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**Biodegradable Multiphase Systems Based on
Plasticized Starch: A Review****Luc Avérous***

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ABSTRACT

The aim of this review is to show the relationships between the structure, the process, and the properties of biodegradable multiphase systems based on plasticized starch (PLS), the so-called “thermoplastic starch.” These mutiphase materials are obtained when associating association between plasticized starches and other biodegradable materials, such as biodegradable polyesters [polycaprolactone (PCL), polyhydroxyalkanoates (PHAs), polylactic acid (PLA), polyesteramide (PEA), aliphatic, and aromatic copolyesters], or agro-materials (ligno-cellulosic fiber, lignin etc.). Depending on materials (soft, rigid) and the plastic processing system used, various structures

(blends, composites, multilayers) can be obtained. The compatibility problematic between these hetero-materials is analyzed. These starchy products show some interesting properties and have some applications in different fields: packaging, sports, catering, agriculture and gardening, or hygiene.

Key Words: Plasticized starch; Agro-polymer; Multiphase system; Biodegradable polyester; Structure; Plastic processing.

1. INTRODUCTION

It is widely accepted that the use of long-lasting polymers for short-lived applications (packaging, catering, surgery, hygiene), is not entirely adequate. This is not justified when increased concern exists about the preservation of ecological systems. Most of the today's synthetic polymers are produced from petrochemicals and are not biodegradable. These persistent polymers are a significant source of environmental pollution, harming wildlife when they are dispersed in nature. For example, the effects of plastic bags are well known to affect sea-life.^[1] Besides, plastics play a large part in waste management, and the collectivities (municipalities, regional or national organizations) are becoming aware of the significant savings that the collection of compostable wastes would provide. Besides, valorizing the plastics wastes presents some issues. Energetic valorization yields some toxic emissions (e.g., dioxin). Material valorization implies some limitations linked to the difficulties to find accurate and economically viable outlets. In addition, material valorization shows a rather negative eco-balance due to the necessity, in nearly all cases, to wash the plastic wastes and to the energy consumption during the process phases (waste grinding and plastic processing). For these different reasons, reaching the conditions of conventional plastic replacements by degradable polymers, particularly for packaging applications, is of major interest for the different actors of the socio-economical life (from the plastic industry to the citizen).

The potential of biodegradable polymers and more particularly that of polymers obtained from agro-resources such as the polysaccharides (e.g., starch) has long been recognized. However, to this day, these agro-polymers largely used in some applications (e.g., food industry) have not found extensive applications in the packaging industries to replace conventional plastic materials, although they could be an interesting way to overcome the limitation of the petrochemical resources in the future. The fossil fuel and gas could be partially replaced by greener agricultural sources, which should also participate in the reduction of CO₂ emissions.^[1]

2. BIODEGRADABLE POLYMERS

2.1. Concepts: Biodegradability and Renewability

2.1.1. Biodegradability and Compostability

According to ASTM standard D-5488-94d, biodegradable means capable of undergoing decomposition into carbon dioxide, methane water, inorganic compounds, or

biomass in which the predominant mechanism is the enzymatic action of micro-organisms that can be measured by standard tests, over a specific period of time, reflecting available disposal conditions. There are different media (liquid, inert or compost medium) to analyze biodegradability. Compostability is material biodegradability using compost medium. Biodegradation is the degradation of an organic material caused by biological activity, mainly micro-organisms' enzymatic action. This leads to a significant change in the material chemical structure. The end-products are carbon dioxide, new biomass and water (in the presence of oxygen: aerobia) or methane (oxygen absent: anaerobia), as defined in the European Standard EN 13432:2000. Unfortunately, depending on the standard used (ASTM, EN), different composting conditions (humidity, temperature cycle) must be realized to determine the compostability level.^[2] Then, it is difficult to compare the results using different standard conditions. We must also take into account the amount of mineralization as well as the nature of the residue left after biodegradation.^[3] The accumulation of contaminants with toxic residues and chemical reactions of biodegradation can cause plant growth inhibition in these products, which must serve as fertilizers. Actually, the key issue is to determine the environmental toxicity level for these by-products, which is known as eco-toxicity.^[4]

Some general rules enable the estimating of the biodegradability evolution. An increase of parameters such as the hydrophobic character, the macromolecular weight, the crystallinity or the size of spherulites decreases biodegradability.^[5] On the contrary, the presence of polysaccharides (blends) favors biodegradation.

2.1.2. Renewability and Sustainable Development

Renewability is linked to the concept of sustainable development. The UN World Commission on "Environment and Development in our Future" defines sustainability as the development which meets the needs of the present time without compromising the ability of future generations to meet their own needs. According to Narayan,^[1] the manufactured products, e.g., packaging, must be designed and engineered from "conception to reincarnation," the so-called "cradle-to-grave" approach. The use of annually renewable biomass, like wheat, must be understood in a complete carbon cycle. This concept is based on the development and the manufacture of products based on renewable and biodegradable resources: starch, cellulose, etc. By collecting and composting biodegradable plastic wastes, we can generate much-needed carbon-rich compost: humic materials. These valuable soil amendments can go back to the farmland and reinitiate the carbon cycle. Besides, composting is an increasing key point to maintain the sustainability of the agricultural system by reducing the consumption of chemical fertilizers.

2.2. Biodegradable Polymers Classifications

Biodegradable polymers are a growing field.^[6-8] A vast number of biodegradable polymers have been synthesized or are formed in nature during the growth cycles of all organisms. Some micro-organisms and enzymes capable of degrading them have been identified.^[6,9,10]

Depending on the evolution of the synthesis process, different classifications of the different biodegradable polymers have been proposed. Figure 1 shows an attempt at

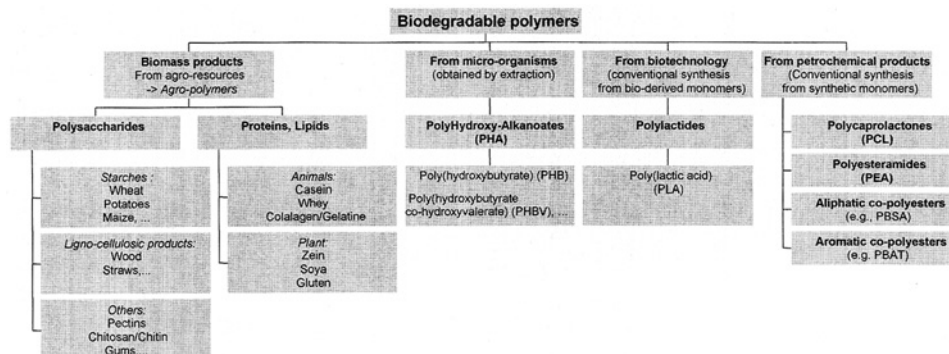


Figure 1. Classification of the biodegradable polymers.

classification. We have four different categories. Only, three categories (a–c) are obtained from renewable resources:

- polymers from biomass such as the agro-polymers from agro-resources (e.g., starch, cellulose),
- polymers obtained by microbial production, e.g., the polyhydroxyalkanoates (PHAs),
- polymers conventionally and chemically synthesized and whose monomers are obtained from agro-resources, e.g., the polylactic acid (PLA),
- polymers whose monomers and polymers are obtained conventionally, by chemical synthesis.

We can also classify these different biodegradable polymers into two main families: the agro-polymers (category a) and the biodegradable polyesters (categories b–d).

2.3. Biodegradable Polyesters

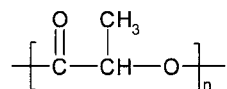
2.3.1. Presentation

Figure 2 shows the chemical structures of various biodegradable polyesters. Table 1 shows main polyesters, which are commercially available. Besides, physical and mechanical properties of some commercial polyesters are given in Table 2.

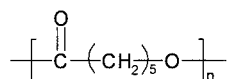
2.3.2. Agro-Resources Based Polyesters

2.3.2.1. PLA

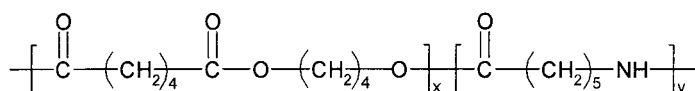
Lactic acid can be produced in different ways: chemical or biological, i.e., by fermentation of carbohydrate from lactobacillus.^[11] The enantiomeric monomers (D and L) are polycondensed via its cyclic dimer (lactide) by ring-opening polymerization (ROP) to a high molecular weight polymer.^[10,12,13]



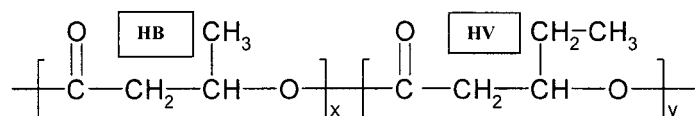
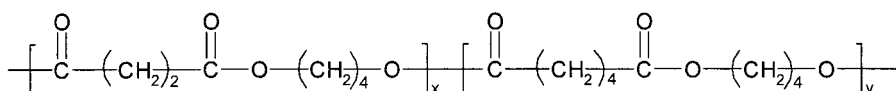
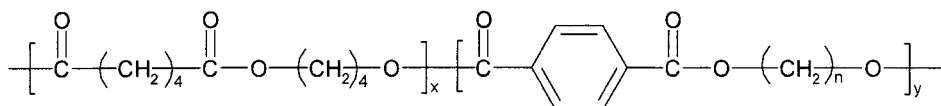
Poly(lactic acid) (PLA)



Polycaprolactone (PCL)



Polyesteramide (PEA)

Polyhydroxyalkanoate: *Poly(hydroxybutyrate-co-hydroxyvalerate)* (PHBV)Aliphatic copolyester: *Poly(butylene succinate adipate)* (PBSA)**Figure 2.** Chemical structures of different biodegradable polyesters.

Compared to the other biodegradable polyesters, polylactic acid (PLA) is the product that at the present time has one of the highest potentials due to its availability in the market and its low price.^[14–16] For instance, Cargill–Dow has developed processes that use corn and other feedstock to produce different PLA grades (NatureWorks®).^[18] For this company, the estimated production in 2002 is 100 ktons. Actually, it is the highest production of biodegradable polyester. In 2004, its price is around 3 €/kg. Different

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Table 1. Classification of main biodegradable polyesters, commercially available.

