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Environmental-Friendly Biodegradable Polymers and Composites

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1. Introduction

Global warming, the growing awareness of environmental and waste management issues, dwindling fossil resources, and rising oil prices: these are some of the reasons why “bio” products are increasingly being promoted for sustainable development.

“Bio” products, such as starchy and cellulosic polymers, have been used for thousands of years for food, furniture and clothing. But it is only in the past two decades that “bio” products have experienced a renaissance, with substantial commercial production. For example, many old processes have been reinvestigated, such as the chemical dehydration of ethanol to produce “green” ethylene and therefore “green” polyethylene, polyvinylchloride and other plastics. Moreover, recent technological breakthroughs have substantially improved the properties of some bio-based polymers, such as heat resistant polylactic acid, enabling a wider range of applications. In addition, plants are being optimized, especially to provide bio-fibres with more stable resource properties over time. An increasing number of applications have emerged recently (including packaging, biomedical products, textiles, agriculture, household use and building) where biodegradable polymers and biocomposites are particularly suitable as sustainable alternatives.

This chapter begins with a summary of the **classification systems for biodegradable polymers and biocomposites** then describes **specific and innovative developments concerning environmental-friendly biodegradable polymers and composites** carried out in recent years, based on several case studies:

- the development of a **multi-layered biocomposite based on expanded starch reinforced by natural fibres** for food packaging applications,
- the development of mulching and silage **films based on proteins extracted from cotton seeds** for agricultural applications,
- the development of a **biocomposite** for automobile applications **associating polylactic acid-based matrices and alterable glass fibres**,
- the formulation of **polylactic acid-based blowing films** for textile applications, such as disposable safety workwear,
- and the processing of **polylactic acid-based foam products** for several industrial sectors such as packaging and transport.

2. Classification systems

2.1 Classification of biodegradable polymers

Biopolymers can be classified in two ways: according to their renewability content (fully or partially bio-based or oil-based) and to their biodegradability level (fully or partially or not biodegradable) (Shen et al, 2009).

An attempt to classify biodegradable polymers into two main groups has been developed (Averous, 2004), these two groups being (i) the **agropolymers** obtained by biomass fragmentation processes (polysaccharides, proteins...), (ii) and the **biopolyesters** obtained either by synthesis from bio-derived monomers (polylactic acid – PLA) or by extraction from micro-organisms (polyhydroxyalkanoate – PHA) or by synthesis from synthetic monomers (polycaprolactone – PCL, aromatic and aliphatic copolyesters – PBAT, PBSA...) (Figure 1).

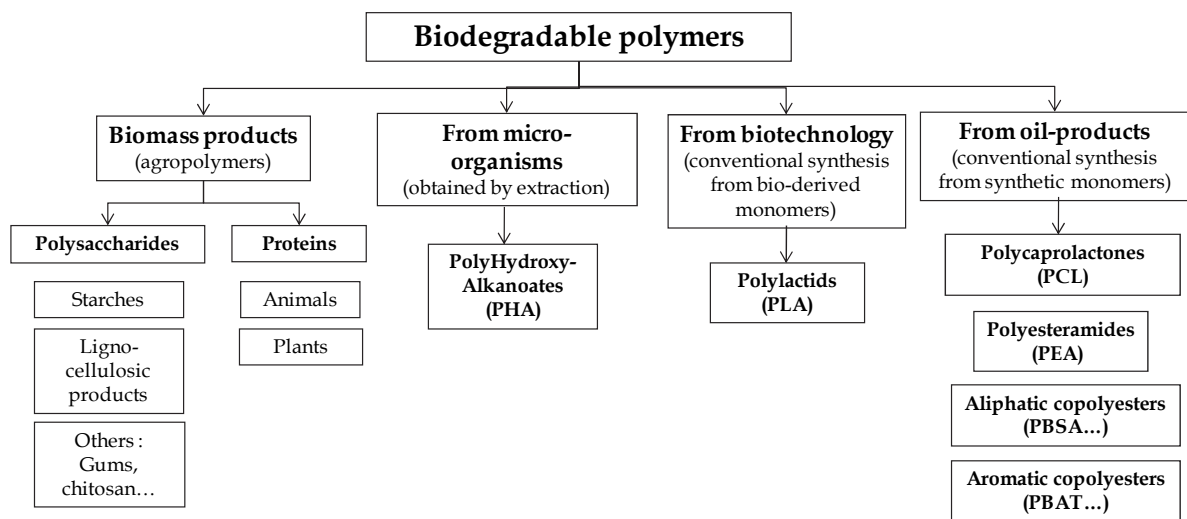


Fig. 1. Classification of biodegradable polymers (Averous, 2004)

2.2 Classification of biocomposites

The materials called biocomposites result from a combination of a biodegradable polymer and biodegradable fillers, usually bio-fibres.

Biocomposites can be classified into three main groups: (i) “**bio¹composites**”, composites in which the production of raw materials is based on renewable resources, (ii) “**bio²composites**” which are bio¹composites whose waste can be managed in an eco-friendly way at the end of their life (composting, biomethanation, recycling...), and (iii) “**bio³composites**”, which are bio²composites where the successive transformation processes from the raw materials to the final products are environmental-friendly (low energy consumption, low emissions).

Nevertheless a problem remains: while it is relatively easy to define a “bio¹composite” by its content of renewable raw materials and a “bio²composite” by its service-life/end-of-life time ratio, how can environmental efficiency be defined for “bio³composite” transformation processes? With regard to the extrusion process, energy consumption can be evaluated from the specific mechanical energy (SME) and specific thermal energy (STE), which correspond respectively to the energy delivered by the screws per unit of mass of extruded biocomposite and to the total heat energy input through the barrel wall and the thermally

regulated screws. A large number of energy efficiency indicators could be proposed for extrusion compounding such as the molten state viscosity of the extruded biocomposite and thermo-physical characteristics (transition temperature and enthalpy, heat capacity, thermal conductivity, density).

3. Agropolymer developments

Agropolymers include starch-based and protein-based polymers. After a general presentation of both types of polymers (microstructure, specific characteristics...) an example of innovative material development will be more extensively presented in each case.

3.1 Starch-based polymers and composites

Starch is the main storage supply in botanical sources such as cereals (wheat, maize, rice...), tubers (potato...) and legumes (pea...). In the past, studies carried on starch esters were abandoned due to their inadequate properties in comparison with cellulose derivatives. It is only in the recent years that a renewed interest in starch-based polymers has been aroused. Starch consists of two major components, amylose and amylopectine. Amylose (Figure 2a) is a linear or sparsely branched carbohydrate based on $\alpha(1-4)$ bonds with a molecular weight of 10^5 - 10^6 . The chains show spiral shaped single or double helixes. Amylopectine (Figure 2b) is a highly multiple branched polymer with a high molecular weight of 10^7 - 10^9 based on $\alpha(1-4)$ bonds and $\alpha(1-6)$ links constituted branching points occurring every 22-70 glucose units (Zobel, 1988; Averous, 2004). In nature starch is found as crystalline beads, in three crystalline modifications according to the botanical source.

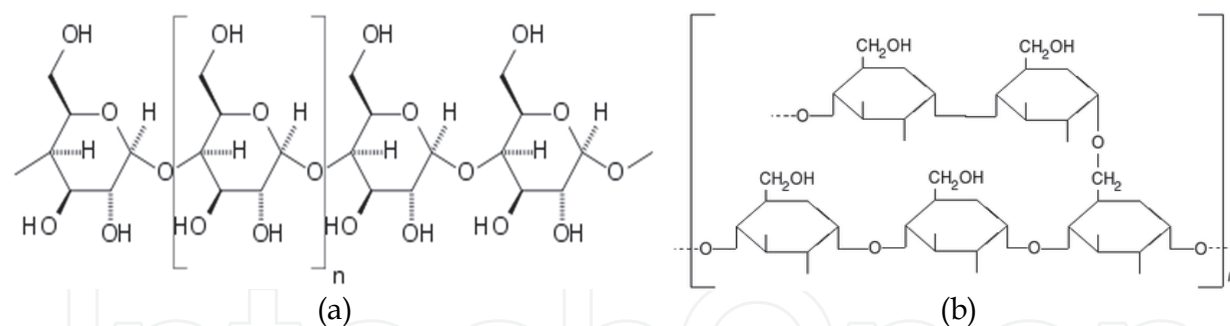


Fig. 2. Structures of (a) amylose and (b) amylopectine

Apart from its use as a filler to produce reinforced polymers (Griffin, 1973), most starch applications require water and the disruption of the granular structure, which is called gelatinization. Starch can swell to form a viscous paste with most of its inter-macromolecule hydrogen bonds being destroyed. A reduction in both melting and glass transition temperatures is observed. It can be shown (Averous, 2004) that different products are obtained in function of the level of destructuring and the water content.

