

Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

EDITORIAL

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Vegetal fiber-based biocomposites: Which stakes for food packaging applications?

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ABSTRACT: Considering the needs of designing suitable food packaging that is able to decrease food losses while reducing the overall environmental impact of the food/packaging system, full biocomposites, i.e., both biodegradable and bio-sourced, are becoming serious candidates for food packaging applications. This article aims at reviewing the knowledge about the functional properties of vegetal fibers-based biocomposites, by considering the specific stakes relative to the food packaging application, i.e., the targeted functional properties, including mechanical properties and mass transfer properties (especially the permeability toward O₂, CO₂, and water vapor), the processability of materials using conventional equipments, the economical competitiveness, and the food safety. The first part summarizes the main characteristics of the constituents, i.e., matrices and fillers, and the processing routes to prepare biocomposites. In the second part, the ways to better understand and control the mass transfer properties in biocomposites will be deciphered by reminding the role of mass transfers in the food/packaging system and by focusing on how mass transfer properties are impacted by the material structure and mechanical properties. Food safety aspects will also be considered, by highlighting the possible undesirable migration from biocomposites toward food. This review will conclude on the main bottlenecks that should be resolved in order to make the use of biocomposites more viable for food packaging applications. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 42528.

KEYWORDS: clay; poly(vinyl chloride); properties and characterization; thermal properties

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INTRODUCTION

Composite materials are made by combining at least two non-miscible components, i.e., the matrix as the continuous phase and the filler as the dispersed phase, in such a way to achieve unique properties that would not be achievable from the individual constituents.¹ Bioplastics are generally defined as biodegradable and/or bio-sourced materials, meaning that a biodegradable petro-sourced material or a nonbiodegradable material from a renewable resource would be equally called bioplastic. In this review, bioplastics being both biosourced and biodegradable will be referred as "full-bioplastics". Full-bioplastics benefit from high yields of natural fabrication with excellent carbon and energy balance, while being completely recyclable into organic waste.²

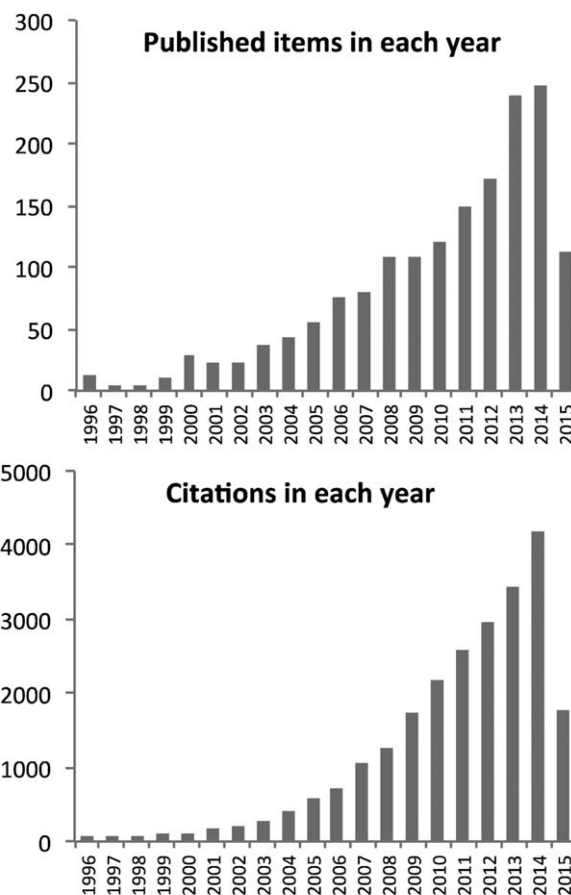
Biocomposites combine both advantages of optimized functional properties of composites and environmental friendliness of bioplastics. The generally admitted definition of biocomposites claims that at least one of the constituents should be biosourced—either the matrix or the reinforce-

ment.³ Thus, as previously mentioned for bioplastics, the term "biocomposites" is often used to describe materials that are only partially environmentally friendly, for example, in the case of polyolefin/natural fibers composites where the main constituent, i.e., the matrix, is petro-sourced and/or not biodegradable. In order to fully benefit from all the positive aspects of full-biomaterials, all constituents of a biocomposite should be biosourced and biodegradable. Such a biocomposite is referred in this article as "full-biocomposite". The development of biocomposites via the incorporation of natural lignocellulosic fibers from different plant origins (hemp, jute, flax, bagasse, cotton, sisal, etc.) is the most commonly proposed strategy and is gaining more and more approval day by day.⁴ The growing importance of these new biocomposites since the 1990s is revealed by the increasing number of publications and citations during the recent years including reviews and books (Figure 1) and the fact that they are now fully integrated within the European strategic reflections. The main specific benefits of using lignocellulosic fibers are their high availability with the existence of sources throughout the

world, low price, low density as compared to conventional glass fibers (allowing to prepare light materials), full biodegradability, high stiffness and tensile strength, and nonabrasive behavior during processing. Furthermore, natural fibers, unlike glass fibers, have less impact on the health of composite manufacturers (irritation of the skin, lung cancer). For all these reasons, lignocellulosic fibers are good candidates for the substitution of glass fibers in thermoplastic reinforcement. However, some manufacturing processes producing natural fibers are known to produce large quantities of dust, which can be harmful in the long term for the production staff. Moreover, the use of vegetal fibers for composite reinforcement could have some limits, due to their poor thermal resistance or their water sensibility.⁵

Regarding the potential applications of such full-biocomposites, they might be used like plastic materials, i.e., for building, construction and automotive applications, but mostly for packaging applications, which represent 40% of the general plastic demand.⁶ It is worth noting that an appropriate food packaging could be an essential actor to reduce food losses, that is about one-third of the edible parts.^{7,8} Indeed, the role of food packaging is, beyond its functions of mechanical protection from physical damage, distribution, marketing, and service, to control the mass transfers responsible for food degradation. The mass transfers are at the heart of the feature of the food packaging: transfers of water vapor, oxygen, and/or carbon dioxide which condition the rates of numerous reactions of food degradation (oxidation, microbial development, physiological reactions, etc.), but also transfers of additives contained in the packaging material, that can be voluntary (active packaging) or to avoid (transfers of packaging additives toward the food). To fulfill these functions, it is primordial that packaging materials display appropriate mechanical properties to ensure physical integrity of the packaging itself, thus being able to preserve their other functional properties such as mass transfer properties. Biocomposites, which ally the bio-sourced character to the structuration at the microscopic scale, appear as innovative and promising materials of future for the sector. The drawbacks hampering currently their growth on the food packaging market are mainly their limited processability, insufficient mechanical and barrier properties, high production cost (e.g., bio-polyesters), or controversial environmental claims. In addition, material sensitivity to water and to microbial spoilage is often incompatible with food safety and quality preservation requirements.

Developing full-biocomposites for food packaging requires taking in account numerous factors, and this is even more important for biodegradable materials compared to conventional plastics, due to the gap in knowledge on the behavior and the potentialities of these complex biodegradable materials. Numerous excellent reviews have already been published on biocomposites^{4,9–16} but they generally stick to presentation of fibers and matrices used and their resultant mechanical properties, without exploring their potential application as food packaging. On the other hand, reviews dealing with food packaging materials only evoke biopolymers^{2,17–19} and/or nanocomposites^{20,21} with a very low or inexistent interest for biocomposites.



Results found : 1680
Sum of the times cited : 24026
Citing articles : 18570
h-index : 70

Figure 1. Citation report for “biocomposites” – ISI Web of Knowledge – April 2015.