	Trade name	Company
Agro-resources based polyesters		
PLA	Natureworks	Cargill-Dow LLC (USA)
	Lacty	Shimadzu (Japan)
	Lacea	Mitsui Chemicals (Japan)
	Heplon	Chronopol (USA)
	CPLA	Dainippon Ink Chem. (Japan)
	PLA	Galactic (Belgium)
PHA		
PHB, PHBV	Biopol	Monsanto-Metabolix (USA) ^a
PHB, PHBV	Biocycle	Copersucar (Brazil)
PHBHx, PHBO, PHBOd	Nodax	Procter & Gamble (USA)
Petroleum-based polyesters		
PCL	CAPA	Solvay (Belgium)
	Tone	Union Carbide (USA)
	Celgreen	Daicel (Japan)
PEA	BAK	Bayer (Germany) ^a
Aliphatic copolyesters (e.g., PBSA)	Bionolles	Showa Highpolymer (Japan)
	EnPol	Ire Chemical Ltd (Korea)
	Skygreen	SK Chemicals (Korea)
	Lunare SE	Nippon Shokubai (Japan)
Aromatic copolyesters (e.g., PBAT)	Eastar Bio	Eastman Chemical (USA)
	Ecoflex	BASF (Germany)
	Biomax	Dupont (USA)
	PHEE	Dow Chemicals (USA) ^a

^aThe production of these polyesters has been stopped.

companies such as Mitsui Chemicals (Japan), Galactic (Belgium), or Dainippon Ink Chemicals (Japan) produce smaller PLA outputs.

Properties of PLA are highly related to the ratio between the two mesoforms D and L. Commercially available, we can find 100% L-PLA which present a high crystallinity (C-PLA) and copolymers of poly(L-lactic acid) and poly(D,L-lactic acid) which are rather amorphous (A-PLA).^[17-19] PLA can show crystalline polymorphism^[20] which can lead to different melting peaks^[21] with a main transition at 152°C for the D,L-PLA (see Table 2). Furthermore, PLA can be plasticized using oligomeric lactic acid (OLA), citrate ester,^[22] or low molecular weight polyethylene glycol (PEG).^[21,23] Table 3 shows the evolution of some properties depending on the plasticizer content. We can notice a T_g shift of 40°C by addition of 20 wt% of OLA. At room temperature, we are close to the rubber plateau with high elongations at break (200%). Besides, the effect of plasticization increases the chain's mobility and then favors the PLA organization and crystallinity we obtain after plasticization, a crystallinity ranging between 20% and 30%.

PLA presents a medium water and oxygen permeability level^[24] comparable to polystyrene.^[25] These different properties associated with its tunability and its availability favor its actual developments in different packaging applications (trays, cups, bottle, films, etc.).^[15,18] McCarthy^[26] showed that A-PLA presents a soil degradation rate

Table 2. Physical and mechanical properties of some biodegradable polyesters.

	PLA	PHBV		PEA Bayer	PBSA Showa	PBAT Eastman
	Dow-Cargill	Monsanto		(BAK 1095)	(Bionolle	(Estar Bio
	(Natureworks)	(Biopol D400G)			3000)	14766)
		HV = 7 mol%				
Density	1.25	1.25	1.11	1.07	1.23	1.21
Melting point (DSC) (°C)	152	153	65	112	114	110–115
Glass transition (DSC) (°C)	58	5	–61	–29	–45	–30
Crystallinity (%)	0–1	51	67	33	41	20–35
Modulus (MPa) (NFT 51-035)	2,050	900	190	262	249	52
Elongation at break (%) (NFT 51-035)	9	15	>500	420	>500	>500
Tensile stress at break or max (MPa) (NFT 51-035)	—	—	14	17	19	9
Biodegradation ^a	100	100	100	100	90	100
mineralization (%)						
Water permeability WVTR at 25°C (g/m ² /day)	172	21	177	680	330	550
Surface tension ^b (γ) (mN/m)	50	—	51	59	56	53
γ _d (dispersive component)	37	—	41	37	43	43
γ _p (polar component)	13	—	11	22	14	11

^aAt 60 days in controlled composting according to ASTM 5336.

^bDeterminations from contact angles measurements of probes liquids.

Sources: Refs. [21,27,33,40,72,132,208].

Table 3. Plasticization effects on some PLA properties.

	T_g (DSC) (°C)	Crystallinity (%)	Modulus (MPa)	Elongation at break (%)
A-PLA	58	1	2,050 (44)	9 (2)
+10% OLA	37	21	1,256 (38)	32 (4)
+20% OLA	18	24	744 (22)	200 (4)
+10% PEG 400	30	26	1,488 (39)	26 (5)
+20% PEG 400	12	29	976 (31)	160 (12)

Note: Standard deviations are given in brackets.

Source: Ref.^[21].

much slower compared with polybutylene succinate/adipate (PBSA). PLA is presumed to be biodegradable, although the role of hydrolysis versus enzymatic depolymerization in this process remains open to debate.^[27] Composting conditions are found only in industrial units with a high temperature (above 50°C) and a high relative humidity (RH) to promote chain hydrolysis. But, according to Tuominen et al.,^[28] PLA biodegradation does not exhibit any eco-toxicological effect.

2.3.2.2. PHAs

PHAs can be produced in different ways, chemically or biologically, by fermentation from feedstock. This family comprises mainly of a homopolymer, polyhydroxybutyrate (PHB), and different copolyesters, polyhydroxybutyrate-*co*-hydroxyalkanoates such as polyhydroxybutyrate-*co*-hydroxyvalerates (PHBV) (see Fig. 2), or polyhydroxybutyrate-*co*-hydroxyhexanoate (PHBHx), polyhydroxybutyrate-*co*-hydroxyoctanoate (PHBO), and polyhydroxybutyrate-*co*-hydroxyoctadecanoate (PHBod).

PHB is a natural polymer. It is an intracellular storage product of bacteria and algae. After fermentation, PHB can be obtained by solvent extraction. Recently, Monsanto has developed a genetic modification of plants to make them produce small quantities of PHB.^[18]

PHB is a highly crystalline polyester (80%) with a high melting point, $T_f = 173\text{--}180^\circ\text{C}$ (Monsanto data), compared with the other biodegradable polyesters. Glass transition temperature (T_g) is around 5°C. The homopolymer shows a narrow window for the process condition. To ease the transformation, PHB can be plasticized with citrate ester, but the corresponding copolymer (PHBV) is more adapted for the process.

PHBV can be produced by bacterial fermentation (e.g., with *Alcaligenes eutrophus*)^[29] of bioproducts such as glucose containing propionic or valeric acid, followed by an extraction step and purification of the polymer. PHBV can be also produced from butyrolactone and valerolactone with an oligomeric aluminosilicate catalyst.^[30] According to the synthesis, we obtain different structures, isotactic with random stereosequences for the bacterial copolyesters and with partially stereoregular block for the synthetic copolyesters.

A large range of bacterial copolymer grades had been industrially produced by Monsanto under the Biopol[®] trade mark, with HV contents reaching 20%. The production was stopped at the end of 1999. Metabolix bought Biopol[®] assets in 2001. Currently, different small companies produce bacterial PHBV, e.g., Copersucar (Brazil) produces PHBV (HV = 12%) 45% crystalline, from sugarcane molasses.^[31] Recently, Procter

and Gamble has begun to develop a large range of polyhydroxybutyrate co-hydroxyalkanoates (PHBHx, PHBO, PHBOd). Industrial production is planned in 2005.

Figure 2 and Table 2 give, respectively, the chemical structure and the properties of some PHBV. Material properties can be tailored by varying the HV content. An increase of the HV content induces an increase of the impact strength and a decrease of

- melting temperature and glass transition,^[32]
- crystallinity,^[33]
- water permeability,^[33]
- tensile strength.^[34]

Besides, PHBV properties can evolve when plasticization occurs, e.g., with citrate ester (triacetin).^[34,35] The PHAs as the PLAs are sensitive to the process conditions. Under extrusion, we obtain a rapid diminution of the viscosity and the molecular weight due to macromolecular linkage by increasing the shear level, the temperature and/or the residential time.^[36]

The kinetics of enzymatic degradation is variable according to the crystallinity, the structure,^[5,31] and then, to the processing history.^[37] Bacterial copolyesters are more biodegradable than synthetic copolyesters.^[38]

2.3.3. Petroleum-Based Polyesters

A large number of biodegradable polyesters are based on petroleum resources obtained chemically from synthetic monomers.^[12–18] We can distinguish (see Table 1), according to the chemical structures (see Fig. 2), polycaprolactones (PCLs), polyester-amides (PEAs), aliphatic or aromatic copolyesters. All these polyesters are soft at room temperature.

2.3.3.1. PCL

Poly(ϵ -caprolactone) is obtained by ROP of ϵ -caprolactone in the presence of aluminum isopropoxide.^[12,13,38] PCL is widely used as a PVC solid plasticizer or for polyurethane applications. But, it finds also some application based on its biodegradable character in domains such as controlled release of drugs, soft compostable packaging, etc. Different commercial grades are produced by Solvay (CAPA[®]), by Union Carbide (Tone[®]), and by Daicel (Celgreen[®]).

Figure 2 and Table 2 give, respectively, the chemical structure and the properties of this polyester. PCL shows a very low T_g (-61°C) and a low melting point (65°C), which could be a handicap in some applications. Therefore, PCL is generally blended^[27,30,39,40] or modified (e.g., copolymerization, crosslink^[41]).

Tokiwa and Suzuki^[42] have discussed the hydrolysis of PCL and biodegradation by fungi. They have shown that PCL can be enzymatically degraded easily. According to Bastioli,^[27] the biodegradability can be clearly claimed but the homopolymer hydrolysis rate is very low. The presence of starch can significantly increase the biodegradation rate of PCL.^[39]

2.3.3.2. PEA

PEA was industrially obtained from the statistical copolycondensation of polyamide (PA 6 or PA 6-6) monomers and adipic acid.^[18,43] Bayer had developed different commercial grades under BAK[®] trademark but their production stopped in 2001. Figure 2 and Table 2 show, respectively, the chemical structure and the properties of this polyester. It is the polyester, which presents the highest polar component, and then it shows good compatibility with other polar products, e.g., starchy compounds. On the other hand, it presents the highest water permeability (see Table 2).