It is for that reason that starchy materials are divided into two categories: (i) with a high water content (between 15 and 30% in volume), **expanded starches** are obtained by expanding starch in the presence of specific blowing and nucleating agents through an extrusion die; (ii) with a low water content (below 15% in volume), **plasticized starches**, also called "thermoplastic starches" (TPS), are obtained after disruption and plasticization of the starch by applying thermo-mechanical energy in a continuous extrusion process.

Starchy materials present some drawbacks compared to conventional oil-based polymers such as a strongly hydrophilic character and rather poor mechanical properties. These weaknesses could be improved by blending with less water sensitive biopolymers and incorporating cellulose-based fibres.

3.1.1 Biocomposites based on plasticized starch

Plasticized starches have been combined with various fibres such as jute fibres (Soykeabkaew et al, 2004), ramie fibres (Wollerdorfer & Bader, 1998), flax fibres (Soykeabkaew et al, 2004; Wollerdorfer & Bader, 1998), tunicin whiskers (Angles & Dufresne, 2001), bleached leaf wood fibres (Averous et al, 2001), wood pulp (De Carvalho et al, 2002) and microfibrils from potato pulp (Dufresne et al, 2000). Most of these authors have shown a high compatibility between starch and cellulose-based fibres leading to higher moduli. A reduction in water sensitivity is also obtained because of the more hydrophobic character of cellulose, which is linked to its high crystallinity. Another reason for the improved properties of fibre reinforced starch biocomposites is the formation of a tight three-dimensional network between the carbohydrates through hydrogen bonds.

3.1.2 Biocomposites based on expanded starch: development of a multi-layered biocomposite for food packaging applications

The materials used for packaging today consist of a variety of petroleum-derived polymers (mainly polyolefin such as polyethylene, polypropylene and polystyrene), metals, glass, paper and combinations thereof. Concerning food products, they must have specific optimum requirements especially regarding storage and interaction with food. The engineering of new bio-based food packaging materials can thus be considered as a tremendous challenge both for academia and industry.

Our research centre and Vitembal Co (Remoulins, France) have joined forces to develop an innovative multi-layered biodegradable composite intended to replace the common Expanded PolyStyrene (EPS) trays used for food packaging, especially fish, meat and vegetables. Starch was considered as a suitable alternative for achieving the required foamed structure. The project was supported by the French organization ADEME.

3.1.2.1 The multi-layer concept

The starch (potato starch provided by Roquette Co, France, with 10-25 wt% amylose, 75-80 wt% amylopectine, 0.05 wt% proteins based on dry weight) used for this study was expanded through a classical co-rotating extruder (Clextral BC21, 900 mm length, 25 mm diameter, 1.5x40 mm² flat die) with 12 heating zones (temperature profile: 30°C (feeder) / 30°C / 50°C / 60°C / 70°C / 80°C / 90°C / 90°C / 100°C / 120°C / 120°C / 160°C (die)) to obtain sheets that were afterwards thermoformed to shape the final tray.

The expansion was induced by water added using a peristaltic pump. An optimized value of 17 wt% of water was obtained, leading to the best expansion. Regular expansion was achieved by adding 2 wt% of talc (Talc de Luzenac Co, France) and 2 wt% of a chemical blowing agent (CBA) based on citric acid and sodium bicarbonate (Hydrocerol ESC5313© supplied by Clariant Co, France). It can be noticed that the foaming aptitude of starch was assessed on the basis of void content induced by extrusion in the final product. The experimental results enabled the definition of an optimum set of extrusion conditions (screw profile and speed, cooling temperature, extrusion temperatures along the screw...) and

material formulations (CBA content, viscosity of polymer during processing...), leading to a maximal void content.

Nevertheless, the main drawbacks of starch are its high water sensitivity and poor mechanical properties. Therefore, firstly, natural fibres were incorporated within the starch. Various natural fibres such as wheat straw fibres, cotton linter fibres, hemp fibres and cellulose fibres (Table 1) and fibre contents (7, 10 and 15 wt %) were compared. In addition, two external biodegradable low hydrophilic polyester films (120 µm) of polycaprolactone (PCL) were calendared on both sides of the core sheet of foamed starch, to limit water absorption and enhance global mechanical properties.

Under these conditions, all the formulations were processed with specific mechanical energy (SME) values between 60 and 90 W.h/kg. The final multi-layered biocomposite structure is presented in Figure 3.

Fibre	Length (mm)	Cellulose content (%)	Supplier
Wheat straw	2.6	30-35	A.R.D. Co (France)
Cotton linter	2.1	80-85	Maeda Co (Brazil)
Hemp	3.2	70-72	Chanvrière de l’Aube (France)
Cellulose	0.13	98-99	Rettenmaier and Söhne (Germany)

Table 1. Main characteristics for different natural fibres used

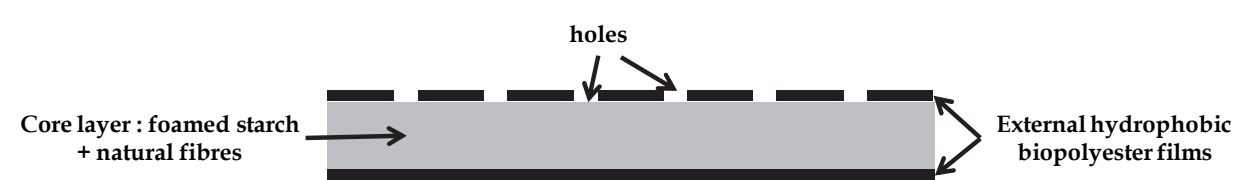


Fig. 3. Multi-layered biocomposite structure

3.1.2.2 Properties of the biocomposite core layer

3.1.2.2.1 Density, expansion index and cell morphology

It is noticeable (Table 2) that the addition of fibres contributed to lowering the core layer density except in the presence of hemp fibres. A slight reduction in expansion index was observed in the presence of cellulose and hemp fibres, whereas an increase was observed in the presence of wheat straw and cotton linter fibres. These effects may result from two competitive mechanisms varying according to the nature of the fibre: on the one hand fibres tend to increase the viscosity of the moulded starch but, on the other hand, fibres act as nucleating agents providing surfaces for cell growth.

As a consequence, reinforced starch foams exhibit smaller cells (mean diameter between 580 and 780 µm compared to 880 µm for unreinforced foamed starch) with thinner walls (between 12.5 µm and 18.6 µm compared to 21.5 µm for unreinforced foamed starch) as shown in Table 3 and Figures 4a to 4c. The results show an open-cell structure (around 80% of open-cells) for all formulations, with little variation between the various formulations, this parameter being mainly influenced by processing conditions and especially cooling speed at the extruder die. The microstructure of industrial multi-layered EPS trays is very different. Indeed, industrial EPS trays are a two-layered system with an open-cell layer (75-85% of open-cells) in contact with the food for optimized absorption of exudates and a closed-cell layer (85-95% of closed cells) to act as a diffusion barrier. Moreover EPS cells are

smaller (about 300 μm) (Figures 4d and 4e). As a consequence it can be concluded that the main challenge was to control the microstructure of the starch foam (i.e. rate of open-cells, cell size, wall thickness).

Fibre	Content (wt%)	Density (g/cm^3)	Expansion index
Wheat straw	7	0.225 ± 0.021	3.0 ± 0.2
	10	0.190 ± 0.012	3.5 ± 0.1
	15	0.186 ± 0.009	3.2 ± 0.2
Cotton linter	10	0.175 ± 0.008	3.2 ± 0.1
Hemp	10	0.242 ± 0.010	2.8 ± 0.2
Cellulose	7	0.161 ± 0.004	2.9 ± 0.1
	10	0.170 ± 0.007	2.8 ± 0.1
	15	0.158 ± 0.004	2.4 ± 0.1

Table 2. Densities and expansion ratios of starch based biocomposites compared to starch (density: 0.236 ± 0.016 ; expansion index: 2.9 ± 0.2)

	D_n (μm)	D_w (μm)	PDI	e (μm)	I_s
Wheat straw	653.8	812.7	0.80	18.61	0.70
Cotton linter	648.9	734.1	0.88	15.12	0.70
Hemp	784.1	966.9	0.81	17.39	0.70
Cellulose	577.6	730.7	0.79	12.54	0.70

Table 3. Size (mean diameter in number, D_n ; mean diameter in weight, D_w), wall thickness of cells (e), polydispersity index (PDI) and sphericity (I_s) of biocomposites reinforced by 10 wt% of fibres compared to starch (D_n : $875.5 \mu\text{m}$; D_w : 1046.6 ; PDI: 0.84 ; e : $21.52 \mu\text{m}$; I_s : 0.72)