In this context, the objective of this state-of-the-art is to review the knowledge about the functional properties of full-biocomposites, i.e., both bio-sourced and biodegradable composites, by considering the specific stakes relative to the food packaging application. The first part will present the main characteristics of the constituents, i.e., matrices and fillers, encountered in literature and the main processing routes to prepare biocomposites. The second part will be devoted on the ways to better understand and control the mass transfer properties in biocomposites, by reminding the role of mass transfers in the food/packaging system, and by focusing on how mass transfer properties are impacted by the material structure and mechanical properties. Food safety aspects will also be considered, by highlighting the possible undesirable migration from biocomposites toward food.

MAIN CONSTITUENTS OF BIOCOMPOSITES

Full-biocomposites are based on a full-bioplastic as matrix and vegetal fibers as fillers. These constituents are available in a very large panel of types and characteristics. An insight on the

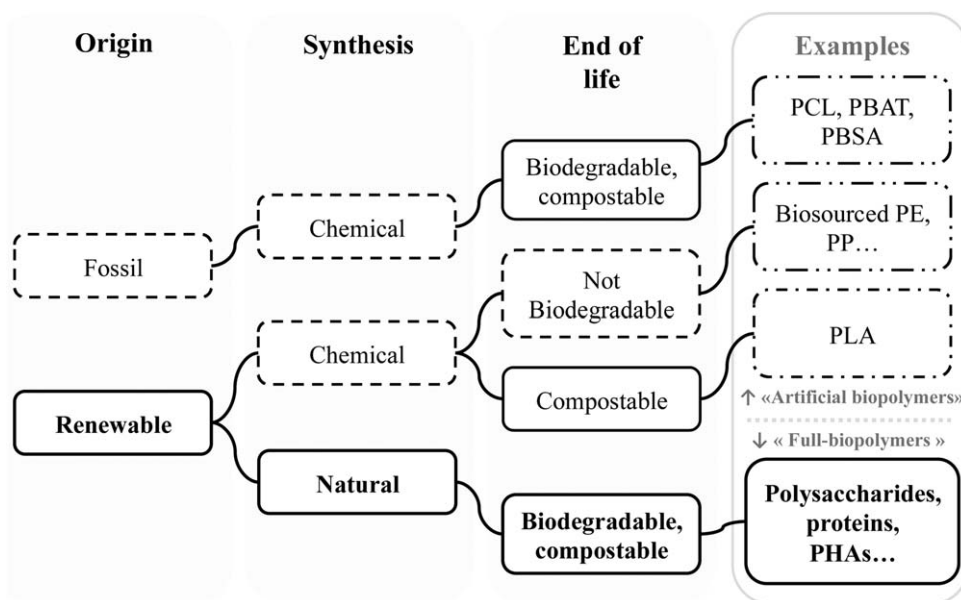


Figure 2. Main groups of bioplastics.

intrinsic properties of both constituents will be given, with a focus on barrier and mechanical properties.

Full-Bioplastics as Matrices

Bioplastics are not a single class of polymers but rather a family of products that are designed to present better environmental impact than conventional plastic materials.²² They can be classified toward three characteristics according to their origin (natural/fossil), the chemistry used to synthesize them (conventional/biosynthesis), and their end life (conventional, composting under industrial conditions, or biodegradation under all conditions).²³ The reference to the term “bio” can be assigned to 1, 2, or 3 of these characteristics (Figure 2). The most promising type of bioplastics would rather be bio-based, naturally produced, and biodegradable polymers, which could be referred as “full-biopolymers,” or bio³-polymers, “bio³” referring to the environmental optimization of all three characteristics.

Then, apart from those polymers, cumulating all “green” characteristics, polymers which source or end of life is not environmentally optimized are “chemically synthesized” polymers, which are also sometimes called “artificial biopolymers”. These polymers are synthesized by conventional chemical polymerization of monomers issued either from fossil oil cracking or from renewable resources “deconstruction” and fermentation.²⁴ The main advantage is the possibility to design polymers with controlled properties but their environmental impact benefit is highly controversial. Among these polymers, polylactic acid (PLA) is mainly produced by chemical polymerization of lactic acid obtained by *Lactobacillus* sp. fermentation of corn starch hydrolysates. PLA properties resemble to those of polyolefins^{24,25} but their rigidity is much higher due to higher glass transition temperature (+5°/+60°C instead of -120°C).²⁶ In 2014, PLA production is slightly above 400 kT/year (with a production that should double in 2020) with an average price of 1.3–2.6 €/kg under the trademark “Ingeo™” from Cargill (USA) or to a lesser extent “Purasorb” from Purac (NL). Bio-

sourced but not biodegradable/compostable plastics polymers (biopolyolefins, biopolyurethan, polycarbonate, ...) produced with monomers coming from renewable resources and “green chemistry” transformation are announced for the near future.¹⁸ Petroleum-based biodegradable polyesters are produced by main chemistry word companies such as BASF with “Ecoflex” (PBAT), Showa Highpolymer with “Bionolle” (polybutene succinate adipate—PBSA), and Solvay with “Capa” (Polycaprolactone—PCL).

The second group of bio-plastics refers to “naturally engineered polymers” produced by vegetal or microbial cells (crop plants, industrial microorganisms), which are extracted, purified, and eventually modified. These polymers are renewable and benefit from the high yields of natural fabrication with excellent carbon and energy balance. In addition, functional properties (e.g., mass transport properties) are often original and far from conventional plastic properties, thus paving the way for new applications such as active or intelligent materials.^{2,22,27} The formulation of bioplastics based on “extractible” agro-polymers implies the use of polyesters, polysaccharides, or proteins.

Today, the availability of both efficient and low-cost biodegradable and bio-sourced polymers is a challenge not yet solved. On the first hand, agro-polymers (starch, proteins, cellulose, and lignin), which are directly extracted from the plant, are generally available at a reasonable cost (around 1 €/kg) and in large quantities. But a downside to their extensive use is often their intrinsic reactivity and thus lower inertia than most conventional petrochemical-based plastics. For example, to overcome the poor moisture barrier properties of starch materials, commercial water-resistant starch-based bioplastics are produced by using fine molecular blends of biodegradable synthetic polyesters (e.g., polycaprolactone (PCL) or polybutyrate adipate terephthalate (PBAT)), which form the continuous phase (and give the water resistance), gelatinized starch (up to 40–60%), and

Table I. Summary of Tensile Properties (Tensile Strength, Tensile Modulus, and Strain at Break) of Some Biodegradable Polymer Matrices

Polymer category	Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Strain at break (%)	References
Polyesters	PCL	19–21	0.21–0.33	300–897	4,50
	PBAT	>84	0.04	>200	102
	PBSA (Bionolle)	20	0.44	20	106
	PLA	21	0.35	3	4
	PHBV	40	3.5	5	4
Protein	Wheat gluten ^a	1.86	0.004	58	103
Polysaccharides	Starch	5	0.13	31	4
	Cellulose	12–13	1.41–1.50	4–5	104
	Chitosan ^b	27–39	–	11–33	105

^a Measured at 25°C and 70% RH.

^b Measured at 25°C and 50% RH.

compatibilizers.²⁸ On the other hand, microbial polyesters such as polyhydroxyalkanoates (PHA), which are produced by bacterial fermentation and constitute a reserve of carbon and energy within the microorganisms, display huge advantages such as their excellent barrier properties and water resistance, but are currently available at a cost that remains high (between 2 and 5 €/kg).^{29,30} A particular interest has been recently given to the copolymer poly(β -hydroxybutyrate/ β -hydroxyvalerate) (PHBV), which is an unbranched polymer predominantly composed of R-3-hydroxyalkanoic acid monomers ranging from 3 to 14 carbons in length with hydrogen or alkyl up to nonyl radicals.³⁰ Some industrial companies are currently commercializing these microbial polyesters. This is the case of Tianan Biologic Material in Ningbo (China) or “Biocycle[®]” produced by PHB Industrial in Brazil. PHAs overall properties are close to polyolefins but their rigidity is much higher due to a higher glass transition temperature (+5°/+10°C instead of –120°C for polyethylene).^{31–33} Actual production of these microbial polyesters is still very low (between 0.6 and 1.2 kT/year with a price between 1.8 and 5.0 €/kg according to the quality and to the production process). A greater diffusion of PHAs has been hampered by their relatively high cost of production.