Currently, the environmental impact of this copolymer is still open to discussion. Fritz^[44] had shown that this biodegradable polyester presented after composting a negative eco-toxicological impact but more recently, Bruns et al.^[45] have confirmed these results. These authors discussed Fritz's experiments and more precisely the composting methods used.

2.3.3.3. Aliphatic Copolyesters

A large number of aliphatic copolyesters are biodegradable copolymers based on petroleum resources. They are obtained by the combination of diols, such as 1,2-ethanediol, 1,3-propanediol, or 1,4-butanediol, and dicarboxylic acid: adipic, sebacic, or succinic acid. Showa Highpolymer (Japan) has developed a large range of polybutylene succinate (PBS) obtained by polycondensation of 1,4-butanediol and succinic acid. Polybutylene succinate/adipate (PBSA), presented in Fig. 2, is obtained by addition of adipic acid. These copolymers are commercialized under the Bionolle[®] trade mark.^[18] Table 2 shows the properties of such a terpolymer. Ire chemical (Korea) commercializes exactly the same kind of copolyesters under EnPol[®] trade mark. Skygreen[®], a product from SK Chemicals (Korea), is obtained by polycondensation of 1,2-ethanediol, 1,4-butanediol with succinic and adipic acids.^[46] Nippon Shokubai (Japan) also commercializes an aliphatic copolyester with Lunare SE[®] trademark. These copolyesters' properties depend on the structure,^[47] i.e., the combination of diols and diacids used.

Biodegradability of these products depends also on the structure. The addition of adipic acid, which decreases the crystallinity^[48] tends to increase the compost biodegradation.^[49] According to Ratto et al.,^[50] the biodegradation results demonstrate that although PBSA is inherently biodegradable, the addition of a starch filler significantly improve the rate of degradation.

2.3.3.4. Aromatic Copolyesters

Compared with totally aliphatic copolyesters, aromatic copolyesters are often based on terephthalic diacid. Figure 2 and Table 2 show, respectively, the chemical structure and the properties of such products (e.g., see Eastar Bio[®] from Eastman). Besides, BASF and DuPont commercialize aromatic copolyesters with Ecoflex[®]^[18] and Biomax[®] trade marks, respectively. Biomax[®] shows a high terephthalic acid content which modifies some properties such as the melting temperature (200°C). But, according to Muller et al.,^[47] an increase of terephthalic acid content tends to decrease the degradation rate, while aromatic like aliphatic copolyesters degrade totally in micro-organisms environment (compost). Ecoflex[®] biodegradation has been analyzed by Witt et al.,^[51] they concluded that there is no indication for an environmental risk (ecotoxicity) when aliphatic–aromatic copolyesters of the Ecoflex-type are introduced into composting processes.

Another kind of polyester can be classified into the group of the aromatic polyesters, the polyhydroxy ester ethers (PHEE). They are obtained from adipic acid and the diglycidil ether of bisphenol A. A commercial PHEE had been developed by Dow chemicals (USA), but the production has stopped.

2.4. Agro-Polymers

2.4.1. Presentation

Agro-polymers are mainly extracted from plants. They are compostable and renewable polymers. We find different families such as the polysaccharides or the lignins. They show some common characteristics such as a hydrophilic character. Most of them can be processed directly, either plasticized as fillers or modified by chemical reactions.

2.4.1.1. Polysaccharides

This family is represented by different products such as starch or cellulose based on glucose units linked in macromolecular chains.

Cellulose is the first agro-polymer in the biosphere. It is a linear polymer consisting of $\beta(1-4)$ linked D-glucose synthesized by plants and bacteria. Table 4 shows that according to the botanical species, we can measure different cellulose contents. It is a cheap semi-crystalline material, which is widely used in paper production but also as a reinforcing element in polymer matrixes. To obtain a thermoplastic material, cellulose is modified by acetylation (cellulose acetate), whose production actually is low. After acidic treatment, and elimination of the amorphous parts of cellulose microfibrils, we obtain the whiskers (mono-crystals), which are used to develop nanocomposites materials.^[52,53]

Table 4. Composition of ligno-cellulose fibers, from various botanical origins.

Fibers	Cellulose content (%)	Lignins content (%)	Hemicellulose content (%)	Ash (silice, ...) (%)
Straw fibers				
Wheat	29–35	16–21	27	5–9
Rice	28–36	12–16	23–28	15–20
Rye	33–35	16–19	27–30	2–5
Wood fibers				
Conifer	40–45	26–34	7–14	<1
Leafwood	38–49	23–30	19–26	<1
Others				
Flax	43–47	21–23	16	5
Jute	45–53	21–26	15	0.5–2
Cotton linters	80–85	—	1–3	0.8–2

Source: Ref.^[192].

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2.4.1.2. Lignins and Ligno-Celluloses

Lignins are second in natural earth abundance. They are aromatic amorphous polymers. Figure 3 shows that the lignin structure is built with a lot of different chemical functions. Depending on botanical resources and fractionation, we obtain a diversity of structures. Lignins are obtained from almost all types of natural plants, in association with cellulose: ligno-cellulose. The architecture of the vegetal tissue is based on a complex composite structure in which the matrix is based on lignins and the reinforcing elements are cellulose fibers. Table 4 gives the lignins contents for different botanical species.

Lignins are by-products of pulp and paper mills and are conventionally treated as a waste material having low economical usage. They are generally used for their calorific energy. Lignins are separated from the cellulose either by strong alkaline or acidic solutions, or by a high-pressure steam treatment followed by solvent extraction. They can be used after fractionation as fillers or as antioxidants.^[54] Lignins can be modified, e.g., by esterification, to decrease the polar character for inclusion in apolar matrixes.

2.4.2. Native Starch

Starch is the main storage supply in botanical resources (cereals, legumes, and tubers). It is a widely available raw material on earth. It presents different industrial applications in fields such as food, paper, textile, and adhesive.

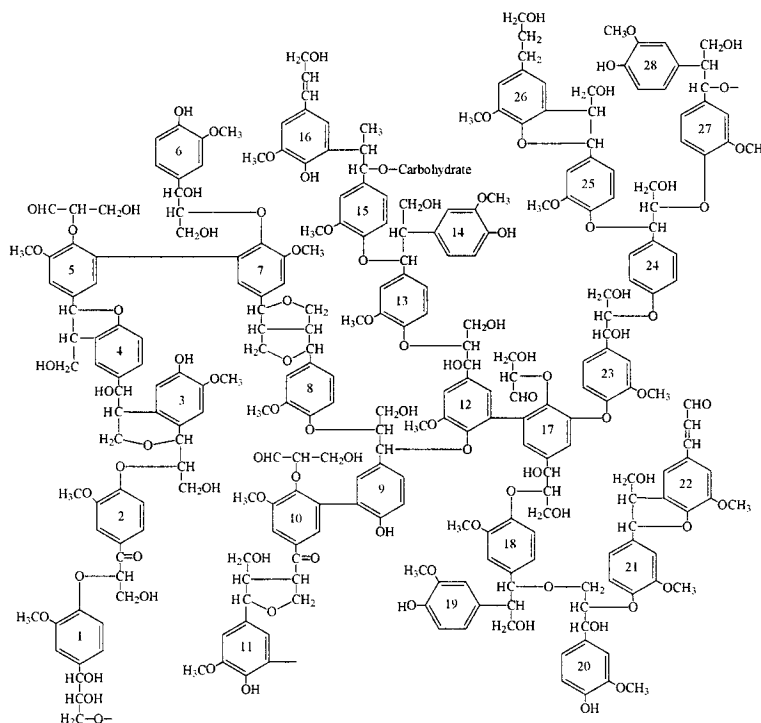


Figure 3. Structural and chemical presentation of wood lignin. Source: Ref.^[54].

Starch granules can be isolated from plants. Main sources come from wheat, potato, maize, rice, cassava, pea, waxy maizes, amylomaizes, etc. According to the resource, native starches have dimensions ranging from 0.5 to 175 μm and appear in a variety of shapes.^[55] For instance, Fig. 4 shows micrographs of the shape of different starch granules (wheat and pea).

Starch is a polysaccharide consisting in D-glucose units, referred to as homoglucan or glucopyranose. Starch is composed of two different macromolecules, amylose and amylopectin. Amylose [Fig. 5(a)] 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 helices. Amylopectin [Fig. 5(b)] is a highly multiple-branched polymer with a high molecular weight: 10^7-10^9 . It is based on $\alpha(1-4)$ bonds but also on $\alpha(1-6)$ links constituting branching points occurring every 22–70 glucose units.^[56]

Table 5 shows that according to the botanical origin, starch composition is variable. Some mutant plant species present some special composition. We can find rich-amylose starch with amylomaize (till 80%) and some rich-amylopectin starch with waxy maize (>99%).

After the different industrial stages of isolation and refining, starch usually shows some traces of lipids, gluten, or phosphate, which can interfere with the starch properties, e.g., by the formation of lipid complexes or with the gluten, by Maillard reactions.

Starch shows a special granular organization,^[57] a high degree of radial organization from hilum. Macromolecules are mainly oriented according to the radial axis. The ultra-structure is obtained by inter-macromolecules hydrogen links, between hydroxyl groups, with the participation of water molecules. Amylose and the branching regions of amylopectin form the amorphous zone in the granule. Amylopectin is the dominating crystalline component in native starch with double helix organizations; we can also find co-crystallization with amylose and single-helical crystallization between amylose and free fatty acids or lipids. Several types of crystallinity are observed in the granule denoted as A, B, C, or V-types. Figure 6 shows that the crystalline regions (20–45%) are arranged as thin lamellar domains, perpendicular to the radial axis.