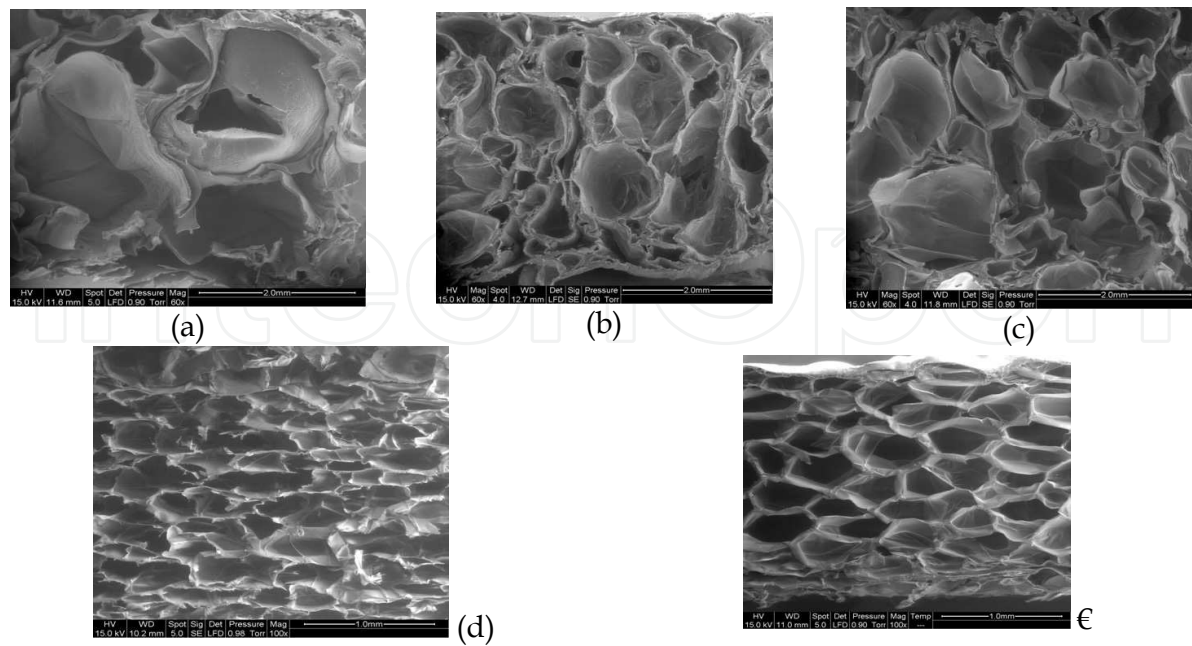


Fig. 4. Cell morphology (a) starch; starch biocomposites reinforced by 10 wt% of (b) wheat straw; (c) cellulose fibres; (d) open- and (e) closed-cells structure of an EPS tray

3.1.2.2.2 Water absorption

Water absorption was measured after storing samples at various relative moistities (33, 56 and 75 RH %) for 200h. This water sensitivity was measured both for the fibres alone (Table 4) and for the core layer of the biocomposites (Table 5). It was observed that the water absorption of the fibres was lower than that of foamed starch under the same conditions (9.1; 12.5 and 16.8 % respectively for 33; 56 and 75 RH %). It would therefore be expected that the presence of fibres would lower the water sensitivity of the expanded starch. However, this decrease in water absorption seems to depend on the type of fibre. Cotton linter fibres show much lower water sensitivity than the other fibres, but such a difference is not observed for the corresponding biocomposite. Two main explanations could be proposed, the first concerns the influence of cell morphology, especially wall thickness, on water vapour diffusion within the material, and The second concerns the potential existence of interactions between fibres and matrix through hydrogen bonds that modify water-fibre and water-starch interactions.

Fibres	33 RH %	56 RH %	75 % RH
Wheat straw	4.5	7.6	11.5
Cotton linter	3.8	6.1	9.0
Hemp	5.0	7.8	11.8
Cellulose	5.3	7.7	11.5

Table 4. Water absorption rate of isolated natural fibres at various relative moistities for 200h

	Wheat straw			Cotton linter	Hemp	Cellulose		
	7 %	10 %	15 %	10 %	10 %	7 %	10 %	15 %
33 %	8.7	8.4	8.3	9.5	8.8	9.2	8.8	9.1
56 %	11.9	11.7	11.4	12.4	12.0	12.5	11.5	12.2
75 %	16.0	15.6	15.3	16.2	16.4	16.7	15.7	15.9

Table 5. Water absorption rate of the core layer of the biocomposites with different weight contents of fibres (7, 10, 15 wt%) and various relative moistities (33, 56, 75 %RH) for 200h

3.1.2.2.3 Mechanical properties

Equivalent E/ρ values (E: bending modulus; ρ: density) for fibre reinforced biocomposites (10 wt% of fibres) are presented in Figure 5 for all humidity rates. It can be observed that cellulose fibres confer the most significant reinforcement effect to the starch foam, followed by hemp and linter cotton fibres. Moreover an increase in relative humidity level results in a decrease in the mechanical properties. This is related to the plasticizing effect of water with respect to starch. Despite the fact that natural fibres are less water sensitive than starch, it is observed that the incorporation of fibres in starch foam does not systematically lead to a reduction in hygroscopicity and thus an improvement in mechanical properties.

3.1.2.2.4 Biodegradation rate

Different degradation tests were investigated on the core layer of the different developed biocomposites. The weight variation of the biocomposite versus composting time was measured (composting test – ISO 14855) (Table 6). The presence of fibres may delay the degradation

rate for short composting times, but a degradation rate of between 38 and 51% was obtained after 4 months whatever the fibre nature due to fungal growth (*Aspergillus*, *Hyphomycetes*).

The oxygen consumption of micro-organisms (BOD: Biological Oxygen Demand - ISO 14432) shows a lower degradation rate after 28 days for biocomposites compared to unreinforced foamed starch (Table 6). This could be explained by the fact that starch degradation may occur before fibre degradation. The activated sludge issued from a wastewater treatment may contain bacteria that can more easily produce enzymes for starch degradation than for fibre degradation. The variations in BOD according to the nature of the fibres may be due to an acclimation period of 28 days for fibre degradation.

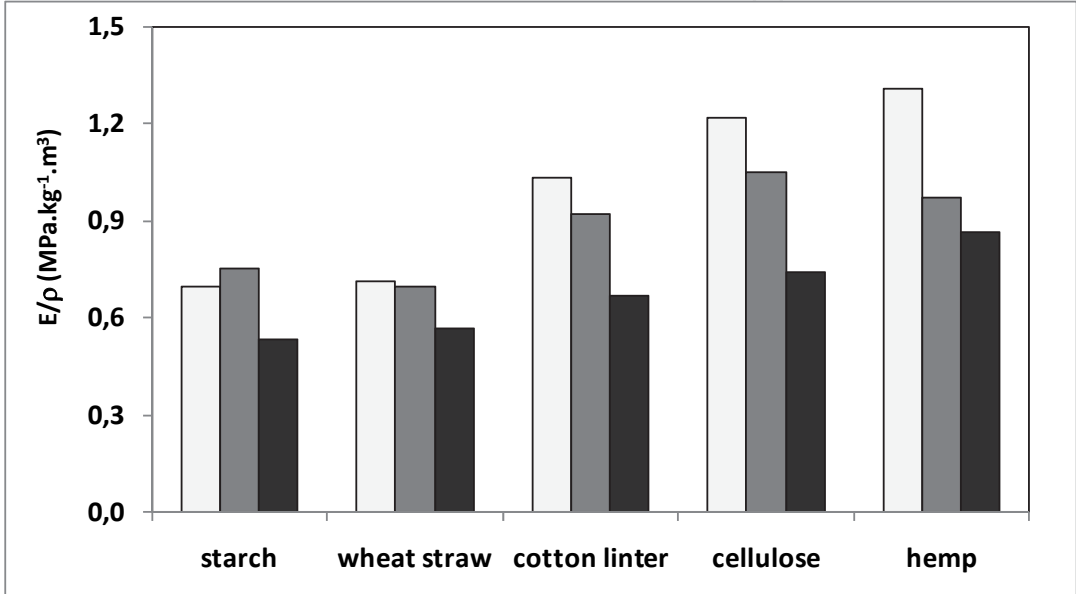


Fig. 5. E/ρ of unreinforced starch and of starch based biocomposite (10 wt% of fibres) as a function of relative humidity ($\square$: 33 HR%; $\blacksquare$: 56 RH%; $\blacksquare$: 75 RH%) (E: bending modulus; ρ : density)

	Composting time	Foamed starch	+10 wt% wheat straw	+10 wt% cotton linter	+10 wt% hemp	+10 wt% cellulose
ISO 14855	32 days	42.7	27.6	30.9	29.2	27.4
	53 days	42.8	32.1	31.4	29.4	25.5
	88 days	41.6	30.3	29.1	28.8	30.8
	122 days	50.9	47.3	43.6	37.8	49.7
ISO 14432	28 days	73	51	52	66	67

Table 6. Degradation rate (%) of the core layer of various biocomposites with composting time according to ISO 14855 and ISO 14432

3.1.2.3 Properties of the multi-layered biocomposite

As concerns the multi-layered biocomposite (Figure 3), results show an increase in density and mechanical properties compared to the core layer alone. Higher impact strengths and

similar E/ρ values were obtained for starch-based biocomposites than for EPS (Figure 6). Nevertheless water sensitivity remained ten times lower for the biocomposite (absorption rate about 1 g/dm² whatever the fibre nature after 24h in contact with a physiological serum) by comparison to EPS (12 g/dm² under the same conditions). At the same time a drastic decrease in mechanical properties was observed. The oxygen consumption of microorganisms (BOD) shows a lower degradation rate for the multi-layered systems compared to the core layer alone, with values between 23 and 28% instead of 51-67%.