Finally, it is worth noting that all the bio-sourced bioplastics present on the market are currently produced from noble food resources. In a period when the basic right of people to the food they need is the greatest challenge facing the world community, the political authorities aimed at stimulating the development of new materials from renewable sources without competition with food usage. For that purpose, many scientists and industrials are recently devoting research activities on the valuation of food by-products (either liquid effluents or solid residues) for the production of materials. Indeed, it is estimated that food processing activities produce in Europe large amounts of by-products and waste of about 250 million tons/year,³⁴ along with relevant amounts of high COD (chemical oxygen demand) liquid effluents. Such waste effluents are only partially valorized at different value-added levels (spread on land, animal feed, composting, anaerobic digestion), whereas the main volumes of them are managed as wastes of environmental concern, with relevant negative effects on the overall sustainability of the

food processing industry.³⁵ The integrated valorization of food processing by-products, wastes, and effluents is a challenging opportunity for the sustainable and competitive development.

Mechanical Properties of Bioplastics. Tensile properties of the main bioplastics are gathered in Table I. Polyesters are known to have mechanical properties closed to classical petro-sourced polymers.⁴ Nevertheless, the limited strain at break of polyesters such as PLA and PHBV, around 3–5%, reveals their brittleness, which limits their use.

Proteins and polysaccharides generally reach lower rigidity and resistance than polyesters, but are more ductile. Their mechanical properties are generally considered as poor and necessitate the use of plasticizers.¹⁷ They present the characteristic of being sensitive to water, which can be seen as a drawback, as they tend to become softer with increasing relative humidity, but it also opens the door to mechanical properties modulation. Recently, a research group revealed the potential shape-memory capacity of starch.³⁶ If this phenomenon has not met yet an application in food packaging, this should still encourage studying atypical structured bio-sourced polymers, which might be richer than classical polymers in terms of mechanical properties diversity.

Barrier Properties of Bioplastics. As for mechanical properties, polyesters display barrier properties close to classical petro-sourced polymers (Table II).³⁷ On the opposite, the water vapor permeability (WVP) values of protein-based films are normally 2–4 orders of magnitude higher than that of low density polyethylene (LDPE).³⁸ This is due to the presence of free hydroxyl groups in the matrix, which interact strongly with migrating water molecules. Moisture considerably affects the WVP and gas permeability of protein films. This is attributed to the plasticization effect of water on protein films. For example, an increase of more than 25-folds was observed by Mujica-Paz and Gontard³⁹ for the oxygen permeability (PO₂) of wheat gluten based films at 24°C between 0 and 100% RH. More interestingly, the permeability toward carbon dioxide is all the more increased than to oxygen, mainly due to the highest solubility of CO₂ in water than O₂, leading to a drastic increase in gas permselectivity (ratio between the carbon dioxide permeability

Table II. Summary of Permeabilities toward Water Vapor (WVP),^a Oxygen (PO₂),^b and Carbon Dioxide (PCO₂)^b of Some Biodegradable Polymer Matrices

Polymer category	Polymer	WVP × 10 ¹⁰ (mol m ⁻¹ s ⁻¹ Pa ⁻¹)	PO ₂ × 10 ¹⁷ (mol m ⁻¹ s ⁻¹ Pa ⁻¹)	PCO ₂ × 10 ¹⁷ (mol m ⁻¹ s ⁻¹ Pa ⁻¹)	References
Polyesters	PCL	0.008	26	-	50,54
	PBAT	0.02	0.3	-	115
	PBSA (Bionolle)	0.0002	-	-	106
	PLA	0.0000024	41	87	2,24
	PHBV	0.002-0.0004	1-7	3-9	10
Protein	Wheat gluten	0.4-0.6 ^a	8-197	88	39,103
Polysaccharides	Starch	0.0005-2	0.1-0.7	-	108
	Cellulose	-	210	4278	104
	Chitosan	85,005-339,056	-	-	105

^a Measured at 25°C and for a difference of relative humidity (RH) equal to 0-100%.

^b Measured at ambient temperature and 0% RH.

(PCO₂) and PO₂).³⁹ Such a property is particularly interesting for the packaging of respiring products such as fruits and vegetable. Polysaccharides, as proteins, exhibit relatively high gas permeability. This feature increasing with relative humidity, modulation of barrier properties can be envisaged, depending on the product to be packaged (Table II).

Vegetal Fibers as Fillers

There are thousands of different fibers in the world and in fact, only few of these have been studied. Natural fibers include those produced by animals (silk, wool), geological processes (asbestos), and vegetal fibers. The present review will voluntarily focus on vegetal fibers, i.e., lignocellulosic fibers, which are widely available all around the world at a quite low cost. They are generally produced annually, except for wood, which generally requires several years before being exploited. Vegetal fibers can be considered as naturally composite materials as they are mainly constituted of cellulose fibrils (fibers) embedded in a lignin matrix (resin). Such materials are inherently fully biodegradable, due to their enzymatic generated structure, which can be depolymerized by other suitable enzymes. As listed by Satyanarayana *et al.*,⁴ lignocellulosic fibers have multiple merits. They display a low density (around 1.5 g cm⁻³) as compared for example to glass fibers (2.5-2.6 g cm⁻³),²¹ giving the possibility to obtain lighter composite materials. They are non-abrasive for machinery, and display high stiffness and less impact on the health of composite manufacturers. It should be mentioned that there are also shortcomings. Their downsides are linked to their chemical structure, thermally sensitive and hydrophilic character,⁵ but also a lack of consistency of fiber qualities, high levels of variability in fiber properties related to the location and time of harvest, processing conditions.⁹

Classification of Fibers. The large variety of vegetal fibers types lead several authors to classify them, generally as a function of their origin in the plant (leaf, seed, or fruit).³ As Faruk *et al.*⁹ suggesting a classification regarding their primary or secondary application, we propose here to classify them regarding their

final use by humans, i.e., technical fibers for manufactured goods vs fibers stemming from food and wood industries by-products.

Technical fibers for manufactured goods. For centuries, vegetal fibers have been exploited for manufactured products such as textile, rope production, furniture, and much more applications. We cite, for example, flax, hemp, cotton lint, or sisal fibers (Table III). Such technical fibers also find secondary applications in food industry (e.g., bamboo, agave, oil from linseed). Even today, these fibers are globally produced up to million tons, each country having a potential of plants to exploit (Table III). As regards their final use constraints, such fibers were chosen due to their good mechanical properties. Indeed, textile and rope are submitted to deformations and tensions they have to resist to. Therefore, most of technical fibers exhibit high tensile strength, around typically 200-800 MPa. They also are quite rigid, as reflected by their generally high tensile modulus. In the field of biocomposites research, craft fibers have been widely studied precisely for these high performances.

By-products fibers. On the opposite, by-product-based composites were studied in order to valorize large amounts of wastes from food industry, regardless of their intrinsic properties. Production of the main product is counted up to billions of tons (Table IV). Their mechanical properties are less documented and generally poorer than craft fibers, i.e., their tensile strength and tensile modulus are lower.

