohydr Polym 65:453–460

Kozempel M, McAloon AJ, Tomasula PM (2003) Drying kinetics of calcium caseinate. J Agric Food Chem 51:773–776

Kristo E, Biliaderis CG (2006) Water sorption and thermo-mechanical properties of water/sorbitol-plasticized composite biopolymer films: caseinate-pullulan bilayers and blends. Food Hydrocolloid 20:1057–1071

Krochta JM (2002) Proteins as raw materials for films and coatings: definitions, current status and opportunities. In: Gennadios A (ed) protein-based films and coatings. CRC Press, Boca Raton, pp 1–44

Krochta JM, De Mulder-Johnston C (1997) Edible and biodegradable polymer films: challenges and opportunities. Food Technology 51:61–77

La Storia A (2012) Development and application of antimicrobial food packaging, Ph.D. Thesis. Universita degli Studi di Napoli Federico II, Napoli, Italy, pp 10–55

Larotonda FS (2007) Biodegradable films and coatings obtained from carrageenan from Mastocarpus stellatus and starch from *Quercus suber*. University of Porto, Portugal

Lee KT (2010) Quality and safety aspects of meat products as affected by various physical manipulations of packaging materials. Meat Sci 86:138–150

Liu G, Song Y, Wang J et al (2014) Effects of nanoclay type on the physical and antimicrobial properties of PVOH-based nanocomposite films. LWT Food Sci Technol 57:562–568

Lopez-Castejon ML, Bengoechea C, Garcia-Morales M et al (2015) Effect of plasticizer and storage conditions on thermomechanical properties of albumen/tragacanth based bioplastics. Food Bioprod Process 95:264–271

Ozdemir M, Floros JD (2001) Analysis and modeling of potassium sorbate diffusion through edible whey protein films. J Food Eng 47:149–155

Pareda M, Ponce AG, Marcovich NE et al (2011) Chitosan-gelatin composites and bi-layer films with potential antimicrobial activity. Food Hydrocolloid 25:1372–1381

Paula GA, Benevides NMB, Cunha AP et al (2014) Development and characterization of edible films from mixtures of κ-carrageenan, ι-carrageenan, and alginate. Food Hydrocolloid 47:140–145

Peressini D, Bravin B, Sensidoni A (2004) Tensile properties, water vapor permeabilities and solubilities of starch-methylcellulose- based edible films. Ital J Food Sci 16:5–16

Perez-Gaga M, Krochta JM (2000) Drying temperature effect on water vapor permeability and mechanical properties of whey protein-lipid emulsion films. J Agric Food Chem 48:2687–2692

Pintado CMBS, Ferreira MASS, Sousa I (2009) Properties of whey protein-based films containing organic acids and nisin to control *Listeria monocytogenes*. J Food Prot 72:1891–1896

Prakash N, Rajkumar E, Sudha PN et al (2014) Antimicrobial activity of binary and ternary composites of chitosan amended with nylon 6 and montmorillonite clay. Int J Pharm Pharm Sci 6:118–120

Ramos OL, Silva SI, Soares JC et al (2012) Features and performance of edible films, obtained from whey protein isolate formulated with antimicrobial compounds. Food Res Int 45:351–361

Rhim JW, Lee JH, Hong SI (2006) Water resistance and mechanical properties of biopolymer (alginate and soy protein) coated paperboards. Lebensm Wiss Technol 39:806–813

Sadek C, Pauchard L, Schuck P et al (2015) Mechanical properties of milk protein skin layers after drying: understanding the mechanisms of particle formation from whey protein isolate and native phosphocaseinate. Food Hydrocolloid 48:8–16

Sanchez-Gonzalez L, Saavedra JIQ, Chiralt A (2013) Physical properties and antilisterial activity of bioactive edible films containing *Lactobacillus plantarum*. Food Hydrocolloid 33:92–98

Schreiber SB, Bozell JJ, Hayes DG et al (2013) Introduction of primary antioxidant activity to chitosan for application as a multifunctional food packaging material. Food Hydrocolloid 33:207–214

Serrano R, Banon S (2012) Reducing SO_2 in fresh pork burgers by adding chitosan. Meat Sci 92:651–658

Sobral PJA, dos Santos JS, Garcia FT (2005) Effect of protein and plasticizer concentrations in film forming solutions on physical properties of edible films based on muscle proteins of a Thai Tilapia. J Food Eng 70:93–100

Srinivasa P, Baskaran R, Ramesh M et al (2002) Storage studies of mango packed using biodegradable chitosan film. Eur Food Res Technol 215:504–508

van Tuil R, Fowler P, Lawther M et al (2000) Properties of biobased packaging materials. In: Weber CJ (ed) Biobased Packaging materials for the food industry—status and perspectives. Department of Dairy and Food Science, The Royal Veterinary and Agricultural University, Copenhagen, pp 8–33

Villaman Dieguez MC, Pelissari FM, do Amaral Sobral PJ et al (2015) Effect of process conditions on the production of nanocomposite films based on amaranth flour and montmorillonite. LWT Food Sci Technol 61:70–79

Wang Q, Padua GW (2005) Properties of zein films coated with drying oils. J Agric Food Chem 53:3444–3448

Weber CJ, Haugaard V, Festersen R et al (2002) Production and applications of biobased packaging materials for the food industry. Food Addit Cont 19:172–177

Weiss J, Takhistov P, Mcclements DJ (2006) Functional materials in food nanotechnology. J Food Sci 71(9):R107–R116

Xiao LS, Jia MW, Yonghong C et al (2010) Antimicrobial and physical properties of sweet potato starch films incorporated with potassium sorbate or chitosan. Food Hydrocolloid 24:285–290

Zhang H, Mittal G (2010) Biodegradable protein-based films from plant resources: a review. Environ Prog Sustain Energy 29:203–220

Zinoviadou K, Koutsoumanis KP, Biliaderis CG (2010) Physical and thermomechanical properties of whey protein isolate films containing antimicrobials, and their effect against spoilage flora of fresh beef. Food Hydrocolloid 24:49–59

Application of Edible Films and Coatings in Food Production

Milan Vukić, Slavica Grujić and Bozana Odzaković

Abstract Today, edible films and coatings can be used for a variety of purposes related to food products, singly or in conjunction with other compounds. There are many variations of edible film and coating, and all can be summarized in the following sentence. Edible films and coatings are thin protective, edible and biodegradable layers deposited on or wrapped around a food's surface. Numerous usages of such films and coatings have been investigated, with reasonable success, one of which is active food packaging. Edible films and coatings are designed by blending edible raw materials with food grade additives. Biopolymers are naturally occurring polymers that are most important for the creation of edible films and coatings, including proteins, polysaccharides and lipids. In proper application, edible films and coatings make it possible to improve the physical characteristics of food products and enhance the distinctive tactile and visual attributes of their surfaces. In other words, edible films and coatings can aid in the function of active substance conveyance for such factors as antioxidants, antimicrobials, colors, and flavors. Protection of food products from oxidation, moisture absorption/desorption, microbial growth, and other chemical reactions is of the greatest importance. Through all these properties, edible films and coatings prolong the quality of food products and improve food safety.

Keywords Edible coatings · Edible films · Lipids · Packaging · Polysaccarides · Proteins

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1 Introduction

The Chinese, in their history, are known to have applied wax coatings to citrus fruits (Hardenburg 1967). Although the entire functional capacity of edible coatings on fresh produce was unknown to them, they had observed that the respiratory gas exchange was slowed by this process, and thus wax-coated fruits could be safely stored for longer time periods than fruits without wax. Any material applied to various foods through enrobing (i.e., deposing film, coating or wrapping) that is safe and can be eaten with that food by the consumers can be called an edible film or coating. For the creation of edible films and coatings, biopolymers can be utilized alone or enforced with plasticizers and other food grade additives for the purpose of adjusting the physical features or performing other functional enforcement of the edible films and coatings (Espitia et al. 2014).

Gennadios et al. (1997) noted that the basic materials from which edible films and coatings can be created are proteins, polysaccharides (carbohydrates and gums), and lipids; two or more components belonging to these basic materials can be united into the desired form. The film-forming mechanism and equipment engaged in the process of creating edible films and coatings must take place within the context of a suitable food process, for instance: pH modification, salt addition, enzymatic modification, etc., and in all reactions, use of food grade solvents or other food grade chemicals must be administered. These basic materials can be molded into a preformed thin layer and placed on the product's surface or between its individual components; this is referred to as edible packaging (Espitia et al. 2014). An edible coating is a thin layer of deposited material on a product's surface that can be eaten along with the product (Kang et al. 2013). The principal difference between these two food packaging systems, films and coatings, is the aggregated state in which they are applied to the food product. An edible coating is deposited in a liquid aggregate state while an edible film is delivered to a food product in the form of thin solid sheets (Falguera et al. 2011).

The objective of edible film and coating utilization on food products is enforcement of quality for longer time periods and protection from physical, chemical, and biological decay throughout the shelf-life of food products (Kester and Fennema 1986). This is accomplished through improvement of the physical strength of food commodities, reduction of particle clustering, and enhancement of distinctive tactile and visual attributes of food surfaces that contribute to the product's attractivity (Cisneros-Zevallos et al. 1997; Cuq et al. 1995) and through protection of foodstuffs from the detrimental developments of moisture migration and other causes of deterioration (Kester and Fennema 1986). Edible films and coatings serve the function of acting as a barrier against oils, gasses, and vapors, and can also convey active substances, such as antioxidants, antimicrobials, coloring, and flavors (Kester and Fennema 1986; Gennadios and Weller 1990; Guilbert and Gontard 1995; Krochta and De Mulder-Johnston 1997; Miller et al. 1998). All things considered, application of edible films and coatings fulfill the objectives of shelf life extension, safety improvement and quality preservation

(Gennadios and Weller 1990). Furthermore, in conjunction with edibility, biodegradability is one of the greatest conveniences of edible films and coatings (Debeaufort et al. 1998).

As a serviceable part of food products, the application of edible materials can significantly alter consumer choice (Petersen et al. 1999). The distinctive organoleptic attributes of a food product that can be altered and adjusted by application of edible films and coatings may encompass pleasant flavor, tastelessness, sensory compatibility with coated or packaged foods, and tactile and visual attributes (Han 2002; Nussinovitch 2003). Safety issues related to the new edible film-forming materials and microflora changes in the coated food product's potential for toxicity or allergenicity should be kept in mind. Marketing factors such as the price of the final product, consumer acceptance of the new materials, cultural hesitation related to religious taboos on some types of food, which can at least in some part be related to the composition of edible films and coatings, should also be reviewed. For the purpose of food packaging, the types of food product, the specific application appropriate for each type, and the major mechanisms of quality deterioration define which edible films and coatings can and, perhaps it is better to say, must be chosen (Guilbert et al. 2002; Petersen et al. 1999). Dear reader, in this text, we authors wish to present an informative overview of the possible applications of edible films and coatings. In such a broad field, we will try to summarize only the most important applications and the logic behind them.

2 Edible Materials

The intended application mainly defines the choice of edible material. When applying edible films and coatings, it is imperative that one choose materials that are compatible with the products from a sensory standpoint, in order not to negatively influence the product's attractivity (Marquez et al. 2017). The principal film-forming materials (proteins, polysaccharides, lipids, and resins) can be applied by themselves or in a mixture. Consequent films and coatings are significantly affected by the physical and chemical attributes of the biopolymers (Sothornvit and Krochta 2000). Regarding the affinity of materials to water, they can either be hydrophilic or hydrophobic or both; however, to maintain the imperative of edibility, the solvents that can be added are restrained to water or ethanol (Peyron 1991). The rate of gas diffusion through edible films and coating is associated with the distinctive physicochemical properties of the material utilized, such as molecular weight, molecular polarity, and structure. Also, the mobility of individual gas molecules plays a major role in permeability. As a method of property enhancement, several film-forming materials can be synergized into edible films and coatings. In an identical principal approach to the production of multilayer blends of plastic films, appropriate edible structures can be designed through the blending of two or more individual film-forming components into a single united and continuous layer (Debeaufort et al. 1998; Were et al. 1999; Yildirim and Hettiarachchy

1997; Basiak et al. 2017), or as a multiple succession of specific layers forming composites. The possible combinations include protein coatings (or film layers) on polysaccharide films or lipid layers of protein/polysaccharide films. In this way, the multi-layered film structure optimizes the characteristics of the final film. Nowadays, when increased awareness of food ingredients is connected with consumer interest in healthy nutrition and food safety, the edible materials used for films and coatings, applied in their natural or modified forms, must be acceptable to the consumer in the same way. Consumers want natural materials, generally listed as safe (GRAS) for application in foods products, for example, beeswax or carnauba wax.

2.1 Proteins

Edible films and coatings formulated with proteins demonstrate exceptional oxygen, carbon dioxide, and lipid barrier properties, particularly at low relative humidities. Likewise, all edible films and coatings formulated on the basis of proteins exhibit adequate mechanical properties, i.e., structural stability, which makes it possible to hold a required form (Kester and Fennema 1986; Peyron 1991). This stands in sharp contrast to the mechanical strength of synthetic polymers that restrain their application in food packaging (Bourtoom 2009). Poor water barrier characteristics relate almost entirely to the hydrophilic nature of proteins (Kester and Fennema 1986; McHugh 2000; Peyron 1991). Raw materials can be obtained from sources of animal and plant origin, including animal tissues, milk, eggs, grains, and oilseeds (Orban et al. 1992; Krochta 2002). However, it must be kept in mind that most of these protein sources are, in fact, mixtures of various protein fractions comprising a range of molecular weights.

2.1.1 Milk Proteins

Whey and caseinates are the main milk protein fractions and have been extensively studied due to their nutritional value in conjunction with their structural appearance (Chen 1995; McHugh and Krochta 1994; Vachon et al. 2000). Caseins represent around 80% of the total milk proteins. In aqueous solutions, caseins form films relatively easily, and due to their random-coil nature, interchain cohesion increases via associated intermolecular hydrogen, electrostatic and hydrophobic bonds (McHugh and Krochta 1994; Chick and Hernandez 2002). Four principal components (αs1-, αs2-, β-, and κ-caseins) constitute caseinates.

Whey proteins are water-soluble milk proteins, obtained from milk serum after caseinate coagulation in the process of making cheese; they can be dehydrated to make whey powder. Of the total protein content in milk, 20% goes to whey proteins (Brunner 1977). Whey contains five essential proteins: α-lactalbumins, β-lactoglobulins, bovine serum albumin (BSA), immunoglobulin, and proteose peptones. The β-lactoglobulin monomer is the most prevalent and accounts for approximately 57% of the protein in whey (Dybing and Smith 1991). The second most plenteous whey protein in milk is α-lactalbumin (20%). BSA represents approximately 7% of the protein in whey and holds 14 S-S bonds and one free thiol group, which makes it a highly structured protein (Morr and Ha 1993).

2.1.2 Collagen and Gelatin

Collagen is a fibrous protein and it accounts for about 30% of total animal body mass (Gustavson 1956). A main functional feature of collagen fibrils within a live animal body is the provision of the tensile strength of the animal's tissues (Trotter et al. 2000). Two principal components constitute collagen, α (MW 100,000 Da) and β (MW 200,000 Da), consisting of two different types of covalently crosslinked chain, pairs α1-α1 and α2-α2 (Piez 1968). Gelatin is produced by hydrolyzing collagen, and its molecular weight spans a broad range from 3000 to 200,000 Da. Molecular weight depends upon the raw material used in the production of gelatin and the handling conditions (Young 1967).

2.1.3 Plasma Proteins

Plasma proteins are mixtures, constituted of albumin and globulins (Herrero et al. 2009; Nuthong et al. 2009). Myofibrillar proteins build the components of muscle and are mainly composed of two principal components, high molecular weight myosin and low molecular weight actin. Protein, from a variety of animal species, has been extracted. Up until now, most work has focused on fish as the main source of protein, for financial reasons. Washing treatments are applied for the removal of lipids, myoglobin, and collagen. The process known as surimi is suitable for obtaining myofibrillar proteins from fish (Cuq 2002). The obtained product is characteristically odorless and colorless. All distinct sources of myofibrillar proteins, such as beef, pork and chicken proteins, can similarly be processed with the surimi process (Sousa et al. 1997; Stanley et al. 1994).

2.1.4 Egg White

Egg white is a protein combination, composed of eight main constituent proteins: ovalbumin, ovotransferrin, ovomucoid, ovomucin, lysozyme, G2 globulin, G3 globulin, and avidin, all of which are globular. Ovalbumin, ovotransferrin, and ovomucoid accounts for 54, 12, and 11% of total proteins, respectively. Of all proteins, free SH groups are found exclusively in ovalbumin protein. Ovotransferrin, ovomucoid, and lysozyme contain S–S bonds (Mine 1995). For adequate film development, S–S bonds have been judged to be the most useful.

2.1.5 Soy Protein

Soy protein isolate is a tertiary product of soy oil production and soy flour purification. Based on relative sedimentation, soy proteins are classified into the following protein fractions: 2S, 7S, 11S, and 15S (Bourtoom 2008). 7S (β-conglycinin) and 11S (glycinin) are particularly vital, with molecular weights of 150–200 and 300–380 kDa, respectively (Fukushima 2004). By their conformation, these proteins are tightly folded proteins, or globulins (Bourtoom 2008).

2.1.6 Wheat Gluten

The precise content of wheat proteins depends upon the variety of wheat. Two substantial fractions of proteins can be denominated from wheat storage proteins. Fractions differ in the range of molecular weights and solubility in aqueous alcohols: the soluble fraction of prolamins called gliadins and the insoluble fraction of glutelin, namely glutenins. These fractions constitute gluten biopolymer. Molecular weights mainly composed of monomeric gliadins range from 28 to 55 kDa, and can further be divided into prolamin subfractions. Those subfractions consist of ω5-, ω1,2-gliadine, as well as α- and γ-gliadin. Glutenins, on the other hand, are aggregated proteins with molecular weights ranging from 500 to 10,000 kDa and can further be divided into two glutelin subfractions, high molecular wheat glutelin (HMW) and low molecular wheat glutelin (LMW). A subfraction of the HMW can be further split into two types, x and y (Shewry et al. 2002; Wieser 2007).

2.2 Polyscchárides

Polysaccharide film-forming materials comprise starch, non-starch carbohydrates, gums, and fibers. The polysaccharides are assembled out of simple monomers in comparison to protein's amino acids, and yet despite this fact, polysaccharides possess much larger molecular weights and complicated conformation structures that are harder to predict and control than those of proteins. By their electrical charge, most carbohydrates are neutral; some gums are charged negatively, while others, in exceptional cases, are positive. Also, scores of hydroxyl groups in neutral carbohydrate structure hydrogen bonds are almost entirely responsible for conducting the most important function in film and coat formation and its characteristics. The basic and underlying advantage of polysaccharide films is in their structural stability and adhesiveness. Polysaccharide compounds in edible films and coatings are the dominant contributors to the following physical properties: hardness, crispness, compactness, and viscosity. They exhibit the ability to slow down the transmission of gasses, through selective permeability of oxygen and carbon dioxide, but are less effective as a water barrier than waxes. Despite this shortcoming, polysaccharides can be used to protect food from oxidation. Retardation of gas transmission can be so effective for polysaccharide films that it can be a challenge to manipulate for an appropriate application. Some polysaccharides exhibit significantly altered rheological properties under acidic conditions, as compared to neutral or alkaline conditions, as well as in the presence of multivalent negatively charged cations. This behavior is of great importance in the film casting process.

2.2.1 Cellulose and Derivatives

Cellulose is the basic structural material of the plant cell wall. The most common derivates of cellulose in commercial usage are carboxymethyl cellulose (CMC), methylcellulose (MC), hydroxypropyl cellulose (HPC), and hydroxypropyl-methylcellulose (HPMC). Besides cellulose of vegetative origin, bacterial cellulose (BC) is also utilized in the production of edible coatings and films. BC is clean of the impurities found in plant cellulose (hemicellulose, pectin, and lignin) (Kurosumi et al. 2009).

2.2.2 Starch and Derivatives

Starch is the most abundant polysaccharide in nature, serving as a reserve polysaccharide in plants. Starch poses a broad range of functionalities for application as a food hydrocolloid, and at relatively low cost. Modified starch has received much attention, both in the field of research and in the field of industrial use. Its increased acceptance stems from the fact that these films exhibit a dramatic enhancement in film properties while maintaining a production expense roughly equivalent to that of native starch films.

2.2.3 Chitosan, Carrageenan and Alginat

Chitosan is a natural linear polysaccharide consisting of 1,4-linked 2-aminodeoxy-β-D-glucan, a partially deacetylated derivative of chitin. After cellulose, chitosan is the most routinely applied polysaccharide in edible food packaging (Bonilla et al. 2012).

Carrageenans are a group of galactans present in red seaweeds with linear chain hydrophilic polymers (Imeson 2000; Osorio et al. 2011). There are three main types of carrageenan, differing in chemical structures and properties: kappa carrageenan (k-carrageenan), iota carrageenan (i-carrageenan) and lambda carrageenan (ι-carrageenan) (Cosenza et al. 2014).

Alginate can be extracted from seaweeds (*Laminaria digitataand*, *Ascophyllum nodosum*), and can also be synthesized by microorganisms (Blanco-Pascual et al. 2014). Its polymer chain structure is composed of linear polysaccharide monomeric units of 1-4-linked α-d-mannuronate and β-L-guluronate, and it is soluble in water. The polymer chain of alginate can be segregated into three kinds of regions or blocks in different ratios and different distributions in the chain. The physical properties of alginates are dependent on the relative contribution of these three blocks in the chain structure.

2.2.4 Pectins

Pectins can be found in plant cells acting as structural components; they are polysaccharides composed of D-galacturonic acid as a principal constituent. They also act as an intercellular cementing substance. Pectins are a by-product of the production of fruit juice, sunflower oil and sugar.

2.3 Hydrophobic Compounds

"Biopolymers" is an inappropriate name for lipids, waxes, and resins, since they are not polymers. Nevertheless, they are still used as film-forming materials. Furthermore, it should be made clear that waxes and fats are the oldest known edible film components. Animal and vegetable oils, fats, mono-, di-, and triglycerides, carnauba wax, beeswax, candelilla, paraffin waxes and resins, as well as essential oils and extracts (camphor, mint), exhibit a hydrophobic nature, which they introduce into the films and coatings formulated from lipid film-forming materials. Lipids can be blended with other film-forming materials to enhance water repellent and low penetration characteristics (Gennadios et al. 1997; Han et al. 2006; Mehyar et al. 2012; Pérez-Gago and Krochta 2002). The extent of improvement of resistance to water penetration in composite films and coatings depends on the type of hydrophobic component used, and the cross-influence of the lipid component with a protein and polysaccharide component (Rhim and Shellhammer 2005). Lipid-based films and coatings are great barriers to water transmission. And yet, they are also able to retard gas diffusion. For example, a wax will affect oxygen and carbon dioxide transmission to such an extent that the final result can be unwanted destructive physiological processes, e.g., commencement of an anaerobic respiratory process in fruits and vegetables leading to quality deterioration.

2.3.1 Waxes

Though there are many other suitable materials, waxes are nevertheless still frequently employed as a raw material in the production of films and coatings for protecting the quality and increasing the sustainability of fruits, vegetables, cheeses, and meat products. The term 'waxes' applies to a series of nonpolar substances of natural or synthetic origin. Waxes, as a diverse group of organic compounds, are defined as the esters of aliphatic acids with a long chain of aliphatic alcohol, and may include various functional groups that express solubility in an organic nonpolar solvent. The waxes available in the market comprise a range of natural waxes such as beeswax, carnauba wax, candelilla wax and paraffin wax, as well as oxidized polyethylene and microcrystalline wax of synthetic origin (Bennett 1975; Hamilton 1995).

2.3.2 Triglycerides and Fatty Acids

Triglycerides, by their chemical composition, represent esters of trivalent alcohol glycerol and three fatty acids. Division of triglycerides can be based on many grounds, but the most frequently used division rests on the presence of unsaturated carbon atoms in the triglyceride chain. Triglycerides are not soluble in water, but at the surface interface, a stable monolayer will form. If a certain concentration is reached, they form aggregates that are similar to micele. In principle, most of the fatty acids that are extracted from vegetable oils are considered to be GRAS substances (Baldwin et al. 1997; Hall 2012). Their physical state, chain length and degree of bond saturation determine the properties of fatty acids. With the chain length, the melting point and hydrophobicity of fatty acids increase, while the number of double bonds causes those same properties to decline.

2.3.3 Resins

Acidic substances secreted by special plant cells or insects are called resins. They can also be synthetically produced. The main representatives of resins are shellac, wood rosin, and coumarone indene. Shellac is the resin most commonly used as a coating for food products, mostly for confectionery, fruits, and vegetables. Resins are soluble in alcohol, while in alkaline solutions, they are compatible with the greatest number of waxes, producing films and coatings with improved moisture barriers and visual attributes.

2.4 Plasticizers

Plasticizers are compounds with low molecular weight combined with film-forming materials to enhance the thermoplasticity of the biopolymers (Guilbert and Gontard 1995). The main plasticizers applied in films and coatings are water and glycerol with applications of, for instance, polyethylene glycol, propylene glycol, or sorbitol.

2.5 Additives

Edible films and coatings can serve as carriers for numerous active compounds, such as antioxidants, antimicrobials, nutraceuticals, flavorings, colorants and many others, fulfilling the function of active packaging for food products. However, this is possible only up to the certain level at which they start to impede the physical and mechanical, as well as tactile and visual, properties of the films (Kester and Fennema 1986; Baldwin et al. 1995, 1997; Howard and Gonzalez 2001; Atarés and Chiralt 2016).

3 Edible Active Packaging Materials

The innovation of active packaging can be summarized and explained as a technique of packaging in which the product environment interacts with the product package and exploits it to prolong shelf-life or enhance safety or organoleptic attributes while maintaining the quality of the product (Cha and Chinnan 2004). Edible films have traditionally been selected as food packaging materials to protect food from unwanted influences of the environment. However, an increasingly new variety of packages and approaches has been utilized to influence food through edible films, providing desirable effects. This methodological approach is often called active packaging, interactive packaging, or intelligent packaging. According to Falguera et al (2011), the term active packaging refers to the application of gas scavengers and emitters or the utilization of antimicrobial and antioxidants factors in sensitive food packaging. When this methodological approach is utilized for edible films and coatings, it can be called active coating or wrapping (Gorrasi and Bugatti 2016). Various compounds can be added to edible films and coatings to serve different functions, such as, to mention just a few, antimicrobial agents, antioxidants to preserve quality, nutrients to increase nutritional value, enhancement of textural attributes, and many other product features.

Antimicrobials such as bacteriocins, antioxidants such as rosemary extract, acidifying agents and curing agents can be fused into edible films. Antifungal compounds, organic acids and bacteriocin are more effective against foodborne microorganisms when added to edible coatings than when an antimicrobial is used by itself. These edible films and coatings have shown many positive effects on food product shelf-life and, consequently, on both nutritional quality and consumer preference. Edible films and coatings as carriers of additives continue to inspire new research into the field of active packaging (Pereira et al. 2016; Ket-on et al. 2016; Espitia et al. 2016; Atarés and Chiralt 2016).

4 Application of Edible Films and Coatings

Edible films and coatings have been accepted as one of many traditional techniques in household food preservation for centuries, while the concept of edible films and coatings in the food processing industry is a new one, with the potential for development of many future applications in an environment of ever more demanding customers. Numerous applications for edible films and coatings have been researched, with reasonable success (McHugh and Avena-Bustillos 2012).

Production of edible films and coatings is accomplished through application of one of the two most dominant technological processes, namely, the "solvent process" and the "thermoplastic process." The first is the most frequently applied, since only certain edible materials, or, to be more accurate, only certain proteins can be molded into a thermoplastic process (e.g., gluten proteins, soy proteins).

It is also possible to implement a variety of techniques for application of edible films and coatings. Which of them should be selected for which particular application is defined by the desired characteristics of the film and the edible materials chosen. Only the most relevant techniques and procedures will be described herein, without going into depth.

The technique of solvent removal is carried out in the following manner: a biopolymer in a film-forming solution is dissolved in a suitable solvent that also contains other additives. The acquired solution is then cast in a thin layer and dried. Enrobing is based on dipping the product into a coating solution (e.g., a chocolate-based coating), whereupon a thick coating layer is obtained. Pan coating, drum coating, and screw coating are very similar techniques. Pan coating is done in a batch process and can apply edible coatings of different thickness through alteration of the process duration, for instance, coating confectionery products with cocoa and sugar. Drum coating is similar to pan coating. Often, it is the best technique for applying either a thin or a thick layer onto hard or solid foods in a continuous process. A screw coater allows for application of a thin layer of coating onto a solid and firm food material in a continuous process. Fluidized-bed coating is a technique based on powder fluidization in a stream of air while simultaneously spraying liquid coating. This technique is paramount because of its ability to apply an edible coating to the particles micronised in size in a thin layer (Palamanit et al. 2016). Finally, it should be noted that the spray coating technique is the one most commonly used for applying an edible coating to food products. The technique of spraying makes it possible to coat using a solution of a liquid, suspension or melted lipid layers of different thickness. Individual wrapping is the most commonly used technique for meat products. It is based on the placing of individual food products into a suitable edible film.

Today, edible films and coatings are being used for a diversity of purposes, even though consumers might not fully comprehend this fact. Consumers should ask themselves, is the shiny surface of an apple in a supermarket provided by nature or there is another explanation? As we shall see, the patent from the nineteenth century to coat meat with gelatin to prevent microbial spoilage and dehydration was merely the inception of edible film and coating usage in the era of industrial food processing (Havard 1869). The following is a short, informative summary of the application of edible films and coatings.