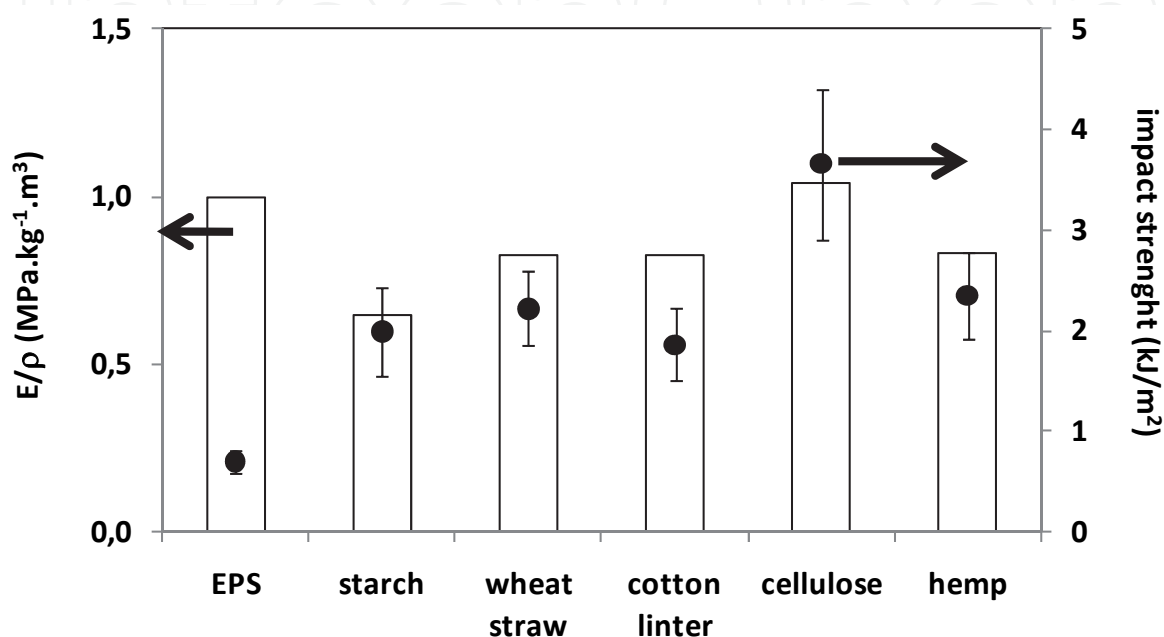


Fig. 6. E/ρ values (E : bending modulus; ρ : density) and impact strengths of the various multi-layered biocomposite (10 wt% of fibres) compared to EPS (commercial tray) at 56 RH %

3.1.3 Further studies

Current studies are focussing on four main topics: (i) optimisation of the cell morphology to reduce the cell size through the incorporation of nanofillers, (ii) control of the open/closed-cells structure through optimisation of the processing conditions, (iii) the use of other natural fibres to modulate the mechanical properties and (iv) the appliance of specific surface treatments on the natural fibres to reduce the water sensitivity of the biocomposite and increase fibre/starch interactions.

3.2 Protein-based polymers and composites: development of mulching and silage films for agricultural applications

3.2.1 General aspects

A wide range of materials have been successfully prepared from proteins, which are abundant and inexpensive. It is well known that the mechanical properties of protein-based materials correlate with the density of the three-dimensional network formed during processing through disulfide-bond crosslinking (Domenek et al, 2002; Shewry & Tatham, 1997). This density increases with the processing temperature and duration, resulting in higher tensile strength and Young's modulus while elongation at break decreases (Morel et al, 2002). Nevertheless optimal processing conditions need to be defined for which thermal

aggregation is maximized while the degradation mechanism is still negligible. Plasticizers, as well as natural fibres, may modify both the processing window and mechanical properties.

The engineering of protein-based biodegradable polymers is therefore providing challenging alternatives for agricultural items, like mulching films, silage films, bags and plant pots. With a worldwide production of about 33 million metric tons, cottonseed cakes are now the most important source of plant proteins after soybeans. These products seem to be very attractive for non alimentary applications such as developing a biodegradable polymer. Nevertheless, in most cases, wet processes such as casting are used for these materials. The objective is to use the dry processing technologies (extrusion, thermo-moulding) currently used for synthetic polymers.

3.2.2 Protein-based films obtained through dry technologies

Our research centre was involved in a FP5 European project to develop protein-based biopolymers through dry processes. This research program was managed by the CIRAD (Centre de Coopération Internationale en Recherche Agronomique pour le Développement, Montpellier, France) and was carried out in collaboration with South American companies and institutions (Brazil, Argentina).

Dry technologies imply that proteins exhibit thermoplastic behaviour, i.e. a viscous flow at high temperature. In many cases, the glass transition of proteins occurs very close to the temperature of thermal degradation. To enlarge the processing range, proteins are mixed with small molecules intended to lower the glass transition temperature by plasticization. Due to the hydrophilic nature of many amino acids, polyols (glycerol, sorbitol...) are commonly used for protein plasticization.

The influence of several parameters was investigated: plasticizer nature and content, storage conditions, presence of shells, presence of lipids, processing conditions. Results highlighted that the presence of plasticizers tends to decrease Young's modulus and tensile strength and to increase elongation at break. This effect increased with plasticizer content and the number of hydroxyl groups supplied by the plasticizer. Storage conditions also have a major influence on mechanical properties, water being a good plasticizer of proteins. The presence of shells tends to reduce the mechanical performance of the films. At very low content (<2 wt %), shells can promote a positive effect by increasing the tensile strength and rigidity. Above 2 wt %, shells decrease the mechanical strength because they act as crack initiators due to their morphology and poor adhesion to the protein matrix. The presence of lipids decreases the rigidity of the materials, with poor cohesion. This was attributed to phase separation between the lipids and proteins. Finally, concerning the influence of processing conditions, the best results were obtained when films were pressurised at 120°C. At lower temperatures, the cohesion of the films was poor (low Young's modulus). At higher temperatures, elongation at break decreased due to potential crosslinking reactions or degradation reactions. The tensile strength =f(elongation at break) curve (Figure 7) shows that the best results were obtained when the films were plasticized with glycerol, were processed at 120°C and contained a small amount of shells.

4. Developments regarding biopolyesters

Biopolyesters are obtained (i) **from biotechnology** (conventional synthesis from bio-derived monomers) such as polylactides (PLA), (ii) **by extraction from micro-organisms** such as

polyhydroxyalkanoates (PHA) and (iii) **from petrochemical products** (conventional synthesis from synthetic monomers) such as polycaprolactones (PCL) and aromatic and aliphatic copolyesters. A wide range of these biodegradable polymers is now commercially available, offering all sorts of properties that enable them to compete with non-biodegradable polymers in several industrial sectors.