Fiber Characteristics. The intrinsic fiber characteristics of interest when considering their use as filler in composite materials for food packaging applications are mainly their mechanical properties, which will affect the mechanical properties of final composite materials, surface properties, including surface free energy and surface physical state, density, composition, crystallinity, morphology, thermal stability, and mass transfer properties. Listings of such characteristics have already been reviewed by several authors.^{9,15,21,40,41} It is worth noting that the properties of vegetal fibers differ among cited works, because of fiber

Table III. Summary of Production, Current Use, and Tensile Properties of Technical Craft Fibers

Plant	World production (tons) ^{1,04}	Main producers ¹⁰⁴	Current use	Tensile strength (MPa) ²¹	Tensile modulus (GPa) ²¹	Strain at break (%) ²¹
Cotton lint	25,955,096	China (26%), India (21%), USA (14%)	Textile	287–800	5.5–12.6	3–10
Jute	3,461,963	India (55%), Bangladesh (42%), China (1%)	Textile and rope	320–800	8–78	1–1.8
Flax	243,115	France (22%), Belarus (21%)	Textile and rope	323–2000	27.6–103	1.2–3.3
Sisal, (a.k.a. Henequen)	220,208	Brazil (40%), Kenya (1.3%), Tanzania (1.2%)	Textile and rope	430–570	10.1–16.3	3.7–5.9
Ramie	154,435	China (97%)	Textile, paper	400–1000	24.5–128	1.2–4
Kapok	99,000	Indonesia (55%), Thailand (45%)	Textile, lifesaving jackets, pillows	-	19	1–2
Abaca	70,000 ^c	Philippines (90%), Ecuador (10%) ^c	Rope and paper	270–900	23.5–90	1–3.5
Hemp	53,495	China (32%), North Korea (26%), Netherlands (1.1%)	Textile and rope	-	-	-
Agave	40,965	Colombia (39%), Mexico (1.5%), Cuba (10%)	Textile fiber	400–980	2–6.2	1–10
Alfa	-	West Mediterranean regions	Paper	35	22	5.8
Bamboo	-	Mainly Asia	Scaffolding, furniture, textile, paper	140–800	11–32	1.5–3.7
Kenaf	340,000	India	Textile and rope, insulation, paper	223–930	14.5–53	1.5–2.7

and testing methods variability. This article will here focus on mechanical properties, surface properties, and gas transfer properties.

Mechanical properties. Extensive studies on the mechanical properties of vegetal fibers are presented in numerous literature reviews as the final composite properties strongly depend on the reinforcing phase. Mechanical properties of fibers are summed up in Tables III and IV. Young's modulus values are ranging from 1–2 GPa for pineapple or agave fibers up to more than 100 GPa for flax or ramie fibers. The majority of lignocellulosic fibers display a tensile strength of about 300–500 MPa, with values ranging from 35 MPa for alfa fibers up to 2000 MPa for flax fibers. Finally, lignocellulosic fibers all display an elongation of about 1–5%. It has been established that lignocellulosic fibers can compete with glass fibers in terms of mechanical properties (Young's modulus of about 80 GPa, tensile strength around 2000 MPa, and elongation at break around 2.5%), even more by viewing fibers in relation to their respective density. However, the range of lignocellulosic fibers mechanical properties is remarkably higher than those of glass fibers, which can be explained by the variability in fiber structure and quality.

It is to be noticed that fiber mechanical properties can be related to their composition, as shown in Figure 3. The following tendencies can be drawn. The tensile strength evolves exponentially with cellulose content, and inversely exponentially with lignin content, while elongation at break increases linearly with lignin content. No clear relationship between Young's modulus and composition was recognizable. Mechanical properties cannot be predicted only regarding fiber composition, which only reflects the structure at the molecular scale. In fact, the mechanical properties of fiber may be governed by the internal structure at the histological level, including mainly cellulose content, spiral angle of the cellulose microfibrils in the inner secondary cell walls along the fiber axis and cellulose crystals size.⁴²

Surface properties. Lignocellulosic fibers display various physical and chemical structures, leading to a wide range of possible interactions with the polymer matrix. Surface properties include surface free energy, which will impact the wettability of fibers by the polymer matrix, and also physical surface state such as roughness, which will govern the ability of the two constituents to interact through mechanical interlocking.

The surface energy of lignocellulosic fibers varies from 30 to 50 mJ m⁻², depending on botanical origin. It is worth noting that for a given sample, results can vary depending on the method, temperature, liquids of reference, and modeling approach used, as revealed for wheat straw fibers in Table V. This value is lower than either pure cellulose or lignin, which display similar magnitude (about 60 mJ m⁻²). In all the cases, lignocellulosic fibers and their pure constituents generally exhibit a polar component as high as the dispersive one, as expected from an OH-rich surface (Table V).

In the case of composite materials, a necessary condition for acceptable interfacial interaction between the reinforcement

Table IV. Summary of Production of Main Food-Used Plants, and Their Respective By-Products Tensile Properties

Plant	World production (tons) ¹⁰⁹	Main producers ¹⁰⁹	By-product fibers	Tensile strength (MPa) ²¹	Tensile modulus (GPa) ²¹	Strain at break (%) ²¹
Sugarcane	1,773,814,608	Brazil (38%), India (20%), China (7%)	Bagasse	222–290	17–27.1	1.1
Rice	719,738,272	China (28%), India (21%), Indonesia (10%)	Straw, husk	-	-	-
Corn	690,668,292	USA (40%), China (30%), Brazil (20%)	Stover	-	-	-
Wheat	670,875,110	China (18%), India (14%), USA (9%)	Straw, husk	50–120 ⁴³	4–13 ⁴³	-
Barley	132,886,519	Russia (10%), France (9%), Germany (8%)	Straw, husk, brewer's spent grains	-	-	-
Banana	101,992,743	India (24%), China (11%), Philippines (9%)	Palm	500	-	1.5–9
Coconut	60,048,837	Indonesia (30%), Philippines (26%), India (18%)	Shell, coir	131–175	4–13	-
Oil palm	50,198,781	Indonesia (47%), Malaysia (37%), Thailand (3%)	Palm	248	3.2	25
Pineapple	23,333,886	Thailand (11%), Costa Rica (11%), Brazil (11%)	Palm	180–1627	1.44–82.5	1.6–14.5
Olive	16,555,375	Spain (22%), Italy (18%), Greece (13%)	Husks	-	-	-
Date	7,548,918	Egypt (19%), Iran (14%), Saudi Arabia (14%)	Palm	-	-	-

and the matrix is that the surface energy of the fiber surface must be greater than that of the matrix. We can note that it is not always the case. Treatments might be thus applied to fibers with the aim to increase their hydrophobic character, including chemical or physical treatments.^{43–47}

Gas transfer properties. As inventoried by Wolf,⁴⁸ water vapor diffusivity coefficients of several lignocellulosic fibers were reported between 1.1×10^{-11} and $179 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ (at 20–25°C and 75–80% RH) whereas PHBV's water vapor diffusivity was reported as $2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. For comparison purpose, LLDPE and EVOH with increasing vinyl alcohol comonomer content diffusivity has been measured between 8.9×10^{-15} and $10.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$.⁴⁹

Due to their chemical composition, lignocellulosic fibers are hydrophilic, therefore are able to let water vapor diffuse through them. According to Ludueña *et al.*,⁵⁰ the sorption behavior is a combination of two processes: absorption due to the micro-cavities and amorphous regions (crystalline regions are considered to be impermeable to vapor molecules) and absorption due to the presence of hydrophilic groups.^{51,52} In the case of fiber treatment, removing amorphous components (e.g., cellulose crystals isolation) and hydrophilic groups (e.g., surface treatment), water sorption might be lower. Also, Belbekouche *et al.*⁵³ observed that the first half sorption diffusion coefficient, corresponding to the diffusion of water through the surface of particles, was higher than the second half sorption diffusion coefficient, more representative of the diffusion at the core. It is an indication that the diffusion of water is rather controlled by the surface than by the core. In such case, a fiber size reduction, related to an extension of its surface area, may favor the controlling mechanism for water diffusion inside the fiber.

To our knowledge, no data are available concerning the diffusivity and sorption of gas such as O₂ and CO₂ in lignocellulosic fibers.