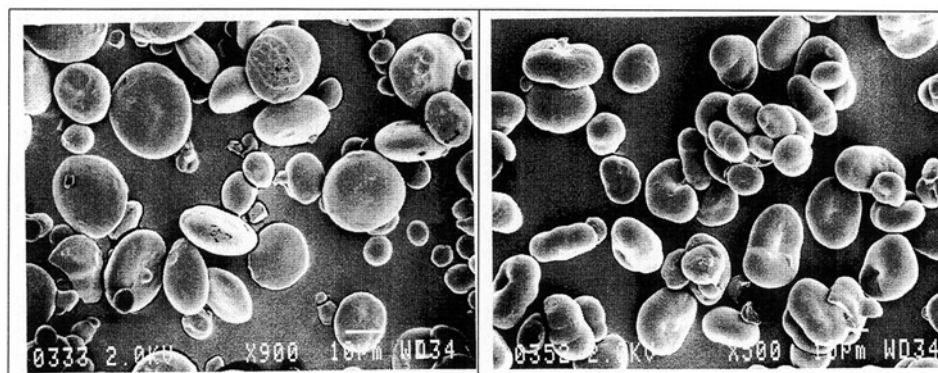


Figure 4. Micrographs of native starch (SEM observations): wheat starch (left) and pea starch (left). White scale = 10 μm .

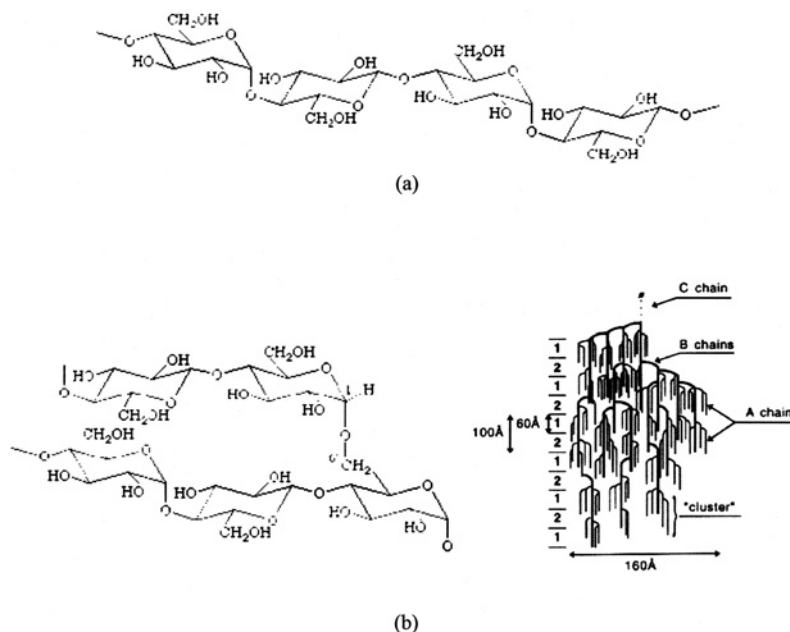


Figure 5. Amylose structure (a), amylopectin structure and cluster model (b).

3. PLS

3.1. Definitions

Except for the purpose as filler to produce reinforced plastics,^[58] native starch must be modified to find applications such as destructured starch. The destructuring agent is usually water. We obtain starch gelatinization with the combination of water (high content) and heat. Gelatinization is the disruption of the granule organization. The starch swells forming a viscous paste with destruction of most of inter-macromolecule hydrogen links. We obtain a reduction of both, the melting temperature (T_m or T_f) and the glass transition (T_g). Figure 7 shows that according to the level of destructuration and the water content, we obtain different products and applications; e.g., we can obtain expanded structures with a rather high water content. Such closed cells structures (foams) have been developed to obtain shock absorbable and isothermal packaging.^[59]

Most starch applications require water dispersion and partial or complete gelatinization. By decreasing the moisture content (<20 wt%), the melting temperature tends to be close to the degradation temperature. For instance, for pure dry starch $T_m = 220\text{--}240^\circ\text{C}$ ^[60] compared to 220°C , which is the temperature at the beginning of starch decomposition.^[61] To overcome this last issue, we add a non-volatile (at the process temperature) plasticizer to decrease T_m , such as glycerol or other polyols (sorbitol, PEG. . .).^[62,63] A mixture of different polyols can also be held.^[64] Other compounds such as those containing nitrogen (urea, ammonium derived, amines. . .) can be used.^[68–70] These plasticized starches (PLS) are also commonly called “thermoplastic starches” or TPS.^[66] The first patents and articles on

Table 5. Composition and characteristics for different kinds of starch.

Starch	Amylose content ^a (%)	Amylopectin content ^a (%)	Lipid content ^a (%)	Protein content ^a (%)	Phosphorus content ^a (%)	Moisture content ^b (%)	Granule diameter (µm)	Crystallinity (%)
Wheat	26–27	72–73	0.63	0.30	0.06	13	25	36
Maize	26–28	71–73	0.63	0.30	0.02	12–13	15	39
Waxy starch	< 1	99	0.23	0.10	0.01	N.d.	15	39
Amylomaize	50–80	20–50	1.11	0.50	0.03	N.d.	10	19
Potato	20–25	79–74	0.03	0.05	0.08	18–19	40–100	25

Note: N.d., not determined.
^aDetermined on a dry basis.
^bDetermined after equilibrium at 65% RH, 20°C.
Source: Refs. [66,209].

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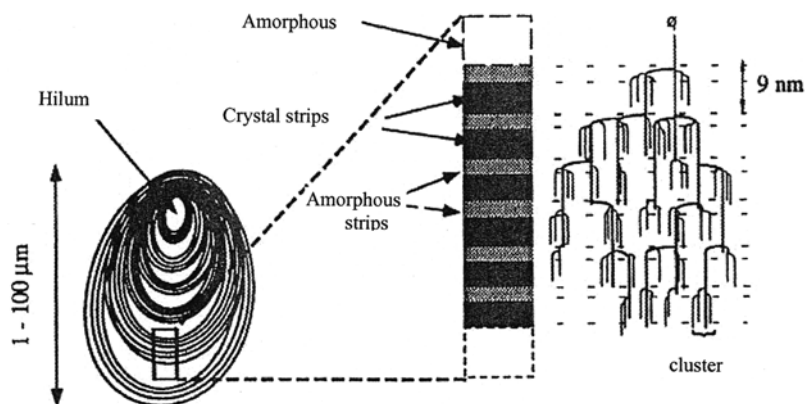


Figure 6. Radial structure of a starch granule (amorphous and crystalline region). *Source:* Ref.^[210].

these processable materials were published at the end of the eighties.^[71–73] PLS combines starch, a non-volatile and high-boiling^[71] plasticizer and often water. Figure 7 shows that PLS are obtained both with low water content and high level of destructure. PLS is usually transformed under thermomechanical treatment as a thermoplastic, using conventional machines for plastic processing (e.g., by extrusion).

3.2. PLS Process

The disruption of granular starch is the transformation of the semi-crystalline granule into a homogeneous, rather amorphous material with the destruction of hydrogen bonds between the macromolecules. Disruption can be accomplished by casting (e.g., with dry drums) or by applying thermomechanical energy in a continuous process. The combination of thermal and mechanical inputs can be obtained by extrusion, a common plastic processing technique. This process can be in one or two stages. In a one-stage process, the extruder, usually a twin-screw extruder, is fed with native starch. Along the barrel, water and liquid plasticizer are successively introduced. In a two-stage process, the first stage is a dry blend preparation.^[72] Into a turbo-mixer, under high speed, the plasticizer is added slowly into the native starch until a homogeneous dispersion is obtained. Then, the mixture is placed in a vented oven allowing the diffusion of the plasticizer into the granule. The plasticizer swells the starch. After cooling, the right amount of water is added to the mixture using a turbo-mixer. This dry blend is then introduced into an extruder. Figure 8 gives the different stages of the extrusion. The starch granules are fragmented. Under temperature and shearing, starch is destructured, plasticized, melted but also partially depolymerized. After the processing, we obtain a homogeneous molten phase.

3.3. Molten State Behavior

The extrusion and viscous behavior of molten PLS is known to depend on temperature, moisture content, and thermomechanical treatment.^[73–76] Viscosity data and rheological models that take into account these variables have been reported in literature.

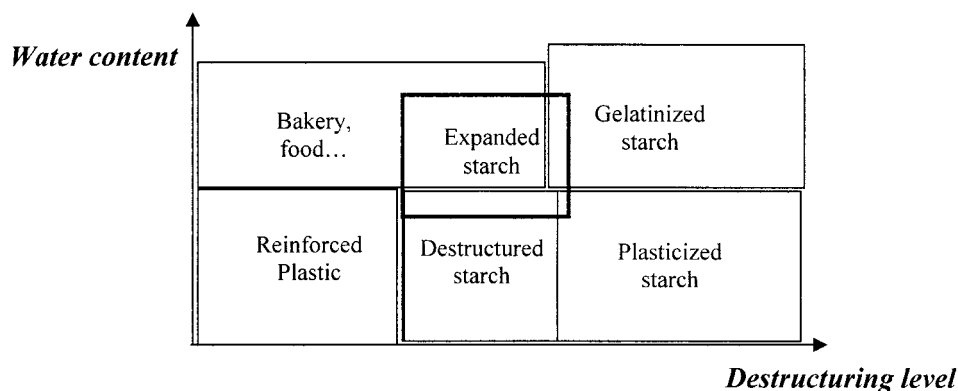


Figure 7. Presentation of different starchy products, depending on water content and destructuring level.