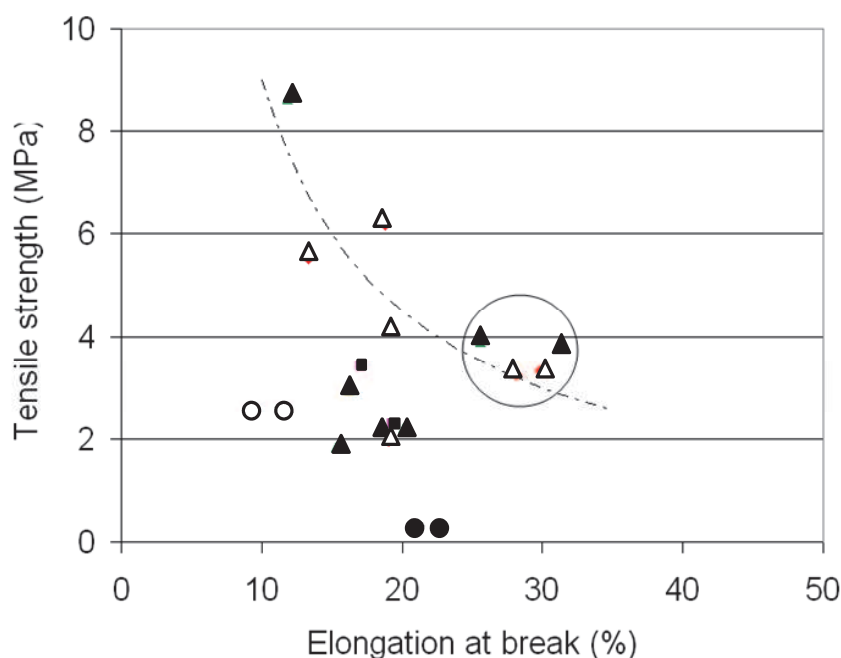


Fig. 7. Tensile strength as a function of elongation at break for various protein-based films prepared under different conditions : plasticized by glycerol and processed at ● 90°C, △ 120°C, ○ 140°C, ▲ 120°C containing shells and ■ plasticized by triethanolamine and processed at 120°C

4.1 Polylactic acid-based polymers

PLA is currently one of the most promising biopolymers. During the last decade PLA has been the subject of an abundant literature, with several reviews and book chapters (Averous, 2004; Garlotta, 2002; Auras et al, 2004; Mehta et al, 2005; Sodergard & Stolt, 2002). Processable by many techniques (blowing films, injection moulded pieces, calendared and thermoformed films...) a wide range of PLA grades is now commercially available with companies such as Cargill (USA), Mitsui Chemical (Japan), Galactic (Belgium), Shimadzu Co (Japan), Purac (Netherland) and many others (Shen et al, 2009).

After a general presentation of the synthesis and properties of polylactic acid, this chapter will detail three case studies.

The first case study concerns a **biocomposite for automobile applications combining a PLA-based matrix and an alterable glass fibre**. The challenge of the work is twofold: maintaining constant mechanical properties under aggressive conditions (temperature, moisture, mechanical stresses) during the in-service life of the automobile and having a material that is easily recycled by composting at the end of its life.

The second study case concerns **PLA-based films for some textile applications**, especially disposable safety workwear. With identical performances to non woven tissues or polyolefin weldable films, PLA films are considered to be competitive alternatives because of their

biodegradability. The required performances (tear resistance, weldability, perforation, thermal resistance, barrier properties...) can be achieved by incorporating specific additives (plasticizers, chain extender molecules, crosslinking agents...) and defined nanoparticles.

The third study case concerns **PLA-based foam products**. With the aim of reducing the environmental impact of plastics, these materials are of major industrial interest, replacing heavy items by lighter bio-based products with identical performance levels. They could be considered as interesting alternative candidates to polyethylene foams, for example, with expansion rates of about 50%. The objective of the studies concerned is to optimize either the processing conditions (extrusion flow rate, temperature, cooling system) or the material formulation (content of chemical blowing agent, PLA characteristics) for maximum foam expansion and good mechanical performances.

Finally it is important to underline that PLA is considered as one of the three biodegradable polymers used for **clinical applications**, together with polyglycolic acid (PGA) and paradiioxanone (PDS). Copolymers of PLA and PGA remain the most interesting alternatives to metals for bone consolidation. These applications will not be detailed in this chapter.

4.1.1 Synthesis and properties of PLA

Lactic acid is extracted from starch and converted to a high molecular weight polymer ($M_w > 100,000$) through an indirect polymerization route via lactide. This route was first demonstrated by Carothers in 1932 (Carothers, 1932) but high molecular weights were not obtained until improved purification techniques were developed (Garlotta, 2002). The mechanism involved is ring-opening polymerization (ROP) and may be ionic or coordination-insertion depending on the catalytic system used (Auras et al, 2004; Sodergard & Stolt, 2002; Stridsberg et al, 2001; Mehta et al, 2005).

All properties of PLA depend on its molecular characteristics, as well as the presence of ordered structures (crystalline thickness, crystallinity, spherulite size, morphology and degree of chain orientation). The physical properties of polylactide are related to the enantiomeric purity of the lactic acid stereo-copolymers. PLA can be produced totally amorphous or up to 40 % crystalline. PLA resins containing more than 93 % of L-lactic acid are semi-crystalline, while those containing 50–93 % are entirely amorphous. The typical PLA glass transition temperature ranges from 50°C to 80°C, whereas the melting temperature ranges from 130°C to 180°C. The mechanical properties of PLA can vary considerably, ranging from soft elastic materials to stiff high strength materials, according to various parameters, such as crystallinity, polymer structure, molecular weight, material formulation (plasticizers, blend, composites...) and processing. For instance, commercial PLLA (92% L-lactide) has a modulus of 2.1 GPa and an elongation at break of 9 %. The CO₂ permeability coefficients for PLA polymers are lower than those reported for crystalline polystyrene at 25°C and 0 % of relative humidity and higher than those for PET. The main abiotic degradation phenomena of PLA involve thermal and hydrolysis degradations.

4.1.2 Polylactic acid-based biocomposites for automobile applications

It is well known that the development of automobile parts requires materials with high mechanical characteristics and good thermal properties that remain constant throughout the in-service life of the automobile in a potential aggressive environment. This challenge could be achieved by the incorporation of reinforcements. Natural fibres are commonly used to reinforce PLA because of their renewability and biodegradability. Moreover, their low price

and low density are complementary advantages. Unfortunately, their main drawbacks are their relative low mechanical properties depending on the production location and crop, the weakness of the matrix/fibre interface and the potential competition with food production. Our research centre and OCV Chambéry International (Chambéry, France) joined forces to develop an innovative biodegradable biocomposite reinforced by glass fibres that can be degraded by water and mineralized by microorganisms without any toxic components being released into the environment. This alterability, combined with the good reproducibility of glass fibre properties compared to plant fibres, shows considerable promise. This research program was supported by the French organizations ADEME and ANR.

4.1.2.1 Alterable glass fibres

Most of the alterable glasses developed in recent years have been used in medical applications. They are based on silicate, calcium and phosphate components, leading to an improvement in micro-organism activity. They are incorporated within several biodegradable polymers such as PLA (Zhang et al, 2004) allowing bone reconstruction. Several steps are involved in glass alteration: inter-diffusion (exchanges between alkaline components of the glass and the solution), glass hydrolysis (direct interaction with intrinsic glass network), gel formation (re-condensation of some components such as silicates), precipitation of secondary phases. Several parameters may influence these mechanisms, such as glass composition, pH, temperature, contact surface and micro-organisms. For this project the main alterable glass formulations were based on silicate and moreover present the advantage of having a lower melting temperature and therefore lower energy requirements for processing than conventional glasses.

4.1.2.2 Mechanical properties of biocomposites

An alterable glass fibre (AGF) and a conventional E-glass fibre (E) were compared, both coated with a standard water based sizing used in traditional polyester composites (such as PET or PBT). A comparison with hemp natural fibre (HNF) will be also carried out. Classical co-rotating extrusion (Clextral BC21) and injection molding (Sandretto) processes were used for the elaboration of PLA (PLA 7000D© provided by Nature Works LCC, USA) reinforced by 30 wt% of fibres.

		PLA	PLA/E	PLA/AGF	PLA/HNF
Bending	Modulus (GPa)	3.36 ± 0.02	10.15 ± 0.25	9.28 ± 0.09	5.78 ± 0.09
	Strength (MPa)	102 ± 1	171 ± 5	138 ± 4	102 ± 2
	Elongation (%)	3.5 ± 0.0	1.8 ± 0.1	1.6 ± 0.1	2.4 ± 0.2
Tensile	Modulus (GPa)	3.61 ± 0.07	10.48 ± 0.28	9.81 ± 0.08	5.89 ± 0.12
	Strength (MPa)	72 ± 1	122 ± 2	116 ± 6	73 ± 1
	Elongation (%)	7.5 ± 1.2	3.3 ± 0.1	3.4 ± 0.3	3.0 ± 0.1
Impact	Resilience (kJ/m²)	30 ± 5	29 ± 2	32 ± 2	14 ± 2

Table 7. Mechanical properties of PLA and PLA composites reinforced by a conventional E-glass fibres (PLA/E), alterable glass fibres (PLA/AGF) and hemp natural fibres (PLA/HNF) (30 wt%)

The mechanical data are summarized on Table 7. The results show that the presence of hemp natural fibres within the PLA slightly increased the tensile and bending moduli but did not improve other mechanical properties (strength and elongation). Moreover a lower resilience was obtained for the HNF reinforced biocomposites compared to unreinforced

PLA. The presence of glass-based fibres led to a significant increase in bending and tensile moduli and strengths and a decrease in corresponding elongations. The impact properties were not influenced by the presence of glass-based fibres. However, AGF-fibres result in lower mechanical properties than E-fibres.

4.1.2.3 Ageing resistance of biocomposites

One of the scientific problems is to be able to maintain consistent properties throughout the in-service use of the biocomposites, while also being able to trigger their ultimate biodegradation/composting at the end of their life, as shown in Figure 8.