Preparation of Full-Biocomposites: Shaping Processes

As conventional plastics for packaging, i.e., polypropylene, polyethylene, and other petro-sourced thermoplastics, full-biocomposites can be manufactured using industrial techniques such as compounding, mixing, extrusion, injection molding, compression molding, and resin transfer molding (RTM).⁹ Though depending on the studied matrix and the aimed application, and often for research purposes, samples are prepared by solvent casting in several studies.^{54–57}

Among the disadvantages associated with classical thermal treatments, there is a risk of degrading both the bioplastic used as matrix and the lignocellulosic fibers. Indeed, most biopolymers are especially sensitive to temperature, their melting temperature being close to their degradation temperature (e.g., PHBV⁵⁸). In the case of proteins, wheat gluten's degradation temperature is even below its melting temperature; therefore, such material has to be plasticized, generally with water and/or glycerol.⁵⁹ Fibers are also sensitive to thermal treatments as degradation can occur that weakens the fibers. The inherent moisture that is naturally bound to the hemicellulose component

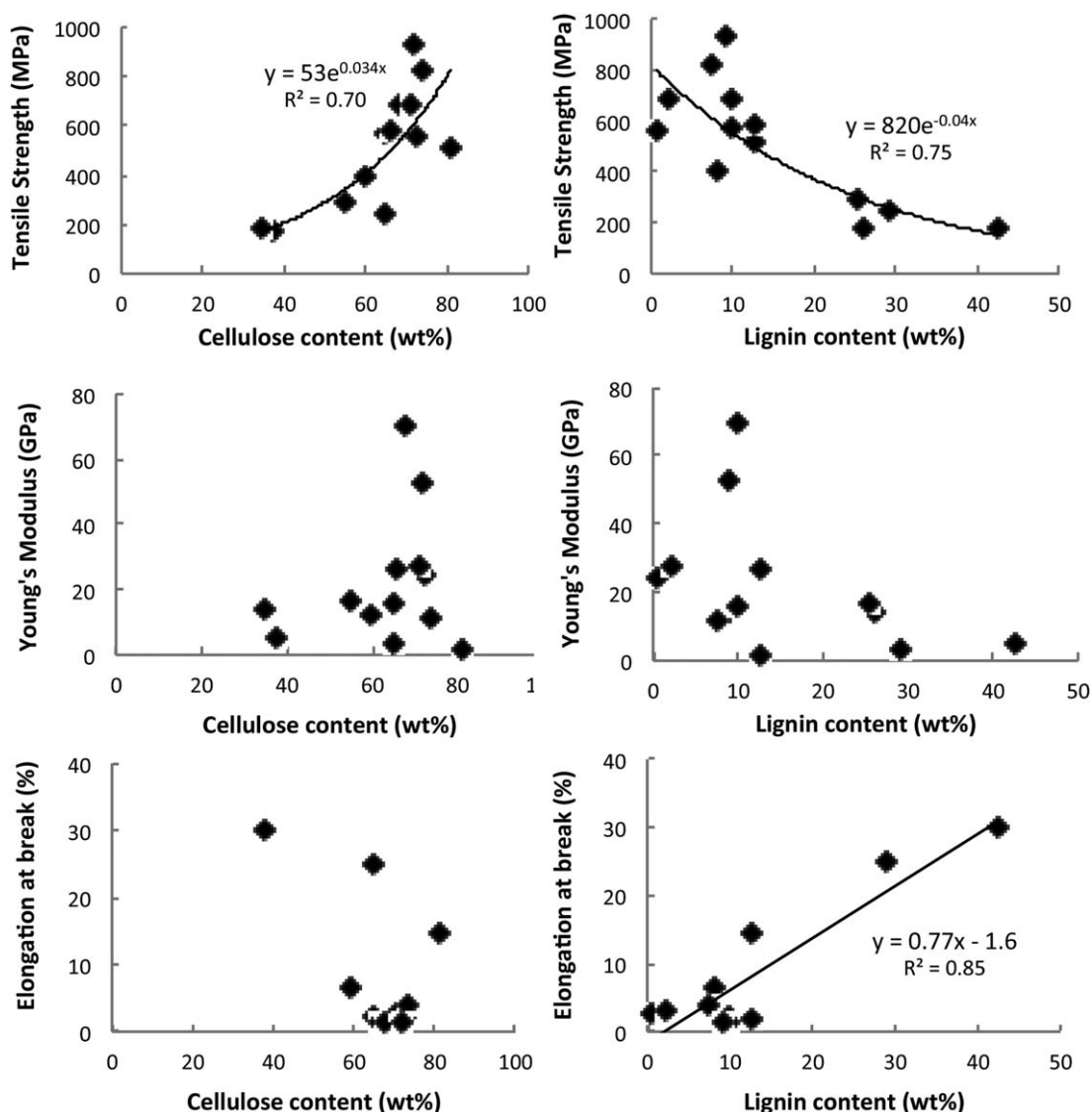


Figure 3. Relationships between the mechanical properties of vegetal fibers (from baca, bagasse, bamboo, coir, curaua, flax, hemp, jute, kenaf, oil palm, pineapple, ramie, and sisal) and their cellulose and lignin contents. Adapted from Faruk *et al.*⁹

can change depending on temperature and exposure time. Furthermore, heat-treated biomass is known to globally become darker and brittle, due to the loss of its tenacious and fibrous nature resulting from the decomposition of hemicelluloses and partial depolymerization of lignin and cellulose. Several publications have investigated these issues and have generally found that exposure to temperatures at or below 170°C did not have a significant effect on the strength of the fibers.⁶⁰

Regarding fibers, processes involving shearing are also known to impact fiber length and morphology.⁶¹ Depending on the process, dispersion of the fibers within the composite might also be affected, thus impacts its mechanical and barrier properties.⁶² Finally, the feeding of melt extrusion equipments could be difficult with some fibers, as reported for flax or hemp fibers, thus imposing the use of a force feeder equipment.

Finally, another key point in is the intrinsically hygroscopic character of vegetal fibers resulting from the polar character of

their main constituents, i.e., cellulose, hemicelluloses, and lignin. Vegetal fibers are found to contain from 8.8 to 15 wt % d.b. of water (for equilibration at 65% RH at 21°C) depending on their botanical origin.⁹ A major limitation of using vegetal fibers in durable composite applications is thus their high moisture absorption or release (depending on environmental conditions) and poor dimensional stability (swelling). Thus, one recommendation commonly done is a cautious drying of lignocellulosic fibers before using them as fillers in composites.⁹

UNDERSTANDING AND CONTROLLING MASS TRANSFER PROPERTIES OF BIOCOMPOSITES

Role of Mass Transfers in the Food/Packaging System

The main functions of packaging are to protect and stabilize food until its consumption. Once these central functions are addressed, all the others (marketing, communication, distribution, etc.) should be equally considered. Packaging should ensure food integrity, which means to avoid exposure to

Table V. Surface Free Energy of Some Lignocellulosic Fibers, Conventional Plastics, and Bioplastics

	γ_s (mJ m ⁻²)	γ_s^d (mJ m ⁻²)	γ_s^p (mJ m ⁻²)	References
Pure cellulose	61 ± 2	39 ± 2	22 ± 2	42
Lignin (softwood kraft)	57	34	23	110
Wheat straw fibers	48 ± 2	33 ± 2	15 ± 2	42
Wheat straw fibers	44 ± 1	21 ± 4	23 ± 1	59
De-retted flax fibers	31	13	18	111
Polyethylene	33	33	0	112
Polypropylene	53 ± 2	40 ± 2	13 ± 2	42
Polyethylene terephthalate	42	37	5	113
Poly(butylene adipate terephthalate)	53 ± 2	40 ± 2	13 ± 2	42
Poly(lactic acid)	49 ± 2	37 ± 2	11 ± 2	114
Polycaprolactone	52 ± 2	41 ± 2	11 ± 2	114
Plasticized wheat gluten	48 ± 1	28 ± 2	20 ± 3	59
Plasticized wheat starch	32 ± 2	20 ± 2	12 ± 2	114

physical damage like mechanical shock, or detrimental environmental elements such as light, dust, chemical, and microbial contamination. In addition, the packaging is also expected to maintain the sensory attributes (texture, color, flavor), the nutritional value (high mineral and vitamin level, low chemical preservative content), and the safety (e.g., by inhibiting or delaying the development of endogenous flora or foodborne pathogens) of the food. Food preservation can be defined in terms of reduction of degradation reactions, i.e., physicochemical and microbial reactions for nonliving products but also physiological reactions for living products that are a function of temperature (controlled via the cold chain), light transmission, and atmosphere composition around the food. Packaging plays a major role hereby defining around the food, a headspace atmosphere whose composition is controlled via mass transfers through the packaging. In food/packaging systems, mass transfers (also called permeability or migration) occurred for many types of molecules (Figure 4), all having an impact on food quality and safety⁶³:

- From the environment toward the headspace and the food, through the packaging materials, permeation of environmental gas and vapor, which are key factors of food quality preservation by controlling food degradation reactions (such as oxygen influencing oxidation of vitamins, essential fatty acids, etc. or microbial growth).
- From the foodstuff toward the packaging, transfer, or sorption of food components, which are important for food sensory properties such as aroma compounds of coffee or carbon dioxide of carbonated beverages for example.
- From the packaging toward the food, migration of undesirable molecules (potentially toxic for human in long-term exposure conditions) such as chemical additives or residual monomers regulated to a maximum limit.

The determination of the barrier properties of a polymer is thus crucial to estimate and predict the product-package shelf-life. The specific barrier requirement of the package system is related

to the product characteristics and the intended end-use application. Generally, plastics are relatively permeable to small molecules such as gases, water vapor, organic vapors, and liquids and they provide a broad range of mass transfer characteristics, ranging from excellent to low barrier values. This broad range of mass transfer properties is important in the case of food products, which display, depending on their nature, different sensitivity to moisture and/or O₂.²

- *Moisture.* Moisture barrier property is an essential basic requirement when packing many foods, whether dry or moist, to preserve the texture (such crispiness, softness, firmness, etc.) and control microbial development of aerobic spoilage and pathogen species. Moisture barrier property is expressed by the water vapor transmission rate (WVTR: amount of water vapor that permeates per unit of area and time through the packaging materials) or more adequately by the water vapor permeability (WVP: taking into account the influence of material thickness and water vapor partial pressure gradient).
- *Oxygen.* Packaging plays also a crucial role for protecting food from oxygen, which is the key element of many degradation reactions occurring in food. Oxygen acts as the main factor of organoleptic and nutritional quality degradation of food through the oxidation of vitamins, aroma compounds, pigments, lipids and proteins compounds, etc. Oxygen is also involved in microbial development and maturation rate of fresh living products such as fresh fruits and vegetables or fermented cheeses. As for water vapor barrier, oxygen barrier property is expressed by the oxygen transmission rate (OTR) or more frequently by permeability (OP).
- *Carbon dioxide.* Carbon dioxide transmission rate or permeability is thus another important selection criterion of many food packaging materials. Carbon dioxide needs to be preserved for many carbonated drinks. It is involved in the inhibition of respiration rate of living produces and is also used as bacteriostatic and fungistatic agent. Carbon dioxide is now

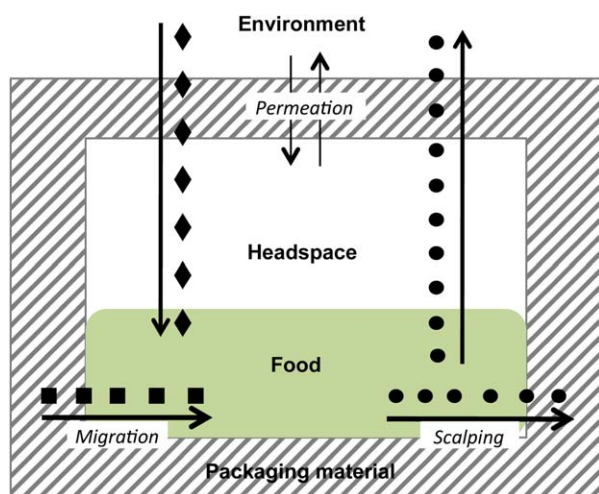


Figure 4. Main possible mass transfers in a food/packaging system: (◆) vapors and gases from the external environment toward the food, (●) food components from the foodstuff toward the packaging or the environment, and (■) undesirable molecules from the packaging toward the food. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

also important for the packaging in modified atmosphere (modified atmosphere packaging (MAP) technology).

Basics on Mass Transfers

Theoretical Definitions. Considering a composite material as a homogeneous material, mass transfer is supposed to obey to Fick's law which related the flux (J) to the gradient of concentration through a proportionality coefficient (D):

$$J = -D \left(\frac{\partial c}{\partial x} \right) \quad (1)$$

where D is the coefficient of diffusion or diffusivity ($\text{m}^2 \text{s}^{-1}$) which characterizes the mobility of a molecular specie in the material.

Henry's law gives the correspondence between the concentration (c) and the partial pressure (p) for dilute system:

$$c = S \times p \quad (2)$$

where S is the solubility coefficient ($\text{mol m}^{-3} \text{Pa}^{-1}$), a thermodynamic parameter which characterizes the number of moles of a molecular species sorbed into the material.

By combining eqs. (1) and (2), the first Fick's law could be expressed for a monodirectional flux through a plane sheet of material as follows:

$$J = \frac{D S (p_1 - p_2)}{h} \quad (3)$$

where p_1 and p_2 are the pressure on the two sides of the film and h is the thickness of the film.

The mass transfer phenomenon in the bi-phasic system could, therefore, be represented by a solution-diffusion mechanism⁶⁴ described by the three coefficients, i.e., solubility (S), diffusivity (D), and permeability (P). The permeability coefficient combines the effects of diffusion and solubility as follows:

$$P = D \times S \quad (4)$$

The permeability coefficient is conventionally used to characterize the barrier properties of composite material in several fields of science such as membrane science, packaging science, etc.

By the addition of permeable particles in a polymer matrix, P of the composite material was a result of the contribution of both permeability of the neat matrix and that of the particles themselves. The composite material is then considered as a biphasic material. A huge part of the works done on mass transfer properties of composite material containing permeable particles have focused on the predictive modeling of the composite permeability from the permeability in the neat matrix and that in the particle itself.

Methods of Analysis. Solubility is a thermodynamic parameter that is measured when the material, initially free of the studied gas or vapor, is put in equilibrium with a surrounding atmosphere of a fixed partial pressure of gas or vapor. For instance, to measure a sorption of gas, the material is first desorbed under a flux of inert gas (e.g., N_2 or He) and after that submitted to a flux enriched with a given pressure of the gas studied. The quantity of gas sorbed in the material at equilibrium could be either measured directly in the sample (e.g., chemical titration, gravimetry) or indirectly by measuring the drop of pressure (occurring subsequently to gas sorption into the sample) in the closed atmosphere in contact with the sample. Methodologies used to measure O_2 and CO_2 solubilities in solid products were recently reviewed.⁶⁵ The most used technique in material science is gravimetry, which is a simple, direct, and powerful experimental procedure to measure the O_2 or CO_2 solubility, but also the O_2 or CO_2 diffusivity when the mass uptake is monitored (see below). Indeed, among the 120 values of CO_2 solubility listed by Tomasko *et al.*⁶⁶ and measured in common synthetic polymers, more than 100 values were obtained by gravimetry, confirming the prevalence of this methodology in the fields of polymer studies and membrane science. Gravimetry was used to measure CO_2 solubility in, for example, wheat gluten films,⁶⁷ polystyrene,⁶⁸ a selection of 10 synthetic polymers,⁶⁹ etc. The measurement of O_2 sorption by gravimetry is trickier than CO_2 sorption due to the lower affinity of O_2 for the matter than CO_2 that lead to very low mass variation. It is well highlighted that one of the main requirements necessary for the use of gravimetry is the accuracy of the balance. Currently, some equipment (Cahn microbalance, quartz crystal microbalance, etc.) enables to perform such an experiment with a sensitivity less than $0.1 \mu\text{g}$.⁷⁰ In the peculiar case of water vapor, solubility is not a constant and varies according to the water vapor pressure (or relative humidity) imposed to the material. Water sorption isotherms, i.e., relationship between relative humidity and moisture content of the material in equilibrium with its surrounding atmosphere, are thus measured.⁷¹ Numerous literature data could be found on the water sorption isotherm of polymer and bio-based materials. Recently, Wolf⁴⁸ measured water sorption isotherm in a biocomposite (PHBV/wheat straw fibers) and its individual components (neat matrix and fiber) in order to decipher the impact of fiber water sorption on the water sensitivity of the composite.