4.1 Meat Products

Improved appearance of a product in retail racks gives a competitive advantage to coated products. Visual changes are reduced by the coatings, while they can also simultaneously be used as carriers of antimicrobial and antioxidant agents. For this purpose, edible films and coatings based on lipids, polysaccharides and proteins, as well as composite materials based on such raw materials, have shown the best results (Khan et al. 2013).

The use of edible protein as a material for food packaging commenced with the application of collagen casing and gelatin films for the packaging of meat products. Nowadays, it can be said, with certainty, that reconstituted or regenerated collagen film sausage casings are the most widely and successfully used in the meat industry. Hams are wrapped in collagen films, and sausages are formed into their desired shape and form in sausage casings (Gennadios et al. 1997). Advancements in the technology of film production created the impetus for using casings made from extruded collagen fibers, or with the addition of, i.e., cellulose and starch derivates to improve the mechanical properties of the coatings. If antimicrobials are built into edible coatings, food safety can be even further increased (Cutter 2006). The development of new types of protein-based edible coatings serves as a continuous field of interest for the meat industry and has been fruitful for food research. These edible coatings are used, and numerous studies have provided evidence for this assertion, because their application on meat products reduces moisture loss, minimizes lipid oxidation, prevents the occurrence of discoloring and reduces water drippage (Gennadios et al. 1997; Vital et al. 2016; Behbahani et al. 2017). The formulation of edible casings influences meat products, and because of that, special attention must be paid to the development of composite casings. For illustration, while composite casing based on pectin or gelatin-sodium alginate casings, including vegetable oil, produce stable sausage products, nevertheless, if only gelatin-sodium casings are used, product shrinkage can occur. This example clearly shows that the type of biopolymer and the amount of vegetable oil have an affect on the sensory properties, water loss and lipid oxidation of the meat products (Liu et al. 2007). Today, carrageenan and alginates receive much attention for possible future use in the production of edible films and coatings for numerous meat products (fresh and frozen meat, poultry and fish) based on their ability to facilitate improvements and satisfy ever-changing consumer preferences.

4.2 *Cereal, Bakery and Confectionary Coatings*

As lifestyles changed in the twentieth century, change in diet also occurred. This change is best represented by food products, most specifically breakfast cereals. The flavor most desired by consumers of breakfast cereals is a sweet taste, and this is the reason why most breakfast cereals coatings are based on sugar. Other additives for the improvement of flavor, consistency, and coating adhesion to the surface can also be added. Edible coatings are used to prevent dehydration and preserve crunchiness (McHugh and Avena-Bustillos 2012). Important attributes of breakfast cereal quality are crunchiness or crispness; if these attributes are lost due to storage under conditions of high humidity, consumers will reject a product. The addition of colorants to make a product more appealing to consumers is also an important trend in this sector. Products with nuts are susceptible to sogginess and lipid oxidation due to moisture uptake (Trezza and Krochta 2002), while crispy cereals are commonly mixed with dried fruit such as raisins, banana, and pineapple. When a food system is made of two components that come into contact, moisture migration occurs from the component with higher water content into that with lower water activity. This water transferal affects the system as a whole, manifesting in unwanted physical and chemical changes (McHugh and Avena-Bustillos 2012). Edible emulsion coatings based on caseinates or composite chitosan coatings have been used to lower water transfer in cereal products with dried fruits. Coatings made from proteins are utilized in an attempt to prevent the passage of oxygen, and thus prevent oxidation of fats in a product with added nuts and peanuts.

Application of bakery coatings is driven mainly by two major boosts. The first is the visual attributes of a bakery product and the second is prolongation of the product's shelf-life. Bakery coatings that address the first impetus are chocolate or sugar-based, while it has been shown that different preservatives can be added to increase a product's shelf-life (e.g., sodium benzoate has been known to increase product shelf-life by at least 100%) while simultaneously increasing product safety.

Confectionary products, even more than bakery products, are coated primarily to enhance visual appearance and increase consumer appeal. Such an application is a confectionary coating of chocolate-paned products with shellac-based coatings to add a shiny coat to the product surface. Aside from these functions, there are also functional reasons for the use of edible coatings, for instance, shellac prevents an outbreak of cocoa butter to the chocolate's surface that would then stain the packaging, performing the role of oil barrier and preventing or hindering fat bloom.

4.3 *Fresh and Minimally Processed Produce*

Despite the formidable potential for the utilization of edible films on fruits and vegetables and the possibility of their extending the sustainability of products, nowadays, commercial use is not represented at a satisfactory level. This can be partially explained by the many difficulties involved in coating different surfaces of fruits and vegetables, which can be slippery, irregular or rough, and the increased complexity of ingredient formulation to ensure an even coating of the produce. Edible films and coatings reduce water vapor transmission and respiration rate by setting up a barrier on the fruit or vegetable's surface and enhancing its appearance through preservation of cell vitality.

The coating is often formed out of waxes, and more and more out of natural coatings composed of biopolymers and lipids. In the recent literature, the effects of new edible coatings have been revised with attention to storability and the postharvest quality of fresh fruits and vegetables (Bai and Plotto 2012; Valencia-Chamorro et al. 2011). Larotonda (2007) found that the water loss from cherries coated with carrageenan was lower by 30% than that from unprotected fruits. Application of the carrageenan coating also has a positive effect on the retention of firmness and glow during storage at 5 °C. Similarly, edible coatings are used on fresh cut fruits because these coatings can act as carriers of antioxidants and antimicrobials that prolong shelf-life and enhance food safety (Dea et al. 2012; Rojas-Grau et al. 2009).

4.4 Coating Application on Fried Foods

Use of an edible coating on fried foods is another novel application of coatings, developed as a response to increasingly present consumer preference for a healthier diet. The coating reduces oil uptake of a fried product during deep-fat frying through use of a protective layer formed on the product surface. The protective effect is based on a mechanism of thermal gelation of the hydrocolloid at temperatures above 60 °C. Reduced absorption of oil during frying improves the nutritional quality of the food product. Edible films and coatings, with their ability to accomplish the functional requirements mentioned, have found much application for meat products in this regard.

5 Future Trends

A stimulating route for the development of packaging materials with unique functionalities is possible through application of edible films and coatings. In regard to many functions, the abilities of edible films and coatings are comparable to those possessed by plastic packaging films. However, there is no single solution for multiple food products; each product demands that a specific edible film or coating be chosen in accordance with the specific applications and the major mechanisms of quality deterioration. More studies regarding the improvement of adhesion between product surface proliferation of films and coatings are needed, as are ones on the all-important factor of durability on the product surface. Organoleptic attributes and consumer acceptance of coated products is also being considered. Future research needs to clarify doubts. Certainly, edible films and coatings will continue to be a vibrant field for research in the future. The research will divaricate into study of new base materials and contrivance of even more innovative methods for modification of edible films and coating properties. Nevertheless, further research should always be focused on commercial applications for the purpose of providing more realistic information that can lead to the commercialization of new and innovative food products.

References

Atarés L, Chiralt A (2016) Essential oils as additives in biodegradable films and coatings for active food packaging. Trends Food Sci Technol 48:51–62

Bai J, Plotto A (2012) Coating for fruits and vegetables. In: Baldwin EA, Hagenmaier R, Bai J (eds) Edible coatings and films to improve food quality. CRC Press, Boca Raton, pp 185–242

Baldwin EA, Nispero-Carriedo MO, Baker RA (1995) Edible coatings for lightly processed fruits and vegetables. Hort Sci 30(1):35–38

Baldwin EA, Nispero-Carriedo MO, Hagenmaier RD et al (1997) Use of lipids in coatings for food products. Food Technol 51(6):56–64

Basiak E, Lenart A, Debeaufort F (2017) Effects of carbohydrate/protein ratio on the microstructure and the barrier and sorption properties of wheat starch–whey protein blend edible films. J Sci Food Agric 97(3):858–867

Behbahani BA, Shahidi F, Yazdi FT et al (2017) Use of Plantago major seed mucilage as a novel edible coating incorporated with Anethum graveolens essential oil on shelf life extension of beef in refrigerated storage. Int J of Biol Macromolecules 94:515–526

Bennett H (1975) Industrial waxes, vol 1. Chemical Publishing, New York

Blanco-Pascual N, Montero MP, Gómez-Guillén MC (2014) Antioxidant film development from unrefined extracts of brown seaweeds Laminaria digitata and Ascophyllum nodosum. Food Hydrocolloids 37:100–110

Bonilla J, Atarés L, Vargas M et al (2012) Effect of essential oils and homogenization conditions on properties of chitosan-based films. Food Hydrocolloids 26:9–16

Bourtoom T (2008) Edible films and coating: characteristics and properties. Int Food Res J 15(3): 237–248

Bourtoom T (2009) Edible protein films: properties enhancement. Int Food Res J 16(1):1–9

Brunner JR (1977) Milk Proteins. In: Witaker JR, Tannenbaum SR (eds) Food proteins. AVI Publishers, Westport, CT, pp 175–208

Cha DS, Chinnan MS (2004) Biopolymer-based antimicrobial packaging: a review. Crit Rev Food Sci 44(4):223–237

Chen H (1995) Functional properties and applications of edible films made of milk proteins. J Dairy Sci 78(11):2563–2583

Chick J, Hernandez RJ (2002) Physical, thermal, and barrier characterization of casein-wax-based edible films. J Food Sci 67:1073–1079

Cisneros-Zevallos L, Saltveit ME, Krochta JM (1997) Hygroscopic coatings control surface white discoloration of peeled (minimally processes) carrots during storage. J Food Sci 62(2):363–366

Cosenza VA, Navarro DA, Fissore EN et al (2014) Chemical and rheological characterization of the carrageenans from Hypnea musciformis (Wulfen) Lamoroux. Carbohydr Polym 102: 80–789

Cuq B (2002) Formation and properties of fish myofibrillar protein films coatings. In: Gennadios A (ed) Protein-based films and coatings. CRC Press, Boca Raton, FL, pp 213–232

Cuq B, Gontard N, Guilbert S (1995) Edible films and coatings as active layers. In: Rooney M (ed) Active food packaging. Blackie, Glasgow, U.K., pp 111–142

Cutter CN (2006) Opportunities for bio-based packaging technologies to improve the quality and safety of fresh and further processed muscle foods. Meat Sci 74:131–142

Dea S, Ghidelli C, Pérez-Gago MB et al (2012) Coatings for minimally processed fruits and vegetables. In: Baldwin EA, Hagenmaier R, Bai J (eds) Edible coatings and films to improve food quality. CRC Press, Boca Raton, FL, pp 243–289

Debeaufort F, Quezada-Gallo JA, Voilley A (1998) Edible films and coatings: tomorrow's packaging: a review. Crit Rev Food Sci Nutr 38(4):299–313

Dybing ST, Smith DE (1991) Relation of chemistry and processing procedures to whey protein functionality: a review. Cult Dairy Prod J 26:4–12

Espitia PJP, Du WX, de Jesús Avena-Bustillos R et al (2014) Edible films from pectin: physical-mechanical and antimicrobial properties—a review. Food Hydrocolloids 35:287–296

Espitia PJ, Batista RA, Azeredo HM et al (2016) Probiotics and their potential applications in active edible films and coatings. Food Res Int 90:42–52

Falguera V, Quintero JP, Jiménez A et al (2011) Edible films and coatings:structures, active functions and trends in their use. Trends Food Sci Technol 22(6):292–303

Fukushima D (2004) Soy proteins. In: Yada RY (ed) Proteins in food processing. CRC Press, Boca Raton, FL, pp 123–145

Gennadios A, Weller CL (1990) Edible films and coatings from wheat and corn proteins. Food Technol 44(10):63–69

Gennadios A, Hanna MA, Kurth LB (1997) Application of edible coatings on meats, poultry and seafoods: a review. Lebensm Wiss Technol 30(4):337–350

Gorrasi G, Bugatti V (2016) Edible bio-nano-hybrid coatings for food protection based on pectins and LDH-salicylate: preparation and analysis of physical properties. LWT-Food Sci Technol 69:139–145

Guilbert S, Gontard N (1995) Edible and biodegradable food packaging. In: Ackermann P, Jägerstad M, Ohlsson T (eds) Foods and packaging materials—chemical interactions. The Royal Society of Chemistry, Cambridge, U.K., pp 159–168

Guilbert S, Gonstard N, Morel MH et al (2002) Formation and properties of wheat gluten films and coatings. In: Gennadios A (ed) Protein-based films and coatings. CRC Press, Boca Raton, FL, pp 69–122

Gustavson KH (1956) The chemistry and reactivity of collagen. Academic Press, New York

Hall DJ (2012) Edible coatings from lipids, waxes, and resins. In: Baldwin EA, Hagenmaier R, Bai J (eds) Edible coatings and films to improve food quality. CRC Press, Boca Raton, FL, pp 79–101

Hamilton RJ (1995) Commercial waxes: their composition and applications. In: Hamilton RJ (ed) Waxes: chemistry, molecular biology and functions. The Oily Press, Dundee, U.K., pp 257–309

Han JH (2002) Protein-based edible films and coatings carrying antimicrobial agents. In: Gennadios A (ed) Protein-based films and coatings. CRC Press, Boca Raton, FL, pp 485–499

Han JH, Seo GH, Park IM et al (2006) Physical and mechanical properties of pea starch edible films containing beeswax emulsions. J Food Sci 71(6):290–296

Hardenburg RE (1967) Wax and related coatings for horticultural products. U.S. Department of Agricultural Bulletin ARS-51-15, pp 1–15

Havard C (1869) U.S. Patent No. 90,944. U.S. Patent and Trademark Office, Washington, DC

Herrero AM, Cambero M, Ordonez MI et al (2009) Plasma powder as cold-set binding agent for meat system: rheological and Raman spectroscopy study. Food Chem 113:493–499

Howard LR, Gonzalez AR (2001) Food safety and produce operations: what is the future? Hort Sci 36(1):33–39

Imeson AP (2000) Carrageenan. In: Phillips GO, Williams PA (eds) Handbook of hydrocolloids. Woodhead Publishing Limited, Cambridge, England

Kang HJ, Kim SJ, You YS, Lacroix M, Han J (2013) Inhibitory effect of soy protein coating formulations on walnut (Juglans regia L.) kernels against lipid oxidation. LWT-Food Sci Tech 51(1):393–396

Kester JJ, Fennema OR (1986) Edible films and coatings: a review. Food Technol 48(12):47–59

Ket-on A, Pongmongkol N, Somwangthanaroj A et al (2016) Properties and storage stability of whey protein edible film with spice powders. J Food Sci Technol 53(7):2933–2942

Khan MI, Adrees MN, Tariq MR et al (2013) Application of edible coating for improving meat quality: a review. Pak J Food Sci 23(2):71–79

Krochta JM (2002) Proteins as raw materials for films and coatings: definitions, current status, and opportunities. In: Gennadios A (ed) Protein-based films and coatings. CRC Press, Boca Raton, FL, pp 1–41

Krochta JM, De Mulder-Johnston C (1997) Edible and biodegradable polymer films: challenges and opportunities. Food Technol 51(2):61–74

Kurosumi A, Sasaki C, Yamashita Y et al (2009) Utilization of various fruit juices as carbon source for production of bacterial cellulose by *Acetobacter xylinum*. Carbohydr Polym 76(2): 333–335

Larotonda FDS (2007) Biodegradable films and coatings obtained from carrageenan from *Mastocarpus stellatus* and starch from *Quercus suber*. Ph.D. Dissertation, University of Porto

Liu L, Kerry JF, Kerry JP (2007) Application and assessment of extruded edible casings manufactured from pectin and gelatin/sodium alginate blends for use with breakfast pork sausage. Meat Sci 75:196–202

Marquez GR, Di Pierro P, Mariniello L et al (2017) Fresh-cut fruit and vegetable coatings by transglutaminase-crosslinked whey protein/pectin edible films. LWT-Food Sci Technol 75:124–130

McHugh TH (2000) Proteinlipid interactions in edible films and coatings. Food/Nahrung 44: 148–151

McHugh TH, Avena-Bustillos RJ (2012) Applications of edible films and coatings to processed foods. In: Baldwin EA, Hagenmaier R, Bai J (eds) Edible coatings and films to improve food quality. CRC Press, Boca Raton, FL, pp 291–318

McHugh TH, Krochta JM (1994) Water vapor permeability properties of edible whey protein-lipid emulsion films. J Am Oil Chem Soc 71:307–312

Mehyar GF, Al-Ismail K, Han JH et al (2012) Characterization of edible coatings consisting of pea starch, whey protein isolate, and carnauba wax and their effects on oil rancidity and sensory properties of walnuts and pine nuts. J Food Sci 77(2):52–59

Miller KS, Upadhyaya SK, Krochta JM (1998) Permeability of d-limonene in whey protein films. J Food Sci 63(2):244–247

Mine Y (1995) Recent advances in the understanding of egg white protein functionality. Trends Food Sci Technol 6:225–232

Morr CV, Ha EYW (1993) Whey protein concentrates and isolates: processing and functional properties. CRC Crit Rev Food Sci Nutr 33:431–476

Nussinovitch A (2003) Water-soluble polymer applications in foods. Blackwell Science, Oxford, U.K, pp 29–69

Nuthong P, Benjakul S, Prodpran T (2009) Effect of phenolic compounds on the properties of porcine plasma protein-based film. Food Hydrocolloids 23:736–741

Orban E, Quaglia GB, Casini I et al (1992) Composition and functionality of sardine native proteins. LWT-Food Sci Technol 25:371–373

Osorio FA, Molina P, Matiacevich S et al (2011) Characteristics of hydroxy propyl methyl cellulose (HPMC) based edible film developed for blueberry coatings. Proc Food Sci 1: 287–293

Palamanit A, Prachayawarakorn S, Tungtrakul P et al (2016) Performance evaluation of top-spray fluidized bed coating for healthy coated rice production. Food Bioprocess Technol 9(8): 1317–1326

Pereira JO, Soares J, Sousa S et al (2016) Edible films as carrier for lactic acid bacteria. LWT-Food Sci Technol 73:543–550

Pérez-Gago MB, Krochta JM (2002) Formation and properties of whey protein films and coatings. In: Gennadios A (ed) Protein-based films and coatings. CRC Press, Boca Raton, FL, pp 159–180

Petersen K, Nielsen PV, Bertelsen G et al (1999) Potential of biobased materials for food packaging. Trends Food Sci Technol 10:52–68

Peyron A (1991) L'enrobage et les produits filmogenes: un nouveau mode de´mballage. Viandes Prod Cares 12(2):41–46

Piez KA (1968) Cross-linking of collagen and elastin. Annu Rev Biochem 37(1):547–570

Rhim JW, Shellhammer TH (2005) Lipid-based edible films and coatings. In: Han JH (ed) Innovations in food packaging. Academic Press, London, U.K., pp 362–383

Rojas-Graü MA, Soliva-Fortuny R, Martin-Belloso O (2009) Edible coatings to incorporate active ingredients to fresh-cut fruits: a review. Trends Food Sci Technol 20:438–447

Shewry PR, Halford NG, Belton PS et al (2002) The structure and properties of gluten: an elastic protein from wheat grain. Philos Trans R Soc London B: Biol Sci 357(1418):133–142

Sothornvit R, Krochta JM (2000) Plasticizer effect on oxygen permeability of β-lactoglobulin films. J Agric Food Chem 48:6298–6302

Sousa SA, Sobral PJA, Menegalli FCM (1997) Desenvolvimento de filmes comestiveis a base de proteinas miofibrilares extraidas de carne bovina. In: Sobral PJA, Chuzel G (eds) Proceedings of workshop sobre biopolimeros. FZEA, Pirrassununga, Brazil, pp 102–106

Stanley DW, Stone AP, Hultin HO (1994) Solubility of beef and chicken myofibrillar proteins in low ionic strength media. J Agric Food Chem 42:863–867

Trezza TA, Krochta JM (2002) Application of edible protein coatings to nuts and nut-containing food products. In: Gennadios A (ed) Protein-based films and coatings. CRC Press, Boca Raton, FL, pp 527–549

Trotter JA, Kadler KE, Holmes DF (2000) Echinoderm collagen fibrils grow by surface-nucleation and propagation from both centers and ends. J Mol Biol 300:531–540

Vachon C, Yu HL, Yefsah R et al (2000) Mechanical and structural properties of milk protein edible films cross-linked by heating and gamma irradiation. J Agric Food Chem 48:3202–3209

Valencia-Chamorro SA, Perez-Gago MB, Del Rio MA et al (2011) Antimicrobial edible films and coatings for fresh and minimally processed fruits and vegetables: a review. Crit Rev Food Sci Nutr 51:872–900

Vital ACP, Guerrero A, de Oliveira Monteschio J et al (2016) Effect of edible and active coating (with rosemary and oregano essential oils) on beef characteristics and consumer acceptability. PLoS ONE 11(8):e0160535

Were L, Hettiarachcky NS, Coleman M (1999) Properties of cysteine-added soy protein wheat gluten films. J Food Sci 64(3):514–518

Wieser H (2007) Chemistry of gluten proteins. Food Microbiol 24:115–119

Yildirim M, Hettiarachchy NS (1997) Biopolymers produced by cross-linking soybean 11S globulin with whey proteins using transglutaminase. J Food Sci 62(2):270–275

Young HH (1967) Gelatin. In: Mark HF, Gaylord NG, Bikales NM (eds) Encyclopedia of polymer science and technology: plastics, resins, rubbers, fibers, vol 7. Interscience, New York, pp 446–460

Biopolymers as Food Packaging Materials

Radoslav Grujić, Dragan Vujadinović and Danica Savanović

Abstract This review examines the recent trends, current technology and future challenges in applications of biopolymers as food packaging materials, together with potential solutions, as well as discussing the major safety concerns regarding food packaging materials produced from sustainable and renewable resources. As food contact materials, biopolymers are increasingly being utilized as alternatives to conventional plastics obtained from oil derivatives. This review covers most of the available polymers, focusing on the general principles of their production, properties, and analysis of the possibilities for potential use in food packaging. The use of biopolymers brings new opportunities, not only from the point of replacing conventional polymers and other materials that are widely used in food packaging (glass, paper, metals, etc.), but also in the way it opens up a whole new level of properties and characteristics. Bio-based resources are the base source for production of biopolymers in food application, while in practice, bioresource content may be different. Biopolymers can be produced by microorganisms through fermentative processes of different bioresources [e.g., polyhydroxyalkanoates (PHAs)] and biomass may be produced directly from different kind of plant (starch, cellulose, etc.). In the context of growing environmental and safety concerns, biopolymers have gained increased attention, related to concerns about conventional plastics traditionally produced from fossil fuel.

Keywords Biopolymers · Biomaterials · Food packaging · Sustainable resources

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1 Introduction

Biopolymers are not new. In the 1850s, a British chemist created plastics from bio-cellulose. Henry Ford, in the early 20th century, experimented with the use of different polymers derived from soy proteins in his automobiles. After that, in the ’70s, biodegradable polymers gained wider interest in the USA during the great oil crisis. The 1980s brought items such as biodegradable films, sheets and mold-forming materials (Tim and Sylvana 2011). Nowadays, a different type of biomaterial is usually combined with glass, metals, board and an assortment of fuel-based plastic polymers, or used for food packaging as a pure biomaterial. These materials are applied in various combinations to provide unique properties that ensure the safety and quality of packed food products, from processing, handling, and storage to final use by consumers. Notably, these materials have to fulfill a significant task in the sense of preventing the quick deterioration of quality and safety, which provides long-term use of food products during their shelf-life and ultimately prevents massive commercial losses of valuable food products (Babu et al. 2013). When contemplating the principle of food packaging, the entire dynamic interaction between food, packaging material and the ambient condition has to be considered. Materials used for food packaging must be capable of providing specific optimal requirements during storage of different types of food product. The engineering and development of new biomaterials suitable for food packaging is a great challenge both in science and industry (Claus 2000).

On account of environmental change, biopolymers have been elevated to important roles by customers, financial specialists and worldwide producers in recent years. A few plastic materials with properties similar to those of petroleum-based polymers (frequently called biopolymers) are now available. Some of these materials are widely available on the market, such as bio-based polyethylene (PE), poly trimethylene terephthalate (PTT), polylactic acid (PLA), starch, thermo-plasticized starch, cellulose, chitosan, pectin, collagen, gelatin, caseins, zein, natural waxes, polybutylenes succinate (PBS), polyp-phenylene (PPP) and microbiological synthesized polyhydroxyalkanoates (PHAs). The afore-mentioned biomaterials and many others have already been successfully used for a long time as materials for packaging various food products (Chen 2010). Each of these biopolymers shows certain mechanical and synthetic properties that permit them to be utilized as a part of the food packaging industry. PHAs can be qualified by their manifold structural variations, resulting in numerous different properties and, subsequently, different spheres of application (Koller et al. 2013; Koller 2014).

According to their origin and production method, biopolymers may be roughly divided into four fundamental classes:

Class 1 Biopolymers obtained by concentrate from biomass (polysaccharides, for instance, starch, pectin, Chitosan, cellulose, etc., proteins like collagen, casein and gluten, etc.);

Class 2 Biopolymers obtained through the usual chemical synthesis from biobased monomers (polylactic acid, a bio-polyester). The fermentation of carbohydrates is the most common way of obtaining such a monomer;
Class 3 Biopolymers produced by microorganism activity. The main representative of this group of biobased polymers mostly consists of polyhydroxyalkanoates (PHAs), however, materials based on bacterial cellulose are currently being advanced;
Class 4 Biopolymers produced through chemical synthesis from both bio-derived monomers and petroleum-based monomers, polybutylene succinate (PBS), bio-based terephthalic acid (TPA) poly trimethylene terephthalate (PTT), biobased PP and PE, etc. (Claus 2000; Robertson 2008; Mittal 2012; Babu et al. 2013).

In this big family, the most common biopolymers used for food packaging applications are: polymer based on starch or cellulose, polylactic acid (PLA), especially, more recently, multilayer (ML) PLA films, polyvinyl alcohol (PVOH), polyhydroxyalkanoates (PHAs) biopolymers, aliphatic-aromatic copolyesters and polyethylene (PE), and polyethylene terephthalate (PET) partially or completely obtained from renewable sources (Bio-PE and/or Bio-PET, Bio PP and Bio PTT) (Timothy 2010; Tim and Sylvana 2011; Babu et al. 2013; Youngjae and Young 2014a, b; Benetto et al. 2015).

2 Biopolymers Based on Starch

Starch is the most plenteous and ordinarily utilized of the renewable crude materials. Starch is comprised of rehashed units of glucose and involved amylose and amylopectin (Gallant et al. 1997). Its unique chemical and physical characteristics and qualities can be recognized apart from all different carbohydrates. Starch is acquired from seeds, legumes, cereals, potatoes and fruits (acorns and chestnuts), among other items (Whistler and BeMiller 2007). Starch polymers are highly sensitive to moisture, with high water vapor permeability and poor mechanical properties that limit their packaging application. Different vegetal source provide the starch used in the form of biodegradable polymers in food application. The characteristic form of natural starch is a crystalline molecular structure, which is not a plastic material. It is necessary that this crystalline form be changed throughout the process of plasticization. During this process, the molecular structure loses its crystalline form and an amorphous material is obtained. The most interesting starch derivative for the food industry is thermoplastic starch (TPS), as it is the most convenient for obtaining various materials. The type and quantity of plasticizer used during production of thermoplastic starch (TPS) strongly determine the physical, chemical and thermal properties of the final products. Its primary application in the food industry is in the sector of production of flexible and solid packaging (bio-films, bags, laminates, etc.). Polymer films produced from starch are biodegradable and possess good properties as an oxygen barrier. The plasticizer, moisture, and amylose content are strongly limiting factors, related to the mechanical properties of TPS (de Vileger 2000; Youngjae and Young 2014a, b). In many cases, in order to modify the properties of TPS, other ingredients or different structural enhancers have been added to the starch-polymer matrix, such as microcrystalline cellulose (MC), fibers, nano-clays, carboxymethylcellulose (CMC), carbon nanotubes, etc., (Ma et al. 2008; Muller et al. 2011; Girones et al. 2012). Sisal and hemp fiber reinforced with TPS through melt processing have been produced very successfully. In this way, TPS enhances their mechanical properties. Beside this combination, starch mixed with PE and PP in the amount of 5% significantly improves their properties. If used in parallel with applied and advanced shaping techniques such as extrusion with supercritical gases, the obtained biopolymer exceeds the conventional polymer properties. Different kinds of this reinforced starch are already being evaluated in the packaging of bread, vegetables and meat products stored under standard conditions (Girones et al. 2012; Chauvet et al. 2017).

Figure 1 depicts the different commercial starch products used for the packaging of processed and fresh food products, as well as dishes. The following table shows the commercial products, the world's largest producers of said products, and examples of products based on starch biopolymers (Table 1).

Fig. 1 Biodegradable starch cups, plates, and cutlery

Table 1 The world's largest manufacturer of commercial starch products for food packaging (Biomass Packaging 2011; Glenn 2014)

Product	Brand Name	Sample products
PSM (Plastarch material), a highly heat resistant biopolymer made from plant starch and polypropylene, with natural modifying agents for a range of applications	PSM is a biobased thermoplastic resin, highly water and oil proof, similar to conventional plastic. It has a high resistance to low and high temperatures	SpudWare cutlery resistant to high heat
Mater-Bi, obtained mainly from starch	Italian-based Novamont is a manufacturer of a Genetically Modified Organism (GMO)-free, starch-based plastic called Mater-Bi used to make BioBag branded certified compostable bags BioBag® is the world's largest brand of certified compostable bags and films made from Mater-Bi	The main products are shopping and waste bags, food service items (plates and cutlery)
TPS (Thermoplastic starch) Made of the cornstarch-derived amylose molecule, whose special chemical properties allow for a wide range of applications in product manufacture	Australian-based Plantic Technologies uses non-GMO corn starch to produce their biopolymer resin. The main area of application is food, cosmetic and pharmaceutical packaging	BioMass Packaging® uses TPS to manufacture water-soluble packing

During 2008, in the UK, the first biodegradable cereal bag was produced by Jordans Organic Cereals and Alcan. The packaging uses two dissimilar types of biopolymer film. The outer layer is made from Innovia Film's clear NatureFlex film. The inside layer is made from Novamont's Mater-Bi film (Hill 2010). In 2009, Novamont launched an improved version of Mater-Bi. This new Mater-Bi integrates Novamont's starch-based technology with the technology of bio-polyesters from vegetable oil. In 2014, Novamont increased their production capacity of their fourth generation of Mater-Bi by more than 120,000 tons per year. This is a good model for the current movement in the food packaging industry towards transitioning from starch to bio-polyester or starch-polyester composites as acceptable food packaging materials (Biomass Packaging 2011; Tim and Sylvana 2011; Youngjae and Young 2014a, b). Figure 2 shows an example of BioBag® commercial product.