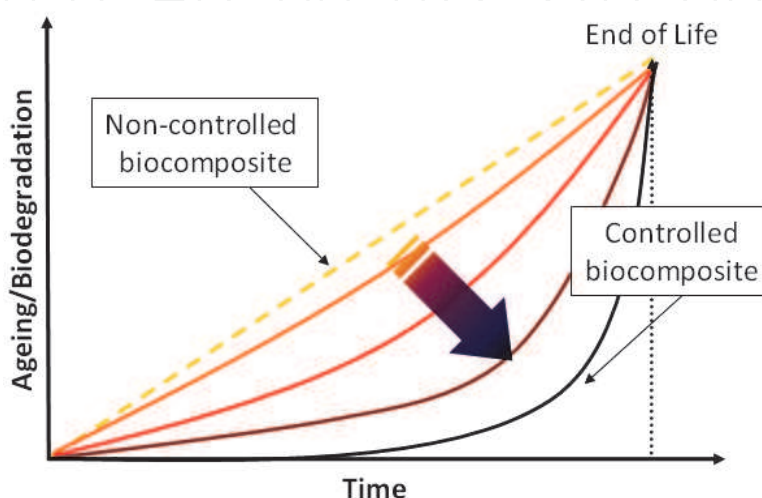


Fig. 8. Control of ageing and biodegradation kinetics of materials

It is well known that the main degradation mechanism of PLA is hydrolysis, which increases markedly above T_g and with ageing time due to the formation of hydrophilic groups such as alcohols and acid functions (Li & McCarthy, 1997). In addition, crystallinity and the presence of microvoids or porosity may affect water permeation (Drumright et al, 2000). Several ageing tests have been developed to analyze the evolution of material properties, among them accelerated ageing tests. For the present study biocomposites were conditioned within an autoclave with 100 RH% and at 65°C (above T_g), simulating several years of in-service use. Figure 9 shows the evolution of mechanical properties together with water absorption and crystallinity rate against ageing time. A significant decrease can be observed for all mechanical properties, with the lowest decrease being obtained for PLA/E biocomposites and the highest for PLA/AGF ones. With regard to water absorption, the presence of E-glass fibres may decrease the water content (0.61% compared to 1.37% for PLA) whereas the alterable fibres did not change the water content. A huge absorption rate was observed for HNF reinforced biocomposites (4.35%) due to the intrinsic hydrophilic character of these fibres. Whatever the biocomposite, an increase in crystallinity rate can be observed at short ageing time (+20% after an ageing time of 24h), then a plateau is obtained except for HNF reinforced PLA.

4.1.2.4 Biodegradation of biocomposites

Different degradation tests were performed on the PLA and biocomposites.

One of them was the previously described BOD test (see § 3.1.2.2.4), which showed no influence of the presence of alterable glass fibres (AGF) either on the latency time (about 10 days) or on the final degradation rate after 28 days (about 15 %) of PLA.

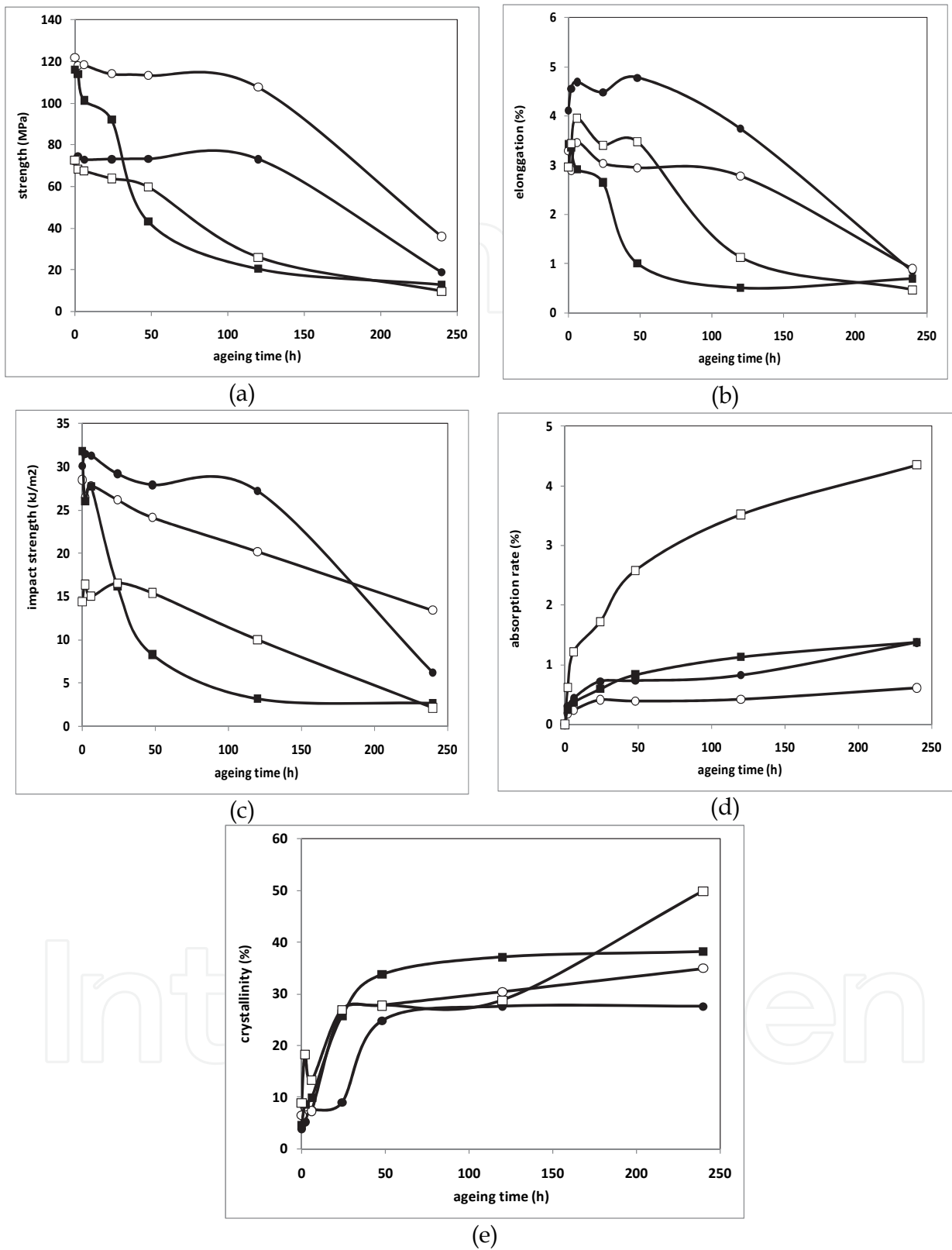


Fig. 9. Variation of (a) ultimate strain, (b) ultimate stress, (c) impact strength, (d) water absorption rate and (e) crystallinity rate of (●) PLA and PLA composites reinforced by by (○) conventional E-glass fibres (PLA/E), (■) alterable glass fibres (PLA/ AGF) and (□) hemp natural fibres (PLA/HNF) (30 wt%) with ageing time (65°C; 100 %RH)

Another test was performed according to XPU 44-163 standards and gave the mineralisation rate of PLA and biocomposites (Figure 10). It was observed that mineralisation rate of PLA does not stop increasing with a value of 170 mg CO₂/g of PLA after 49 days with a final pH of the soil of 4.24. In the case of the biocomposites, a decrease in this mineralisation rate can be observed with various behaviours according to the fibre nature. In presence of AGF a plateau is reached after 25 days (120 mg CO₂/g of composite) and acidification of the soil is observed (final pH at 4.06) which may induce a decrease in microbial activity. The lowest mineralisation rate, together with acidification of the soil (final pH at 3.91,) was obtained in the presence of HNF (60 mg CO₂/g of composite).

One purpose of this study was to propose glass formulation that may buffer the soil to avoid acidification and therefore the decrease in microbial activity.