Martin et al.^[77] have summarized the main rheological studies performed on starch, including the measurement technique and models used. They all report a thermoplastic-like behavior of low hydrated starch, with an Arrhenius dependence on temperature and similar for moisture content. Conversely, structural modifications of starch, which affect the viscosity of the product, are reflected differently by specific mechanical energy (SME), by the screw speed, or even by the extruder barrel pressure, which depend on the machine characteristics. This discrepancy underlines the need to ascertain the dependence of starch melt viscosity upon structural factors or variables directly involved in its transformation. Some authors have introduced terms relating to the modification of starch, such as conversion, degree of transformation, or extent of degradation.^[78–82] Lai and Kokini^[83] studied the rheological properties of high amylose (70%) and high amylopectin (98%) cornstarches, and showed the strong influence of the processing history undergone by products prior to viscosity measurements. Zheng and Wang^[82] identified the contribution of shear and thermal energies in the conversion of waxy cornstarch. Della Valle et al.^[84,85] took into account the starch transformation and the resulting macromolecular degradation, evaluated by chromatography (SEC profiles) and intrinsic viscosity,^[86,87] by confirming the importance of the term noted β . This latter is reported in Eq. (1),

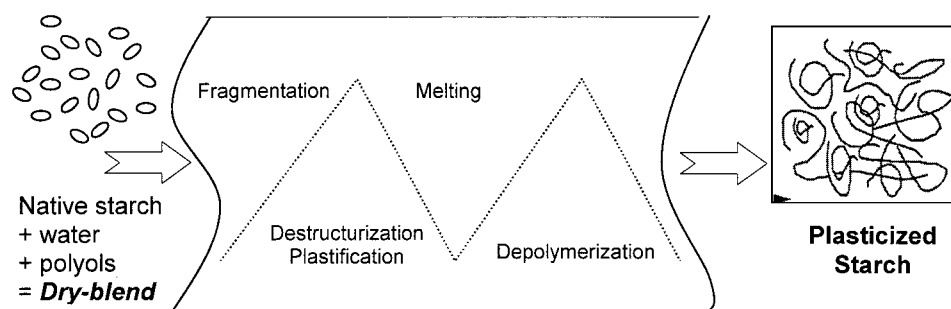


Figure 8. Schematic of starch process by extrusion.

which presents a pseudo-plastic model with the pseudo-plastic index (m) and the consistency (K). The influence of SME on the degradation of starch products was evaluated by intrinsic viscosity $[\eta]$ measurements. The gradual decrease of $[\eta]$ with increasing SME confirmed that macromolecular degradation occurred.^[77,88]

$$\eta = K|\dot{\gamma}|^{m-1} \quad \text{with the consistency: } K = K_0 \times \exp\left[\frac{E}{RT} - \alpha MC - \alpha' GC - \beta \cdot \text{SME}\right] \quad (1)$$

where MC, moisture content; GC, glycerol content; α , α' , and β , dimensionless coefficients.

A common difficulty of rheological studies is that a thermomechanical treatment is needed to obtain a homogeneous molten starch phase prior to measurement. This material shows a behavior not totally thermoplastic but thermo-mechano-plastic.^[77] Both, mechanical energy and temperature are required to obtain a molten material to cause it to flow. Consequently, traditional rheometry (rotational, capillary) is not appropriate for the study of the rheological behavior of low-moisture starches. In that respect, extruder-fed slit rheometry is well adapted.^[89–93] Martin et al.^[77,88] have also shown great interest in combining capillary and slit dyes on an in-line viscometer attached to the head of an extruder (a large shear rate range can be covered: 4 decades) with thermomechanical conditions (shear rate, SME, temperature) comparable to those used during the processing. Also of interest is the Rheoplast[®], known as a reliable commercial tool,^[94,95] to perform capillary viscometry measurements or to simulate extrusion of starchy products.

Finally, starch melts are commonly considered to exhibit viscoelastic behavior. The measurement of elastic components of PLS molten phases, associated with the first normal stress difference (N_1), is not trivial because conventional rheometers do not allow to perform mechanical treatment and cannot prevent volatilization of plasticizers. In a recent study using plane-plate geometry, PLS was shown to behave mainly as a solid-like material, because subjected to insufficient mechanical treatment.^[96] As an alternative, Senouci and Smith^[90] related the entrance and exit pressure losses in a slit viscometer dye to the elastic properties of potato starch-based materials. Entrance and exit pressure effects have been also used to evaluate the elasticity of melt of plasticized wheat starch. Some authors^[77] have concluded that significant elastic properties may be expected.

3.4. Solid-State Behavior

3.4.1. Crystallinity

Compared with native starch, PLS shows a lower crystallinity. According to Van Soest et al.,^[97] two kinds of crystallinity are obtained after PLS processing: residual crystallinity from native starch (A, B, C types) and processing induced crystallinity (V and E types). Crystallinity induced by processing is influenced by parameters, such as the extrusion residence time, the screw speed, or the temperature. It is mainly caused by the fast recrystallization of amylose into single-helical structure. After post processing aging,

Van Soest^[98] proposed a complex model for PLS with amorphous and crystalline amylose and amylopectin and probable co-crystallization between amylose and amylopectin.

3.4.2. Plasticizer and Water Interactions

The evolution of the moisture content are of consequence on the evolution of properties or transitions such as the glass transition, because water also acts as a plasticizer^[99] but it is a volatile plasticizer which is equilibrated in mechanisms of sorption–desorption with the environment.^[66] Lourdin et al.,^[100] and Mathew and Dufresne^[63] have determined according to the RH, the nature and content of the plasticizer and the moisture content after equilibrium on starch. They have shown that for low RH, water content decreases when plasticizer increased. In this case, plasticizer molecules then occupy some sites initially occupied by water. For higher activities (>43% RH) water content tends to increase with the plasticizer content due to plasticizer–water interactions (e.g., see Table 6). According to Lourdin et al.,^[100] this evolution is not linear but very well marked for high plasticizer content (e.g., more than 18 wt%, for glycerol), i.e., above the limit where phase separation between the polysaccharide and the plasticizer can occur, with constitution of plasticizer-rich phases.^[101] This concentration threshold corresponds to one glycerol molecule per three-anhydroglucose unit.

Lourdin et al.^[102] have shown that at low plasticizer content an antiplastification effect occurs. Due to strong interaction between the plasticizer and the starch, a hydrogen links network appears and we obtain a material reinforcement. Then, when the plasticizer contents increase (e.g., >12 wt% for glycerol into potato starch), interactions between plasticizer–plasticizer occur with a material swelling and a plastification effect.

3.4.3. Post Processing Aging

Different authors^[40,103,104] have shown that after processing, PLS shows an aging with a strong evolution of mechanical properties such as the tensile modulus, which increase during several weeks. PLS presents two kinds of aging behavior depending on glass temperature value. In the sub- T_g domain, PLS shows a physical aging versus time, with a material densification.^[104,105] At a temperature above T_g , PLS shows retrogradation phenomena with the evolution of the crystallinity and rearrangements of plasticizer molecules into the material^[103] versus storage time. The retrogradation kinetic depends on the macromolecules mobility, on the plasticizer type and content.^[104]

3.4.4. PLS Properties

According to the plasticizer/starch ratio, PLS presents a large range of attributes. Table 6 shows for increasing glycerol/starch ratio, the evolutions of different properties, including physical and mechanical behaviours. Figure 9 shows the thermograms' evolution for the formulations given in Table 6. Figure 9 illustrates that the C_p variations at glass transitions are very low, although DMTA determinations are generally more desirable to obtain PLS glass transitions. DMTA evolutions are drawn in Fig. 10 for the same formulations. The evolutions of $\tan \delta$ versus temperature show two transitions. Main and broad relaxation (α -transition) can be linked to the PLS glass transition.^[40] Secondary relaxation (between -50°C and -60°C) could be connected to glycerol

Table 6. Plasticized starch—formulations and properties.

	Glycerol/ dry starch ratio ^a (w/w)	Water ^a (wt%)	Density ^a	T _g (DSC) (°C)	α-Transition (DMTA) (°C)	Modulus ^a (MPa)	Max tensile ^a strength (Mpa)	Elongation at break ^a (%)
S74G10W10 ^b	0.14	9	1.39	43	63	1144 (42)	21.4 (5.2)	3 (0)
S74G18W12 ^b	0.25	9	1.37	8	31	116 (11)	4.0 (1.7)	104 (5)
S67G24W9 ^b	0.35	12	1.35	-7	17	45 (5)	3.3 (0.1)	98 (5)
S65G35W0 ^b	0.50	13	1.34	-20	1	11 (1)	1.4 (0.1)	60 (5)

Note: Standard deviations are in brackets.

^aContents and properties after equilibrium at 23°C and 50% RH, 6 weeks.

^bInitial formulation (S₁G₃W₂): S, starch (x wt%); G, glycerol (y wt%); W, water (z wt%).

Source: Refs.^[40,132].

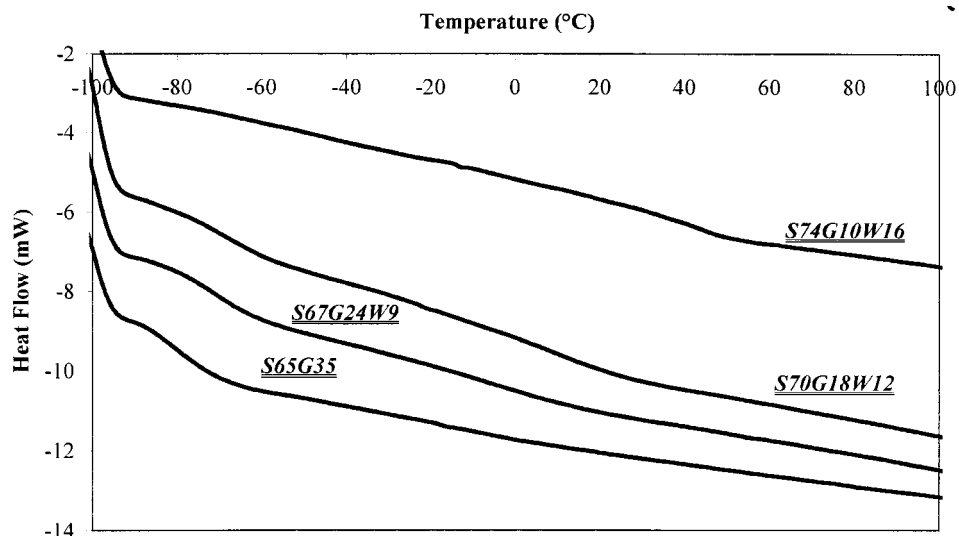


Figure 9. DSC evolutions with different glycerol/starch ratios. Source: Ref.^[72].

glass transition.^[40] According to Lourdin et al.,^[101] this latter relaxation could be an indicator of the level of interactions between the plasticizer and the polysaccharides. In the explored domains, Figure 10 shows that this relaxation temperature decreases when glycerol content increases and then, the phase segregation.