Fig. 2 Biodegradable thermoplastic starch food pack bags

3 Biopolymers Based on Cellulose

A number of cellulose derivatives are produced commercially, most commonly methylcellulose (MC), carboxymethyl cellulose (CMC), ethyl cellulose (EC), hydroxyl propyl cellulose (HPC), hydroxyethyl cellulose (HEC) (Sanchez et al. 2011) and cellulose acetate (CA). In relation to the derivatives mentioned, only CA is widely used for food packaging (baked goods and fresh produce). CA is characterized by low resistance to gasses and moisture and must be conducted through a plastification process if used for the development of film. This is a direct consequence of the crystalline structure of cellulose, which makes the initial steps of derivatization difficult and costly (Claus 2000; Jafarizadeh et al. 2011). Emulsified cellulose-based biofilm composed of corn starch, microcrystalline cellulose (MCC), and soybean oil extended the shelf-life of wrapped crackers stored in different RH values, compared to unwrapped ones, by reducing moisture loss. The excellent film-forming properties possess many cellulose derivatives, but they are just too expensive for wider industrial usage. To change this situation and produce lower-cost cellulose packaging materials, we will be obliged to create effective processing technologies for the production of cellulose derivatives (Bravin et al. 2006; Sauperl et al. 2009). Table 2 shows the largest commercial producers of cellulose products around the world.

Figure 3 shows the oxygen permeable cellulose commercial films for packaging various kinds of food.

Table 2 The world's largest manufacturers of commercial cellulose products for food packaging (Biomass Packaging 2011)

Product	Brand Name	Sample Products
Cellophane: natural biopolymer obtained from wood	BioMass Packaging® carries cellophane products made with Nature Works LLC, a 100% cellulose biopolymer with excellent oxygen, grease, oil, and moisture barrier characteristics	Used as a packaging film for bakery product wraps, confectionery product wraps, other food wraps, and food-grade transparent bags
Cellophane is one of the first ever biopolymers made from cellulose, the main component of trees and plants	Nature Flex bags generally compost in several weeks in a home compost pile or a commercial compost facility	
It is produced from renewable resources	Nature Flex™, Innovia Films (U.K.)	

Fig. 3 Cellulose films for packaging of different kinds of food

4 Biopolymers Based on Chitosan

Chitosan biopolymer films are strong and difficult to break. They are also flexible, with mechanical properties similar to those of commercial polymers traditionally produced from petroleum-based derivatives. They are sensitive to humidity and have a low moisture barrier, which has limited their wider use in food applications. Because of that, as with other biopolymers based on polysaccharides, special attention must be paid to a moist environment. In order to reduce the water vapor permeability (WVP) of the chitosan coatings and polymer films, various other biopolymers may be incorporated into chitosan to form stable and mechanically compact films such as, e.g., lipids and other polysaccharides (Bonilla et al. 2012). Emulsion films based on caseinates or chitosan have been successfully applied to dried fruit products (partially-dehydrated pineapple) and different types of cereal products. Chitosan films are poorly resistant to moisture and water vapor. During the storage of cereals treated with chitosan-based films, the critical moisture content for cereal products was reached (Talens et al. 2012). New techniques of chitosan synthesis in many ways solved these problems. Advanced catalytic systems, such as pincer-type PdII, produce chitosan-based polymers with significantly improved properties and durability (Baran and Menteş 2017).

At Harvard, Wyss Institute researchers have developed fully degradable biopolymers isolated from shrimp shells. This new material can be very well molded into different shapes, as much as conventional plastics, but without any environmental hazards. As a cheap and environmentally friendly alternative to conventionally produced plastic based on petroleum derivatives, the chitosan biopolymers could be used as a base for production of different kind of bags, food packaging in different shapes, and diapers that decompose in just a few weeks while releasing rich nutrients that are suitable for cultivation and growth of plants.

5 Polylactic (PLA)-Based Biopolymers

Polylactic acid (PLA) is a biodegradable, thermoplastic, renewable biopolymer obtained through the polymerization of the lactic acid monomer. Lactic acid (LA), as a basic monomer, is obtained from the bacterial fermentation of polysaccharides or through chemical synthesis. The biopolymer's production can be roughly divided and considered through the production of lactic acid (LA) as a basic monomer in the first stage and polymerization of the lactic acid in the second final stage. PLA has a high potential for application as a hygiene and packaging material in the food industry. The most commonly used polymer for food packaging applications may be 90% L-lactide and 10% racemic D, L-lactide. This material is reported to be readily polymerized, easily melt processable and easily oriented (Linnemann et al. 2003; Wang et al. 2005; Rasal et al. 2010).

The PLA composite obtained through polymer modification with 2-methacryloyloxyethyl isocyanate (MOI) significantly improved the physicomechanical and thermal properties of the final biopolymer (Chen et al. 2012). The MOI-PLA composite had a 20 times higher percentage of stretching than the pure PLA. Copolymerized PLA with other bio-polyesters significantly improved its physical properties (Sodergard and Stolt 2002). There are also synthesized polylactide-polyisoprene-polylactide thermoplastic elastomers with various compositions, and the excellent stretching and elastomeric copolymers (Frick et al. 2003; Youngjae and Young 2014a, b).

PLA polymers are GRAS (Generally Recognised As Safe), permitting their use in direct food contact with aqueous, acidic and fatty foods under 60 °C and aqueous and acidic drinks served under 90 °C. Therefore, PLA polymers are designed for direct food contact (Yokesahachart and Yoksan 2011). In Europe, lactic acid is listed as an approved monomer for food contact applications in Amendment 4 of the Monomers Directive, 96/11/EC (1996). The high elastic modulus and low hardness are characteristic physical features of PLA that are similar to polystyrene (PS). PLA in its amorphous form is clearly transparent, with excellent thermal and physical properties. It is a very versatile polymer, suitable for a large number of applications, flexible (for labels, composites, etc.), or rigid and foaming (for food use) packaging (Chen 2010; Chen et al. 2012).

For example, from NatureWorks PLA, Wilkinson Industries produces various thermoformed dishes and biofilms. This kind of PLA material provides an optimal aroma barrier and high strength. Mighty Leaf Tea launched 100% bio-pouches, while Revolution T Organics presented PLA tea bags. College Farm Organic Candy uses individual packages made from PLA for organic candy products. Similarly, Noble launched a line of PLA bottles and labels in 2008. It was one of the first “all renewable” bottles to be used for juice packaging (Raithatha 2009).

In 2010, Walmart began utilizing Nature Works Ingeo as packaging materials for organic salad, salsa, spinach, fresh-cut fruit, vegetables, and tomatoes, while in 2011, Danone introduced the Ingeo cup for yogurt on the EU market. Compared to previous packaging, by introducing the Ingeo PLA packaging, the company’s carbon footprint was reduced by around 25%, which resulted in a decrease in the use of fossil raw materials of more than 40% (Sanjay and Ackmez 2011; Youngjae and Young 2014a, b). Figures 4 and 5 show a common example of commercial PLA products.

Although PLA is not a commonly used material, some companies have found specific uses for it, such as:

- **Bags for salads**. Salad bags and similar promotional materials for new food applications accounted for more than 40% of PLA use in 2006. It is reckoned that the food service industry is the most probable source of growth for this material, and it is proposed that the use of PLA could have a 24% annual increase rate. The use of PLA in the packaging of processed and fresh food is generally preferred by companies promoting a sustainable and organic life culture (Casey 2010).

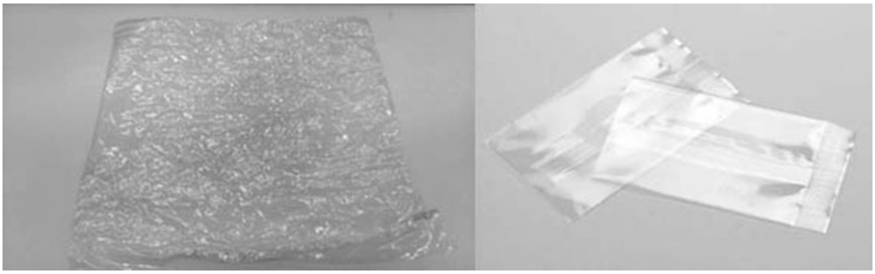

Fig. 4 Polylactic Acid (PLA) bags from corn

Fig. 5 PLA cup and bowl

- **Coca-Cola** is another company that is looking to implement PLA into its operation. They are currently developing a PET "Plant Bottle" that will contain 25% PLA. This, however, could make an existing recyclable PET bottle no longer recyclable, as well as non-bio-degradable (Youngjae and Young 2014a, b). Combining the two ingredients in concert would make separation at a recycling level impossible, which could push the bottles into the landfill. This is the type of critical thinking that is necessary when assessing a new idea (Sanjay and Ackmez 2011).

Some of the problems with PLA are in its production. A vast amount of corn is needed to produce commercially-used PLA. According to projections, calculated by the 116,000 metric tons of PLA in use by 2011, the demand for corn can be estimated using the conversion of 2.5 kg of corn needed to get 1 kg of PLA. Separating the portion of the grain used for PLA production from that utilized for human and animal food could affect the marketplace by increasing the cost of corn, which would mostly impact the poorest countries already suffering due to a lack of basic foodstuffs. Additionally, taking into account the fact that only two countries produce the majority of the world's corn could create inflated prices as well (Casey 2010). Table 3 shows the largest commercial PLA products producer around the world.

Table 3 The world's largest manufacturers of commercial PLA (Polylactic Acid) products for food packaging (Biomass Packaging 2011)

Product	Brand Name	Sample Products
PLA (Polylactic Acid) is plastic made from vegetable starch A clear alternative to petrochemical-based plastic, such as PET (polyethylene terephthalate) and PS (polystyrene)	Most PLA is marketed as Ingeo™ by the U.S. company Nature Works, LLC Nature Works, LLC ferments animal-feed corn dextrose into lactic acid	Takeout containers, coated paper and cold drink cups, various other cups, and fresh produce packaging

6 Polyhydroxyalkanoate (PHA) Biopolymers

PHAs are very suitable for food packaging applications because their moisture barrier is comparable to conventional packaging materials. Generally, PHAs are bio-polyesters of alkanoic acids, containing a hydroxyl group and at least one functional group attached to the carboxyl group. PHAs polymers could be different in their properties according to their chemical composition (homo or co-polyester, contained hydroxyl fatty acids, etc.) (Lee 1996). They are water-insoluble, being based on a thermoplastic biopolymer with high surface energy. Because of that, PHAs are very suitable for printing and dye. PHAs possess oxygen UV resistance in their level of commercial ethyl vinyl alcohol (EVOH). Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is suitable for heat-shaping and producing a flexible plastic used in the food packaging sector, where biodegradable materials are desirable. PHAs are currently mostly used as flexible food packaging with high oil content (marinated olives, cheese, nuts and others), and for frozen foods and food that is declared as organic (Innocentini et al. 2003; Shen et al. 2009).

PHAs can be embedded in a matrix of biomaterials, such as bio-coatings, laminates, and biodegradable dye printing. Additionally, PHA structures can include different kinds of thermoplastic elastomer, waxes, adhesives, different binders and others. Depending on the type and relationship of different inclusions, mechanical properties vary from elastomeric to resins as stiff as nylon or polycarbonate. PHAs are most commonly shaped via film extrusion, injection, hollow bodies, etc. The first two commercial PHA products launched on the market were extrusion coating and cast films. Other current potential applications are as mulch films, stretch films, different kinds of bag, and surfactant soluble packagings. An injection molding procedure is also under continuing development by academia and industry, with new methods and techniques for obtaining cheaper and more suitable packaging materials being studied. Currently, Metabolix alone is developing and commercializing PHAs for film and bag applications, such as PHA Latex Barrier Coating for Paper and Cardboard. Other major worldwide PHA-based product producers with main world market shares are the Kaneka Corporation (Japan), GreenBio (China), Tianan Biologic Material Co. (China), and Meridian

Fig. 6 Different kinds of PHA bags used in food packaging

Fig. 7 PHA thermoformed cups

(Bainbridge, GA). GreenBio built a PHA production plant in Tianjin, China, that began operation in 2009 and has the capacity to produce 10,000 tons of PHA per year (Modi et al. 2011). The basic requirement which is imposed if PHAs are used for food packaging is that they should not be in direct contact with the food. PHAs are a natural material whose life cycle is completely renewable, produced by microorganisms and completely decomposed by microorganisms (Doi et al. 1994; Bugnicourt et al. 2014) (Fig. 6).

Mirel's thermoformed cups. Mainly produced from PHA resins. These resins are known as aliphatic polyesters, made biologically by converting products of photosynthesis using microbial or plant biofactories. The main raw materials for the microbial production of PHA are corn and various sugars (different carbohydrates). The resins obtained in this way have mainly been used for the production of thermoformed cups. The properties of the PHA cups are noted as being comparable to polypropylenes, offering good stiffness and tensile strength (Casey 2010; Koller et al. 2013; Koller 2014). Figure 7 illustrates an example of a PHA thermoformed cups commercially used in food packaging.

7 Other Biopolymers Used in Food Packaging

Biopolymers, for example, poly trimethylene terephthalate (PTT), are a kind of bio-polyester which have extraordinary mechanical properties, processability, and thermal steadiness. The 1,3-propanediol (PDO) and pure terephthalic acid (PTA) or dimethyl terephthalate (DMT) are the main compounds for PTT production. Succinic acid can be synthesized through bacterial fermentation from either a bioresource or oil-based resources (Shen et al. 2009). Monomers produced in this way can be used for the synthesis of polybutylenes succinate (PBS). The mechanical properties of PBS are similar to those of PP and PE. That kind of bio-polyester has a relatively high melting temperature (T_m), around 113 °C (Kabasci and Bretz 2012). The main chemical composition of polyethylene terephthalate (PET) includes around 30% ethylene glycol (EG) and 70% terephthalic acid (TPA) (Shen et al. 2009). Biobased TPA can additionally be produced by the bio-route from isobutanol, n-butanol, isobutylene, muconic acid, limonene, terpenes, and carbohydrates, while commercial TPA is still being produced from oil resources (Berti et al. 2010). In polyethylene (PE) production, ethylene represents a basic monomer. It can be produced from ethanol obtained via fermentation of a different kind of sugar, sugarcane or corn. PE and PP obtained in this way are mechanically and physically identical to the traditionally produced plastic packaging materials. PE and PP produced from bioresources are not biodegradable; in any case, they can be recycled like conventional PE and PP (Timothy 2010).

Basically, fully biodegradable polymers are not recyclable from the aspect of currently applied technologies used in the recycling of conventional petroleum-based polymers. In 2009, Coca-Cola launched "PlantBottle," bottles made out of up to 30% of plant-based monomers with the same mechanical, chemical physical, and functional properties as conventional PET plastics. One of the most important advantages of this new bottle is a recyclability performance as full as a conventional one. In the conventional PET, ethylene glycol (EG) and terephthalic acid (TPA) are irreplaceable base components. To produce a PlantBottle, a monomer of EG is bio-produced from sugarcane through the fermentation process. Coca-Cola is currently trying to produce fully bio-based terephthalic acid (TPA) from natural resources such as stems, fruit peels, and bark. In this way, they will achieve their goal of fully bio-based bottles (Hill 2010; Ying 2014).

In 2011, Heinz introduced the PlantBottle for their ketchup sold in the retail markets of U.S. and Canada. In 2012, Heinz, Nike, Coca-Cola, Ford Motor, and Proctor & Gamble founded the Plant PET Technology Collaborative (PTC), a strategic working group with the mission of accelerating and promoting research of bio-PET. In 2011, PepsiCo produced the world's first 100% bio-based PET made from pine bark, switchgrass, and corn husks, with the same structure and physical and mechanical properties as conventional PET. They are also researching and developing technology for the production of bio-based PET from other natural resources, such as oat hulls, orange peels, and potato scraps (Youngjae and Young 2014a, b; Ying 2014).

Changes in retail patterns, such as the globalization of markets resulting in longer distribution distances, present major challenges for the food-packaging industry, which ultimately act as driving forces for the growth of novel and improved packaging concepts that extend shelf-life while sustaining the safety and defined quality of the packed food. Novel active and bioactive packaging technologies, combined with bio-packaging and nanotechnology, can best help in achieving the goals of both the food industry and consumers. Therefore, the proper combination of these three technological concepts will provide the driving force towards innovation in the food sector over the next few years (Biopolymers Market Forecast 2014).

The use of polymeric packages for food applications has increased considerably over recent decades. Apart from the intrinsic benefits associated with polymers, significant improvements in their physicochemical characteristics,specifically regarding barrier, mechanical, and thermal properties, have been attained as a consequence of extensive research work. Furthermore, due to the deficit of petroleum resources and waste management issues, the focus of the research is switching from synthetic oil-based plastics to biomass-derived biodegradable and non-environmentally harmful polymers. The main drawbacks of biopolymers in regard to wide industrial and commercial application stem from their poor barrier properties and high instability. The progress of research is in novel applications, making polymers an ideal partner for active and bioactive packaging,in which the package is no longer a passive barrier,but actively contributes to the preservation of food. Biopolymers have an ideal structural matrix for the incorporation and controlled release of a number of substances to be added to foods (Sanjay and Ackmez 2011; Ying 2014).

8 Biopolymers Used in Paper Packaging

Paper biopolymers, besides making for rigid packaging, could be used for wrapping food products (e.g., flexible paper). In this way, non-biodegradable plastic materials would no longer be required. According to Khwaldia et al. (2010), the association of biopolymers to paper provides an interesting functionality while maintaining the environmentally-friendly characteristic of the material. Caseinates (Khwaldia 2010; Khwaldia et al. 2010), whey protein isolate (Lin and Krochta 2003), isolated soy protein (Rhim et al. 2006), wheat gluten (Gallstedt et al. 2005), corn zein (Trezza et al. 1998), chitosan (Despond et al. 2005; Ham-Pichavant et al. 2005), carrageenan (Rhim et al. 1998), starch (Matsui et al. 2004), and alginate (Rhim et al. 2006) have been the usual substances researched and applied as biomaterials for the coating of various kind of papers. Han and Krochta (2001) have found that use of paper for food packaging shows significant performance improvement (reducing moisture permeability and resisting oil oxidation) when the paper biopolymer film is made based on whey protein. Despond et al. (2005) write about packaging products in paper covered with a film of chitin/carnauba wax that gets great results, owing to the paper having improved barrier properties in regard to water and gasses.

In addition, it is necessary that any given biopolymer packaging material fulfill all requirements pertaining to conventional packaging materials. This refers to the properties of permeability (permeability to water vapor and gases, aroma substances, and light) and mechanical and optical properties (e.g., transparency) (Debeaufort et al. 1998; Chan and Krochta 2001; Weber et al. 2002; Hong et al. 2004; Gallstedt et al. 2005; Kjellgren et al. 2006; Bordenave et al. 2007; Khwaldia 2010). Figure 8 shows examples of lined paper bags and cups commercially used products.

Fig. 8 PLA, PHAs, Cellulose, Chitosan-Lined Paper Bags and cups

Tetra Pak has launched the industry’s first entirely plant-based, renewable packaging materials. This was the first packaging to have 100% bio-low-density polyethylene (LDPE) films and caps made from 100% bio-high-density polyethylene (HDPE). All of these products were obtained from sugar and laminated on paperboard certified by the Forest Stewardship Council (FSC™). This kind of package has been commercially available starting in 2015.

The Table 4 presents an overview of the use of biopolymers for the production of packaging materials.

Table 4 Properties of biopolymers used in paper coating (Khaoula et al. 2010)

Type of commercial biopolymers	Main functions/properties	Reference
WPI	Suitable for printing with water-based ink	Han and Krochta (1999)
	Fat and oil barrier/resistant	Han and Krochta (2001)
		Chan and Krochta (2001)
NaCAS	Oxygen barrier	Khwaldia (2004)
NaCAS/paraffin wax bilayer	Water vapor barrier	Khwaldia (2010)
Corn zein	Grease barrier	Trezza and Vergano (1994)
	Prevention of drying/brittleness	
Corn zein/paraffin wax bilayer	Water vapor barrier	Parris et al. (1998)
	Grease barrier	
SPI	Gas and lipid barrier	Park et al. (2000)
SPI with $CaCl_2$ posttreatment	Water vapor barrier	Rhim et al. (2006)
WG	Oxygen barrier	Gällstedt et al. (2005)
Carrageenan	Grease barrier	Rhim et al. (1998)
HPMC/beeswax	Water vapor barrier	Sothornvit (2009)
Chitosan	Fat barrier	Ham-Pichavant et al. (2005)
	Gas barrier	Kjellgren et al. (2006)
Chitosan/sodium alginate bilayer	Fat barrier	Ham-Pichavant et al. (2005)
Chitosan/carnauba wax bilayer	Gas barrier	Despond et al. (2005)
Chitosan/sodium alginate bilayer	Fat barrier	Ham-Pichavant et al. (2005)
Paraffin wax	Water vapor barrier	Parris et al. (1998)

9 Advantages of Biopolymers

Packaging is a system of preparing goods for transport, distribution, storage, retailing and end use. It means that a product must be safely shipped to the final retail market in a defined condition at reasonable cost. All conventional polymers used for the production of different kinds of food package could be roughly categorized according to their application, functional properties in packaging, and contents of containment in the package. The presence of various contaminants in conventional plastics, as well as their possible migration into the food, is one of the main reasons they need to be replaced with biopolymers. Another key reason is the environmental issue and lack of biodegradability, a byproduct of the use of plastic produced from petroleum derivatives. Production of 1 kg of conventional plastics requires 65% more energy than does the same amount of biopolymers. Conventional plastic has an unreasonably long degradation period, resulting in huge environmental impact and contamination. In spite of all this, for a long period of time, using conventional plastic was considered as viable concept, regardless of all the benefits of use sustainable materials such as biopolymers. More or less all conventional plastics are toxic due to the need to use different ingredients and, as such, limited in terms of their safe use in the food packaging industry. Biopolymers save 30–80% in greenhouse gas emissions and provide longer shelf-life than normal plastic (Chen 2010; Raiand and Roy 2011; Sanjay and Ackmez 2011; Babu et al. 2013).

Most of the materials obtained on the basis of biopolymers are biodegradable and suitable for the production of compost, which carries nutrients and organic material to the soil. The result of this is an increase in water and nutrient retention, reduction in chemical input and prevention of plant diseases. Starch-based biopolymers have been shown to degrade 10–20 times quicker than conventional plastics (Liu et al. 2009). Incineration of conventional plastics generates smoke and fumes that are toxic to humans, wildlife, and the environment. It was not necessary to investigate the Incineration of biopolymers in regard to their biodegradability over a short period of time, but were such incineration to happen, the fumes released would not be hazardous to the environment. Biopolymers have a more diversified structure, chemical composition and architecture, which permits researchers a vast number of opportunities to customize the properties of the final packaging material (Tokiwa et al. 2009; Wei et al. 2011; Mittal 2012). The great advantage of the use of biopolymers is the possibility of incorporating nanoparticles that carry a number of positive characteristics, such as heat and cold stability, impermeability to gasses, strength, firmness, antimicrobial properties, impermeability to oxygen, etc. (Huang et al. 2015; Cazóna et al. 2016; Van Long 2016).

10 Toxicity Concerns Related to Biopolymers in Food Applications

The monomers of cellulose and starch-based biopolymers, as well as those of poly3-hydroxybutyrate (PHB) and PLA, have been estimated not to cause health problems. The main concerns associated with the use of PHAs as materials for food packaging refer to microorganisms, considering that some strains used in their production could be potentially hazardous (Conn et al. 1995; Zhu et al. 2014). Different kinds of additive are usually used in biopolymer material production than those used in conventional plastics. The physicochemical properties of biopolymers and their environmental condition determine the potential migration rate of their ingredients. The pure biopolymers (additive-free) usually have fewer properties than conventional ones. The additive migration rate from PLA and starch-based biopolymers was reported to be very low (Avella et al. 2005; Clarke et al. 2012). The most common source of chemical migrants is oxo-biodegradable plastics. Ammala (2011) and colleagues gave a detailed overview of potential additives for commercial use, including dithiocarbamates and benzophenones. Related to bio-nano-composites, the studies viewed demonstrated the cytotoxic effects of nano-clays consolidated into nano-bio-composite polymers. Nonetheless, these studies did not take into consideration a conclusion reached on the poisonous capability of bio-nano-composites, because of the incredible variety of nanomaterials, even those obtained from the same batch, and an absence of accepted standardized testing conditions (Maisanaba et al. 2013; Houtman et al. 2014).

11 Conclusion

Biopolymer materials are already widely used in developed countries, having practically replaced conventional polymers as food packaging materials, especially in the packaging of organic, natural and functional foods. Biopolymers have been set up in many applications, from food packaging to hi-tech. Despite the benefits that biopolymers possess, there are a number of drawbacks that prevent the widespread commercial use of these materials, particularly in the field of food packaging. This is usually because of performance and price when compared with their conventional doublets. In accordance with the method of production and use in the food industry, biopolymers can be classified into different categories and quality groups. The widest commercial use in the food packaging sector is occupied by cellulose-based biopolymers; with the exception of these, very few other biobased materials have commercial use in the packaging of conventional food products. Advancements are taking place at increasing speed in the development of commercial products using starch- and PLA-based biomaterials for a different kind of food packaging that has already been created. In this way, biopolymers have increasing significance in food application. The primary reason for this is that they are created from renewable resources, and the fact that they can be reused through the recycling process. The researchers focused on applications of biopolymers have demonstrated not only that they have suitable properties for wider use in the food industry, but also that they could achieve an acceptable commercial price in the future. If we compare them with petroleum recyclable products, packaging materials made from renewable bioresources could very soon have a low cost and suitable properties for food packaging applications.