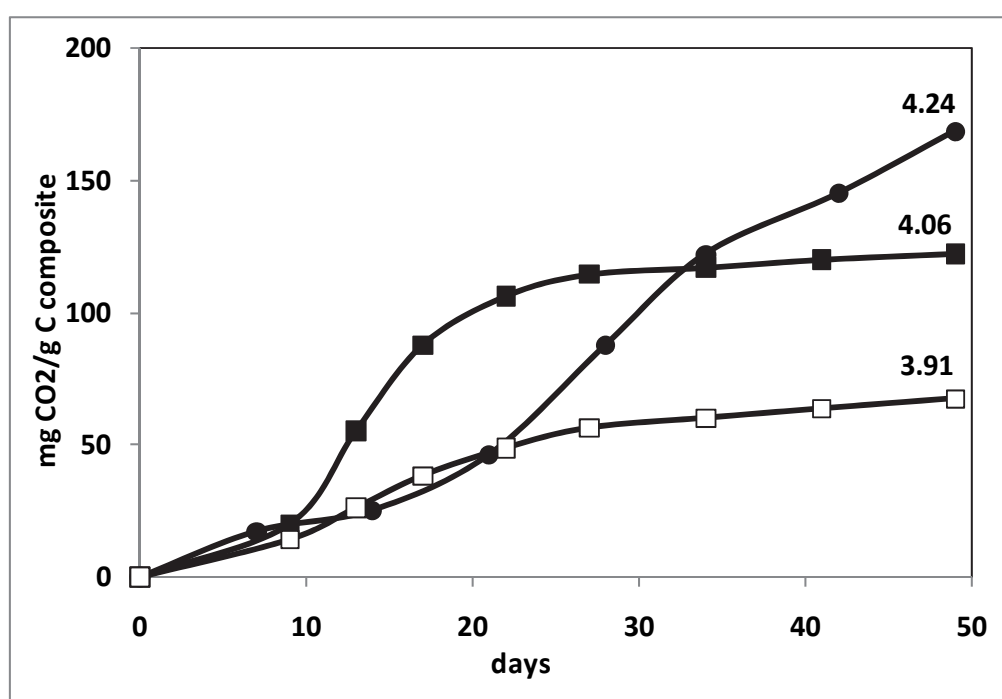


Fig. 10. Mineralisation rate and final pH of the soil for (●) PLA and PLA composites reinforced by (■) alterable glass fibres (PLA/AGF) and (□) hemp natural fibres (PLA/HNF) (30 wt%)

4.1.2.5 Further studies

Current studies are focussing on improving both the glass formulation and the PLA-based matrix properties. Concerning the glass, new glass compositions are being developed to control either the mechanical properties of the alterable fibre in order to be comparable to conventional E-glass fibres (with a Young's modulus about 73 GPa) or the alteration mechanism. For the PLA-based matrix, investigations are being carried out to increase impact properties as well as durability by incorporating impact modifiers and/or blending with other biodegradable polymers that are more ductile and less hydrophilic than PLA.

4.1.3 Polylactic acid-based films for textile applications

This second case study concerns PLA-based films for some textile applications, especially disposable safety workwear. The required performances (among them tear resistance,

weldability, perforation, thermal resistance, barrier properties) were achieved by incorporating nanoclays and specific additives.

Various mechanical behaviours were obtained according to the nature of the nanoparticles and their surface modifications. A fibrillar sepiolite and a lamellar montmorillonite (called MMT) were compared for a content of 2.5 wt%. They were respectively treated with a silane coupling agent (γ -methacryloxy-propyltriethoxysilane) and a quaternary ammonium salt. PLA (PLA4032D© provided by Nature Works LCC, USA) was plasticized (18 wt% of tributylacetylacetate from Sigma Aldrich). A chain extender (styrene-co-glycidyl methacrylate, trademarked Joncryl 4368© from BASF) was also added. A three-step process was involved including (i) twin screw extrusion to obtain a PLA/clay masterbatch (85/15 w/w), (ii) dilution and addition of plasticizer and chain extender through twin screw extrusion and (iii) blowing extrusion to obtain 50 μ m thick films.

The first analysis of the behaviour was performed using the tensile tests performed for each formulation. These tests were carried out using an optical extensometer combining a Charge Couple Device (CCD) camera associated with Digital Image Correlation (DIC) software. This revealed the evolution of the in-plane strains (transverse and longitudinal components) (Figure 11). Table 8 summarizes all mechanical characteristics. While it can be observed that a lower yielding stress was obtained for PLA films filled with sepiolite clay, on the other hand they showed higher work hardening (K).

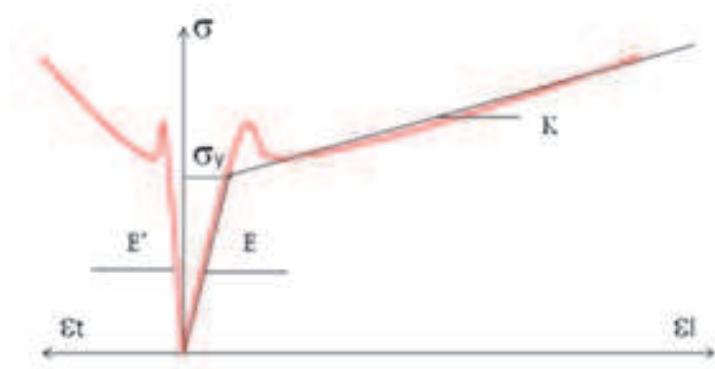


Fig. 11. Evolution of the in-plane strains (transverse and longitudinal components)

	E (MPa)	σ_y (MPa)	K
PLA	1100 (10)	26 (11)	1 (8)
PLA/sepiolite	390 (10)	16 (8)	17 (3)
PLA/mod-sepiolite	600 (14)	15 (7)	17 (3)
PLA/MMT	700 (10)	21 (4)	12 (5)
PLA/mod-MMT	1100 (10)	27 (2)	13 (5)

Table 8. Longitudinal mechanical characteristics obtained from loading curves of stress vs deformation (100 mm/min, sample 150x50x100 mm³) for PLA and PLA composites reinforced by unmodified and modified (mod) sepiolite and montmorillonite – (): variance

4.1.4 Polylactic acid-based foam products

Obtaining PLA-based foam products is of major industrial interest, in order to replace high-mass products by lighter bio-based ones with identical performances. They can be considered as interesting alternative candidates.

The objective of the studies concerned was to optimize either the processing conditions (extrusion flow rate, temperature, cooling system) or the material formulation (content of chemical blowing agent, PLA characteristics) for maximum foam expansion and good mechanical performances.

Results show that the nature of the PLA (PLA 7000D© and PLA4032D© provided by Nature Works LCC, USA) had no major effect on the void content of the foams extruded under the same conditions (screw range temperature: 150-180°C) (Figure 12). The density varied between 893 and 879 kg/m³ for a CBA content of 2 wt% (corresponding to a density reduction of 29 % and 30 %, respectively). Moreover, the void content increased gradually (the foam density decreased) with the CBA content, regardless of the PLA type or temperature profile. This evolution is related to the amount of gas formed and available for the expansion process (Klempner & Sendjarevic, 1991). Similar results have been reported for extruded foams based on polyolefins (Lee, C.H. et al, 2000; Lee, S.T., 2004, 2008).

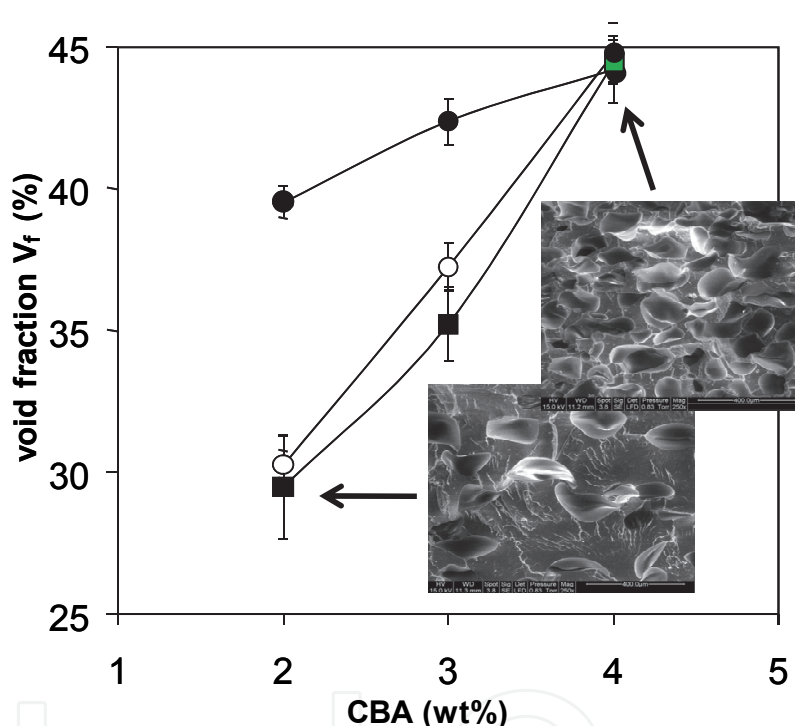


Fig. 12. Void fraction of PLA foams as a function of the chemical blowing agent content (CBA), the processing conditions (screw range temperature : ● 130-190°C; ■,○ 150-180°C) and the PLA nature (○ PLA4032D©, ●,■ PLA7000D©) and corresponding microstructures (ESEM observations; magnitude 250X)