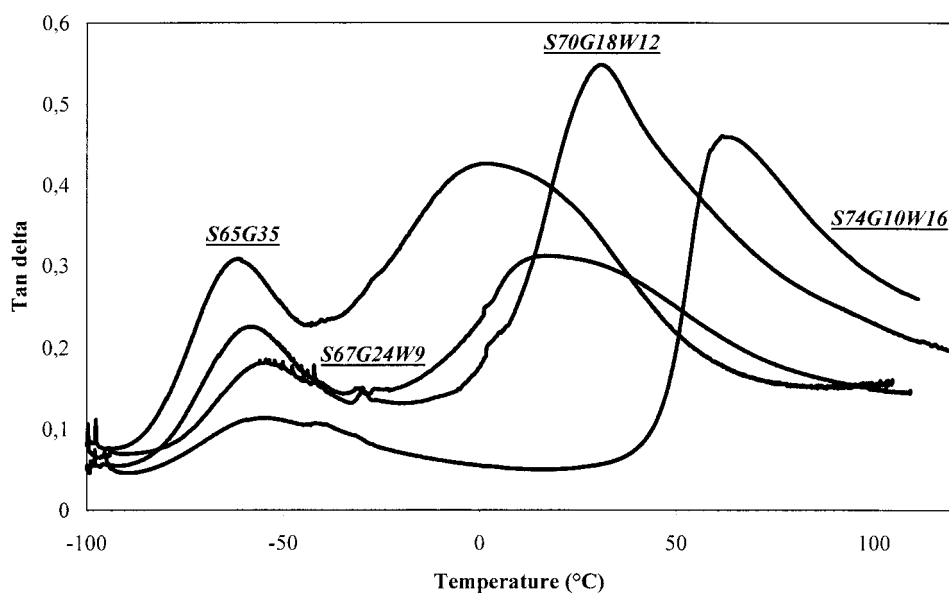


Figure 10. DSC evolutions with different glycerol/starch ratios. Source: Ref.^[72].

Table 6 exemplifies that we can achieve a large range of mechanical properties by variation of the plasticizer content. Further, PLS shows different levels of permeability (moisture and oxygen).^[100,106,107] Although PLS water permeability is high due to its polar character, oxygen permeability is found low compared with most polyesters.^[24] Permeability increases drastically at the glass transition, and continues to rise on the rubber plateau, with the plasticizer content.

3.4.5. PLS Issues and Strategies

As a material, PLS shows strong attributes: a total compostability without toxic residues, the renewability of the resource. Besides, compared with synthetic thermoplastic, it is a rather cheap material. Compared with fossil resources, the price of starch resources remains stable and even tends to decrease due to overproduction of cereals in the world. In addition, PLS can be easily processed with plastic processing machines. It shows a wide properties range according to the plasticizer level and the starch botanical source. But unfortunately, PLS shows various issues for some applications (e.g., packaging) such as a great moisture sensitivity, rather weak mechanical properties compared with synthetic polymers. To overcome these weaknesses, during the last decades different strategies were elaborated.

Chemical starch modification has been carried out, since the first half of the twentieth century, in the continuity of research on modified cellulose. Yet in 1942, Mullen and Pacsu^[108] published a critical analysis of the different methods of starch (tri)ester preparation. In 1943, the same authors^[109] presented an industrial usage of such a compound. Since then, a large literature has been published on this subject. Starch esterification (e.g., by acetylation) improves its water resistance.^[110] In addition, we can control the degree of substitution (DS, between 0 and 3) to obtain the accurate hydrophobic character. Besides, these compounds can be plasticized with, for instance, ester citrate.

But, the strategy of chemical modification is strongly limited as far as toxicity and diversity of by-products obtained during the chemical reactions are concerned. Another limitation lies in the cost of both process stages, that of the modification and product purification (to eliminate the by-products). Besides, the chemical reactions lead to some incidences on the polysaccharide molecular weight, with a decrease due to chain linkages. Consequently, the mechanical properties are altered.^[111] Such products do not fulfil the requirements for the substitution of PLS for material applications. Yet for one or two decades, another more promising strategy has been developed for the association of PLS with other biodegradable compounds to obtain compostable multiphase materials. We can obtain different structures with corresponding properties. This approach induces some problematics linked with the quality of the interfaces, i.e., concerning the continuity between the phases and the compatibility between the different materials.

4. PLS-BASED MULTIPHASE SYSTEMS

4.1. Structures Classification

Two different materials can be associated to PLS to obtain compostable materials: biodegradable polyesters or agro-materials (lignins, cellulose, etc.). Figure 11 shows the different sorts of structures, which can be obtained by associations, and the related process.

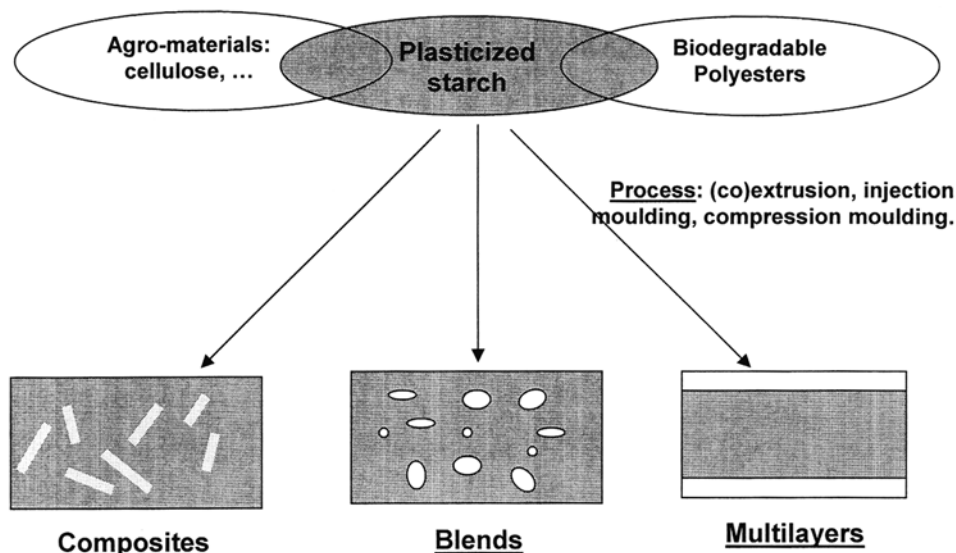


Figure 11. Schematic of multiphase systems based on plasticized starch—process and structures.

4.2. Biodegradable PLS-Based Blends

Blend shows different attributes.^[112,113] Blending is the easier process to associate different polymers together. Blending provides a powerful route to obtain materials with improved property/cost performances. This approach is cheaper than the development of new polymers. Besides, blends are also commonly used as models to test the compatibility between different polymeric phases because a blend presents a great surface of interphase compared with, e.g., multilayer structures.

PLS has been widely used in blends with other polymers.^[114,115] A lot of patents were published on this topic (see Table 7). These considerable research efforts have led to starch-based blends being commercialized, Mater-Bi[®]^[30,71] from Novamont (Italy) or Bioplast[®] from Biotec (Germany).^[115] Starch blends production, for this latter, is now managed by Novamont. To produce these commercial blends, starch is blended with non-biodegradable polymers (polyolefins) or with biodegradable polyesters (e.g., PCL). Applications concern packaging, disposable cutlery, gardening, leisure, hygiene and the like.

In the past, blends with synthetic polymers, such as PE^[116] or EVOH,^[117] were developed leading to non-fully biodegradable materials.^[118,119] Because these controversial materials were presented as biodegradable, they have been named bio-fragmentable. To maintain the compostability feature, different biodegradable blends were developed. A great number of patents have been published on this topic (see Table 7). We find some associations of PLS with agro-polymers such as proteins^[118–121] or pectins.^[120,122] But, most of the research is focused on the blending of PLS with biodegradable polyesters: PCL,^[32,39,40,123–129] PEA,^[39] PHBV,^[126,127,130,131] PBSA,^[50,132] poly(butylene adipate-co-terephthalate) (PBAT),^[132] PLA^[21] or PHEE.^[27] These commercially available polyesters show some interesting and reproducible properties such as a more hydrophobic

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Table 7. Main patents disclosing biodegradable PLS-based materials.

Patents no.	Inventors (assignee)	Comments
Plasticized starch (PLS)		
EP 282 451	Dobler et al. (1988)	Destructured starch and PLS
EP 304 401	Tomka et al. (1989)	Destructured starch and PLS
WO 90/05161	Tomka (1990)	PLS
EP 400 531	Bastioli et al. (1990)	PLS
WO 92/04408	Cole and Egli (1992)	PLS and process
US 5,275,774	Bahr et al. (1994)	Extrusion with water removing during the process
EP 609 983	De bock and Bahr (1994)	Plasticizers: mixture of sugar alcohols
WO 94/28029	Lorcks et al. (1994)	PLS and process
WO 96/35748	Haschke and Tomka (1996)	Plasticizers: graft copolymers
EP 758 669	Bastioli et al. (1997)	PLS
WO 97/48764	Loerck et al. (1997)	Plasticizers: polymers system
WO 98/51466	Feil et al. (1998)	PLS foam moulding
Biodegradable PLS-based blends		
EP 327 505	Rehm et al. (1989)	PLS + PHB
EP 535 994	Tokiwa et al.	PLS + PCL
FR 2 691 467	Van Hoegaerden (1993)	PLS + proteinaceous material
US 5,280,055	Tomka (1994)	PLS + cellulose ester
EP 580 032	Dehennau and Depireux (1994)	PLS + PCL
EP 596 437	Tomka (1994)	PLS + biodegradable polymers
WO 94/25493	Fishman and Coffin (1994)	PLS + pectines
WO 95/24447	Narayan and Krishnan (1995)	PLS + PCL, in absence of water
EP 704 495	Muramatsu and Hino (1996)	PLS + PBSA or PHBV, or PCL
WO 97/03120	Seppala et al. (1997)	PLS–polyester compatibilization with poly-isocyanate
JP 9 137 069	Shimoozono and Hino (1997)	PLS + aliphatic bio. polyester
JP 9 294 482	Shimoozono and Hino (1997)	PLS + aliphatic bio. polyester
WO 98/20073	Bastioli et al. (1998)	PLS + bio. polyester + non-ionic surfactant
WO 99/02595	Bengs et al. (1999)	PLS + biodegradable polymer + phosphate
EP 947 559	Bastioli et al. (1999)	PLS + bio. polyesters + non-ionic surfactant
EP 965 615	Bellotti et al. (1999)	PLS + bio. polyesters (heterophase)
US 6,025,417	Willett et al. (2000)	PLS + PHEE
US 6,218,321	Lorcks et al. (2001)	Production of fibers: PLS + bio. polyester
Biodegradable PLS-based multilayers		
US 5,391,423	Wnuk et al. (1995)	Multilayers with biodegradable polymers
US 5,512,378	Bastioli et al. (1996)	Multilayers PLS/wax fabrication
WO 97/27047	Shogren and Lawton (1997)	Coating by spraying solutions

(continued)

Table 7. Continued.