References

Ammala A, Bateman S, Dean K et al (2011) An overview of degradable and biodegradable polyolefins. Prog Polym Sci 36:1015–1049
Avella M, de Vlieger JJ, Errico ME et al (2005) Biodegradable starch/clay nanocomposite films for food packaging applications. Food Chem 93:467–474
Babu RP, O'Connor K, Seeram R (2013) Current progress on bio-based polymers and their future trends, review paper. Prog Biomater 2(8):1–16
Baran T, Menteş A (2017) Construction of new biopolymer (chitosan)-based pincer-type Pd(II) complex and its catalytic application in Suzuki cross coupling reactions. J Mol Struct 1134:591–598
Berti C, Binassi E, Colonna M et al (2010) Bio-based terephthalate polyesters. US Patent 2,010,168,371, 1 July 2010
BenettoE Jurya C, Igosa E et al (2015) Using atmospheric plasma to design multilayer film from polylactic acid and thermoplastic starch: a screening Life Cycle Assessment. J Clean Prod 87:953–960
Biomass Packaging (2011) Bioplastics, bioplastic packaging products. http://www.biomasspackaging.com/education/bioplastics
Bioplastics Market Forecast 2014–2024 (2014) Prospects for biobased/non-biodegradable packaging, consumer electronics/products, catering, agriculture & pharmaceuticals, Visiongain, pp 1–172. http://www.reportlinker.com/p02229693/Bioplastics-Market-Forecast-2014-2024.html
Bonilla J, Atarés L, Vargas M et al (2012) Effect of essential oils and homogenization conditions on properties of chitosan-based films. Food Hydrocollilod 26:9–16
Bordenave N, Grelier S, Pichavant F et al (2007) Water and moisture susceptibility of chitosan and paper-based materials: structure–property relationships. J Agric Food Chem 55:9479–9488
Bravin B, Peressini D, Sensidoni A (2006) Development and application of polysaccharide—lipid edible coating to extend shelf-life of dry bakery products. J Food Eng 76:280–290
Bugnicourt E, Cinelli P, Lazzeri A et al (2014) Polyhydroxyalkanoate (PHA): review of synthesis, characteristics, processing and potential applications in packaging. Express Polym Lett 8 (11):791–808
Casey K (2010) PLA: a critical analysis. In: Proceedings of Italian Packaging Technology, Award, Milano, p 13
Cazóna P, Velazqueza G, Ramírez JA et al (2016) Polysaccharide-based films and coatings for food packaging: a review. Food Hydrocolloids (in press)
Chan MA, Krochta JM (2001) Grease and oxygen barrier properties of whey-protein-isolate coated paperboard. Tappi J 84(10):57–67
Chauvet M, Sauceau M, Fages J (2017) Extrusion assisted by supercritical CO_2: a review on its application to biopolymers. J Supercrit Fluids 20(2):408–420
Chen B, Shih C, Chen AF (2012) Ductile PLA nanocomposites with improved thermal stability. Appl Sci Manuf 43:2289–2295

Chen GQ (2010) Introduction of bacterial plastics PHA, PLA, PBS, PE, PTT, and PPP, Plastics from bacteria. Nat Fun App 14:1–16

Clarke K, Tchabanenko K, Pawlosky R et al (2012) Oral 28-day and developmental toxicity studies of (R)-3-hydroxybutyl (R)-3-hydroxybutyrate. Regul Toxicol Pharmacol 63:196–208

Claus JW (ed) (2000) Biobased packaging materials for the food industry status and perspectives. The Royal Veterinary and Agricultural University, Copenhagen

Commission Directive 96/1 1/EC (1996) Amending Directive 90/ 128/EEC relating to plastic materials and articles intended to come into contact with foodstuffs, O J Euro. L 61/26

Conn RE, Kolstad JJ, Borzelleca JF et al (1995) Safety assessment of polylactide (PLA) for use as a food-contact polymer. Food Chem Toxicol 33:273–283

de Vileger JJ (2000) Green plastics for food packaging. In: Ahvenainen R (ed) Novel food packaging techniques. CRC Press, Boca Raton, pp 519–534

Debeaufort F, Quezada-Gallo JA, Voilley A (1998) Edible films and coatings: tomorrow's packagings. Crit Rev Food Sci Nutr 38(4):299–313

Despond S, Espuche N, Cartier N, Domard A (2005) Barrier properties of paper-chitosan and paper-chitosan-carnauba wax films. J Appl Polym Sci 98:704–710

Doi Y, Mukai K, Kasuya K et al (1994) Biodegradation of biosynthetic and chemosynthetic polyhydroxyalkanoates. Stud Pol Sci 12:39–51

Frick EM, Zalusky AS, Hillmyer MA (2003) Characterization of polylactide-b-polyisoprene-b-polylactide thermoplastic elastomers. Biomacromolecules 4:216–223

Gallant DJ, Bouchet B, Baldwin PM (1997) Microscopy of starch: evidence of a new level of granule organization. Carbohydr Polym 32:177–191

Gallstedt M, Brottman A, Hedenqvist MS (2005) Packaging-related properties of protein- and chitosan-coated paper. Packag Technol Sci 18(4):161–170

Girones J, Lopez JP, Mutje P et al (2012) Natural fiber-reinforced thermoplastic starch composites obtained by melt processing. Compos Sci Technol 72:858–863

Glenn GM, Orts W, Imam S et al (2014) Starch plastic packaging and agriculture applications. USDA-ARS/ UNL Faculty, pp 421–452

Gällstedt M, Brottman A, Hedenqvist MS (2005) Packaging-related properties of protein- and chitosan-coated paper. Packag Technol Sci 18:161–170

Ham-Pichavant F, Sebe G, Pardon P et al (2005) Fat resistance properties of chitosanbased paper packaging for food applications. Carbohydr Polym 61:259–265

Han JH, Krochta JM (2001) Physical properties and oil absorption of whey-protein-coated paper. J Food Sci 66:294–299

Han JH, Krochta JM (1999) Wetting properties and sodium water vapor permeability of whey-protein-coated paper. Trans ASAE 42:1375–1382

Hill J (2010) Successful brand enhancement through packaging, best practice in leveraging unique brand attributes and innovative products. Business Insight, London

Hong SI, Han JH, Krochta JM (2004) Optical and surface properties of whey protein isolate coatings on plastic films as influenced by substrate, protein concentration, and plasticizer type. J Appl Polym Sci 92:335–343

Houtman J, Maisanaba S, Gutiérrez-Praena D et al (2014) Toxicity assessment of organomodified clays used in food contact materials on human target cell lines. Appl Clay Sci 90:150–158

Huang J-Y, Li Xu, Weibiao Zhou (2015) Safety assessment of nanocomposite for food packaging application. Trends Food Sci Tech 45:187–199

Innocentini MLH, Bartoli JR, Baltieri RC (2003) Mechanical and thermal properties of poly (3-hydroxybutyrate) blends with starch and starch derivatives. Macromol Symp 197:77–88

Jafarizadeh MH, Osman A, Tan CP et al (2011) Evaluation of effectiveness of three cellulose derivative-based edible coatings on changes of physicochemical characteristics of 'Berangan' banana (Musa sapientum cv. Berangan) during storage at ambient conditions. Food Res Int 18(4):1381–1386

Kabasci S, Bretz I (2012) Succinic acid: synthesis of biobased polymers from renewable resources. In: Mittal V (ed) Renewable polymers. Synthesis, processing, and technology. Scrivener, Salem, MA, pp 355–379

Khaoula K, Elmira AT, Stephane D (2010) Biopolymer coatings on paper packaging materials. Compr Rev Food Sci Food Saf 9:82–91

Khwaldia K (2004) Mise au point, caractérisation et application d'un emballage biodégradable complexe à base de fibres cellulosiques (papier) et de protéines animales (caséinate de sodium). Dosertatoion, Institut National Polytechnique de Lorraine

Khwaldia K (2010) Water vapor barrier and mechanical properties of paper-sodium caseinate and paper-sodium caseinate-paraffin wax films. J Food Biochem 34(5):998–1013

Khwaldia K, Arab-Tehrany E, Desobry S (2010) Biopolymer coatings on paper packaging materials. Compr Rev Food Sci Food Saf 9:82–91

Kjellgren H, Gallstedt M, Engstrom G et al (2006) Barrier and surface properties of chitosan-coated greaseproof paper. Carbohydr Polym 65:453–460

Koller M (2014) Poly(hydroxyalkanoates) for food packaging: application and attempts towards implementation. Appl Food Biotechnol 1(1):1–13

Koller M, Salerno A, Muhr A et al (2013) Polyhydroxyalkanoates: biodegradable polymers and plastics from renewable resources. Mater Tehnol 47:5–12

Lee SY (1996) Bacterial polyhydroxyalkanoates. Biotechnol Bioeng 49:1–14

Lin SY, Krochta JM (2003) Plasticizer effect on grease barrier and color properties of whey-protein coatings on paperboard. J Food Sci 68:229–233

Linnemann B, Sri HM, Gries T (2003) Polylactide fibers (PLA). Chem Fibers Int 53:426–433

Liu HS, Xie FW, Yu L et al (2009) Thermal processing of starch based polymers. Progr Polym Sci 34:1348–1368

Ma X, Yu J, Wang B (2008) Glycerol plasticized-starch/multiwall carbon nanotube composites for electroactive polymers. Compos Sci Technol 68:268–273

Maisanaba S, Puerto M, Pichardo S et al (2013) In vitro toxicological assessment of clays for their use in food packaging applications. Food Chem Toxicol 57:266–275

Matsui KN, Larotonda FDS, Paes SS et al (2004) Cassava bagasse-Kraft paper composites: analysis of influence of impregnation with starch acetate on tensile strength and water absorption properties. Carbohydr Polym 55:237–243

Mittal V (2012) Polymers from renewable resources. In: Mittal V (ed) Renewable polymers synthesis, processing, and technology. Scrivener, Salem, MA, pp 1–22

Modi S, Koelling K, Vodovotz Y (2011) Assessment of PHB with varying hydroxyvalerate content for potential packaging applications. Eur Polym J 47:179–186

Muller CMO, Laurindo JB, Yamashita F (2011) Effect of nanoclay incorporation method on mechanical and water vapor barrier properties of starch-based films. Ind Crop Prod 33:605–610

Park HJ, Kim SH, Lim ST et al (2000) Grease resistance and mechanical properties of isolated soy protein-coated paper. J Am Chem Soc 77:269–273

Parris N, Vergano PJ, Dickey LC et al (1998) Enzymatic hydrolysis of zeinwax-coated paper. J Agric Food Chem 46:4056–4059

Raiand R, Roy I (2011) Polyhydroxyalkanoates: the emerging new green polymers of choice. In: Sharma SK, Mudhoo A (eds) A handbook of applied biopolymer technology. Synthesis, degradation and applications. Royal Society of Chemistry, London, pp 79–101

Raithatha C (2009) Innovation in food and drinks packaging. Business Insight, London

Rasal RM, Janorkar AV, Hirt DE (2010) Poly(lactic acid) modifications. Progr Polym Sci 35: 338–356

Rhim JW, Hwang KT, Park HJ et al (1998) Lipid penetration characteristics of carrageenan-based edible films. Korean J Food Sci Technol 30:379–384

Rhim JW, Lee JH, Hong SI (2006) Water resistance and mechanical properties of biopolymer (alginate and soy protein) coated paperboards. Lebensm Wiss Technol 39:806–813

Robertson G (2008) State of the art biobased food packaging materials. In: Chiellini E (ed) Environmentally compatible food packaging. CRC Press, Boca Raton, FL, pp 3–28

Sanchez GL, Pastor C, Vargas M et al (2011) Effect of hydroxypropylmethylcellulose and chitosan coatings with and without bergamot essential oil on quality and safety of cold-stored grapes. Postharvest Biol Technol 60:57–63

Sanjay KS, Ackmez M (2011) A handbook of applied biopolymer technology. Royal Society of Chemistry, Cambridge

Sauperl O, Stana-Kleinschek K, Ribitsch V (2009) Cotton cellulose 1, 2, 3, 4 buthanetetracarboxylic acid (BTCA) crosslinking monitored by some physical-chemical methods. Text Res J 79:780–791

Shen L, Haufe J, Patel M (2009) Product overview and market projection of emerging bio-based plastics. Utrecht University, Utrecht

Sodergard A, Stolt M (2002) Properties of lactic acid based polymers and their correlation with composition. Progr Polym Sci 27:1123–1163

Sothornvit R (2009) Effect of hydroxypropyl methylcellulose and lipid on mechanical properties and water vapor permeability of coated paper. Food Res Int 42:307–311

Talens P, Pérez-Masía R, Fabra MJ et al (2012) Application of edible coatings to partially dehydrated pineapple for use in fruit-cereal products. J Food Eng 112:86–93

Tim AO, Sylvana GR (2011) History of sustainable bio-based polymers. In: Sanjay KS, Ackmez M (eds) A handbook of applied biopolymer technology: synthesis, degradation and applications. Royal Society of Chemistry, Cambridge, pp 1–123

Timothy A (2010) Carbohydrate route to para-xylene and terephthalic acid. WO Patent 1.513.46, 29 Dec 2010

Tokiwa Y, Calabia BP, Ugwu CU et al (2009) Bio-degradability of plastics. Int J Mol Sci 10:3722–3742

Trezza TA, Wiles JL, Vergano PJ (1998) Water vapor and oxygen barrier properties of corn zein-coated paper. Tappi J 81:171–176

Trezza TA, Vergano PJ (1994) Grease resistance of corn zein-coated paper. J Food Sci 59: 912–915

Van Long NN, Joly C, Dantigny P (2016) Active packaging with antifungal activities. Int J Food Microbiol 220:73–90

Wang S, Cui W, Bei J (2005) Bulk and surface modifications of polylactide. J Anal Bioanal Chem 381:547–556

Weber CJ, Haugaard V, Festersen R et al (2002) Production and applications of biobased packaging materials for the food industry. Food Addit Contam 19:172–177

Wei XW, Guo G, Gong CY et al (2011) Biodegradable polymers: research and applications. In: Sharma SK, Mudhoo A (eds) A handbook of applied biopolymer technology synthesis, degradation and applications. Royal Society of Chemistry, London, pp 365–387

Whistler RL, BeMiller JN (2007) Starches, modified food starches, and other products from starches. In: BeMiller JN (ed) Carbohydrate chemistry for food scientists. American Association of Cereal Chemists, St. Paul, MN, pp 117–151

Ying JC (2014) Bioplastics and their role in achieving global sustainability. J Chem Pharm Res 6 (1):226–231

Yokesahachart CC, Yoksan R (2011) Effect of amphiphilic molecules on characteristics and tensile properties of thermoplastic starch and its blends with polylactic acid. Carbohydr Polym 83: 22–31

Youngjae B, Young TK (2014a) Utilization of bioplastics for food packaging industry. In: Han JH (ed) Innovations in food packaging. Elsevier, London, pp 369–389

Youngjae B, Young TK (2014b) Bioplastics for food packaging: chemistry and physics. In: Han JH (ed) Innovations in food packaging. Elsevier, London, pp 353–365

Zhu J, Li X, Huang C et al (2014) Structural changes and triacetin migration of starch acetate film contacting with distilled water as food simulant. Carbohydr Polym 104:1–7

New Technologies for Microclimatic and Indoor Air Quality Analysis for the Protection of Cultural Heritage: Case Studies of the Classense Library and “Tamo,” The Museum of Mosaics at Ravenna

Massimo Andretta, Floriana Coppola and Ana Pavlovic

Abstract In recent decades, analysis and monitoring of the concentration of indoor pollutants and the microclimate has become more important; the reasons for this interest can be found in the fact that people spend a great deal of their time in confined environments. Furthermore, detailed assessment of the consequences of exposure to air pollutants requires considering concentrations of indoor pollutants. In fact, general indoor microclimatic conditions (i.e., temperature, relative humidity, lighting, pollutant concentration) play an important role in all aspects related to the conservation of works of art and cultural heritage housed in museums, galleries and libraries. In this paper, we present two case studies focused on the application of new methodologies for microclimatic and indoor air quality analysis, specifically devoted to preventive conservation and the enhancement of cultural heritage. In particular, we will describe some case studies in which modern and up-to-date technologies for the monitoring of microclimatic conditions have been applied to study the characteristics of two important monuments in Ravenna: the Biblioteca Classense and the “TAMO” mosaic museum. In particular, in both of these cases, we have used new portable testers for recording indoor thermo-hygrometric conditions and newly developed passive samplers for monitoring indoor and outdoor air pollution concentrations. In this article, we specifically describe the characteristics and main

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innovative peculiarities of the new instruments we have adopted for these measurement campaigns, devoted to the characterization of the indoor microclimatic conditions and to the evaluation of the so-called environment-work of the art system.

Keywords Microclimatic quality · Thermo-hygrometric sensors · Passive diffusive samplers · Innovative methods for cultural heritage conservation · Heritage science

1 Introduction

In recent decades, the problem of microclimate monitoring and control of indoor conditions has assumed great importance, both for the risk assessment of people spending a great deal of their time in confined environments and also for the protection of cultural heritage. In particular, this latter aspect has assumed increasing importance as a result of many factors, like, for example, the wide variety and great value of the exhibited artworks (e.g., in museums or houses in the archives), the increasing number of visitors to these art insitutions, the different materials of which the cultural goods are composed, etc. (Corgnati et al. 2006, 2009; Thomson 1986; Camuffo 1998).

Nowadays, it is well known that microclimate conditions and concentrations of indoor pollutants play a relevant role in the deterioration processes of the different constituents of the works of art; for this reason, any preservation assessment and policies of cultural heritage management have to consider the indoor microclimatic parameters and their mutual interrelationship with the outdoor conditions. These days, the instruments and methodologies for monitoring microclimatic and air quality conditions can take advantage of the development of new sampling methodologies and the advancement of micro-electronic technologies. In particular, new models of portable, passive air pollutant samplers have been placed on the market and new electronic testers for the recording of microclimatic parameters are now available.

In this paper, we describe, specifically, the instruments that we have used for the monitoring of indoor conditions during two measurement campaigns: one conducted at the Classense Library of Ravenna during a summer period (from July 21th to August 7th, 2014) and another one that took place, again, at the Classense Library and also at the TAMO mosaic museum in Ravenna during a winter period (from December 9th to December 22th, 2014). We have chosen these two periods in order to analyze the microclimatic conditions of the two buildings under extreme and, in a certain sense, “worst case” conditions. Furthermore, the Classense Library and the TAMO museum are housed in two neighboring buildings. In this way, we have been able to compare the microclimatic scenarios and the performances of two different buildings under similar outdoor conditions, but with different designs, structural characteristics and functionalities. In particular, in this paper, we describe the electronic thermo-hygrometers and the passive diffusive samplers (for NO_2 and O_3 concentration analysis) we have used to monitor the indoor and outdoor conditions of the above-mentioned monuments. The pollutant concentrations and the thermo-hygrometric data of the internal microclimatic parameters recorded during the two campaigns have been compared with the external ones, obtained from nearby measuring points. *Inter alia*, the aim of these measurements has been to determine the so-called Indoor/Outdoor ratio of pollutant concentrations and other parameters useful for the characterization of the so-called "environment - work of an art system," such as, for example, the air exchange rate of the buildings' rooms and the related pollutant deposition velocities. Furthermore, the monitored data allowed us to compare the analyzed microclimatic data with the specific values recommended by different international norms and standards, in order to verify the conditions of preservation of the precious texts. In this way, we have been able to evaluate the so-called "Performance Index" (PI) of the buildings too (Corgnati et al. 2009); this index determines the percentage of time in which the microclimatic parameters do not match the value recommended for the purposes of preservation of the precious artworks. Some of the results of these monitoring campaigns will be presented in Sect. 4 of this work, in which some of the advantages and disadvantages of the proposed techniques will be reported as well. In this article, we will also describe, in detail, the technical characteristics of the innovative instruments we have used for these researches and their chemical/physical functional principles.

2 Description of the Area of Study and the Sampling Locations

As previously reported, we have used the innovative instruments that are the object of this paper for two measurement campaigns: one campaign in the rooms of the Classense Library and another one in the TAMO museum of mosaics. The Classense Library is housed in a historic building that overlooks, on one side, high-traffic areas and, on the other one, limited traffic areas. It owes its origins and its name to the monks of the "Congregation of the monks of Camalodoli," who had an abbey in Classe, a hamlet of Ravenna, about five kilometers distance from it.

These monks left their suburban residence of Class after the so-called "Battle of Ravenna" in 1512, undertaking the construction of this abbey that, in the course of the subsequent centuries, has become one of the most important abbeys belonging to the Camaldolese order. In the time that followed the abbey's founding, especially in the seventeenth and eighteenth centuries, numerous enlargements and changes were performed (Domini 2001). These have come to define, along with the temporal succession of architectural styles, the current imposing building, which extends over an area of about twenty-two thousand square meters in the center of Ravenna. The collections of the Classense Library represent about 800,000 bibliographic units of different categories: prints, manuscripts, engravings, maps, etc., coming from different sources, from library markets to other ecclesiastical libraries and legacy donations (Morlotti 2013).

On the other hand, the TAMO Museum (acronym of the Italian: “Tutta l’Avventura del Mosaico”—All the adventure of the mosaic) is hosted at the Complex of San Nicolò. The exhibition proposes a suggestive tour through important finds (some of which are still unknown to the public) belonging to Ravenna and its territorial heritage of mosaics. It includes works from the antique, late-antique and medieval periods, up to productions by modern and contemporary artists. The innovative presentation of these works of art distinguishes TAMO for its interactive set-ups and multimedia devices, as well as its plastic models, working tools, materials, animated reconstructions and advanced technological solutions (TAMO 2015).

Both of these two buildings are situated in the urban area of Ravenna, a city of the Emilia Romagna Region in Northern Italy, on the shores of the Adriatic Sea.

Figures 1 and 2 show the geographic position of the area of study and of the sites in the urban area of Ravenna.

The meteo-climatic conditions of the region are strongly influenced by the topography of the Padanian Valley, a floodplain formed by the Po River, the longest river in Italy; in particular, the presence of the mountains causes the air to stagnate very frequently. The climate of the Province of Ravenna has the typical characteristics of the sub-continental climate of the inland areas; in particular, one can note that, obviously, the marine influence becomes more and more relevant as we approach the coast (Righi et al. 2013).

In the Classense Library, during the first summer measurement campaign, from July 21th to August 7th, 2014, we placed the samplers and the detectors into four inner rooms of the building: the so-called Hall of the Holy Fathers (Santi Padri, in Italian), the Dante Hall (Sala Dantesca), the Great Hall (Aula Magna) and the Former Refectory (Ex Refettorio). The choice that was made was dictated, in particular, by the possibility of analyzing heterogeneous indoor environments, each different from the others in terms of geometry, type of ventilation, use and attendance. The indoor measures were compared with the outdoor ones. The outdoor data was obtained from two measuring points: one point located just nearby the Classense Library and the other one represented by one of the air quality monitoring

Fig. 1 Geographic location of the area of study. Italy (*left*), district subdivision of Ravenna City

Fig. 2 The sites investigated in the research, located in the urban area of Ravenna City

stations of the Regional Environmental Protection Agency (ARPA-RER) (ARPA 2014a, b; Sistema DEXTER 2014).

Monitoring of the indoor microclimate was focused on the following thermo-hygrometric parameters: temperature (T), relative humidity (RH) and their daily excursions (ΔT_{24} and ΔRH_{24}). We also measured the indoor and outdoor concentrations of the following pollutants: NO_2 and O_3, which can be considered key pollutants for this kind of heritage building in Ravenna (Tétreault 2003). During the winter campaign, from December 9th to December 22th, 2014, we placed two sets of the same thermo-hygrometric detectors and air pollutant concentration samplers in the TAMO museum, one just near the entrance and the second one near the deep end of the great nave room of the Complex of San Nicolò that houses the museum.

3 Instrument Descriptions

3.1 *The Thermo-Hygrometric Testers*

For the measurement of the thermo-hygrometric parameters, we used five USB PCE-HT71© thermo-hygrometers of the PCE Instruments. This environmental tester is equipped with a Pt100 resistance thermometer and a capacitive sensor for humidity. It can store readings in its internal memory.

Fig. 3 USB PCE-HT71© thermo-hygrometer

Figure 3 shows the specific thermo-hygrometer described herein.

A resistance thermometer, like the devices we used, is also defined as a Resistance Thermal Detector (RTD); RTDs are passive transducers with a positive temperature coefficient of resistance, i.e., they increase their resistance when their temperature augments. They are characterized by a high accuracy and repeatability (Deric 2010). In its more widely used configuration, an RTD is built of a fine coiled wire wrapped around a ceramic or glass core. The element is usually quite fragile, so it is often placed inside a sheathed ceramic probe to protect it. The element of an RTD is typically copper, nickel or platinum. These materials change their resistivity as the temperature changes, and this well-defined behavior is used to determine temperature. Among all of the above-mentioned materials, platinum is the best material for use in RTDs, because of its linear and highly repeatable resistance-temperature dependence, typically ranging from −272.5 to 960 °C. As reported above, the other metals normally used for resistance thermometers are nickel and copper. For all these metals, the relationship between resistance and temperature (and also humidity) can be described with good approximation through the “Callendar-Van Dusen” equation:

$$R = R_0\left[1 + At + Bt^2 + C(t - 100)t^3\right],$$

where

R is the resistance, function of the temperature t [Ω],
R_0 is the resistance at 0 °C [Ω],
and A, B, C are constants that depend on the metal used in the RTD.

Usually, the constant C is null for $t > 0$ °C and $t < 100$ °C, and the term $B \ll A$; therefore, the terms with higher power of t can be ignored if you operate in the range 0–100 °C and you can consider the "Callendar-Van Dusen" relationship to be linear. In particular, the PCE-HT71© data-loggers we used in our measurement campaigns were equipped with a Pt100 thermo-resistance, i.e., a platinum RTD with a resistance of 100 Ω at 0 °C.

For measurement of the Relative Humidity (RH), the sensors we used were equipped with a capacitive humidity sensor; this kind of device is usually used for long-lasting, continuous sampling (Roveti 2001). The working principle of these devices is the change of the dielectric constant of a metal oxide or of a polymer as an effect of the humidity. With these sensors, one can have an accuracy of ±2% RH in the range of 5–95% RH. Furthermore, these devices are also robust against external, undesirable and potentially harmful effects such as condensation and high temperatures. They consist of a thin film of polymer or metal oxide deposited between two conductive electrodes. The sensing surface is protected with a porous metal electrode to prevent contamination and possible condensation phenomena. The substrate is typically glass, ceramic, or silicon, as in the PCE-HT71© we used. The change in the dielectric constant of this kind of sensor is nearly directly proportional to the relative environmental humidity. The capacitance range is, typically, 0.2–0.5 pF for a 1% RH change, while the bulk capacitance ranges from 100 to 500 pF at 50% RH at 25 °C. These sensors are characterized by a low temperature coefficient, high temperature (up to 200 °C) operative conditions and reasonable resistance to chemical vapors. The normal response time spans from 30 to 60 s for a 63% RH change (Roveti 2001).

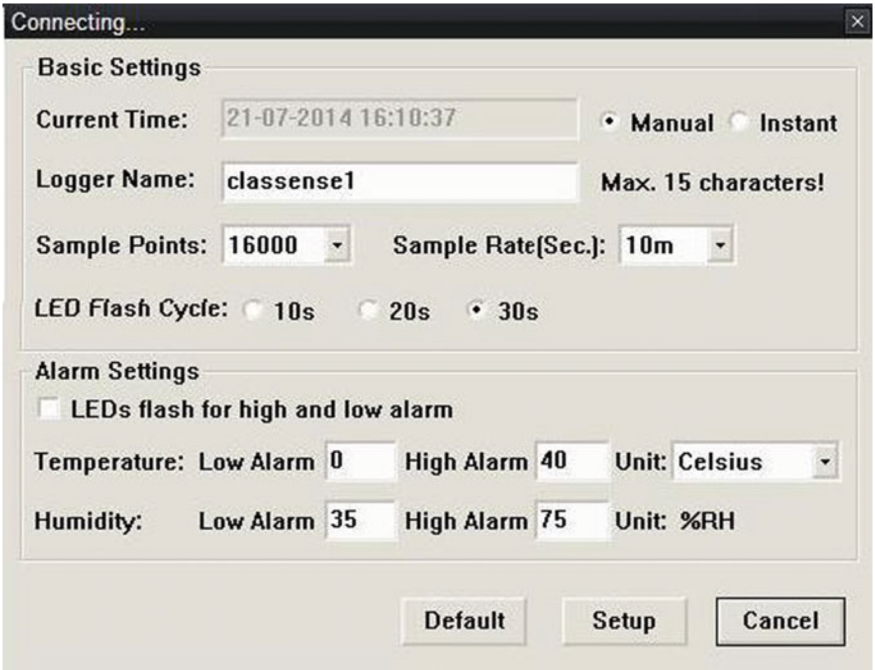
Nevertheless, these sensors can be subject to contamination, drift and, generally speaking, "aging effects."

The PCE-HT71© testers used for our measurement campaigns were compact devices with enough memory to store up to 32,000 readings (i.e., 16,000 for T and RH parameter). These devices can be activated manually or can be pre-programmed to start and stop on specific dates, and at specific times as well. You can also set the intervals at which the measurements will be taken, allowing them to be left to record data unsupervised. Once transferred with specific software, the data can be analyzed on a computer. The internal clock allows the user to accurately assess the results. The PCE-HT71© tester is powered by a removable 3.6 V, long-life lithium battery, which could last, depending on use, up to a year (PCE 2015). The main technical characteristics of the PCE-HT71© thermo-hygrometer are summarized in Table 1.

In Fig. 4, we show the main window of the SW Datalogger Graph (Vers. 2.2)© that allows the user to set all the parameters of the sampler:

Table 1 Technical specifications of the thermo-hygrometer PCE-HT71 (PCE 2015)

Variable	Temperature	Relative humidity
Measurement range	−40 to +70 °C	0–100%
Accuracy	±1 °C	±3%
Resolution	0.1 °C	0.1%
Environmental conditions	−40 to +70 °C	0–100% (no condensed)
Sensors	Pt100	Capacitive
Sampling frequency	2 s to 24 h	
Start/End	Free programmable	
Memory	32,000 samples	
Power	3.6 V lithium battery	
Dimensions	30 × 25 × 130 mm	
Weight	25 g	



Basic Settings

Current Time: 21-07-2014 16:10:37 ● Manual ○ Instant

Logger Name: classense1 Max. 15 characters!

Sample Points: 16000 Sample Rate(Sec.): 10m

LED Flash Cycle: ○ 10s ○ 20s ● 30s

Alarm Settings

☐ LEDs flash for high and low alarm

Temperature: Low Alarm 0 High Alarm 40 Unit: Celsius

Humidity: Low Alarm 35 High Alarm 75 Unit: %RH

Fig. 4 The main window of the Datalogger Graph (Vers. 2.2)© SW to set the USB PCE-HT71© samplers

- *Sample Rate* (i.e., the monitoring frequency, from 1 per minute to 1 for a day)
- *Sample Point* (i.e., the maximum amount of parameter data recorded, Temperature and Relative Humidity, from 1 to 16,000 for each parameter)

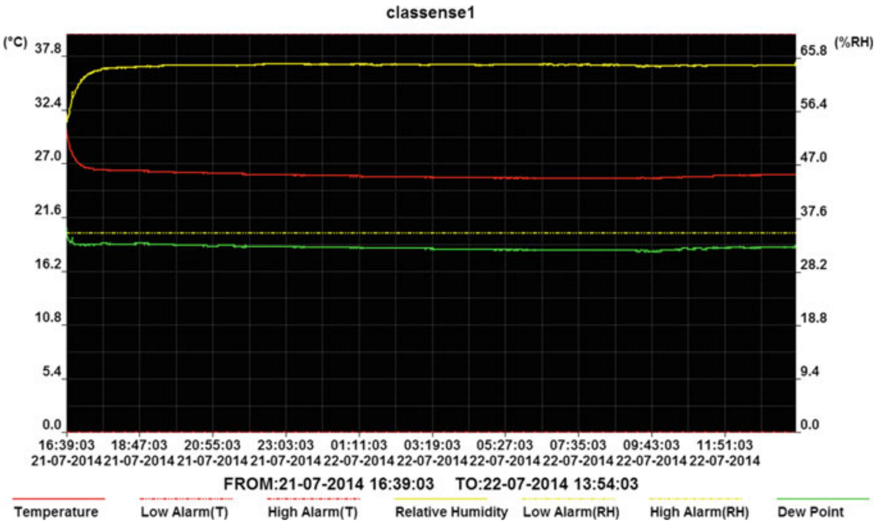


Fig. 5 An example of data visualization: Temperature (*continuous red line*), Relative Humidity (*continuous yellow line*), Dew Point (*continuous green line*), Set Alarms (*red dot lines*)

- *Led Flash Cycle* (i.e., the frequency of flashing of the control LED), usually set at 30 s, to allow a longer battery life
- *Alarm Settings* (i.e., the range of acceptable values for both the Temperature and the Relative Humidity); in our case, we set the acceptable range between 0 and 40 °C for the temperature and between 35 and 75% for the RH. Outside of these ranges, a red LED on the sampler flashes.