In addition, both PLAs investigated provided foams with homogeneous cellular structures (polydispersity PDI close to 1) (Table 9). In all cases, the open-cell ratio was low, below 26 %. Similar results have been reported for polyolefin foams (Klempner & Sendjarevic, 1991; Ray & Okamoto, 2003; Ema et al, 2006). An increase in the open-cell ratio with the CBA content is observed which is related to the amount of gas release. This trend has already been reported by other authors (Klempner & Sendjarevic, 1991; Lee, C.H. et al, 2000). A higher open-cell ratio range is obtained for PLA4032D© (ratio between 19 and 27% for CBA content between 2 and 4 wt%) compared to PLA7000D© (ratio between 11 and 19%). This is related to the higher temperatures involved in the temperature profile used for PLA4032D© inducing a

higher gas yielding as well as a lower PLA viscosity. The cell density of the PLA7000D©-based foams processed with a screw temperature range 130-190°C was significantly higher than that of PLA4032D©-based foams processed with the screw temperature range 150-180°C. This is undoubtedly related to gas loss through the first barrel zones during extrusion-foaming of the PLA4032D©. Moreover, for PLA7000D©, the cell density decreases with the CBA content as the cell size increases with no variation in the cell wall thickness. For PLA4032©, a slight increase in cell density is observed with a non monotonous variation in cell size and a significant decrease in the cell wall thickness. It can be assumed that several competitive mechanisms may occur: (i) the increase in gas yielding and decrease in viscosity due to barrel temperatures, (ii) the plasticization induced by the gas products during decomposition and (iii) the presence of a higher content of nucleating agents present in the CBA masterbatch. Complementary work is in progress to evaluate the relative contributions of these mechanisms. The average cell diameter and cell-wall thickness in the present study were similar to those reported for polyolefin foamed with CBA (Klempner & Sendjarevic, 1991; Lee, C.H. et al, 2000), but significantly higher than those reported by other authors for microcellular PLA foams (Ray & Okamoto, 2003). Nevertheless, the cases reported in the literature concern mainly physical foaming processes, and PLA modified by nanofillers (which may act as cell nucleating agents) and/or chain extenders.

Finally, for both types of PLA investigated, the increase in CBA content led to a reduction in stresses at yield and break in tension (Table 10), due to the increase in void content (reduction of the effective sample cross-section). On the contrary, elongation at yield and break were low and independent of the CBA content. Similar results were reported for PVC and PUR-based foams (Kabir et al, 2006; Lin, 1997).

PLA	CBA1 (%wt)	d _n (µm)	d _w (µm)	PDI	N _c (cells.cm ⁻³) ×10 ⁵	δ (µm)	C _o (%)
7000 D©	2	90 (2)	105 (1)	0.86 (0.01)	11.25 (0.78)	48 (1)	10.91 (0.24)
	3	95 (2)	104 (1)	0.91 (0.01)	10.13 (0.70)	46 (1)	14.72 (1.08)
	4	107 (2)	122 (2)	0.88 (0.01)	7.38 (0.51)	49 (1)	19.22 (0.69)
4032 D©	2	134 (3)	144 (2)	0.93 (0.01)	2.72 (0.19)	95 (2)	19.12 (1.47)
	3	125 (3)	174 (2)	0.72 (0.01)	4.02 (0.28)	71 (2)	24.49 (1.3)
	4	130 (3)	152 (2)	0.86 (0.01)	4.19 (0.29)	58 (1)	26.76 (1.11)

Table 9. Cell dimensions (d_n, d_w), cell density (N_c), cell size polydispersity (PDI), cell-wall thickness (δ) and open-cell ratio (C_o) as function of CBA content – PLA 7000D© screw temperature range 130-190°C and PLA 4032D© screw temperature range 150-180°C; screw speed 30 tr/min; die temperature 195 °C; free cooling - () : standard deviation

4.2 Polyhydroxyalkanoates

Like polylactic acids, polyhydroxyalkanoates (PHAs) are aliphatic polyesters (Figure 13) produced via fermentation of renewable feedstock. Whereas PLA production is a two-stage

process (fermentation to monomer followed by a conventional polymerization step), PHAs are produced directly via fermentation of carbon substrate within the microorganism. The PHA accumulates as granules within the cytoplasm of cells and serves as a microbial energy reserve material. PHAs have a semicrystalline structure, the degree of crystallinity ranging from about 40% to around 80% (Averous, 2004).

PLA	CBA (wt%)	Void fraction (%)	$\sigma_{\max}$ (MPa)	$\epsilon_{\max}$ (%)	σ_r (MPa)	ϵ_r (%)
7000D©	2	42 (1)	36.00 (2.84)	8.41 (0.32)	33.38 (2.18)	9.95 (0.71)
	3	45 (1)	25.65 (1.33)	8.84 (0.39)	21.51 (1.72)	11.59 (0.92)
	4	47 (1)	23.71 (0.90)	8.37 (0.55)	20.49 (1.08)	10.28 (1.16)
4032D©	2	34 (1)	40.54 (3.27)	10.24 (0.89)	37.91 (3.90)	11.51 (1.23)
	3	41 (1)	30.68 (2.40)	8.61 (0.70)	27.14 (3.44)	10.43 (1.11)
	4	48 (1)	26.77 (1.24)	9.44 (1.36)	22.87 (1.12)	11.50 (1.60)

Table 10. PLA-foams tensile properties. Processing conditions: PLA 7000D© screw temperature range 130-190°C and PLA 4032D© screw temperature range 150-180°C; screw speed 30 tr/min; die temperature 195 °C; free cooling. ($\sigma_{\max}$: yield stress, $\epsilon_{\max}$: elongation at yield stress, σ_r : stress at break, ϵ_r : elongation at break) - () : standard deviation

Table 11 shows the generic formula for PHA where x is 1 (for all commercially – relevant polymers) and R can be either hydrogen or hydrocarbon chains of up to around C16 in length. A wide range of PHA homopolymers, copolymers and terpolymers have been produced, in most cases at the laboratory scale. A few of them have attracted industrial interest and been commercialized in the past decade.

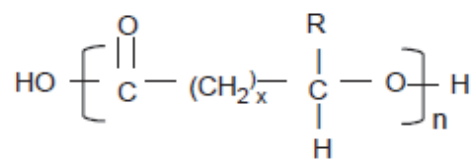


Fig. 13. PHA molecule

PHA	full name	x	R
PHB	Poly(3-hydroxybutyrate) P(3HB)	1	-CH ₃
PHV	Poly(3-hydroxyvalerate) P(3HV)	1	-CH ₂ CH ₃
PHBV	Poly(3-hydroxy butyrate-co-valerate) P(3HB-co-3HV)	1	-CH ₃ and -CH ₂ CH ₃
PHBHx	Poly(3-hydroxy butyrate-co-hexanoate) P(3HB-co-3HHx)	1	-CH ₃ and -CH ₂ CH ₂ CH ₃
PHBO	Poly(3-hydroxy butyrate-co-octanoate) P(3HB-co-3HO)	1	-CH ₃ and -(CH ₂) ₄ CH ₃

Table 11. Examples of structures of PHA

Like PLA, PHA is sensitive to processing conditions. Under extrusion, a rapid decrease in viscosity and molecular weight can be observed due to macromolecular linkage by

increasing the shear level, the temperature and/or the residual time (Ramkumar & Bhattacharia, 1998). The kinetics of enzymatic degradation varies according the crystallinity and processing history (Parikh et al, 1998).

At present, packaging (bags, boxes), agriculture mulching films and personal care items (razors, tooth brush handles) are the most important market for PHA. In the future, the applications will become broader: building, textile, transportation, electronics, houseware, etc.

4.3 Biopolyesters obtained from petrochemical products

Several biopolyesters can be obtained from petrochemical products, among the most commonly used is polycaprolactone (ring opening polymerization of caprolactone resulting from moderate oxidation of cyclohexanone). The other biopolyesters are produced through condensation reactions between diols and diacides, for example polybutylene succinate (PBS), polybutylene adipate terephthalate (PBAT). All these biodegradable polymers have interesting ductile properties, and are thus frequently combined with rigid PLA.

PCL is widely used as a PVC solid plasticizer or for polyurethane applications. There are also some applications based on its biodegradable character in the controlled release of drugs and soft compostable packaging.

5. Conclusion

The progress made in the field of environmental-friendly biodegradable polymers and composites over the past ten years has been impressive. A large number of companies are now involved in this area, producing a wide range of products. There are also major ongoing advances in research and development, contributing to the increased attractiveness of chemical sciences and technology for a new generation of scientists and engineers. All in all, these developments have converted bio-based polymers and composites from a minor niche into a mainstream activity. However, the challenges that need to be successfully addressed in the years and decades to come are the lower material performance of some bio-based polymers, the control of the lifetime during in-service life regardless of their end-of-life biodegradation, their relatively high production and processing costs, and the need to minimize the use of agricultural land and forests, thereby also avoiding competition with food production and adverse effects on biodiversity and other environmental impacts.

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CEA (Commissariat à l’Energie Atomique), Marcoule; Ecole des Mines de Douai, Douai) involved in the various studies presented in this chapter.

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