Patents no.	Inventors (assignee)	Comments
FR 2 791 603	Avérous et al. (2000)	Coextrusion: bio. polyester/PLS/ bio. polyester
Biodegradable PLS based composites		
WO 95/04111	Rettenbacher and Mundigler (1995)	PLS + wood cellulose
WO 97/03121	Happonen et al. (1997)	PLS + cellulose fibers
US 5,666,216	Tomka (1997)	PLS + natural cellulose fibers
US 5,705,536	Tomka (1998)	Foam: PLS + cellulose fibers
EP 842 977	Rothe (1998)	PLS + natural fibers (milling industry)
WO 99/56556	Wang (1999)	Foam: PLS + cellulose fibers + proteins
US 6,136,097	Heuer et al. (2000)	PLS + ligno-cellulose fibers + proteins
US 6,231,970	Andersen et al. (2001)	PLS + natural fibers + mineral fillers
WO 01/68762	Fischer and Fischer (2001)	Nanocomposites: PLS + organoclays
US 6,406,530	Boehm and Bengs (2002)	PLS + lignins

Note: Bio. polyester = biodegradable polyester.

character, a lower water permeability and some improved mechanical properties, compared with PLS.

4.2.1. Blends Properties

Solid-state properties of the blends depend on the nature of the polyester phase. At ambient temperature, polyesters can be rigid (e.g., PLA) or soft (e.g., PCL, PBSA, PBAT). Then, corresponding mechanical properties are tuneable.

Young's Modulus can be evaluated between two boundaries determined by the serial model from Reuss [cf. Eq. (2)] and the parallel model from Voight [cf. Eq. (2)] for respectively, the lower and the higher boundary.^[21,40,72] In the case of a co-continuous structure, as shown on some PLS/PLA blends,^[21,133] modulus can be evaluated with a rather good agreement by Davies model [cf. Eq. (2)].^[134]

$$E_{\text{Reuses}} = \phi_1 E_1 + \phi_2 E_2$$

$$\frac{1}{E_{\text{Voight}}} = \frac{\phi_1}{E_1} + \frac{\phi_2}{E_2} \quad (2)$$

$$E_{\text{Davies}}^{1/5} = \phi_1 E_1^{1/5} + \phi_2 E_2^{1/5}$$

where E_i and ϕ_i are, respectively, the modulus and the volume fraction of the i th phase.

Starch and more hydrophobic compounds such as biodegradable polyester are rather immiscible and mixing produces blends with separated phases with rather poor interfacial

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properties. This is illustrated by the results of different micro- or macro-structural approaches:

- The shifts of both glass transitions before and after blending which can be compared with the evaluations determined with the Couchmann-Karasch's model.^[135]
- MEB observations of the structure and phase dispersion.
- Tensile test values at break,^[21] elongations and strengths.
- Peel test measurements.^[21]
- Calculation of the theoretical work of adhesion from contact angles of probes liquids.^[136–138]

For instance, Table 2 shows that PEA presents the highest surface tension, a high polar component, and PLA the lowest. These different determinations allow the establishment of a classification from the least compatible (PLA) to the most compatible polyesters (PEA).

However, this low compatibility induces special behaviors and properties. During the injection moulding process, we have a preferential migration of the polyester, the low-viscosity polymer,^[139] towards the mould surface. After cooling, we obtain a polyester-rich skin and a starchy core.^[40,140] Imaging NMR has highlighted this pseudo-multilayer structure. Compared with PLS, this stratified structure gives to the blend rather good water resistance^[40,72] due to the polyester surface protection. Water sensitivity, determined by contact angle measurements with water drops deposit decreases drastically for contents lower than 10 wt% of polyesters in the blend.^[132] Biodegradability of such blends is modified, degradation occurs from the starchy core toward the skin.^[141]

4.2.2. Blends Compatibilization

To improve the compatibility between two phases, compatibilization strategies are generally developed. This strategy implies the addition of a compound: the compatibilizer, which can be obtained by modification of at least one polymer initially present in the blend.^[142] For compatibilization, authors have followed different ways:

- The functionalization of the polyester, with maleic anhydride,^[143–145] with pyromellitic anhydride^[146] with polyacrylic acid^[147] or by producing telechelic polyester phosphate.^[148]
- The functionalization of starch with polyglycidyl methacrylate^[149] or, with urethane functions by reaction of *n*-butylisocyanate.^[150]
- The starch–polyester reticulation with coupling agents such as peroxides,^[41,151,152] or polyisocyanates.^[153–157]
- The development of copolymers: starch-graft polyester. To compatibilize starch and PCL, different authors have developed PCL-grafted starch or dextran.^[158–163] The grafting is obtained by ROP of ϵ -caprolactone on the polysaccharide. Reaction can be catalyzed with stannous octoate and initiated with aluminum alkoxides. The length of the grafts can be controlled to obtain a comb structure.^[162,163] The same approaches can be used with PLA-grafted polysaccharides (unpublished work).

Results are improving for the interphase continuity, observed by MEB and by DSC, and for the mechanical properties.

4.3. Biodegradable PLS-Based Multilayers

Compared to blends, multilayer structures present some attributes. Moisture sensitivity is not fully addressed in a blend because of starch phase distribution close to the surface. Development of moisture-resistant starch-based products shall be undertaken through multilayers, allowing for the preparation of sandwich-type structures with PLS as the central layer and the hydrophobic biodegradable component as the surface outer layers. On this topic, some patents were published (see Table 7). For instance, Bastioli et al.^[164] proposed different processes (coextrusion, casting and hot melt techniques) to protect starch-based materials with wax layers. Stratified materials can be obtained by a multistep process based on compression moulding.^[165] The case of coating is also mentioned in literature. Coating has been achieved by spraying^[166] or painting^[167] different dilutes liquid such as biodegradable polyester solutions onto the starch-based material.

Coextrusion seems the best option, since it offers the advantages of being a one-step, continuous and versatile process. Multilayer coextrusion has been widely used in the past decades to combine the properties of two or more polymers into one single multilayered structure.^[168] However, some problems inherent to the multiphasic nature of the flow are likely to occur during coextrusion operations, such as non-uniform layer distribution, encapsulation, and interfacial instabilities, which are critical since they directly affect the quality and functionality of the multilayer products. The layer encapsulation phenomenon corresponds to the surrounding of the more viscous polymer by the less viscous one, as shown by Lee and White.^[169] Figure 12 illustrates interfacial instabilities with wavy interfaces. Yih^[170] and Hickox^[171] pioneered studies on interfacial instabilities, suggesting that viscosity differences may cause instabilities of stratified flow. Schrenk and Alfrey^[172] investigated the factors responsible for the onset of instabilities, and suggested the existence of a critical shear stress value beyond which interfacial instabilities are likely to occur. Han and Shetty^[173,174] described in detail the factors responsible for the occurrence of instabilities, such as critical shear stress at the interface, viscosity and elasticity ratio, and layer thickness ratio. Khomani,^[175,176] Su and Khomani^[177,178] examined theoretically the elastic and viscosity effects on the interfacial stability, according to the die geometry and layer depth ratio. They determined the role of elasticity in the mechanism of instabilities. Wilson and Khomani^[179–181] studied the propagation of periodic flow disturbances experimentally and numerically and determined the stable and unstable flow conditions, in a good agreement with models.

Despite the number and diversity of studies on multilayer flows and stability, only few articles^[165,182,183] and patents^[164,184] reported the use of PLS and polyester in coextrusion processes. Different stratified structures were processed by coextrusion and studied: with PCL,^[165,182] PBSA,^[165,182] PEA,^[165,182] PLA,^[165,182,183] PBAT,^[182] or with PHBV.^[183,185]

4.3.1. Interfacial Instabilities

Martin and Avérous^[183] have shown on a PLS/PEA/PLS systems, that the key parameters are the skin-layer viscosity and thickness, the global extrusion rate and the dye geometry after determining the stable and unstable flow conditions. They have found that the occurrence of instabilities is strongly related to the shear stress at the interface.

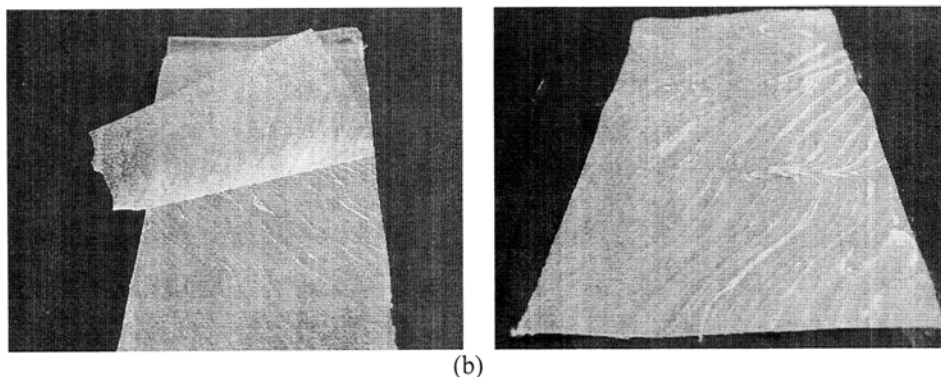
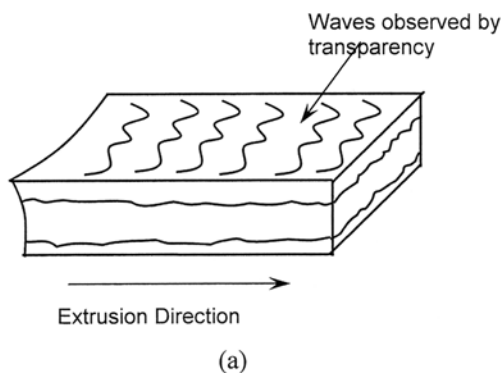


Figure 12. (a) Schematic of a multiplayer film exhibiting wavy instabilities at the interface. (b) Photographs of a delaminated film (PLS/PLA/PLS) exhibiting wave-like instabilities. *Source:* Ref.^[77].