The monitored data can be displayed as shown in Fig. 5, herewith included and saved in many different formats (e.g., .rec, .txt, .xls, .bmp).

3.2 The Air Pollutant Concentration Samplers

Devices and technologies for measurement of the concentration of contaminants in the air are varied and characterized by a state of rapid evolution. Generally speaking, the different methods can be traced back to two approaches, one active and the other passive (or diffusive).

In active sampling, through the action of a pump, the instrument funnels the air into a detector or a filter; in this way, determination of the pollutant concentration is done by analyzing the sampled air. An example of this type of sampling is the so-called "diffusion pipes," also known as a "denuder"; they consist of cylindrical glass tubes, at a length of about ten centimeters, with an inner diameter of a few millimeters. Their internal surface is coated with a substance that chemically reacts with the gaseous species of interest. By means of a pump, the air is drawn through the “denuder”; during the passage of the air, the gaseous species diffuse on the walls of the tube, where they react with the coating and are retained by it. At the end of the sampling, the “denuder” is first extracted using appropriate solutions; then, the resulting samples are analyzed by, for example, ion chromatography.

Among the most common methods of active sampling and analysis, we can also mention the type of analyzer in which the air is continuously sent into a chamber (or cell) where the concentration is determined by infrared absorption, ultraviolet or electrochemical detectors, depending on the species you want to determine.

Since its invention in the ’70s, the technology of diffusive sampling has been widely used for environmental monitoring. From the first demonstration of the validity of the passive samplers, initially designed only for air gaseous pollutants, there has been rapid development of their application (Palmes and Guinnison 1976). Recently, such devices have also been used for analysis of aqueous and solid matrices. The principle of the air pollutant passive samplers’ functioning is based on the molecular diffusion of a gas to an absorbent means. This phenomenon is described by Fick’s first law; according to this law, in the case of steady state conditions and assuming only one direction of diffusion, the flow is proportional to the gradient of concentration, i.e.,

$$J = -D\frac{dC}{dx},$$

where

J is the “diffusion flux,” expressed as the amount of substance per unit area per unit time [g m^{-2} s^{-1}],
D is the molecular diffusion coefficient, also called “diffusivity” [m^2 s^{-1}],
and $\frac{dC}{dx}$ is the concentration gradient along the x direction [g m^{-4}].

Depending on the pollutant you want to analyze (e.g., NO_2, O_3, SO_2, NH_3, HCOH), the sampler will be equipped with a specific adsorbent that fixes the pollutant diffusing inside the tube of the sampler. From the foregoing reasoning, it is clear that, due to its intrinsic characteristics, the result of a measurement with a diffusive sampler is the average concentration of the analyte during a known time period; that is to say, it is the so-called “TWA concentration” (Time-Weighted Average concentration) (Seethapathy et al. 2008).

Even if passive sampling has been widely used and recognized as a valuable tool for environmental monitoring, in the past, the reliability of this technique under different environmental conditions has been a subject of controversy. In fact, the theoretical principle of passive samplers is based on Fick’s first law. This law hypothesizes, precisely speaking, the “steady state” conditions. In the field, under certain specific and “extreme” conditions, the effective absorption of the samplers could vary depending on many factors and chemical/physical conditions; for example, a significant change in the temperature or the humidity, which can affect the diffusivity (Seethapathy et al. 2008).

However, some authors (Gerboles et al. 2006), in evaluating the uncertainty of the measurements of different passive samplers available on the market at that time, cited field tests showing that most of the passive samplers meet the uncertainty requirements of 25–30% for NO_2 and O_3; these relative uncertainties match the European Community's requirements for the analysis of these air pollutants (Gerboles et al. 2006).

Table 2 summarizes the equations, the most important parameters and the possible effects of environmental conditions on passive diffusive samplers.

In our measurement campaigns, the subjects of this paper, the concentrations of air pollutants have been determined through the use of passive samplers, produced by the PASSAM Company (ATTALEA 2014). These samplers are of the so-called axial diffusion type, also known as *Palmes tubes* (Palmes and Guinnison 1976). They consist of a tube, open at one end, with an absorbent at the other, closed end; this absorbent matrix fixes the specific pollutant from the surrounding air (Targa et al. 2008). In particular, for our studies, given the duration of the monitoring campaigns, directed towards determination of the average indoor concentrations for

Table 2 Main equations, parameters and possible effects of environmental conditions on passive diffusive samplers (Seethapathy et al. 2008)

Fick's Law	$\left(\frac{M}{t} = D\left(\frac{A}{L_d}\right)(C_0 - C)\right)$ M is the total quantity of the pollutant absorbed in the time t D is the molecular diffusion coefficient A is the cross-section area of the sampler L_d is the length of the diffusion path C_0 is the pollutant concentration at the open end of the sampler C is the pollutant concentration at the absorbent end
Gauge constant	$K = \frac{L_d}{(AD)}$
TWA Concentration	$C_0 = \frac{KM}{t}$
Side effects of the temperature	Resulting from the dependence on the temperature of the diffusivity D $D = D_0 exp\left(\frac{-Q_d}{RT}\right)$ In general: where: D_0 is a temperature-independent coefficient Q_d is the diffusion activation energy R is the gas constant (8.31 J/(mole K)) T is the absolute temperature
Side effects of the humidity	Possible saturation of the absorbent substance
Response time of the samplers	$R_d = \frac{L_d^2}{2D}$ R_d = Response time
Effect of pollutant concentration on the sampling rate	Non-influential

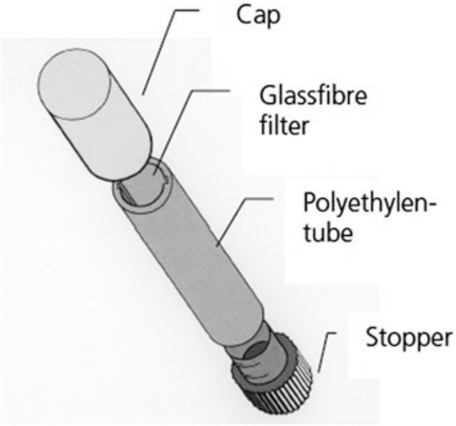


Fig. 6 Passive sampler for O_3 (ATTALEA 2014)

a sufficiently long and representative period of time, we used samplers for long-term monitoring (i.e., 2 weeks for NO_2 and 1 week for O_3).

A typical sampler such as the one we used for ozone, shown in Fig. 6, is constituted by a cylindrical tube, 4.9 cm long, with an internal diameter of 0.9 cm, where the air can circulate via molecular diffusion.

As we have previously mentioned, one side of the tube is open to allow for the diffusion of gases, while on the bottom of the sampler, there is a filter made of glass fiber, supported by a network. A substance that reacts with the ozone is deposited on this filter. In particular, in the samplers we used, the filter is soaked with a solution of 1,2-di (4-pyridyl) ethylene (DPE), which reacts with O_3 and produces formaldehyde. The ozone concentration is determined by spectrophotometrical analysis; in particular, by reading the line at 442 nm produced by the ozonide. The samplers for nitrogen dioxide consist, on the other hand, of a polypropylene vial 7.35 cm in length with an internal diameter of 0.98 mm. At one end, a filter impregnated with trietanolammina (TEA) which reacts with NO_2, is positioned. Dioxide binds to the TEA via a covalent bond. The concentration of NO_2 is determined by adding N-(1-naphthyl) ethylenediamine hydrochloride (NEDA) and reading the absorbance at 540 nm through spectrophotometry (Cape 2009).

In Table 3, we summarize the main characteristics of the passive samplers we used for our researches.

4 Case Studies of Indoor Air Quality Analysis Monitoring Campaigns

We herewith present some of the results of the monitoring campaigns for indoor quality analysis, with the main purpose of highlighting the peculiarities and advantages related to the use of new methodologies in the present work.

Table 3 Technical specification for diffusive samplers produced by the Passam Company (ATTALEA 2014)

	NO_2	O_3
Sampling rate	0.8536 $ml\,min^{-1}$ (estimated at 9 °C) 0.7340 $ml\,min^{-1}$ (estimated at 20 °C)	0.0255 $mg\,m^{-3}\,h^{-1}$ (estimated at 9 °C) 0.2805 $mg\,m^{-3}\,h^{-1}$ (estimated at 2 °C)
Working range	1–200 $\mu g\,m^{-3}$	5–240 $\mu g\,m^{-3}$
Detection limit	0.3 $\mu g\,m^{-3}$	5.1 $\mu g\,m^{-3}$
Exposure period	1–4 week	1–2 week
External influences Wind speed	<10% to 4.5 $m\,s^{-1}$	<10% to 2 $m\,s^{-1}$
Temperature	No influence between 5 and 40 °C	No influence between 10 and 30 °C
Humidity	No influence between 20 and 80%	No influence between 20 and 80%
Storage	24 months before use 6 months after exposure	6 months before use 4 months after exposure
Extended uncertainty	18.4% at concentration levels of 20–40 $\mu g\,m^{-3}$	20.5% at concentration levels >80 $\mu g\,m^{-3}$

As mentioned before, we used these instruments during two monitoring campaigns in two different seasons.

The summer campaign was carried out in the indoor spaces of the Classense Library, while the winter campaign was performed inside the TAMO Museum. In this section, we present some partial results in order to explain the features, peculiarities and advantages of these instruments.

First of all, we present partial results about the summer monitoring that took place from July 21st to August 7th. In this regard, we report the thermo-hygrometric parameters recorded starting from 4.30 PM on July 21st to 4.30 PM on July 22nd, uninterrupted for 24 h.

In Fig. 7, the positioning of both the thermo-hygrometer and the passive diffusive sampler for the measuring of temperature, relative humidity and the concentration levels of NO_2 is illustrated.

These instruments do not need a power supply, and thus they can be installed in place with no correlated visual impact or other undesirable negative effects, e.g., noise, vibration, etc. In fact, as can be seen in Fig. 7, it is also possible hide the instruments in certain areas that are not accessible to the public, and that do not require frequent maintenance.

Through the use of the thermo-hygrometer, and by elaborating the data with DataLogger Graph, we can obtain some very interesting statistical information on the time trends of the temperature and the relative humidity, summarized in Table 4 and Fig. 8, respectively. In this case, the sample rate was fixed to 1 min, and so there are a considerable number of observations.

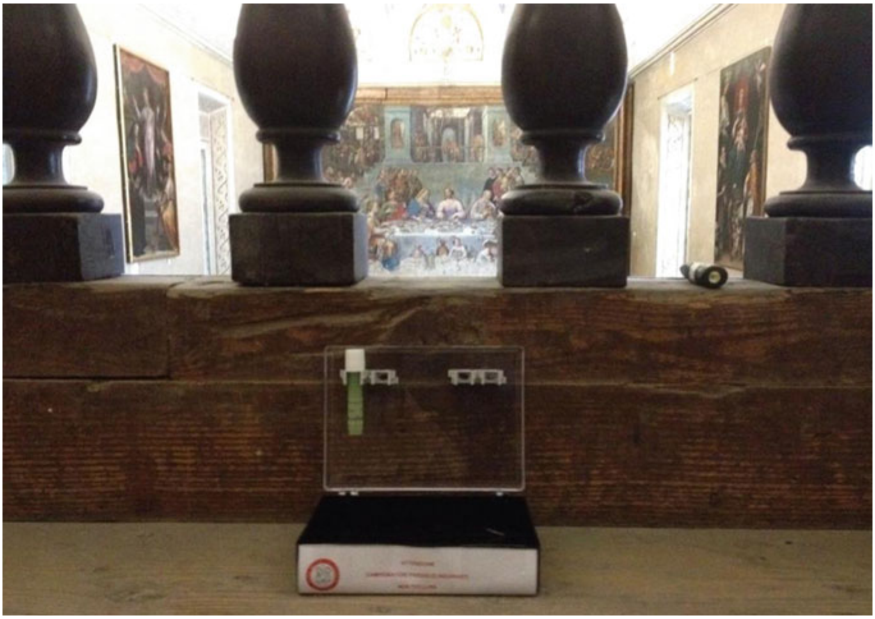


Fig. 7 Positioning of the thermo-hygrometer and passive diffusive sampler in the Former Refectory, a room investigated during the monitoring campaign inside the Classense Library. At the *top* of this photo, it is possible to admire the painting *Le nozze di Cana* by Luca Longhi (1507–1590)

Table 4 Statistical information about the summer monitoring campaign (July 21st–July 22nd, 2014) in the Former Refectory of the Classense Library

Statistics	Temperature (°C)	Relative Humidity (%)
Number of observations	1437	1437
Minimum	25.5	54.6
Maximum	30.3	65.1
Average	25.9	64.4
Std. Dev.	0.4	0.9

Now, we present some results obtained from the monitoring campaign performed inside the TAMO Museum from December 16th to December 22nd, 2014. In this case, the sample rate was 30 min. Thus, we report thermo-hygrometric data recorded over 24 h, continuously, in Table 5 and Fig. 9.

Finally, we report, in the form of histograms, the indoor levels of NO_2 measured by a passive diffusive sampler made by PASSAM in the Former Refectory and the TAMO Museum. These samplers were exposed for two weeks in both the summer and the winter (Fig. 10).

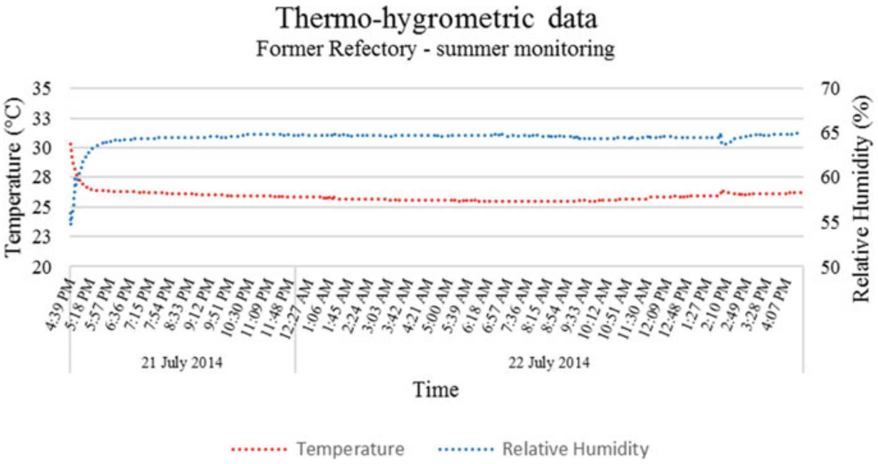


Fig. 8 Graph showing the trends of the temperature and the relative humidity in the considered period of time (July 21st–July 22nd)

Table 5 Statistical information about the winter monitoring campaign (December 16th–December 17th, 2014) in the open space in the TAMO Museum

Statistics	Temperature (°C)	Relative humidity (%)
Number of observations	49	49
Minimum	13.2	64.7
Maximum	16.7	72.9
Average	14.5	69.7
Std. Dev.	1.1	2.8

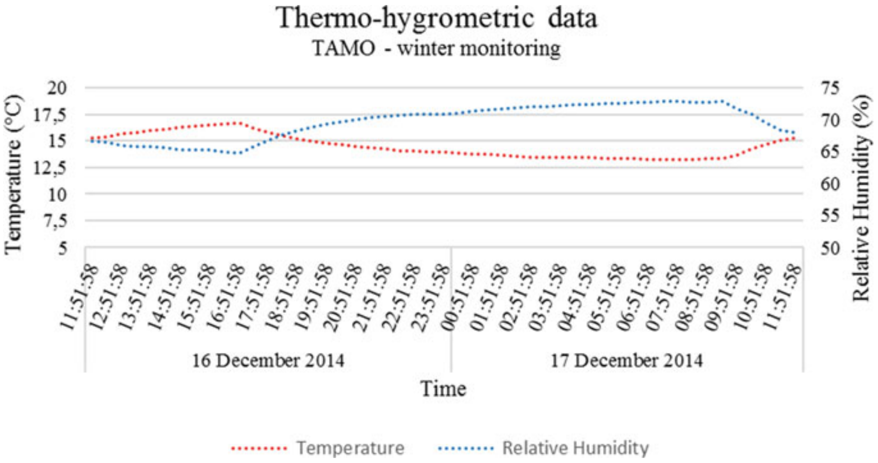


Fig. 9 Graph showing the trends of the temperature and the relative humidity in the considered period of time (December 16th–December 17th)

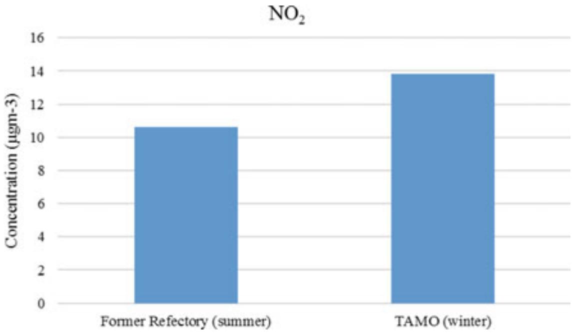


Fig. 10 Histograms with the levels of nitrogen dioxide in the Former Refectory (from July 21st to August 4th) and in the TAMO Museum (from December 9th to December 22nd)

We have reported these data as an example of the results of the data collected by the instruments described in the previous sections. Thus, we can highlight some advantages of these instruments in investigating indoor microclimatic conditions, especially in areas like museums and libraries where there are exhibition requirements, as well as a need for silence and low visual impact.

5 Conclusion

In this paper, we present two kinds of innovative instrument for the monitoring of the indoor microclimate of rooms in museums and libraries, with an eye specifically towards the conservation of cultural heritage and the assessment of the correct conditions for preservation. Specifically, we have analyzed the main technical/functional features of two kinds of innovative portable device particularly suited to monitoring campaigns in indoor museum environments; the mini and electronic testers for recording data on temperature and relative humidity and the portable passive diffusive samplers, or *Palmes tubes*, for air pollutant concentration analysis.

The attention of the scientific literature towards the use of these passive samplers, ever since the studies done by Saunders et al. (1981) and Namiesnik et al. (1984), can be explained by a number of practical, indisputable advantages that distinguish these kinds of sampler from the active ones. These samplers are, for many reasons, a convincing alternative to the traditional automatic analyzers of pollutant concentration measurements for medium or long periods: in fact, these analyzers have no energy limits of autonomy, they do not cause visual disturbance or noise, they do not require supervision, and they can make multiple measurements simultaneously (Brown 2000). They have also small dimensions, which facilitate their transport, and they do not require daily maintenance.

Although in the beginning, they were mainly applied to analysis of workplace environments, thanks to the above-described features, passive diffusive samplers represent a very versatile technique, which is well-adapted to different contexts:

from environmental applications [for example, they are widely used to monitor remote forest areas (Cox 2003)] to those of health (e.g., for epidemiological investigations) to those of cultural heritage conservation (Camuffo et al. 1999), as in the measurement campaigns that are the object of the present work.

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References

ARPA (2014a). La Rete di monitoraggio della qualità dell'aria a Ravenna. http://www.arpa.emr.it/v2_rete_di_monitoraggio.asp?p=RA&s=9000015&idlivello=134. Accessed 30 Dec 2014

ARPA (2014b). Accesso diretto ai dati - Sistema dexter. http://www.arpa.emr.it/sim/?osservazioni_e_dati/dexter. Accessed 21 Dec 2014

ATTALEA (2014) Environmental protection and monitoring. http://www.attalea.net/#/home-en/4585643796. Accessed 5 Jan 2015

Brown RH (2000) Monitoring the ambient environment with diffusive samplers: theory and practical consideration. J Environ Monit 2(1):1–9

Camuffo D (1998) Microclimate for cultural heritage. Elsevier, Amsterdam

Camuffo D, Brimblecombe P, Van Grieken R, Busse H, Sturaro G, Valentino A, Bernardi A, Blades N, Shooter D, De Bock L, Gysels K, Wieser M, Kim O (1999) Indoor air quality at the Correr Museum, Venice, Italy. The Science of the Total Environment 236(1–3):135–152

Cape JN (2009) The use of passive diffusion tubes for measuring concentrations of nitrogen dioxide in air. Crit Rev Anal Chem 39(4):289–310

Corgnati SP, Fabi V, Filippi M, Perino (2006) A new approach for the IEQ (Indoor Environment Quality) assessment. In: Fazio P, Ge H, Jiwu R, Desmarais G (eds) Proceeding of 3rd international conference, Montreal, 27–31 August 2006. Research in building physics and building engineering, Taylor &Francis, pp 837–844

Corgnati SP, Fabi V, Filippi M (2009) A methodology for microclimatic quality evaluation in museums: application to a temporary exhibit. Build Environ 44(6):1253–1260

Cox RM (2003) The use of passive sampling to monitor forest exposure to O_3, NO_2 and SO_2: a review and same case of studies. Environ Pollut 126(3):301–311

Domini D (2001) La storia della Biblioteca Classense. In: Domini D, Giuliani C, Malkowski L (eds) Classense. Longo Editore, Ravenna, pp 15–55

Fabbri P (1981) L' Escuriale de Camaldolesi. In: Domini D (ed) Cultura e vita civile a Ravenna: secoli XVI - XX. University of Bologna, Almamater studiorum, pp 27–94

Kyriacou PA (2010) Biomedical sensors: temperature sensor technology. In: Deric PJ (ed) Biomedical sensors. Momentum Press, New York, pp 1–38

Gerboles M, Buzica D, Amantini L, Lagler F (2006) Laboratory and field comparison of measurement obtained using the available diffusive samplers for ozone and nitrogen dioxide in ambient air. J Environ Monit 8(1):112–119

Giuliani C (2001) La Biblioteca Classense. I fondi speciali. L'Ottocento. In: Domini D, Giuliani C, Malkowski L (eds) Classense. Longo Editore, Ravenna, pp 56–80

Gorecki T, Namiesnik J (2002) Passive sampling. TrAC Trends Anal Chem 21(4):276–291

Morlotti E (2013) Indagine microclimatica nel caso studio della camere blindata della Biblioteca Classense. Bachelor thesis, Alma Mater Studiorum, University of Bologna

Namiesnik J, Gorecki T, Kozlowski E, Torres L, Mathieu J (1984) Passive dosimeters—an approach to atmospheric pollutants analysis. Sci Total Environ 38:225–258

Palmes ED, Guinnison AF (1976) Personal sampler for nitrogen dioxide. Am Ind Hyg Assoc J 37 (10):570–577

PCE Instruments (2015) Environmental Tester PCE-HT 71N. https://www.pce-instruments.com/english/measuring-instruments/meters/environmental-tester-pce-instruments-environmental-tester-pce-ht-71n-det_287613.htm?_list=qr.art&_listpos=5. Accessed 4 Jan 2015

Righi S, Farina F, Marinello S, Andretta M, Lucialli P, Pollini E (2013) Development and evaluation of emission disaggregation models for the spatial distribution of non-industrial combustion atmospheric pollutants. Atmos Environ 79:85–92

Roveti DK (2001) Humidity/Moisture. Choosing a humidity sensor: a review of three technologies. Sensor online. http://www.sensorsmag.com/sensors/humidity-moisture/choosing-a-humidity-sensor-a-review-three-technologies-840. Accessed 21 Jan 2015

Ryhl-Svendsen M, Padfield T, Smith VA, De Santis F (2003) The indoor climate in historic buildings without mechanical ventilation systems. Healthy Buildings 2003:278–283

Seethapathy S, Gòrecki T, Li XJ (2008) Passive sampling in environmental analysis. J Chromatogr A 1184(1–2):234–253

Saunders KJ, Brown RH, Charlton J (1981) The development of an improved diffusive sampler. Am Hyg Assoc J 42(12):865–869

TAMO Museum—All the Adventure of the Mosaic (2015) http://www.turismo.ra.it/eng/Discover-the-area/Art-and-culture/Museums-and-galleries/Tamo-Museum-All-the-adventure-of-the-mosaic. Accessed 23 Jan 2015

Targa J, Loader A, Collings A (2008) Diffusion tubes for ambient NO_2 monitoring: practical guidance. Diffusion tubes for ambient NO_2 monitoring: practical guidance for laboratories and users. Defra and the Devolved Administrations. http://laqm.defra.gov.uk/documents/0802141004_NO2_WG_PracticalGuidance_Issue1a.pdf. Accessed 23 Jan 2015

Tétreault J (2003) Airborne pollutants in museums, galleries, and archives: risk assessment, control strategies, and preservation management. Canadian Conservation Institute, Ottawa

Thomson G (1986) The museum environment, 2nd edn. Buttherworths, London

Potential Application of Nano Zero Valent Iron in Environmental Protection

Dragana Tomašević Pilipović, Đurđa Kerkez, Božo Dalmacija, Milena Bečelić-Tomin and Aleksandar Došić

Abstract Nanoscale zero-valent iron particles (nZVI) have been studied intensively in recent years as a new and promising technology for environmental remediation. nZVI is a readily available and low-cost reducing agent, which also has high reactivity towards a broad range of contaminants. Nonetheless, pivotal points to be addressed are its stability against aggregation, its mobility in subsurface environments, and its longevity. This chapter gives an extensive review of the progressive research and development activities in regard to environmental protection through iron-based nanoparticles. Methods for synthesis of different types of supported iron-based nanomaterial, as well as their characterization, are discussed. The lack of knowledge is evident regarding use of the same nanomaterials for treating different environmental mediums and various chemical species. Thus, the chapter includes two case studies, covering the usage of several supported nZVI for remediating solid porous media polluted with metals, as well as for treating wastewaters containing dye molecules. Case studies also indicate a broader applicability of these processed materials, emphasizing the possibility for further commercialization of supported nZVI.

Keywords Supported nano zero valent iron · Environmental remediation · Toxic metal polluted sediment · Dye wastewater

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1 Introduction

The rapid rise of nanotechnologies originates from the different physico-chemical, magnetic and optical properties of nanomaterials. These nanomaterials have potential applications in a wide range of areas, such as electronics, pharmaceuticals, cosmetics and personal care items, transportation, construction, energy, medicine, and agriculture, to name a few. Efforts have been aimed towards the synthesis and design of nanomaterials for environmental remediation.

As a consequence of the impressive field of nanotechnology development, the broader environmental impacts of nanotechnology will also need to be considered. Among others, such considerations might include cost, size, availability and the benefit of applying advanced technological devices, as well as the risks of nanotechnology with respect to their effects on the environment and human health.

The initial application of nanotechnology was remediation using nanoscale iron particles, which eventually expanded to include all different kinds of contaminant. nZVI has become an efficient material for pollutant removal due to its higher reactivity, compared to the analogous bulk material. However, due to their small particle size, magnetic interactions and surface corrosion, nZVI and other metals show surface area reduction and electro transfer inhibition for redox reactions (Li et al. 2012; Zhang et al. 2012, 2013; Kim et al. 2013; Luo et al. 2013), which surely presents a challenge for additional research.

Former investigations regarding the use of nZVI addressed different approaches to environmental protection. Some of these articles described environmental applications, which include environmental remediation, water and wastewater treatment (Hua et al. 2012; Feng et al. 2013; Ruiz-Hitzky et al. 2013), removal of pollutants such as heavy metals/metalloids (Sánchez et al. 2011; Xu et al. 2012; Wang et al. 2013), dyes (Zhao et al. 2011; Park et al. 2013; Singh et al. 2013; Udom et al. 2013; Wang et al. 2013), and removal of other organic pollutants, such as pesticides, chlorinated compounds, amines, phenols, and organic acids (Zhao et al. 2011; Singh et al. 2013; Wang et al. 2013). nZVI particles can also remove nutrients such as nitrogen from activated sludge (Wu et al. 2013) and phosphorus from aqueous solutions (Liu et al. 2013). Several publications describe methods for the preparation, modification, and characterization of nanomaterials, because they can change in size, shape, crystallinity phase, surface area, stability, and other factors, seriously affecting their utilization (Zhao et al. 2011; Hua et al. 2012; Gupta et al. 2013; Shukla et al. 2013; Tosco et al. 2013; Wang et al. 2013). Other researchers have investigated the nanoparticles/adsorbent binding mechanisms (for example, adsorption, degradation, photocatalysis) (Fu et al. 2013; Gupta et al. 2013; Tang and Lo 2013). Articles on the efficiency of the method utilized and the reactivity of the nanoparticles were also found (Gupta et al. 2013; O'Carroll et al. 2013; Tang and Lo 2013; Udom et al. 2013). Others pointed out the advantages and disadvantages of using nanomaterials (Crane and Scott 2012; Feng et al. 2013; O'Carroll et al. 2013; Tang and Lo 2013; Tosco et al. 2013), and their potential risk to living organisms such as *Daphnia magna* (Sánchez et al. 2011), bacteria and edible plants (Tang and Lo 2013).

Summing up a great number of published researches, there is an evident lack of knowledge regarding the use of those same iron-based nanoparticles for treating different environmental mediums and various chemical species. So, in this chapter, we will discuss usage of several supported nZVI for remediating solid porous media, such as sediments contaminated with metals. The tendency of metals to incorporate into sediments creates a potential environmental risk at both the local and global levels, but only a few surveys have explored the possibility of using iron-based nanoparticles to address this issue. On the other hand, the chapter will also discuss usage of the same supported nZVI materials for remediating wastewaters containing dye molecules (as representatives of an organic compound), namely, because dye molecules are recognized as one of the major pollutants in the environment because textile industries all over the world discharge vast amounts of wastewater.

2 Synthesis, Support and Characterization of nZVI Particles

2.1 Synthesis Techniques of nZVI

Numerous techniques for the production of nZVI particles have been successfully implemented in recent years. These techniques can be divided into bottom-up approaches (generation of iron nanoparticles from ions or smaller particles via deposition, nucleation, precipitation, agglomeration, etc.) and top-to-bottom approaches (size reduction of larger particles, e.g., via milling, ablation, etc.) (Crane and Scott 2012). The synthesis techniques, reported in the literature, usually follow the first approach, including decomposition of iron pentacarbonile [$Fe(CO)_5$] through the standard chemical vapor condensation process in organic solvents (Karlsson et al. 2005), in argon (Choi et al. 2001), or in NH_3 (Kim et al. 2003), liquid precipitation of Fe^{3+} ions via reduction in the presence of sodium borohydride ($NaBH_4$) (Wang and Zhang 1997), and hydrogen reduction of goethite ($FeOOH$) and hematite (Fe_2O_3) (Nurmi et al. 2005). Ultrasound effects during synthesis in the presence of sodium borohydride was recently considered, and had positive results in reducing the nZVI particles' size and modifying their structural form (Jamei et al. 2014).