Contrary to the solubility coefficient, the diffusivity value cannot be directly measured. For this purpose, a gradient of concentration or partial pressure must be imposed to the sample, and the subsequent mass transfer must be measured against time and/or position. The diffusivity is then identified by fitting a mathematical model to the experimental data. The diffusivity value is the one that minimizes the sum of squared error between the 2 datasets. Sorption kinetic measured by gravimetry (see above) could be used to identify diffusivity value as it could be done for water vapor diffusivity from dynamical water sorption measurements.^{71–73}

Permeability is calculated from a measure of flux across the material in a permanent state. This rate is obtained for a given partial pressure difference in gas or vapor which is imposed to the material by mean of a permeation cell. For water vapor permeability, the permeation cell containing pure water (100% RH) or a saturated salt solution is hermetically sealed with the film and stored in a desiccator at a given RH different from that in the cell (usually 0% RH) (American ASTM E96-80; ASTM 1980). Due to the difference of RH, loss of water by the cell occurs which is gravimetrically monitored as a function of time. Slope of the curve, loss of mass vs time, corresponds to the flux of water vapor that permits to calculate WVP. For gases such as O₂ and CO₂, the cell is flushed on one side by a given partial pressure of O₂ or CO₂ (usually 100%) and on the other side by an inert gas (namely vector gas). The quantity of O₂/CO₂ that permeates through the film and is present in the flux of vector gas could be assayed, for example, by gas chromatography. An alternative to this dynamic method is the static method: in that case, the cell on which the film is sealed is flush by the inert gas or the permeant gas, and then hermetically closed. The quantity of O₂ or CO₂ entering or going out the cell toward external atmosphere due to the gradient of gas created is monitored as a function of time. Only the initial part of the curve is used to calculate the permeability (from the initial slope) when a pseudo steady state could be assumed. Permeability is the most used parameter to characterize the mass transport properties of thin films. Therefore numerous permeability values could be found in original peer-reviewed papers, handbooks such as that of Massey.⁷⁴

Gas (O₂, CO₂) Transfer Properties in Biocomposites

Studies dealing with gas transfer properties in biocomposites are very rare. Only two studies were found to report gas transfer properties in biocomposites.^{75,76}

Sonia and Dasan⁷⁵ studied cellulose microfibrils (CMF)/poly (ethylene-co-vinyl acetate) (EVA) with an increasing fiber content, up to 13 wt %. It occurred that the introduction of low fiber content (up to 5 wt %) lead to an improvement of the barrier properties, whereas above this limit value, the 200 μm fibers provoke an increase of oxygen permeability through the materials.

Valdés García *et al.*⁷⁶ studied a composite based on almond skin residues in a poly (β -caprolactone) matrix. Since composites contained 10, 20, and 30 wt % of 50 μm fibers, no information about low fiber content is given, and oxygen transfer

rate (OTR) displayed the same evolution than observed by Sonia and Dasan⁷⁵ for highest fiber loads. In all cases, fiber introduction increased OTR, with a 5-times step up at 30 wt % of fibers content. Sonia and Dasan,⁷⁵ considering the fibers as impermeable, explained that diffusion through the polymer can be related to two interconnected phenomena: fibers introduction (1) replaced a space that would otherwise be occupied by the permeable polymer and (2) increased of the tortuosity for gaseous molecules diffusing through the membrane. However, in opposition to the expected OTR decrease, OTR increase above 5 wt % of fiber content. This behavior was ascribed to a nonuniformity in fiber distribution at microlevel for high fiber loading. Another hypothesis brought by the authors could be that a percolation network has been formed above a limit concentration, which then would create preferential pathways for gases. Valdés García *et al.*⁷⁶ also suggest an agglomeration of the fibers at high fiber content, which is confirmed by scanning electron microscopy (SEM) observations.

Water Vapor Transfer Properties in Biocomposites

Literature was richer concerning water vapor than gas transfer properties of full-biocomposites (Table VI). Main parameters evoked to control water vapor permeability (WVP) are fiber content and size, fiber/matrix adhesion, and crystallinity and plasticisation of the matrix.^{50,55} From a theoretical point of view, supposing that fibers are impermeable and well dispersed in the matrix, WVP is likely to decrease due to tortuosity effect. Actually, as evoked previously in this article, lignocellulosic fibers are not fully impermeable. Therefore, in most of the cases, WVP of the composite increased with fiber addition. Thus, the fiber hygroscopic character should be added to the list of the main parameters controlling WVP.

WVP would increase due to aggregation and percolation phenomena. The first one might occur for small fibers and/or poor fiber/matrix adhesion. Poor fiber/matrix adhesion would also generate voids in the polymers, which might ease the transport of the water molecules throughout these regions.⁵¹ Percolation will appear shortly afterward agglomeration for higher fiber content and also, more likely, in the case of higher fiber size. WVP would increase also due to a decrease of the matrix crystallinity and/or matrix plasticization induced by fiber addition.

In the case of cellulose microfibrils in PCL, PLA, and PHBV,⁵⁵ a competitive effect hypothesis has been proposed, between fibers aggregation, creating pathways increasing gas permeability, and the supposed intrinsic barrier capacity of cellulose crystals. Though the crystallinity of the matrix has been shown to decrease in the presence of fibers, water vapor permeability decreases, at least for the lowest fiber contents (all fiber contents tested being below 10 wt %).

On the opposite, Valdés García *et al.*,⁷⁶ testing 10, 20, and 30 wt % of almond skin residue content in PCL, observed a gradual increase of WVP, though no significant differences were found for neat PCL and PCL10% composite ($p > 0.05$). Such results were ascribed solely to fiber agglomeration causing reduction in the matrix homogeneity and cohesion.

Table VI. Water Vapor Permeability ($\times 10^{13}$ mol m⁻² s⁻¹ Pa⁻¹) of Some Biocomposites

Matrix	Fibers	Fiber size	Conditions of measurement	WVP $\times 10^{13}$ (mol m/m ² s Pa)											Reference		
				0	1	2	3	4	5	10	15	20	30	50			
PHBV	Cellulose	Length: 60 μ m; width: 20 μ m	24°C, 40% RH	7.1	2.1	2.7		5.2	2.9	3.7							55
PCL				19	11	12		14	16	24							
PLA				13	12			16	18	23							
PCL	Almond skin	d_{50}^a : 50 μ m	20°C, 50% RH	14				12	17	18							76
PCL	Cotton	Length: 3870 μ m; width: 59 μ m	Room temperature, 68% RH	8.9				11	13								50
	Cellulose	Length: 1191 μ m; width: 9 μ m	[emsp]					8.9	9.4								
	Hydrolyzed cellulose	Length: 1.78 μ m; width: 0.2 μ m						11	11								
PHBV	Wheat straw fibers	d_{50}^a : 109 μ m	Room temperature, 100% RH	8.3				29									117
	Olive mills	d_{50}^a : 46 μ m						2.9									
PHBV	Ball milled wheat straw fibers	d_{50}^a : 17 μ m	Room temperature, 100% RH	9.7				8.6	18	21							116
	Impact milled wheat straw fibers	d_{50}^a : 109 μ m						8.4	20	65							
	Cut milled wheat straw fibers	d_{50}^a : 469 μ m						14	49	130							
Alginate	Cellulose microfibrils	Not precised (<100 μ m)	23°C, 50% RH	470,000													380,000
Starch	Softwood	Length: 1.2 mm; width: 0.1 mm	25°C, 33-64% RH	53				65	58	48							79
Cassava starch	Fibers	d_{50}^a : <53 μ m	20°C	53				130									80

^a d_{50} is the median apparent diameter of particles and corresponds to the size achieved by at least 50% of the particles, considered as spheres.