Viscosity differences, high extrusion rates, and low cap layer thickness have been shown to promote the occurrence of instabilities. Conversely, moderate extrusion rate, appropriate dye geometry and lesser viscous component at the dye wall have favored the stability of the combined flow.

4.3.2. Interfacial Adhesion

Different authors^[165,182] have shown that in the absence of compatibilizer according to the level of PLS–polyester compatibility and to the process, we obtain different levels of interfacial strength, as illustrated in Fig. 13. Elsewhere, Wang et al.^[182] have shown that the addition of plasticizer to the starch, or a decrease of the polyester molecular weight (PCL), tends to decrease the peel strength. Martin and Avérous^[183] have found that the interfacial strength of biodegradable multilayer films can be improved by a controlled extent of instabilities at the interface, via mechanical interlocking between respective layers.

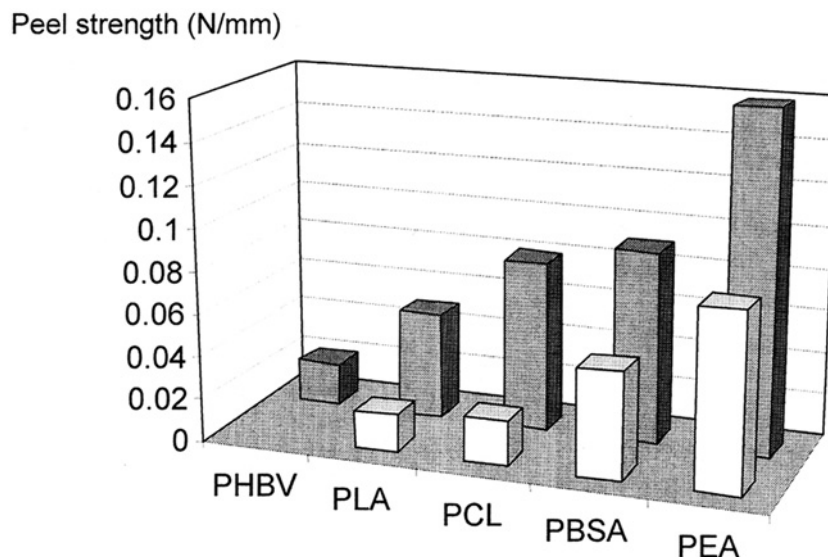


Figure 13. Peel test results at 90°, 50 mm/mm, 23°C and 50%RH. Effect of the polyester type and process on the peel strength of PLS–polyester films. (White bars represent the hot pressed films by compression moulding. Dark bars represent coextruded films). Source: Ref.^[165].

4.4. Biodegradable PLS-Based Composites

4.4.1. Cellulose Fibers Reinforcement

Different types of fibers or microfibrils were tested in association with PLS: microfibrils from potato pulp,^[52,53] bleached leafwood fibers,^[186–189] fibers from bleached eucalyptus pulp,^[190] flax and jute fibers.^[191] The different authors have shown high compatibility between both polysaccharides. For instance, Avérous et al.^[187] have found a T_g increase of 28°C by addition of 10 wt% of cellulose fibers into a PLS matrix. This evolution is linked to the fiber–matrix interactions, which decrease starch chains mobility. In another example, Fig. 14 shows a MEB image of a cryogenic fracture; the cellulose fibers are imbedded in the starchy matrix. Similar results have been found by Curvelo et al.^[190] After mixing, authors have found high improvements of the material performance; some of them are linked to a usual matrix reinforcement,^[192] some others are brought by the inter-relations fiber-matrix:

- higher modulus,^[186–189]
- reduced water sensitivity due to fiber–matrix interactions and to the higher hydrophobic character of the cellulose, linked to its high crystallinity,^[52,53,186,187,190]
- higher thermal resistance,^[52] due to the transition shift and an increase of the rubber plateau,
- reduced post processing aging, due to the formation of a 3D network between the different carbohydrates, through hydrogen bonds.^[189]

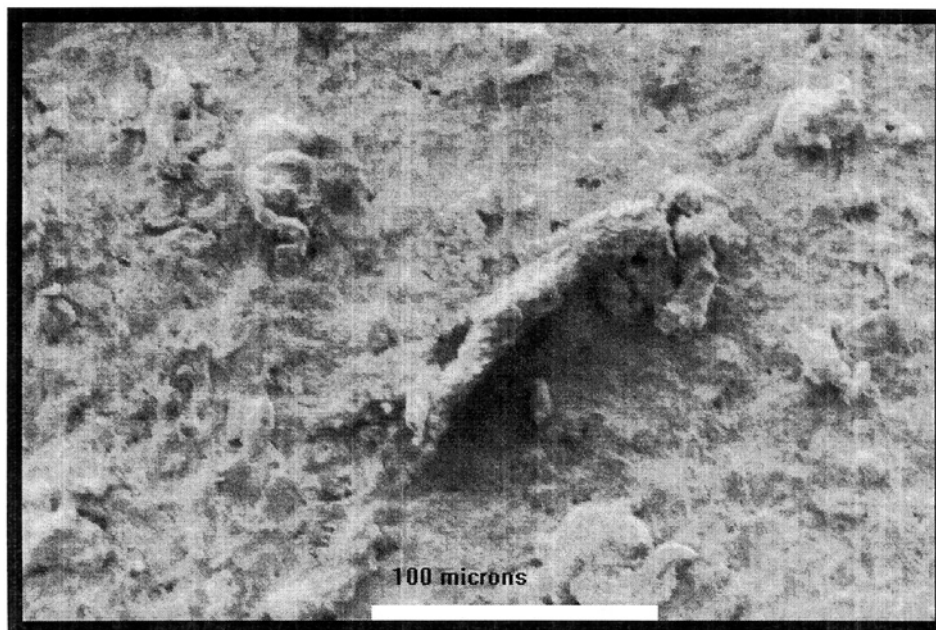


Figure 14. MEB observation. Cryogenic fracture of composites: PLS-leafwood cellulose fibers (white scale = 100 μm). Source: Ref.^[187].

On this topic, a large number of patents were published (see Table 7) during the last decade with some complex formulations, also based on proteins and even on biodegradable polyesters.

4.4.2. Lignin Fillers

Different kinds of fractioned or modified lignins (Kraft lignins, Acell[®] lignins) have been investigated in association with PLS obtained by film casting preparation or by extrusion.^[193–195] According to Baumberger,^[194] both systems are quite compatible with lignins acting as fillers or as extender of the PLS matrix, with the soluble lignin fractions.

4.4.3. Nanocomposites and Mineral Microfillers

Two kinds of nanoparticles have been tested into PLS composites: whiskers obtained from cellulose and organoclays.

By acid hydrolysis of cellulosic materials, we obtain whiskers, which are mono-crystals from cellulose. Some authors^[196–198] used tunicin (an animal cellulose) whiskers, slender parallelepiped rods of 500 nm to 1–2 μm length and 10-nm-width,^[196] into PLS matrixes. As for cellulose fibers, whiskers–matrix interactions are important. The high shape ratio of the nanoparticles (50–200), the high specific area ($\approx 170 \text{ m}^2/\text{g}$) increases the interfacial phenomena then properties are improved, compared with PLS–cellulose composites. Tunicin whiskers favor the starch crystallization due to a nucleating effect of the filler.^[198]

Different authors^[199–201] developed layered silicate nanocomposites to be compatibilized with the biodegradable polyester phase, such as PLA,^[202] PCL,^[201] or PBSA.^[46] The organoclay incorporation is generally between 1 and 10 wt%. These nanocomposites are based on montmorillonites, which are generally modified by cations exchange with alkyl-ammonium.^[200–202] From this latter, Kubier et al.^[203] have in situ polymerized polyesters by ROP of ϵ -caprolactone using tin alkoxide catalyst, to obtain intercalated or exfoliated nanocomposites.

The addition of modified organoclay into biodegradable polyester phase tends to modify the material properties such as the mechanical properties. The tensile modulus and strength are increased; on the other hand, the elongation at break is slightly decreased.^[46,201,204] According to Lepoittevin et al.,^[201] thermal stability determined by thermogravimetric analysis (TGA) is improved. Krook et al.^[204] have shown that oxygen and water transmission rates are rather decreased. According to Lee et al.,^[46] the kinetic of biodegradation is decreased.

On a recent patent based on PLS–montmorillonites,^[204] Fischer and Fischer^[205] present clay-based compounds as processing aids, which decrease the viscosity during extrusion. Besides, the mineral compounds act to prevent plasticizer loss during aging and then, improves the PLS stability. On PLS-biodegradable polyester blends, McGlashan and Halley^[206] have shown that nanocomposites tend to improve the mechanical properties (tensile and impact tests), the barrier properties and the transparency by crystallinity modification.

Mineral micro-fillers were tested into a PLS matrix.^[207] Kaolin particles, with an average size of 0.5 μm , were incorporated by extrusion. Due to significant inter-compatibility, subsequent behaviors, such as a glass transition decrease, a reduction of water uptake, and an increase of the stiffness can be observed.

5. CONCLUSION AND PERSPECTIVES

In this review, the relationships between the structure, the process, and the properties of biodegradable multiphase systems based on PLS, the so-called “thermoplastic starch” was analyzed. Besides, this review tried to show the high potential presented by plasticized starch-based materials. Because of its low cost, its renewable and biodegradable character, starch seems to be nowadays an important challenger for the development of future agro-based products. Compared to petrochemical polymers, plasticized starch should be a future good competitor, when petroleum resources will drastically decrease. Besides, these agro-materials are totally in agreement with the emergent concept of sustainable development.

The association of plasticized starch with other biodegradable polymers is a good solution to overcome main starch issues, e.g., compared to the limitations linked to starch chemical modifications (process cost, toxicity of the by-products etc.). Besides, with the different structures, we can obtain (blend, composite, multilayer) can fulfil the requirements of different applications fields, such as packaging or other short-lived applications (catering, agriculture, sport, hygiene) where long-lasting polymers are not entirely adequate.