In addition, in recent years, several authors have been developing and promoting a greener bottom-up method that involves the utilization of extract from natural products (usually leaves or peels) (Hoag et al. 2009; Machado et al. 2013). These extracts have high reductive capacities and assure the reduction of iron (III)/(II), producing nZVI. This 'green' method also enhances the stability of the nZVI through the capping action of the polyphenols present in the extract, which delays the agglomeration process and increases the reactivity and efficiency of the remediation (Hoag et al. 2009).

The typical range of primary nZVI particles, obtained through the different methods, is 10–100 nm, with a corresponding specific surface area on the order of 10–50 m^2/g (Sun et al. 2006). In aqueous dispersions of nZVI, dendritic aggregates, tens or hundreds of times larger than primary particles, are usually observed (Tiraferri et al. 2008), as a consequence of strong particle-particle interactions (Fig. 2). X-ray diffraction (XRD) analysis performed over a number of nZVI samples, synthesized at both the laboratory and industrial scales (Liu et al. 2005b), revealed that particles are composed of a core of zero valent iron and a shell of iron oxides and hydroxides, including magnetite $Fe(II)Fe(III)_2O_4$, goethite α-FeO(OH) and wustite FeO. The existence of the oxide layer does not totally inhibit iron reactivity, enabling the transfer of electrons from the Fe^0 core to the particle surface, where reactions with contaminants adsorbed on the particle's oxide shell, or in its proximity, can take place (O'Carroll et al. 2013). The composition, size and shape of the shell are significantly affected by the synthesis process. nZVI obtained from the reduction of borohydride are smaller (a few dozen nanometers), more regular and smooth in shape, and the Fe^0 structure in the core is amorphous (Liu and Lowry 2006), while particles obtained from the reduction of goethite and hematite are, as a general rule, larger (up to 100 nm), more irregularly shaped, and the core has a crystalline structure (Yan et al. 2013). Larger particles (50 nm–1 μm, approximately) are found in other commercial products (e.g., NanoFer 25 and NanoFer 25S, Nano iron, CZ), with a nominal specific surface of 20–25 m^2/g (Laumann et al. 2013). Diversity in size and shape also has an impact on nZVI reactivity and aging (Christian et al. 2008). Fresh nZVI particles are primarily composed of Fe^0, with a thin layer of oxides which increases over time. Oxidation is extremely fast in the first few days after synthesis. After the formation of the oxide shell, the Fe^0 core is partly protected from undesired reactions, and corrosion is slower (Yan et al. 2013). As a general rule, Fe^0 content ranges from 98% in fresh particles obtained through a borohydride-based process to approximately 40% in aged particles obtained via hydrogen-based reduction. Zero valent iron percentage is strongly affected by the particle size, since the thickness of the oxide layer is approximately constant regardless of the particle size (Crane and Scott 2012). Very small particles may result in higher degradation rates towards contaminants, due to the specific surface area increase, and also in more pronounced inadmissible reactions, and consequently in faster corrosion and waste of material. The impact of corrosion and aging on nZVI reactivity has been deeply revised (Yan et al. 2013).

2.2 Support and Characterization of nZVI

The high reactivity of nZVI alone is not sufficient to ensure an effective remediation, and some important issues need to be addressed for successful full-scale application. Central points are stability against aggregation, mobility in subsurface environments, and durability under subsurface conditions (Tosco et al. 2012). To be effective for remediation, iron particles should remain in suspension for a time sufficient to allow slurry preparation, handling and injection into the subsurface. Iron particles should have a sufficient mobility in the subsurface to be transported for some extent around the point of injection (Kanel et al. 2007). Studies have shown that nZVI is barely mobile and stable in both laboratory studies (Liu et al. 2005a) and field-scale tests (Quinn et al. 2005). The main reason was found in the strong tendency of nZVI particles to aggregate when dispersed in water, due to the strong magnetic attractive forces which develop among particles, thus forming big dendritic flocs, and subsequently network structures, which may widely exceed the micron. This kind of aggregate significantly limits transport by plugging the pores of the aquifer, showing reduced specific surface area, and consequently reduced reactivity (He and Zhao 2005). Another reason for further limitation of nZVI mobility, in the subsoil, is the eventual affinity between the iron particles and minerals of the soil grains, resulting in nZVI deposition onto the porous medium. Particle surface modification and the viscosity of the dispersant fluid were shown to be effective in improving both the colloidal stability and the mobility of nZVI. In order to address this issue and to improve colloidal stabilization, nZVI have been supported by adsorbents such as clays, zeolites, activated carbon, polymers, and bacterial strains. Polyelectrolyte or polymer coatings can inhibit nZVI aggregation through a combination of electrostatic and steric repulsion forces when these interactions are large enough to overcome inter-particle magnetic and van der Waals attractive forces. The nZVI colloidal stabilization by polymers has been shown to reduce the deposition of nZVI onto granular media, thus increasing its mobility, relative to that of bare nZVI (Raychoudhury et al. 2012).

Selection of the most appropriate stabilizing agent and stabilization approach for improving mobility, and consequently delivery into the subsurface, is not a straightforward process, as it depends on a number of factors. As a general rule, non-toxic, cheap and widely available polymers and carrier fluids should be selected so as to avoid any possible negative impact on the environment and to restrict the additional cost associated with their use. The presence of an adsorbed polymer is known to partly hinder nZVI reactivity, even if the effect is reversible when the polymer is removed (Phenrat et al. 2009). As a consequence, easily degradable polymers are to be preferred for nZVI stabilization (Kirschling et al. 2011).

Kerkez et al. (2014a) and Tomašević et al. (2014a) have shown that clays like bentonite (B-nZVI), kaolinite (K-nZVI) and native clay (NC-nZVI) and polymers like carboxymethyl cellulose (CMC-nZVI) have the potential to act as stabilizers and dispersants during the synthesis of supported nZVI materials (Fig. 1). Clays, as low-cost and efficient adsorbents, have great potential as an ideal support material for nZVI, due to their large specific surface area and developed mesoporous and microporous structure. Also, the use of native clay instead of commercial ones, can contribute to commercialization of the entire process. Recently, carboxymethyl cellulose (CMC) was used as a stabilizing agent for preparing iron-based nanoparticles. Ordinarily, polymers such as CMC, guar gum, chitosan and poly

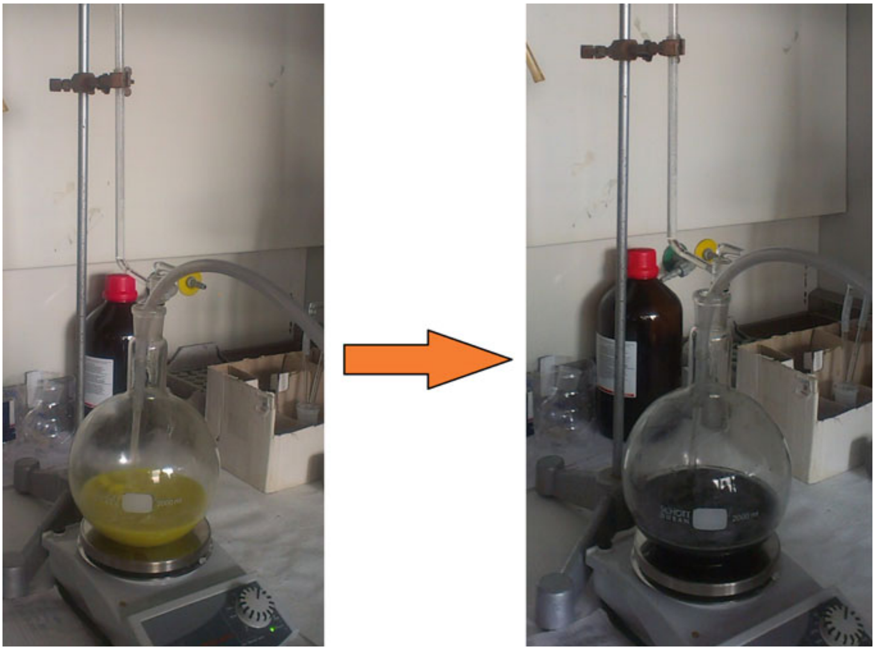

Fig. 1 Supported-nZVI synthesis using the conventional liquid-phase method of the reduction of ferric iron by borohydride

(acrylic acid) provide steric stabilization that exhibits a larger repulsion force than electrostatic repulsion, and hence, they can help to stabilize Fe^0 nanoparticles and superparamagnetic ferrofluid via carboxylate binding. CMC-stabilized nZVI exhibited better dispersity and reactivity relative to many other stabilized forms. CMC is a commercial, environmentally-friendly material that has high water solubility and biocompatibility. It is therefore predictable that we might witness booming prospects for CMC-nZVI, owing to its superior physicochemical properties (Wang et al. 2010a, b; Zhou et al. 2014).

Kerkez et al. (2014a) and Tomašević et al. (2014a) show the morphology and nanoparticle distribution of nZVI and nZVI on kaolin, bentonite, native clay and a carboxymethyl cellulose structure, analyzed using transmission electron microscopy (TEM) and a scanning electron microscope (SEM). Bare nZVI particles in the form of chain-like aggregates were observed in Fig. 2a. In comparison, as revealed in Fig. 2b–d, the nZVI particles supported on native clay, kaolinite and bentonite were clearly discrete and well dispersed in the clay carriers, without aggregation. The obtained particles are close to spherical, with a grain size ranging from 20 to 100 nm in diameter. These results showed that native clay, kaolinite and bentonite prevented the nZVI particles from aggregating together. However, it can be seen that there is a difference between average nanoparticle sizes depending on the clay used.

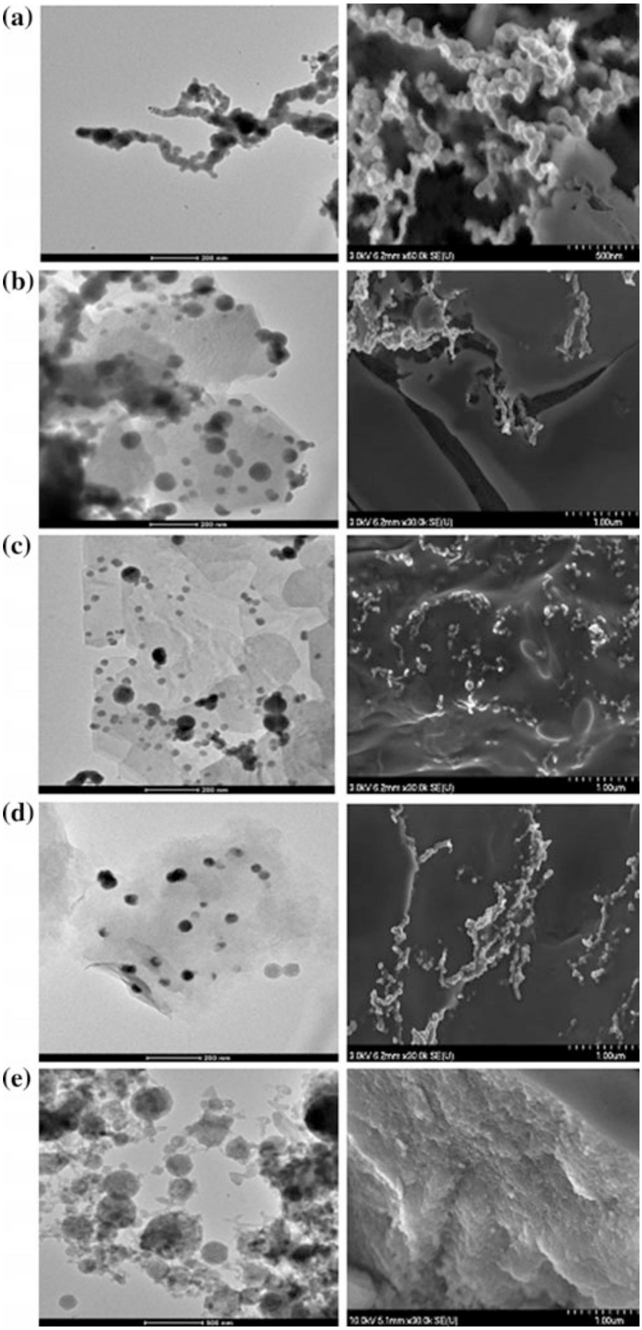

Fig. 2 **a** TEM and SEM of nZVI, **b** TEM and SEM of K-nZVI, **c** TEM and SEM of B-nZVI, **d** NC-nZVI, **e** TEM and SEM of CMC-nZVI (Kerkez et al. 2014a; Tomašević et al. 2014a, partial reprint)

Nanoparticle size decreased in a series of 80 nm > 50 nm > 30 nm when native clay, kaolin and bentonite were used to support nZVI, indicating that there is a clear link between the dispersion of synthesized nZVI particles and the BET-specific surface area and the porosity of materials used for support. Namely, bentonite had almost triple the BET-specific surface area of kaolin and native clay. From the aspect of mesopores, there is almost no difference between kaolin and bentonite, while the native clay shows the highest volume in this range (Kerkez et al. 2014a). Regarding CMC-stabilized Fe^0 nanoparticles, they also appear to be clearly discrete and well-dispersed, close to spherical in shape, and their sizes range from 20 to 250 nm in diameter (Fig. 2e).

SEM images (Fig. 2b–d) indicated that there were many nodular protrusions over the clay surface. These nodules were the in situ prepared Fe^0 particles. They were spherical in shape and distributed throughout the surface of the clays without observable aggregation, compared with bare nZVI (Fig. 2a). These observations were consistent with the explanation that the ion-exchanged Fe^{3+} were mainly located in the hexagonal prism and the sodalite cage near the surface of the clay's framework, acting as nucleuses causing the growth of Fe^0, which resulted in the production of dispersed nanoscale iron particles on the clay surface according to Wang et al. (2010a, b). Bentonite shows the most uniform nZVI particle distribution, followed by native clay and kaolin. Consequently, the presence of CMC minimized agglomeration of the resulting iron particles, and thus maintained the high surface area and potential reactivity of those particles. These results further confirmed that the presence of CMC also prevented agglomeration of the resulting Fe^0 nanoparticles, and thus maintained the high surface area and potential reactivity of those particles as well.

3 nZVI for Treating Sediment Contaminated with Metals

Rapid industrial development has greatly influenced the degradation of the environment, especially water resources, and therefore the sediment. The need for sediment analysis stems from the fact that sediment shows a strongly pronounced binding tendency, and thus represents a reservoir of toxic and persistent compounds, predominantly of anthropogenic origin. Metals show a tendency to incorporate into sediment. The sorption of heavy metals as persistent, bioaccumulative and toxic substances in sediment creates a potential environmental risk at both the local and global levels. In the case of the contaminated sediment, depending on the degree of pollution, it is sometimes necessary to conduct remediation, as disposal is not recommended in a controlled area. Selection of appropriate methods of sediment remediation depends on the specific characteristics of the given sediment, metal concentrations in the individual fractions, the concentration, and the type of pollutant to be removed, as well as the end use of the contaminated sediments. However, it is necessary to take into account the great specificities of sediment in the sample site ("site-specific") and the necessary modifications in order to include all relevant characteristics of a given place that can affect the toxicity of metals.

Nano zero valent iron can be used as the immobilization agent in the remediation treatment of dredged sediment, as well as the treatment that is performed on-site (in situ) (Tomašević et al. 2014a). nZVI particles consist entirely of zero valent iron (Fe^0), and their small particle size and high surface area make them highly reactive and extremely volatile. At large surface areas and surface reactions, as compared to a granular form, the nano particles allow for remediation of contaminants at a higher rate and with a lower generation of hazardous byproducts.

nZVI reaction to inorganic contaminants is controlled by the redox potential of the inorganic species (O'Carroll et al. 2013):

- if it is notably higher than the redox potential of Fe^0, the compound is removed by reduction and subsequent precipitation or co-precipitation;
- if it is notably lower, then the reduction is not possible, and the compound can be eliminated only via adsorption into the iron particles;
- if the redox potential is moderately higher, a conjunction of reduction and (co)precipitation could be observed.

O'Carroll et al. (2013) classified the predominant removal mechanism for the most common inorganic contaminants (mostly metals and metalloids) into the following 5 categories:

- Reduction: As, Ag, Cu, Cr, Co, Hg, Ni, U, Se, Pb, Pd, Pt.
- Adsorption: As, Ba, Cd, Cr, Co, Ni, Se, U, Pb, Zn.
- Oxidation/reoxidation: As, Se, Pb, U.
- Co-precipitation: As, Cr, Ni, Se.
- Precipitation: Cd, Co, Cu, Pb, Zn.

The reaction processes and pathways that occur on the iron surface are greatly influenced by a number of factors, namely the nZVI chemical properties and structure, the presence of contaminant species, and, in general, the hydrochemistry of the aqueous environment (pH, redox, naturally dissolved species, etc.) (Li and Farrell 2000). A deep and extensive overview on nZVI reactivity has been reported in recently published reviews by O'Carroll et al. (2013) and Yan et al. (2013).

3.1 In situ and Ex situ Sediment Remediation by Supported Nanoscale Zero-valent Iron Materials—Case Study

In this section, we will show the experimental results regarding nZVIparticle usage for both in situ and ex situ sediment remediation, as sediment polluted with toxic metals and As represents the greatest concern in the Vojvodina region (Serbia). These researches represent the basis for a pilot scale experiment installation, which would further lead to commercialization of this kind of treatment. In the research conducted, supported nano zero valent iron has been used as the immobilization agent in the remediation treatment of dredged sediment, as well as the treatment that is performed on-site (in situ) as a laboratory scale experiment.

Sediment was taken from the most ecologically-endangered sections of the Nadela watercourse, in Vojvodina (Serbia). It was characterized on the basis of the pseudo-total metal content, in which the concentration of chromium, nickel, copper, arsenic and lead represents an extreme risk to the environment, and it belongs to the fourth and last quality class according to the national regulation that lays down the criteria for assessing the quality of the sediment (Official Gazette of RS, no. 48/12). Such sediment is considered severely polluted with analyzed metals (class 4) and requires dredging, disposal in special reservoirs and, if possible, sediment clean-up measures.

Stabilization is one of the most adequate methods for reducing the availability of toxic metals in soil by transforming toxic or potentially hazardous phases into less hazardous ones (Phenrat et al. 2007).

At the moment, there is not enough data on stabilization treatments of contaminated sediments with supported nZVI, but there are some data about the stabilization of soil. For example, Kumpiene et al. (2006) examined the efficiency of Fe(0) in reducing the mobility and bioavailability of Cr, Cu, As and Zn in chromate copper arsenate (CCA)-contaminated soil. The treatment notably decreased As and Cr concentrations in soil leachates, in soil pore water and in plant shoots.

This study aims to find a better understanding of the potential for extraction of toxic metals and the effectiveness of the treatment applied. For evaluating the effectiveness of treatments, leaching tests were used. To determine the long-term behavior of ex situ-treated sediment, leaching tests were performed in accordance with an ANS 16.1 (1986) diffusion test over a period of 90 days.

Mixtures for the ex situ process were prepared by addition of 0.4, 0.8 and 1.2% nZVI supported by bentonite, kaolinite, carboxymethyl celulose and native clay, as compared to the total weight of the sediment. The treated sediment samples were prepared by mixing them with supported nanomaterial according to standard method ASTM D1557-00 and cured at 20 °C in sealed sample bags for 28 days. Samples were then put into inert plastic bags and placed in hanging plastic containers within deionized water, with the ratio of liquid/solid (L/S) 10:1 (l/kg).

The effectiveness of the stabilization treatment, according to the Canadian Agency for Environmental Protection (1991), means that LX values can be taken as a criterion for the use and disposal of stabilized treated waste. When LX values are higher than 9, treatments can be considered effective and the stabilized treated waste can be used when properly controlled, for example, in the rehabilitation of quarries, for closing a lagoon, as the basis for roads, etc. For LX values between 8 and 9, the stabilized waste can be disposed of in sanitary landfills, and for values below 8, it is considered unsuitable for disposal and stabilized treatment is considered ineffective.

It can be concluded that the investigated compounds for Cr, Cu and Pb are suitable for further, controlled use of the LX, because the values were in the range of 9.1–11.4 (Fig. 3). On the basis of the adopted criterion, all mixtures for arsenic, and mixtures of treated sediment with B-nZVI and K-nZVI for Ni with LX values

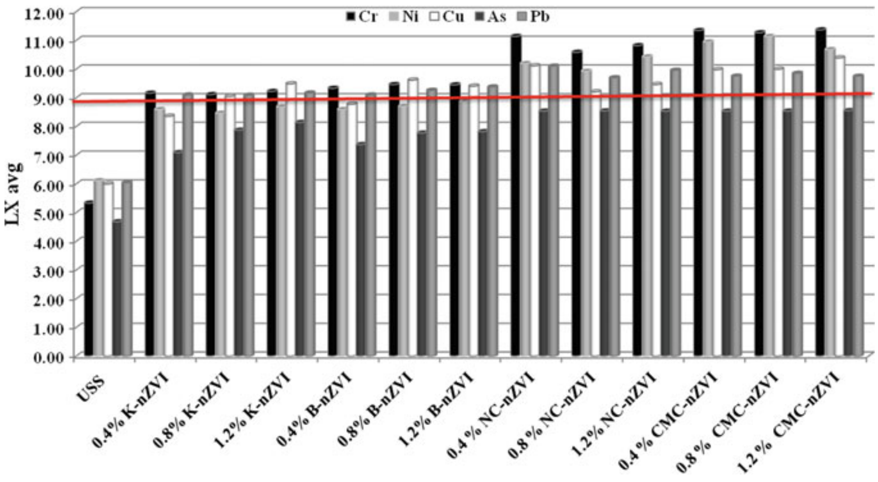

Fig. 3 Mean leachability index (LX)

less than 9, the selected treatments may be considered effective, but only if the treated wastes are about to be disposed of in segregated or sanitary landfills.

As mentioned previously, the specific removal mechanisms involved in the treatment of heavy metal contamination with nZVI depend on the standard redox potential (E^0) of the metal contaminant. Metals that have an E^0 that is more negative than, or similar to, that of Fe^0 (e.g., Zn $E^0 = -0.76$ V) are removed purely by adsorption to the iron (hydr)oxide shell. Metals with E^0 that is much more positive than Fe^0 (e.g., As $E^0 = 0.24$ V) are preferentially removed through reduction and precipitation. Metals with slightly more positive E^0 than Fe^0 (e.g., Pb $E^0 = -0.13$ V) can be removed through both reduction and adsorption. Oxidation and co-precipitation by iron oxides are the other possible reaction mechanisms, depending upon the predominant geochemical conditions, such as Eh, pH and initial concentration and speciation of the contaminant metals.

Lower immobilization with supported nZVI can be justified with a high reactivity and difficulty in handling this material in an ex situ treatment.

Simulation of in situ conditions was carried out by injection of nanomaterial into small vessels with 750 g of contaminated sediment. After injection of the nanomaterials, with mixing of the sediment, a complete distribution of nanomaterials in the sediment was performed (Tomašević et al. 2014b).

The use of zero valent iron (Fe^0) in the in situ remediation technique is currently undergoing evaluation. The basic mechanism for removal, as originally suggested, involves the reduction of metal contaminants, and then their subsequent precipitation of insoluble forms. These processes are accompanied by the oxidation of nano zero valent iron. The ability of B-nZVI, K-nZVI, NC-nZVI and CMC-nZVI to remove metal ions from the sediment is presented in Fig. 4, and it shows a significant change in the percentage of metals removed (As, Cu, Ni, Cr, Pb) after 4 weeks.

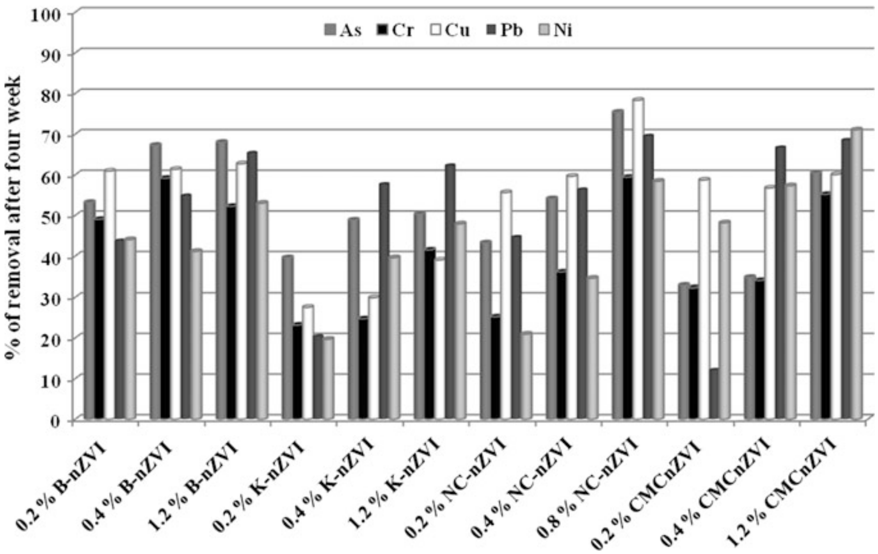

Fig. 4 Percentage of metals removed from the mixture of sediment and K-nZVI, B-nZVI, NC-nZVI and CMC-nZVI (%) after 4 weeks

If we observe the percentage of metals removed as a criterion of the treatment's efficiency, then the in situ laboratory sediment treatment with the nZVI stabilized with kaolinite, bentonite, native clay and carboxymethil cellulose as immobilization agents proved to be very effective in the case of all metals. From Fig. 4, it can be concluded that with increasing amounts of nanomaterials, metal concentration decreases. If we use the metal concentration removal as a criterion of the treatment's efficiency and compare it with the values for assessing the quality of sediments by national legislation (Official Gazette of RS, no. 48/12), then the sediment treated with nanomaterials proved to be very effective in the case when the higher percentage of immobilization agent is added. In this case, all metals tested, when the highest percentage of nanomaterial was added, met the target values for which metal concentrations below these values show a negligible adverse impact on the environment.

Results also showed better As removal, which is probably due to adsorption of both As^{3+} and As^{5+} by iron nanoparticles that occurs through the formation of inner-sphere complexes with the (hydr)oxide shell of nZVI, as decribed in Kanel et al. (2007). Furthermore, good results regarding Pb indicate that Pb^{2+} reacts with nZVI, precipitating as $Pb(OH)_2$ and oxidizing as α-PbO_2, according to Lien and Zhang (2007).

Based on the above findings, the in situ treatment in the laboratory proved to be very effective, providing the choice of optimal doses of nanomaterials towards the concentration of toxic metals in the sediment.

When applying a nanomaterial, as the immobilization agent in sediment treatment, using two remediation options (ex situ and in situ), a high stability of the metals was achieved in the treated sediment.

4 nZVI for Treating Coloured Waste Water

Dyes can be considered important sources of water pollution and their degradation products may be carcinogenic and toxic to mammals. The estimation is that about 15% of total dye production is lost and discharged in the effluent created during dye production and the dyeing process. The remediation of colored wastewater is complex, because dyes are stable organic molecules due to their conjugated electron systems. Dyes can remain in an aqueous medium for a long time, affecting photosynthetic processes (Debrassi et al. 2012). Furthermore, some dyes, together with their precursors and degradation products, are also toxic and carcinogenic (Chen et al. 2013). Azo dyes are the main group (60–70%) of dyes applied in textile processing and are considered to be recalcitrant, non-biodegradable and persistent (Fu et al. 2010; Al-Amrani et al. 2014). Several supported nanomaterials have been used for the removal of these organic molecules from aqueous solutions. A great deal of interest has developed in the degradation of dyes by nZVI particles, as they are inexpensive, environmentally-friendly, and easy to operate, and the low iron concentration in their effluent results in no further treatment demands (Chang et al. 2006; Sun et al. 2009). In most studies, the sole nZVI or supported nZVI was used for the effluent treatment, and the main mechanism was the reductive degradation of the dye molecule (Eq. (1)). More recently, nZVI has been widely applied for wastewater treatment and organic compound degradation in the Fenton system (Choi and Lee 2012). Under acidic conditions, the surface of the nZVI corrodes and generates in situ ferrous ions, which leads to Fenton reactions in the presence of hydrogen peroxide (Eqs. (2), (3) and (4)). The nZVI surface can then reduce the ferric ions down to ferrous ions, and faster recycling of ferric iron at the iron surface occurs through Eq. (5) (Fu et al. 2010). This process is called the advanced Fenton process (AFP) (Namkung et al. 2008).

$$\mathrm{Fe}^0 \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^- \tag{1}$$

$$\mathrm{Fe}^0 + 2\mathrm{H}^+ \rightarrow \mathrm{Fe}^{2+} + \mathrm{H}_2 \tag{2}$$

$$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+} + \mathrm{HO}^\bullet + \mathrm{HO}^- \tag{3}$$

$$\mathrm{HO}^\bullet + \mathrm{dye} \rightarrow \text{oxidized dye} + \mathrm{H}_2\mathrm{O} \tag{4}$$

$$2\mathrm{Fe}^{3+} + \mathrm{Fe}^0 \rightarrow 3\mathrm{Fe}^{2+} \tag{5}$$

Thus far, experiments for the removal of several dyestuffs have been conducted in batch techniques using synthetic aqueous solutions. However, an important factor is the use of these nanocomposites in more realistic scenarios, including in the presence of a mixture of organic, inorganic, and biological pollutants. In this context, Chen et al. (2011, 2013) performed experiments with wastewater from a textile printing and dyeing company in China. After treatment with a bentonite–nZVI composite, the removal efficiency of methyl orange was 99.75%, while use of a kaolinite–nZVI composite created a removal efficiency of crystal violet of 99.95%.

4.1 Supported Nanoscale Zero-valent Iron Materials for Dye Degradation—Case Study

In this section, we will show the experimental results regarding the use of nZVI particles for treatment of wastewaters containing the dyes Rosso Zetanyl B-NG (RZ B-NG), Reactive Red 120 (RR120), both belonging to the largest group of azo dyes, and Reactive Blue 4 (RB4), an anthraquinone dye. These dyes were chosen for the study because azo and anthraquinone dyes are extensively used in the textile industry in Serbia. Large amounts of textile wastewater containing dyes are discharged into the environment without any kind of treatment, so the investigation for the optimal treatment technique is necessary. Treatments of different synthetic solutions containing the chosen dye molecules were performed with nZVI, K-nZVI, NC-nZVI, B-nZVI and CMC-nZVI. Reductive degradation and the Fenton system were chosen as the main mechanisms for synthetic dye solution decolourization.

Under established optimal conditions, the investigation also included mineralization efficiency testing. Furthermore, the application of supported-nZVI on a real textile industry effluent was performed to indicate the possible commercialization of the entire process.

General conclusions regarding decolourization experiments on synthetic solutions can be drawn from the collective research. Namely, the decolourization efficacy when using supported nZVI for synthetic dye solutions is distinctly higher compared to the sole use of nZVI, indicating that the presence of support materials caused dispersion and stabilization of nZVI particles, leading to enhanced reactivity of the supported-nZVI. Also, when the heterogeneous Fenton system was employed, the decolourization rates achieved were enhanced, indicating that this process is superior to reductive degradation and fully applicable regardless of the dye molecule structure (Fig. 5).

During further investigation of the Fenton process with the use of supported nZVIs, optimization of process variables was performed, such as: nanomaterial dosage, H_2O_2 concentration, solution pH, initial dye concentration and reaction kinetics.

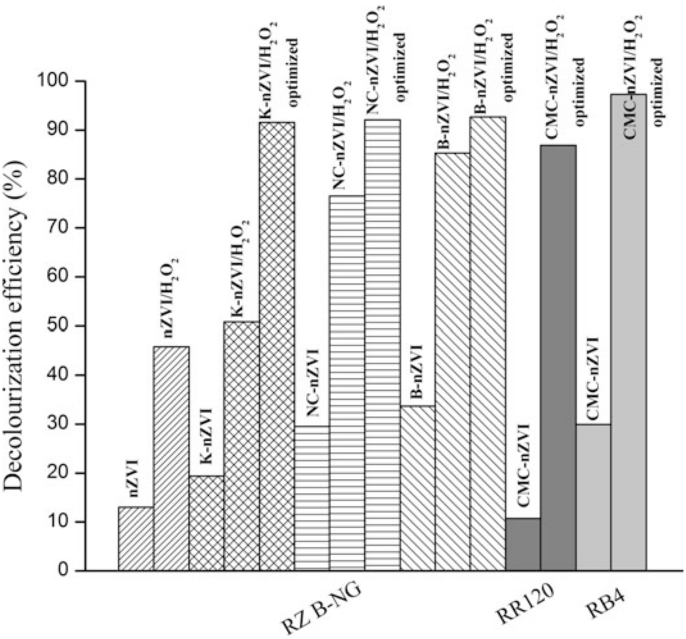

Fig. 5 Decolourization efficiencies of RZ B-NG, RR120 and RB4 in different reaction systems using supported-nZVI

Optimization indicated that the investigated parameters greatly influenced the efficacy of the process. In addition, a relatively uniform influence of the variation of investigated parameters on dye decolourization was established (Kerkez et al. 2014a, b).

To justify usage of the supported-nZVI/H_2O_2 processes, the mineralization efficiency was further investigated by measuring the total organic carbon (TOC) removal rate under previously established optimal conditions for each material. During the Fenton process, solution decolourization is caused by the destruction of the chromophore groups of dye molecules, while the removal of the TOC depends on the degree of color mineralization. The mineralization efficiency after approximately 60 min is about 50% TOC reduction, which represents satisfactory levels when compared to similar research (Fu et al. 2010; Duarte et al. 2013; Yu et al. 2014). The reduction in TOC values is primarily attributed to the fragmentation of highly-complex structures of dye molecules on relatively simpler organic fragments, such as carboxylic acids, aldehydes, ketones, alcohols, etc. As a result, the intermediate products of dye degradation are difficult to oxidize, and the complete oxidation may proceed for a longer time.

In addition, several experiments were performed on a real textile industry effluent containing the dyes investigated (Fig. 6).

Both the decolourization and mineralization efficiencies were lower in comparison to synthetic dye solutions. Namely, textile wastewater composition can

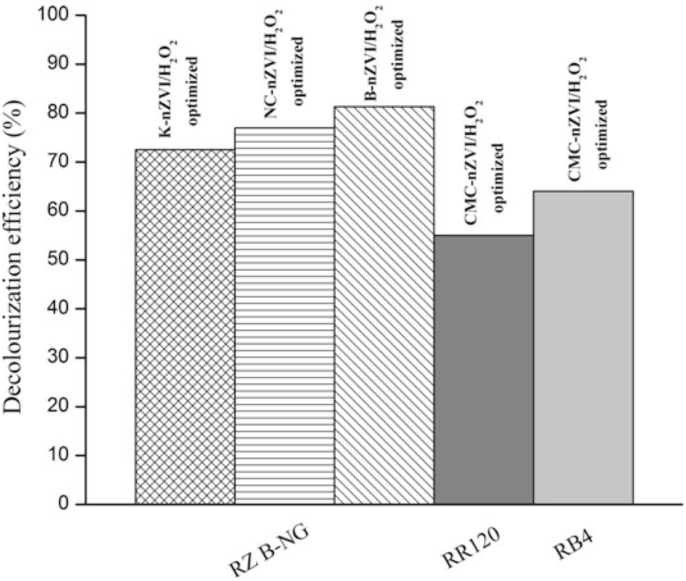

Fig. 6 Decolourization efficiencies of a real textile industry effluent containing the dyes investigated under the optimal conditions in a supported nZVI/H_2O_2 system

greatly influence the advanced oxidation processes (Guimarães et al. 2012; Babuponnusami and Muthukumar 2014; Liu et al. 2014), due to its complex composition. The composition of the effluents tested, beside the dyes, included: NH_3 ~ 5 mgN/l, NO_3^- ~ 0.1 mgN/l, NO_2^- ~ 0.02 mgN/l, Total P ~ 1.05 mgP/l, anionic detergents ~ 0.5 mg/l, alkalinity ~ 40 mval/l, etc. Additionally, the conductivity of textile industry effluents was approximately 1000 µS/cm, much higher compared to the conductivity of synthetic solutions (roughly 20 µS/cm). Therefore, certain inorganic ions found at high concentrations in textile wastewater can affect the process and have an inhibiting effect. They can act as hydroxyl radical scavengers and compete for active sites. Therefore, it is assumed that such results are the consequence of the presence of various inorganic ions, and also other organic species in the raw textile effluent, which together form a complex matrix that is more challenging to treat.

5 Conclusion and Further Challenges in Using Nano Zero Valent Iron in Environmental Protection

This chapter has highlighted the fact that environmental nanotechnology, with an emphasis on iron-based-nanoparticles, is considered to play a key role in the shaping of current environmental engineering and science. An overview of the most recent researches indicated that nZVI have great potential to remediate all sorts of contaminants, regardless of the matrix in which they are implemented. Furthermore, supporting nZVI particles with different kinds of material, such as clays and polymers, overcame the problem of aggregation and reactivity loss, enhancing their applicability. Findings from case studies showed that there is no obstacle to using the same supported nZVI for treating different environmental mediums and various chemical species. Nevertheless, there are still issues that must be given special attention, mainly regarding the commercialization of these materials for remediation purposes. Challenges such as cost, on-site synthesis, and possible collection and recuperation from the environment need further investigation. Furthermore, a careful weighing of the opportunities and risks of nanotechnology with respect to their effects on the environment is needed in order to achieve sustainable water, soil and air quality improvement.

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References

Al-Amrani WA, Lim PE, Seng CE, Ngah WSW (2014) Factors affecting bio-decolorization of azo dyes and COD removal in anoxic–aerobic REACT operated sequencing batch reactor. J Taiwan Inst Chem Eng 45:609–616

ANS (American National Standard) ANSI/ANS 16.1 (1986) American National Standard for the measurement of the leachability of solidified low-level radioactive wastes by short-term tests procedures. American National Standards Institute, New York

ASTM D1557-00 Standard test method for laboratory compaction characteristics of soil using modified effort American Society for Testing Materials. Annual book of ASTM standards: ASTMD1557-91, vol 4.08. ASTM, Philadelphia

Babuponnusami A, Muthukumar K (2014) A review on Fenton and improvements to the Fenton process for wastewater treatment. J Environ Chem Eng 2(1):557–572

Chang MC, Shu HY, Yu HH (2006) An integrated technique using zero-valent iron and UV/H_2O_2 sequential process for complete decolorization and mineralization of C.I. Acid Black 24 wastewater. J Hazard Mater 138:574–581

Chen Z, Jin X, Chen Z, Megharaj M, Naidu R (2011) Removal of methyl orange from aqueous solution using bentonite-supported nanoscale zero-valent iron. J Colloid Interface Sci 363: 601–607

Chen Z, Wang T, Jin X, Chen Z, Megharaj M, Naidu R (2013) Multifunctional kaolinite-supported nanoscale zero-valent iron used for the adsorption and degradation of crystal violet in aqueous solution. J Colloid Interface Sci 398:59–66

Choi K, Lee W (2012) Enhanced degradation of trichloroethylene in nano-scale zero valent iron Fenton system with Cu(II). J Hazard Mater 211–212:146–153

Choi CJ, Dong XL, Kim BK (2001) Microstructure and magnetic properties of Fe nanoparticles synthesized by chemical vapor condensation. Mater Trans 42(10):2046–2049

Christian P, Kammer F, Baalousha M, Hofmann T (2008) Nanoparticles: structure, properties, preparation and behaviour in environmental media. Ecotoxicology 17(5):326–343

Crane RA, Scott TB (2012) Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. J Hazard Mater 211–212:112–125

Debrassi A, Correa AF, Baccarin T, Nedelko N, Slawska-Waniewska A, Sobczak K, Dłuzewski P, Greneche JM, Rodrigues CA (2012) Removal of cationic dyes from aqueous solutions using N-benzyl-O-carboxymethyl chitosan magnetic nanoparticles. Chem Eng J 183:284–293

Duarte F, Morais V, Maldonado-Hódar FJ, Madeira LM (2013) Treatment of textile effluents by the heterogeneous Fenton process in a continuous packed-bed reactor using Fe/activated carbon as catalyst. Chem Eng J 232:34–41

Environment Canada (1991) Proposed evaluation protocol for cement-based solidified wastes, Environmental Protection Series. Report No. EPS 3/HA/9

Feng C, Khulbe KC, Matsuura T, Tabe S, Ismail AF (2013) Preparation and characterization of electro-spun nanofiber membranes and their possible applications in water treatment. Sep Purif Technol 102:118–135

Fu F, Wang Q, Tang B (2010) Effective degradation of C.I. Acid Red 73 by advanced Fenton process. J Hazard Mater 174:17–22

Fu F, Han W, Tang B, Hu M, Cheng Z (2013) Insights into environmental remediation of heavy metal and organic pollutants: simultaneous removal of hexavalent chromium and dye from wastewater by zero-valent iron with ligand-enhanced reactivity. Chem Eng J 232:534–540

Guimarães JR, Maniero MG, Nogueira de Araújo R (2012) A comparative study on the degradation of RB-19 dye in an aqueous medium by advanced oxidation processes. J Environ Manage 110:33–39

Gupta VK, Kumar R, Nayak A, Saleh TA, Barakat MA (2013) Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. Adv Colloid Interface Sci 193–194:24–34

He F, Zhao D (2005) Preparation and characterization of a new class of starch stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water. Environ Sci Technol 39:3314–3320

Hoag GE, Collins JB, Holcomb JL, Hoag JR, Nadagouda MN, Varma RS (2009) Degradation of bromothymol blue by 'greener' nano-scale zero-valent iron synthesized using tea polyphenols. J Mater Chem 19:8671–8677

Hua M, Zhang S, Pan B, Zhang W, Lv L, Zhang Q (2012) Heavy metal removal from water/wastewater by nanosized metal oxides: a review. J Hazard Mater 211–212:317–331

Jamei MR, Khosravi MR, Anvaripour B (2014) A novel ultrasound assisted method in synthesis of NZVI particles. Ultrason Sonochem 21(1):226–233

Kanel SR, Nepal D, Manning B, Choi H (2007) Transport of surface-modified iron nanoparticle in porous media and application to arsenic(III) remediation. J Nanopart Res 9(5):725–735

Karlsson MNA, Deppert K, Wacaser BA, Karlsson LS, Malm JO (2005) Size controlled nanoparticles by thermal cracking of iron pentacarbonyl. Appl Phys A Mater Sci Process 80(7):1579–1583

Kerkez D, Tomašević D, Kozma G, Bečelić-Tomin M, Prica M, Rončević S, Kukovecz Á, Dalmacija D, Kónya Z (2014a) Three different clay-supported nanoscale zero-valent iron materials for industrial azo dye degradation: a comparative study. J Taiwan Inst Chem Eng 45:2451–2461

Kerkez Đ, Bečelić-Tomin M, Prica M, Tomašević D, Pucar G, Dalmacija B, Rončević S (2014b) Decolourization of Reactive Red 120 by an advanced Fenton process in conjunction with ultrasound. Paper presented on International symposium on graphic engineering and design "GRID2014", November 13–14, Novi Sad, Serbia

Kim TS, Sun W, Choi CJ, Lee BT (2003) Microstructure of Fe nanoparticles fabricated by chemical vapor condensation. Rev Adv Mater Sci 5(5):481–486

Kim SA, Kamala-Kannan S, Lee KJ, Park YJ, Shea PJ, Lee WH, Kim HM, Oh BT (2013) Removal of Pb(II) from aqueous solution by a zeolite-nanoscale zero-valent iron composite. Chem Eng J 217:54–60

Kirschling TL, Golas PL, Unrine JM, Matyjaszewski K, Gregory KB, Lowry GV, Tilton RD (2011) Microbial bioavailability of covalently bound polymer coatings on model engineered nanomaterials. Environ Sci Technol 45(12):5253–5259

Kumpiene J, Ore S, Renella G, Mench M, Lagerkvist A, Maurice C (2006) Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil. Environ Pollut 144:62–69

Laumann S, Micic V, Lowry GV, Hofmann T (2013) Carbonate minerals in porous media decrease mobility of polyacrylic acid modified zero-valent iron nanoparticles used for groundwater remediation. Environ Pollut 179:53–60

Li T, Farrell J (2000) Reductive dechlorination of trichloroethene and carbon tetrachloride using iron and palladized-iron cathodes. Environ Sci Technol 34(1):173–179

Li Y, Li J, Zhang Y (2012) Mechanism insights into enhanced Cr(VI) removal using nano scale zero valent iron supported on the pillared bentonite by macroscopic and spectroscopic studies. J Hazard Mater 227–228:211–218

Lien HL, Zhang WX (2007) Nanoscale Pd/Fe bimetallic particles: catalytic effects of palladium on hydrodechlorination. Appl Catal B: Environ 77:110–116

Liu Y, Lowry GV (2006) Effect of particle age (Fe^0 content) and solution pH on NZVI reactivity: H_2 evolution and TCE dechlorination. Environ Sci Technol 40(19):6085–6090

Liu YQ, Choi H, Dionysiou D, Lowry GV (2005a) Trichloroethene hydrodechlorination in water by highly disordered monometallic nano iron. Chem Mater 17(21):5315–5322. doi:10.1021/Cm0511217

Liu YQ, Majetich SA, Tilton RD, Sholl DS, Lowry GV (2005b) TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. Environ Sci Technol 39(5):1338–1345

Liu H, Chen T, Zou X, Xie Q, Qing C, Chen D, Frost RL (2013) Removal of phosphorus using NZVI derived from reducing natural goethite. Chem Eng J 234:80–87

Liu X, Wang F, Chen Z, Megharaj M, Naidu R (2014) Heterogeneous Fenton oxidation of Direct Black G in dye effluent using functional kaolin-supported nanoscale zero iron. Environ Sci Pollut Res 21:1936–1943

Luo S, Qin P, Shao J, Peng L, Zeng Q, Gu JD (2013) Synthesis of reactive nano scale zero valent iron using rectorite supports and its application for Orange II removal. Chem Eng J 223:1–7

Machado S, Pinto SL, Grosso JP, Nouws HPA, Albergaria JT, Delerue-Matos C (2013) Green production of zero-valent iron nanoparticles using tree leaf extracts. Sci Total Environ 445–446:1–8

Namkung KC, Burgess AE, Bremner DH, Staines H (2008) Advanced Fenton processing of aqueous phenol solutions: a continuous system study including sonication effects. Ultrason Sonochem 15:171–176

Nurmi JT, Tratnyek PG, Sarathy V, Baer DR, Amonette JE, Pecher K, Wang CM, Linehan JC, Matson DW, Penn RL, Driessen MD (2005) Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry, and kinetics. Environ Sci Technol 39(5):1221–1230. doi:10.1021/Es049190u

O'Carroll D, Sleep B, Krol M, Boparai H, Kocur C (2013) Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. Adv Water Resour 51:104–122

Official Gazette of RS, 67 (2011) and 48 (2012) Regulation on limit values of pollutants in water and deadlines for their achievement

Park H, Park Y, Kim W, Choi W (2013) Surface modification of TiO_2 photocatalyst for environmental applications. J Photochem Photobiol, C 15:1–20

Phenrat T, Marhaba T, Rachakornkij M (2007) XRD and unconfined compressive strength study for a qualitative examination of calcium–arsenic compounds retardation of cement hydration in solidified/stabilized arsenic–iron hydroxide sludge. J Environ Eng-ASCE 133:595–607

Phenrat T, Liu Y, Tilton RD, Lowry GV (2009) Adsorbed polyelectrolyte coatings decrease Fe^0 nanoparticle reactivity with TCE in water: conceptual model and mechanisms. Environ Sci Technol 43(5):1507–1514

Quinn J, Geiger C, Clausen C, Brooks K, Coon C, O'Hara S, Krug T, Major D, Yoon WS, Gavaskar A, Holdsworth T (2005) Field demonstration of DNAPL dehalogenation using emulsified zero-valent iron. Environ Sci Technol 39(5):1309–1318

Raychoudhury T, Tufenkji N, Ghoshal S (2012) Aggregation and deposition kinetics of carboxymethyl cellulose-modified zero-valent iron nanoparticles in porous media. Water Res 46(6):1735–1744

Ruiz-Hitzky E, Darder M, Fernandes FM, Wicklein B, Alcântara ACS, Aranda P (2013) Fibrous clays based bionanocomposites. Prog Polym Sci 38:1392–1414

Sánchez A, Recillas S, Font X, Casals E, González E, Puntes V (2011) Ecotoxicity of, and remediation with, engineered inorganic nanoparticles in the environment. Trends Anal Chem 30(3):507–516

Shukla SK, Mishra AK, Arotiba OA, Mamba BB (2013) Chitosan-based nano-materials: a state-of-the-art review. Int J Biol Macromol 59:46–58

Singh S, Mahalingam H, Singh PK (2013) Polymer-supported titanium dioxide photo catalysts for environmental remediation: a review. Appl Catal A: Gen 462–463:178–195

Sun YP, Li XQ, Cao J, Zhang WX, Wang HP (2006) Characterization of zero valent iron nanoparticles. Adv Colloid Interface Sci 120(1–3):4–56

Sun SP, Li CJ, Sun JH, Shi SH, Fan MH, Zhou Q (2009) Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: effect of system parameters and kinetic study. J Hazard Mater 161:1052–1057

Tang SCN, Lo IMC (2013) Magnetic nanoparticles: essential factors for sustainable environmental applications. Water Res 47:2613–2632

Tiraferri A, Chen KL, Sethi R, Elimelech M (2008) Reduced aggregation and sedimentation of zero-valent iron nanoparticles in the presence of guar gum. J Colloid Interface Sci 324(1–2):71–79

Tomašević DD, Kozma G, DV Kerkez, Dalmacija BD, Dalmacija MB, Bečelić-Tomin MR, Kukovecz A, Konya Z, Rončević S (2014a) Toxic metal immobilization in contaminated sediment using bentonite- and kaolinite-supported nano zero-valent iron. J Nanopart Res 16:2548

Tomašević D, Dalmacija M†, Kerkez D, Bečelić-Tomin M, Dalmacija B, Rončević S, Maletić S (2014b) In situ remediation of toxic metal contaminated sediment using kaolinite supported nZVI. Paper presented at the 4th meeting of new remediation technologies "Remediation 2014", 12–14 May, Zrenjanin, Serbia

Tosco T, Coisson M, Xue D, Sethi R (2012) Zero valent iron nanoparticles for groundwater remediation: surface and magnetic properties, colloidal stability, and perspectives for field application. In: Chiolerio A, Allia P (eds) Nanoparticles featuring electromagnetic properties: from science to engineering. Res Signpost, Kerala, pp 201–223

Tosco T, Papini MP, Viggi CC, Sethi R (2013) Nanoscale zero valent iron particles for groundwater remediation: a review. J Clean Prod 77:10–21

Udom I, Ram MK, Stefanakos EK, Hepp AF, Goswami DY (2013) One dimensional-ZnO nanostructures: synthesis, properties and environmental applications. Mater Sci Semicond Process 16:2070–2083

Wang CB, Zhang WX (1997) Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. Environ Sci Technol 31(7):2154–2156

Wang Q, Qian H, Yang Y, Zhang Z, Naman C, Xu X (2010a) Reduction of hexavalent chromium by carboxymethyl cellulose-stabilized zero-valent iron nanoparticles. J Contam Hydrol 114(1–4):35–42

Wang W, Zhou M, Mao Q, Yue J, Wang X (2010b) Novel NaY zeolite-supported nanoscale zero-valent iron as an efficient heterogeneous Fenton catalyst. Catal Commun 11:937–941

Wang S, Sun H, Ang HM, Tadé MO (2013) Adsorptive remediation of environmental pollutants using novel graphene-based nanomaterials. Chem Eng J 226:336–347

Wu D, Shen Y, Ding A, Mahmood Q, Liu S, Tu Q (2013) Effects of nanoscale zero-valent iron particles on biological nitrogen and phosphorus removal and microorganisms in activated sludge. J Hazard Mater 262:649–655

Xu P, Zeng GM, Huang DL, Feng CL, Hu S, Zhao MH, Lai C, Wei Z, Huang C, Xie GX, Liu ZF (2012) Use of iron oxide nanomaterials in wastewater treatment: a review. Sci Total Environ 424:1–10

Yan W, Lien HL, Koel BE, Zhang WX (2013) Iron nanoparticles for environmental clean-up: recent developments and future outlook. Environ Sci: Process Impacts 15(1):63–77. doi:10.1039/c2em30691c

Yu R, Chen H, Cheng W, Lin Y, Huang C (2014) Monitoring of ORP, pH and DO in heterogeneous Fenton oxidation using nZVI as a catalyst for the treatment of azo-dye textile wastewater. J Taiwan Inst Chem Eng 45(3):947–954

Zhang Y, Li Y, Li J, Sheng G, Zhang Y, Zheng X (2012) Enhanced Cr(VI) removal by using the mixture of pillared bentonite and zero-valent iron. Chem Eng J 185–186:243–249

Zhang M, Bacik DB, Roberts CB, Zhao D (2013) Catalytic hydro dechlorination of trichloroethylene in water with supported CMC-stabilized palladium nanoparticles. Water Res 47:3706–3715

Zhao X, Lv L, Pan B, Zhang W, Zhang S, Zhang Q (2011) Polymer-supported nanocomposites for environmental application: a review. Chem Eng J 170:381–394

Zhou L, Thanh TL, Gong J, Kim JH, Kim EJ, Chang YS (2014) Carboxymethyl cellulose coating decreases toxicity and oxidizing capacity of nanoscale zero valent iron. Chemosphere 104:155–161

Development of New Composites Made of Waste Materials for Wood Pallet Element

Fatima Zivic, Nenad Grujovic, Dragan Adamovic and Dejan Divac

Abstract The recycling of waste products and its further use for new products is of the utmost importance nowadays. The quantities of waste product originating from industries involving plastics, paper, wood, textile and metal foils, such as the related automotive, paper, wood and food industries, represent extremely large numbers, strongly indicating the need for efficient waste management. On the other side of things, companies are always looking for ways to lower material costs. The combination of different waste materials can be used for production of new composite materials. This paper will present a brief overview of existing possibilities in the development of new composites completely made of waste materials, as well as further research directions. A preliminary study of material combinations that can provide a composite aimed at load bearing applications is given, for the purpose of replacing elements such as wood blocks in transport pallets. Several combinations of waste material from different industries were studied in a composite structure: paper, cardboard boxes, tetra-pak containers, expanded polystyrene (styrofoam), polyurethane (PU) foam, artificial leather, textile, wood chips and dust. Preliminary compressive tests were performed. The results indicated unsuitable combinations, but also some that provided a stable compact composite which endured high compressive loads. An important result is that such a composite can be made without adding any adhesives. Waste materials from different industries can be efficiently used for new composites, and further study of this is clearly needed.

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1 Introduction

As a result of increasing environmental pollution and the health risks associated with it, as well as the questionable sustainability of many products and technologies used today, the circular economy, green production and green products have emerged recently as a significant model for support in overcoming these issues. Environmental sustainability has become a necessity in order to preserve life on the planet. Many new classes of industrial biomaterial have been studied, aimed at preventing or minimizing pollution and/or reducing waste. It is not easy to provide materials and environmentally-friendly green products, since this was not a consideration within traditional technologies and products for the vast majority of the time since societies began to become industrialized. Existing production technologies and materials are well-established, and their total costs are usually the lowest possible with well-defined properties for the final product. Numerous articles can be found in the scientific literature pertaining to green products and environmental sustainability from different economic or material and production aspects (de Medeiros and Ribeiro 2017; Zhang et al. 2017; Väisänen et al. 2016; Faruk et al. 2014; De Paola et al 2013; Pickering et al. 2016; Gurunathan et al. 2015; Pereira et al. 2015; Linke et al. 2012; Satyanarayana et al. 2009).

Waste management has become a necessity nowadays. and many different research groups are in the process of studying its various aspects (Vivekanandhan et al. 2017; Vermeulen et al. 2011; Williams 2013; Ignatyev et al. 2014; Miller et al. 2014; Väisänen et al. 2016). The amounts of waste produced by numerous industries are huge, with the plastic, paper, automotive, and food industries being some of the worst contributors to environmental pollution. There is wide interest in determining methods for sorting out the waste in such a way as to enable its further utilization. The possible practical use of recycled waste materials is beneficial from many other aspects as well. Recycled paper for notebooks, newspapers or other printed materials is perhaps the best known example. There are several issues related to the use of waste materials, starting from the adequate technologies for sorting and separation, followed by cutting, shredding, milling, melting or otherwise fragmenting the materials into particulate, fiber, small piece or liquid forms, which can be further used as raw materials for some other purpose. Additionally, national and international legislative regulations and economic drivers impose certain boundaries on strategies related to waste management (Triguero et al. 2016; Pires et al. 2011; Forton et al. 2006; Pati et al. 2006). Composite materials made of recycled waste have been recognized as representing valuable new materials that will provide high added value, even in cases when only a part of the constituting composite components are made of waste materials. New research results have even shown possibilities for producing carbon nanotubes from renewable resources (Vivekanandhan et al. 2017).

Very rough and approximate estimates of existing quantities of waste material throughout the world showed that around 300 million tons of plastic were used in 2015 alone, according to plastic-pollution.org. Use of paper has increased, even with the growth of online communication tools and e-documents, and the paper industry foresees a doubling of its spending on raw materials, with estimates of up to 500 million tons of paper to be produced in 2020. 50% of all waste originating from companies is some form of paper waste, as well as 25% of landfill pollution and 33% of city pollution. The wood industry generates around 5 million tons of waste per year in the UK alone, out of which around 2.3 million tons is recycled. The food industry, and the food packaging subindustry within it, generates around an $11.4 billion value in just used food vessels and containers, as estimated from the production data of only the seven largest producers of food and beverages. In 2007, more than 137 billion products were sold in tetra-pak containers around the world (Korkmaz et al. 2009). The latest data from just one large international Tetra Pak company indicates more than 10 billion fabricated packages, a number supported by the fact that many foods previously sold in cans or jars are subsequently transferred into tetra-pak containers and carton packages.

The waste resulting from the automotive industry is very significant, with an additional issue in this area being that waste materials from this sector are very diverse in their nature and form, comprising scrap metal, textile, rubber, plastics, glasses and others, most of which go directly into landfills, after shredding (Miller et al. 2014; Zorpas and Inglezakis 2012; Vermeulen et al. 2011; Morselli et al. 2010; Forton et al. 2006). The largest number of vehicles is produced in the EU, with around 30% of the world's production, around 15 million cars, produced each year, resulting in around 2–2.5 million tons per year of shredded waste or 10% of the entire dangerous waste generated in the EU (Zorpas and Inglezakis 2012). The most significant part of automotive waste is related to that generated after the end of the functional life of the vehicles, or the changing of damaged and/or failed parts, especially tires (Williams 2013). A large amount of waste is made of different polymers (e.g., polyurethane foam). Waste materials resulting from old or damaged cars are contaminated with different residues, such as oils. However, very large quantities of clean waste are also generated during the process of vehicle production that cannot be directly reused in a production process. For example, during the production of car seats, large amounts of textile and plastic foam are wasted after the cutting of desired shapes to be used in a new car. It is estimated that in the UK automotive industry alone, around 40% of such shredded waste can be efficiently recycled and used again (Forton et al. 2006). The recycling of polymers is important in general, with degradable plastics being one of the hottest topics today (Ignatyev et al. 2014), and the recycling of plastics originating from the automotive industries has also been given serious consideration (Miller et al. 2014). Waste management has become a potentially very profitable area, with significant opportunities for small and medium enterprises (SMEs), especially considering the fact that companies which can further utilize these materials can get them at almost no cost, or even get paid to collect it from the sites.

Wood waste is produced in numerous sectors, including off-cuts from untreated raw wood, as well as processed wood products and a number of different post-consumer types of waste. Almost all companies (manufacturers, warehouses, markets, hospitals, hotels, etc.) produce some wood waste, such as disposed pallets after delivery of transported products. Also, paper production is closely related to the wood industry, since it involves wood processing at one phase of the paper manufacturing process. Generally, all paper products can be recycled, including used newspapers, glossy magazines, office papers and cardboard. Several other waste categories can also be fully recycled, especially if they are clean and untainted by certain industrial pollutants (e.g., oil), such as fabrics, textiles, cloth, some types of plastic, glass bottles and jars, aluminium foils in packaging, cans, etc. The total cost of recycled waste comprises several general categories: cost of waste, transportation, processing by appropriate technologies, inventory and disposal (Pati et al. 2006).

Many recycled materials have been used for production of certain consumer products, such as shopping bags out of recycled papers or beverage containers, plastic coasters from plastic bottles, gypsum boards from paper, different boards from newspapers, new foams from reground polyurethane foam, etc. (Rhamin et al. 2013; Hwang et al. 2006; Grigoriou 2003; Yang et al. 2002). Different boards can be used in furniture for which wood fibers are commonly used, such as in cases of medium density fiberboard (MDF) or high density board (HDF). Wooden boards are very suitable for the application of new composites that can contain recycled materials (Grujovic et al. 2016). Recycled paper fibers are especially suitable for these applications. Different types of paper waste, such as office paper, magazines and newspapers, were studied for fabrication of composites aimed at manufacturing boards for interior use as replacements for gypsum or plaster boards (Rhamin et al. 2013; Hwang et al. 2006; Grigoriou 2003; Yang et al. 2002). In general, boards are suitable as an end application, because paper waste that has not gone through a deinking process can be used as a raw material, while some other possible applications would require removal of the printing ink from recycled paperfibers. The deinking process has significant influence on the properties of recycled paper fibers (Negaresh et al. 2013). In economic analysis related to wood products, such as furniture, the origin of the raw materials is shown to be one of the most significant attributes in obtaining a green product (De Medeiros and Ribeiro 2017). Another large market is production of well-known wood pellets (10 million tons per year on the international market), through the use of wood residues (e.g., chips, fibers), straw, grass and/or other biomasses, but the main constituent is usually wood chips (Whittaker and Shield 2017).

The new concept of the circular economy faces many challenges (Geissdoerfer et al. 2017; Lieder and Rashid 2016). There are still many issues and ambiguities. It is not a straightforward process to use novel materials in real products, even in cases when they show some initial exquisite properties related to eco-efficiency. Prior to real market utilization, novel material classes need comprehensive investigation from many aspects, starting from the fundamental material properties (physical and chemical properties, such as composition, weight, density, wettability, water intake) and mechanical properties, moving up to a range of characteristics related to their specific end applications (e.g., ductility, wettability, fatigue resistance, compressive and/or tensile strength). It is important to consider all factors that can influence the mechanical properties of the final material, in order to enable efficient bio-composite design depending on the specific end applications (Pickering et al. 2016; De Camargo et al. 2016). It is also very important to establish a suitable production technology to support eco-efficiency (Gurunathan et al. 2015; Linke et al. 2012). However, sometimes even small changes in the fabrication of well-known materials can produce significant changes in their mechanical properties (Zivic et al. 2012), and every new material must undergo comprehensive investigation in relation to its final application. The development of composites reinforced with natural fibers has gained attention in recent years, and reviews of some results and new bio-composites are given in Faruk et al. (2014), Väisänen et al. (2016), Gurunathan et al. (2015), Pereira et al. (2015) and Satyanarayana et al. (2009), whereas the very low price of raw materials is emphasized as the major reason for extensive research in this area. Another important aspect of new bio-composites is that they can efficiently use waste as raw materials, after some processing, such as, for example, fabrication of fibers made of natural waste materials. Industries that utilize extremely high material amounts (e.g., construction materials - concrete for dams, roads, bridges) can efficiently substitute certain constituents with certain recycled materials. However, such infrastructural objects need very detailed investigation from the point of view of additional safety aspects (Grujovic et al. 2012; Stojanovic et al. 2013). The cost of such recycled materials is usually significantly lower than, for example, that of carbon fibers or other newly utilized materials that are often aimed at providing better mechanical properties. In the case of many products, comparable properties can be achieved by using low cost natural materials, thus simultaneously providing better environmental sustainability as well.

Different weight percentages of waste paper flakes mixed with wood particles, with additions of polymeric diphenylmethane 4-4-Diisocyanate (PMDI) resin and wax in different percentages, have been studied (Grigoriou 2003). Composites made with additions of up to 50% of flakes made of newspapers showed the most suitable mechanical properties (density, static bending, internal bond and screw-holding strength) and thickness swelling, but they also showed a more artistic visual appearance in comparison with pure wood boards. They showed that pure waste paper, without any other additional material, was unsuitable for making boards (Grigoriou 2003). Generally, adhesives that support internal bonding of the wood fibers have significant influence on several mechanical properties of the board material, especially on elastic properties and tensile strength, and investigations related to recyclable adhesives have gained attention in recent years (Jasiukaitytė-Grojzdek et al. 2013; Reis et al. 2015).

A mixture of recycled cartons from used milk containers and melamine-Urea formaldehyde resin has been studied as a material for the production of boards

(Rhamin et al. 2013). Several material properties (water absorption, thickness swelling, elasticity modulus, internal bonding, screw withdrawal) were investigated depending on the pressing time and the amount of resin content added, and it was concluded that even without the resin, the material exhibited physical properties satisfactory to serve as a raw material for boards that are not subjected to high loading (Rhamin et al. 2013). Another study with recycled beverage containers (paperboards laminated with aluminium foil or plastic) for making composite boards, with the addition of urea resin, also showed promising results, either with pure recycled constituents or with the addition of wood particles and resin (Hwang et al. 2006). Some researchers tried to treat recycled paper fibers with fire retardants, and these composites showed very good mechanical properties, even comparable to MDF or HBF boards (Yang et al. 2002). This research indicated that composite boards made of recycled paper waste can also be used for making furniture, besides the possibilities of efficiently substituting interior boards such as gypsum boards or different insulation boards. Another promising direction for the utilization of recycled wood fibers is their use as reinforcements in polymer composite foams, especially in bioorganic composites (Gu et al. 2013).

All business sectors involved in the storage and transportation of different products, directly or indirectly, utilize wood pallets. One estimate, based on the comprehensive study by Phil Araman from the US Forest Service, states that there are around 2 billion pallets in service in the USA alone; on average, 500 million new pallets are manufactured per year (around 400 million were produced in 2011), 150 million pallets are recycled into some other product, and still another 190 million annually end up in landfills. Again, these extremely high numbers only represent the USA, whereas pallets are used extensively all over the world. One of the largest producers of pallets, RP Technologies, evaluates that the world market for pallets is worth around $9 billion, with wood accounting for more than $7 billion. In some countries, the pallet market is rather stable, like in the USA, but in others, it shows growth on an annual level (e.g., 12% per year in Mexico). The same study by the US Forest Service showed that around 90% of pallets are made of solid wood, and pallet production represents the largest sector in hardwood lumber. Boards and blocks of different size and shape are standard elements of the wood pallets, which are commonly made of such solid wood species as spruce, pine, aspen, birch or alder. It is obvious that pallets are related to very high waste, as well as the use of natural resources (forests and solid wood) whose preservation is essential for a healthy environment. Accordingly, any possible savings related to pallet elements would result not only in a significant cost decrease, but would also contribute to environmental sustainability.

New composites made of recycled materials could potentially be an effective substitution for solid wood in standard pallet elements. This paper presents a preliminary investigation related to possible combinations of different waste materials in order to make such low cost composite material aimed for use as pallet blocks. The focus has been on achieving a suitable composite made completely out of waste materials, without using any commercial adhesives or resins. Complete avoidance of such adhesives, commonly used to glue wood chips into solid elements (e.g., boards and blocks), additionally contributes to environmental sustainability, since almost all existing adhesives have toxic effects, not to mention their high cost. The new composite that we studied in this article would need to be designed to endure high compressive loads, as any material suitable for use as a pallet block would, and several combinations proved to be feasible.

2 Experimental Study: Materials and Methods

New composite materials, made of waste materials, were investigated with the aim of using them to replace the block in a wood pallet. A schematic of the basic elements of a wood pallet is given in Fig. 1.

Several types of recyclable waste material produced in different industries were used for fabrication of the composites: old papers (newspapers and magazine papers), old cardboard boxes, tetra-pak containers (beverage containers), expanded polystyrene (styrofoam) from cut-offs in the manufacturing of food containers and from the automotive industry, cut-offs of polyurethane (PU) foam from the manufacturing of car seats, cut-offs of artificial leather and textile from the manufacturing of car seats, and wood chips and dust from the wood processing industry (waste generated during production of boards and furniture). Samples of composite material were made with different combinations of compositions, 13 different composite material samples in total, denoted composites 1–13 (C1–C13), as shown in Table 1.

Firstly, all waste materials were either cut, shredded or milled to form suitable initial material for fabricating composites. Afterwards, 13 homogenous mixtures of different material combinations were realized (Table 1), including approximately equal weight percentages of each constituent, by using large industrial mixers. Prior

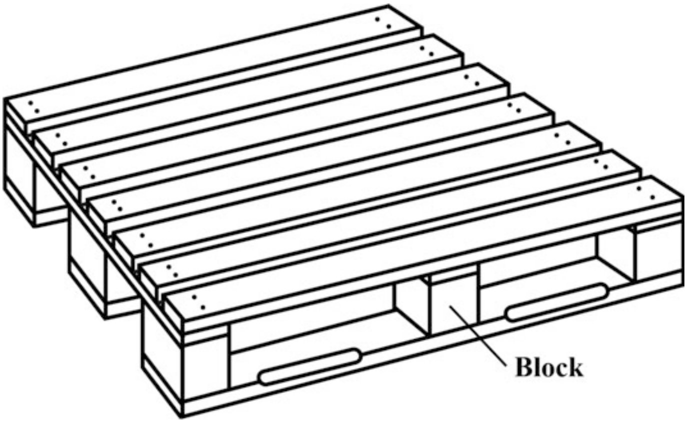

Fig. 1 Schematic of a wood pallet, with the block denoted by a *line*

Table 1 Combination of recycled materials in a final composite

Sample	Composition of composite (approximately equal weight percentages)	Origin of the material
C1	Paper strands and cardboard flakes	Waste paper (mixture of magazine papers and old newspapers) and cardboard boxes
C2	Paper strands and flakes of beverage carton	Waste paper (mixture of magazine papers and old newspapers) and tetra-pak containers
C3	Cardboard flakes	Waste cardboard boxes
C4	Expanded polystyrene (styrofoam) and cardboard flakes	Waste cut-offs from the manufacturing of styrofoam containers and cardboard boxes
C5	Expanded polystyrene (styrofoam); cardboard flakes and paper strands	Waste cut-offs from the manufacturing of styrofoam containers; waste paper (mixture of magazine papers and old newspapers) and cardboard boxes
C6	Cardboard flakes and dust of beverage carton	Waste cardboard boxes and tetra-pak containers
C7	Paper strands; cardboard flakes; dust of beverage carton; expanded polystyrene (styrofoam)	Waste paper (mixture of magazine papers and old newspapers); cardboard boxes; cut-offs from the manufacturing of styrofoam containers
C8	Polyurethane (PU) foam and wood dust	Waste cut-offs from the manufacturing of vehicle seats (automotive industry)
C9	Polyurethane (PU) foam and expanded polystyrene (styrofoam)	Waste cut-offs from the manufacturing of vehicle seats (automotive industry); cut-offs from the manufacturing of styrofoam containers
C10	PU foam and cardboard flakes	Waste cut-offs from the manufacturing of vehicle seats (automotive industry) and cardboard boxes
C11	Wood chips	Wood chips from the wood processing industry
C12	Wood dust	Wood chips from the wood processing industry
C13	PU foam and cloth	Waste cut-offs from the manufacturing of vehicle seats: PU foam and artificial leather and textile (automotive industry)

to mixing, all raw materials were sieved through an industrial sieve machine (8 × 8 mm sieves). In none of these combinations was a commercial adhesive added. Afterwards, compact samples of composite materials were made by using a large industrial extruder, at 200 °C temperature. All fabricated samples are shown in Fig. 2. All samples were left in a normal indoor environment for three months to see if any spontaneous decompositions of the material would occur.

Fig. 2 Samples of 13 different composite materials completely made of waste materials

Out of the 13 fabricated composites, the last three in Table 1 (samples C11, C12 and C13) were not subjected to any testing, because they exhibited significant spontaneous decomposition of the initial materials, that, is the samples began crumbling at the touch of a finger and were either found to be surrounded by wood dust (C11, C12 samples) or traces of cloth (C13). It was obvious that these three material combinations could not provide a compact material structure without the use of some type of commercial adhesive, which was not the focus of this study. Samples C1–C10 (Table 1) were subjected to further testing. Compression tests were realized through the use of a compressive test device with a constant increase of loading from 0 up to the maximum load of 10,000 kg, followed by instant complete unloading. These tests were conducted to indicate which material combinations could withhold their compact structure under high compressive loads, without fracture or leakage of some of the material constituents. Permanent deformation after unloading of the sample was also recorded and monitored, being defined as the difference in the height of the sample before and after unloading and resting. Typically, each block within a pallet is subjected to high compressive loading over a long period of time, and thus the compressive test is an essential one in order to eliminate unsuitable material combinations.

3 Results and Discussions

All tested samples (C1–C10) endured all compressive tests without catastrophic failure, though they did exhibit some degree of small cracks, with the exclusion of samples C1 and C7, which exhibited no cracks. Maximum compressed length [mm] and permanent plastic deformation [mm] for each sample after unloading are shown in Fig. 3, while load-displacement curves are shown in Fig. 4.

Samples C1 and C2 exhibited almost complete elastic recovery after unloading, which can be attributed to the elastic properties and low hardness of the paper or cardboard used as their largest constituent material. However, after the test, all samples except C1 and C7 had rather large cracks in the direction of loading. Sample C7 prior to and after the test is shown in Fig. 5. In the case of the C1 sample, this is probably due to its elastic properties (Fig. 3). Samples C8 and C9 exhibited pronounced rounding of the shape of the sides during the compression test, which was not completely recovered after unloading; the same happened in the

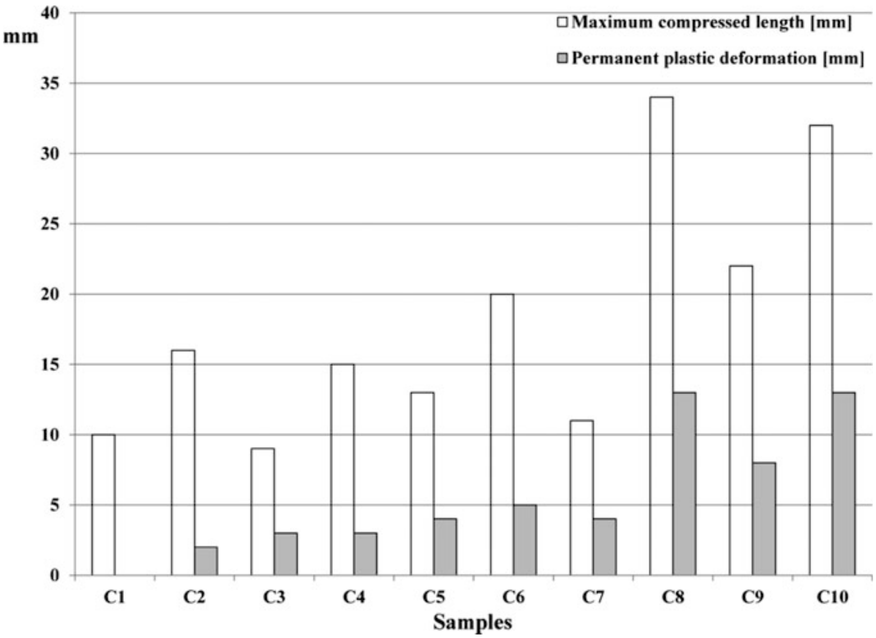

Fig. 3 Maximum compressed length [mm] and permanent plastic deformation [mm] for each sample after unloading (C1–C10)

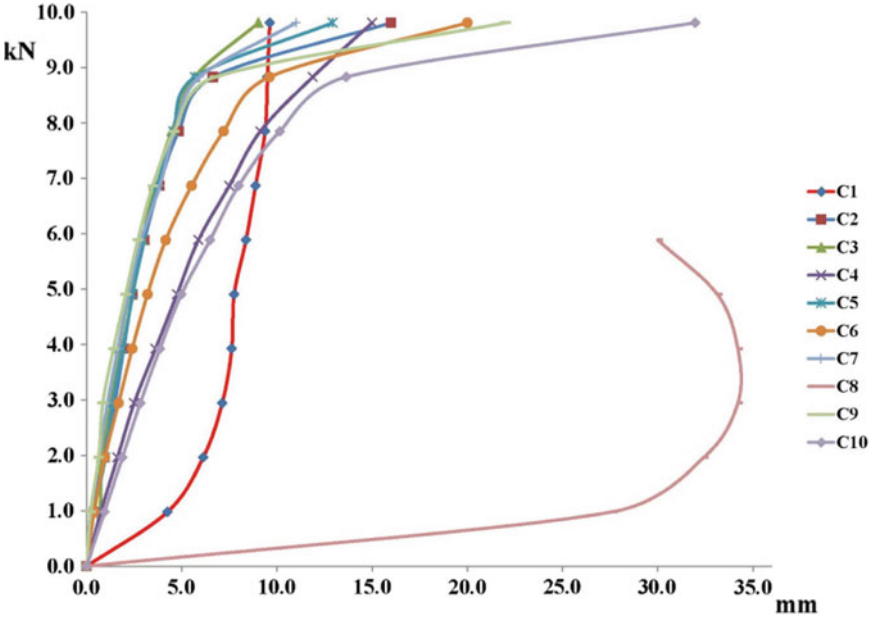

Fig. 4 Load-displacement curves for all samples during the compressive tests: compressed length [mm] as a function of the compressive force, Fn [kN]

Fig. 5 Sample C7 prior to (*left*) and after (*right*) the compressive loading test

case of the C10 sample, with a slightly lower level of roundness, unlike all of the other samples. Also, a certain amount of constituent material, mainly residue from PU foam, were found in the surroundings of samples C8–C10, indicating leakage of the materials from the composite structure. This is probably the influence of the behavior of the polymers, resulting in a rather non-homogenous composite material structure. PU foam and expanded polystyrene both have a significant amount of empty space (usually in a form of bubbles) within their structure, thus resulting in the different visco-elastic and plastic behaviour of the C8–C10 composites in comparison to other compositions. Accordingly, the highest displacements (compressed lengths) were exhibited in the cases of the C8–C10 samples (Fig. 3). PU foam belongs to a group of thermosetting polymers, a term indicating that they do not soften or melt with the temperature increase during the extrusion process. Under the influence of a high compressive load, the material will change its shape and the bubbles might break, but the general foam structure should be retained. A high level of crosslinking in this polymer results in a high level of stretching without failure, which is in accordance with the compressive tests results in this study. The small amounts of debris found around the C8 and C9 samples were mostly made of PU foam residue. Another material in composites C8 and C9 is expanded polystyrene (styrofoam), which behaves differently due to its glass transition temperature of 100 °C, over which it flows, becoming rigid again after cooling down. This should mean that the styrofoam in the composites investigated in this study could play the role of an adhesive in a composite structure. The results obtained in this study support this, because the only residue in any form that was not visible in the vicinity of any of the samples, under any conditions, was that of styrofoam. This indicates that it had been tightly incorporated within the composite structure during the extrusion process at 200 °C.

In the cases of the C1 and C8 samples, the stress curves exhibited a different trend in comparison with all of the other samples, as shown in Fig. 4, indicating that these two composites exhibited no load bearing capabilities. Accordingly, the C1 and C8 composites are not suitable for load bearing applications, such as serving as a block in a pallet. All samples exhibited some amount of leakage of constituent materials, as shown by the dust or flakes or granules of different raw materials that surrounded the samples after the test, except in case of the C7 sample. Also, the lowest amount of post-test dust around a sample was found in the case of the C1 sample. If we compare samples C1 and C7, the C7 sample did not exhibit any leakage of constituent material, whereas the C1 sample had certain small amounts of cardboard flake surrounding the sample after the compressive test was finished. This might indicate that some decomposition of the material could appear over time under conditions of compressive loading. Other authors who have studied the behavior of waste paper flakes have also concluded that they showed a tendency to agglomerate at one site within a composite, resulting in a non-homogenous composite structure throughout the bulk (Grigoriou 2003).

Based on the material behavior under compressive loading, preliminary screening of composite materials can be made and sample C7 can be noted as being a promising candidate (Fig. 5). The smaller amount of expanded polystyrene added to this composite structure probably served as an adhesive, making the material very compact and lending it good load bearing capacity. Also, the beverage carton dust probably contributed to the internal bonding of the other two components (paper strands and cardboard flakes of small sizes) and decreased the elastic part of the material behaviour under compression, in comparison with the C2 sample (combination of paper strands and flakes of beverage carton only), which exhibited a hyper elastic response, making it unsuitable as a pallet block.

4 Conclusions

The investigated combinations of waste materials for fabrication of a composite material by extrusion under elevated temperature, aiming for load bearing applications such as service as a pallet block, showed promising results. Unsuitable combinations were clearly indicated (C1, C8, C11–C13 samples). Paper with cardboard (C1 sample) and PU foam with wood dust (C8 sample) did not show a proper load bearing capacity, even though they formed rather compact material. PU foam in larger weight percentages was particularly indicated as an unsuitable component in a composite for high compressive loads. Wood chips (C11 sample), wood dust (C12 sample) and PU foam with artificial leather (C13 sample) all proved that these types of composite cannot be made without the addition of some adhesive material, since they spontaneously decomposed. Further studies will indicate the exact material combinations and their weight percentages, since these preliminary investigations indicated that fine particles or powders, especially with the addition of styrofoam to serve as an adhesive (such as in the case of the C7 sample), can efficiently withstand large compressive loads, up to 10 t. The strong conclusion of this work is that utilization of certain waste materials can greatly contribute to waste recycling, but also to the preservation of natural resources, such as wood, which can be substituted with new eco-composites. Another advantage is the possibility for small companies to introduce production of this element due to the low cost of processing of the materials studied. However, this is only a preliminary investigation, and further study is necessary from several aspects, starting with optimization of composition, and followed by further comprehensive testing that will involve other necessary properties, such as wettability or aging, and other mechanical properties, such as complex loading and fatigue.

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References

De Camargo FV, Guilherme CEM, Fragassa C et al (2016) Cyclic stress analysis of polyester, aramid, polyethylene and liquid crystal polymer yarns. Acta Polytech 56(5):402–408

De Medeiros JF, Ribeiro JLD (2017) Environmentally sustainable innovation: expected attributes in the purchase of green products. J Clean Prod 142:240–248

De Paola S, Fragassa C, Minak G et al (2013) Green Composites: a review of state of art. In: Proceedings of 30th Danubia Adria Symposium, Symposium on Advances in Experimental Mechanics, DAS 30, Code 125164:77-78, Primošten, Croatia, 25–28 September 2013

Faruk O, Bledzki AK, Fink HP et al (2014) Progress report on natural fiber reinforced composites. Macromol Mater Eng 299:9–26

Forton OT, Harder MK, Moles NR (2006) Value from shredder waste: ongoing limitations in the UK. Resour Conserv Recycl 46:104–113

Geissdoerfer M, Savaget P, Bocken NMP et al (2017) The Circular Economy—A new sustainability paradigm? J Clean Prod 143:757–768

Grigoriou AH (2003) Waste paper–wood composites bonded with isocyanate. Wood Sci Technol 37:79–89

Grujovic N, Divac D, Zivkovic M et al (2012) An inelastic stress integration algorithm for a rock mass containing sets of discontinuities. Acta Geotech 8:1–14

Grujovic N, Zivic F, Zivkovic M et al (2016) Custom design of furniture elements by fused filament fabrication. Proc Inst Mech Eng C-J Mech Eng Sci, Published online before print April 19, 2016. doi:10.1177/0954406216646401

Gu R, Sain MM, Konar SK (2013) A feasibility study of polyurethane composite foam with added hardwood pulp. Ind Crop Prod 42:273–279

Gurunathan T, Mohanty S, Nayak SK (2015) A review of the recent developments in biocomposites based on natural fibres and their application perspectives. Compos A Appl Sci Manuf 77:1–25

Hwang GS, Wang EIC, Su YC (2006) Preparation of composite board using foil-laminated and plastic-laminated liquid packaging paperboard as raw materials. J Wood Sci 52(3):230–235

Ignatyev IA, Thielemans W, Vander Beke B (2014) Recycling of polymers: a review. Chem Sus Chem 7:1579–1593

Jasiukaitytė-Grojzdek E, Kunaver M, Kukanja D et al (2013) Renewable (waste) material based polyesters as plasticizers for adhesives. Int J Adhes Adhes 46:56–61

Korkmaz A, Yanik J, Brebu M et al (2009) Pyrolysis of the tetra pak. Waste Manage 29:2836–2841

Lieder M, Rashid A (2016) Towards circular economy implementation: a comprehensive review in context of manufacturing industry. J Clean Prod 115:36–51

Linke B, Huang YC, Dornfeld D (2012) Establishing greener products and manufacturing processes. Int J Precis Eng Manuf 13:1029–1036

Miller L, Soulliere K, Sawyer-Beaulieu S et al (2014) Challenges and alternatives to plastics recycling in the automotive sector. Materials 7:5883–5902

Morselli L, Santini A, Passarini F et al (2010) Automotive shredder residue (ASR) characterization for a valuable management. Waste Manage 30:2228–2234

Negaresh E, Antony A, Cox S et al (2013) Evaluating the impact of recycled fiber content on effluent recycling in newsprint manufacture. Chemosphere 92:1513–1519

Pati RK, Vrat P, Kumar P (2006) Economic analysis of paper recycling vis-a-vis wood as raw material. Int J Prod Econ 103:489–508

Pereira PHF, De Freitas Rosa M, Cioffi MOH et al (2015) Vegetal fibers in polymeric composites: a review. Polimeros 25:9–22

Pickering KL, Efendy MGA, Le TM (2016) A review of recent developments in natural fibre composites and their mechanical performance. Compos A Appl Sci Manuf 83:98–112

Pires A, Martinho G, Chang NB (2011) Solid waste management in European countries: a review of systems analysis techniques. J Environ Manage 92:1033–1050

Reis JML, Amorim FC, da Silva AHMFT et al (2015) Influence of temperature on the behavior of DGEBA (bisphenol A diglycidyl ether) epoxy adhesive. Int J Adhes Adhes 58:88–92

Rhamin H, Madhoushi M, Ebrahimi A et al (2013) Effect of resin content, press time and overlaying on physical and mechanical properties of carton board made from recycled beverage carton and MUF resin. Life Sci J 10(4s)

Satyanarayana KG, Arizaga GGC, Wypych F (2009) Biodegradable composites based on lignocellulosic fibers—an overview. Prog Polym Sci (Oxford) 34:982–1021

Stojanovic B, Milivojevic M, Ivanovic M, Milivojevic N, Divac D (2013) Adaptive system for dam behavior modeling based on linear regression and genetic algorithms. Adv Eng Softw 65:182–190

Triguero A, Álvarez-Aledo C, Cuerva MC (2016) Factors influencing willingness to accept different waste management policies: empirical evidence from the European Union. J Clean Prod 138:38–46

Väisänen T, Haapala A, Lappalainen R et al (2016) Utilization of agricultural and forest industry waste and residues in natural fiber-polymer composites: a review. Waste Manage 54:62–73

Vermeulen I, Van Caneghem J, Block C et al (2011) Automotive shredder residue (ASR): reviewing its production from end-of-life vehicles (ELVs) and its recycling, energy or chemicals' valorisation. J Hazard Mater 190:8–27

Vivekanandhan S, Schreiber M, Muthuramkumar S et al (2017) Carbon nanotubes from renewable feedstocks: a move toward sustainable nanofabrication. J Appl Polym Sci 134(4):44255

Williams PT (2013) Pyrolysis of waste tyres: a review. Waste Manage 33:1714–1728

Whittaker C, Shield I (2017) Factors affecting wood, energy grass and straw pellet durability—a review. Renew Sustain Energy Rev 71:1–11

Yang HS, Kim DJ, Kim HJ (2002) Combustion and mechanical properties of fire retardant treated waste paper board for interior finishing material. J Fire Sci 20(6):505–517

Zhang Y, Hafezi M, Zhao X et al (2017) The impact of development cost on product line design and its environmental performance. Int J Prod Econ 184:122–130

Zivic F, Babic M, Grujovic N et al (2012) Effect of vacuum-treatment on deformation properties of PMMA bone cement. J Mech Behav Biomed Mater 5:129–138

Zorpas AA, Inglezakis VJ (2012) Automotive industry challenges in meeting EU 2015 environmental standard. Technol Soc 34:55–83

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