Ludueña *et al.*⁵⁰ also observed an increase of WVP with cotton-based fibers content (0, 5, and 15 wt %) in PCL but also assessed the impact of fibers size. A competitive effect occurs between fibers size and their affinity with water, therefore with the matrix. The smallest fiber (0.20 μm) type, being the more hydrophilic, increases composites WVP almost in the same extent than the longest fibers (59 μm), while the medium size fiber (9.1 μm), the most hydrophobic ones, preserves composite's WVP at the same level than pure PCL.

In most recent studies on PHBV,^{116,117} wheat straw fibers introduction in the matrix has been found to increase resultant composites' WVP, along with fiber content increase. WVP alteration was all the more drastic that the fibers were rougher (up to 469 μm diameter). Indeed, for the highest amount of cut milled wheat straw fibers (30 wt %), PHBV's WVP was raised up to 1000% of its initial value.¹¹⁷ Since hydrophilic character of the different wheat straw fibers was not affected by the successive grindings, WVP increase toward fiber size increase was ascribed to other concurrent phenomena: at macroscopic scale, a preferential pathway for water vapor was supposed to be created by the poor fiber/matrix adhesion, and at molecular scale, a polymer degradation in presence of the fibers might have also affected the matrix structure. Nevertheless, a decrease of PHBV's WVP could be observed at relatively high fiber content (20 wt %) of olive mills,¹¹⁶ thanks to their smaller size, limiting the risk of percolation, and better adhesion than wheat straw fibers. The supposed increased tortuosity would then lead to conclusion that olive mills have a better intrinsic barrier to water vapor than wheat straw fibers.

Regarding polysaccharide matrices, due to their high hydrophilicity, they present low water vapor barrier properties.⁷⁸ Therefore, introduction of up to 50 wt % of cellulose microfibrils in alginate films leads Sirvio *et al.*⁷⁹ to observe a decrease of WVP, which was ascribed to an increase in tortuosity due to introduction of less permeable fibers than the matrix. Same theory than for polyesters is suggested: increased pathway tortuosity because of fibers introduction.⁷⁸ Another hypothesis, from Müller *et al.*,⁷⁹ attributes WVP decrease, for increasing fibers content (10–50 wt %) of 1.2 mm softwood in starch, to the lower hygroscopicity of cellulose fibers compared to starch's.

However, low contents (0–3 wt %) of 53 μm fibers in cassava starch display an increase of WVP.⁸⁰ This increase is explained by the major effect of fiber-induced defects against the plasticization of starch by glycerol. Citing López *et al.*,⁸¹ Versino *et al.*⁸⁰ describe an interference of glycerol with polymeric chain association, leading to soften of the network; thus a less ordered film structure without pores or cracks is obtained, decreasing WVP. Nevertheless, it must be concluded that, in the frame of this study, the effect of plasticizer on films water vapor barrier properties is less significant than filler's.

To conclude, biocomposites can achieve a broad range of WVP. Moreover, this property can be controlled through formulation, with a proper choice of the constituents. Hence, besides the choice of the matrix, one must take in account the fiber/matrix affinity and fibers' ability to disperse themselves within the matrix, and last but not least, the fibers' intrinsic WVP.

Undesirable Migrations from Biocomposites

To ensure food safety, the mass transfer process of components from the packaging toward the food and vice versa should be controlled. This process is called “food/packaging interaction” and includes the so-called “chemical migration” (migration of migrants from the packaging toward the food). In the EU, an important effort of harmonization on Food Contact Material (FCM) regulations has been undertaken since 1976, when the Framework Directive was adopted laying down the general principles of FCM safety.⁸² European regulation 1935/2004⁸³ is the basic community legislation that sets the general guidelines for the compliance of all Food Contact Materials. The plastics Directive 10/2011/EC⁸⁴ translates the requirements of Regulation 1935/2004 to plastics (monolayers and multilayers that consist only of plastic) as limits that must be respected for migration tests. The requirement of inertia for the materials becomes an overall migration limit (OML), i.e., the total mass released by the packaging material during a migration test, which is set to 60 mg kg^{-1} of food. The directive 10/2011/EC also establishes a specific migration limit (SML) for every substance listed in a positive list. The recommended migration tests are chosen as worst case conditions and are in practice applicable only to water-resistant materials even though the use of water-sensitive materials, such as paper, board, or bioplastics, is particularly widespread. Recently, Mauricio-Iglesias *et al.*⁸⁵ demonstrated that conventional tests (based on the use of liquid simulants) were not adapted to assess suitability of protein-based films as food contact materials. They proposed the use of solid simulants as alternative for such water sensitive material. In accordance with the conditions set in the directives 10/2011/EC and 882/2004⁸⁶ of the European Regulation, demonstration of compliance of migration into foodstuffs shall be carried out under the most extreme conditions of time and temperature foreseeable in actual use.

The introduction of new materials, such as bioplastics and lignocellulosic fibers, has deeply changed the panorama of food packaging. In absence of specific regulation, bioplastics should lie within the scope of European regulation (EC) 1935/2004.⁸³ So far, only little literature is available on the topic of migration from biodegradable packaging materials. One critical key point is the sensitivity balance of biodegradable packaging in the respect that the material should be durable enough for protection but still biodegradable.²³ Substances arising from physical–chemical material degradation as well as breakdown products and/or intentionally added additives could migrate during the contact of the materials with the food. A work has been recently published to highlight the relationships between the structural and physical–chemical stability and the inertness of PHBV films with respect to the targeted food packaging application.⁸⁷ It was concluded that the functional properties of PHBV films (mechanical properties and water vapor permeability) were very stable after contact at 40°C during 10 days with all food simulating liquids tested (water, acetic acid 3% (w/v), ethanol 20% (v/v)m and iso-octane), except with ethanol 95% (v/v), which was also identified as the worst case in terms of overall migration. This was mainly explained by a significant plasticizing effect, together with a decrease in both the molecular weight

and the crystallinity degree of PHBV films. From an industrial point of view, such a study is very useful to assess that the packaging functions of PHBV are fulfilled all over the food supply chain. However, knowledge is still missing on the dependency of the chemical safety (evaluated through migration tests) with the structural and physical–chemical stability of biodegradable materials.

In the case of lignocellulosic fillers, potential toxicological substances able to migrate toward food are mainly pesticide residues (including herbicides, insecticides, and fungicides) and ubiquitous environmental pollutants. Environmental pollutants include polycyclic aromatic hydrocarbons, but also additives used in all life-products materials, and especially plasticizers like phthalates that are commonly used in the formulation of packaging materials. A special attention should be thus paid to evaluate the decontamination efficiency of the respective production and extraction processes used to prepare lignocellulosic fibers. For that purpose, “challenge tests” could be used, which consists in enriching materials with surrogates (molecules representative of the contaminants) and quantify their residual amount at each step of the preparation process.

Mechanical Properties in Relationships with Mass Transfers

Maintaining physical film integrity is essential to guarantee its barrier properties. Mechanical properties are thus essential requirements for food protection. In general, the functional properties of short-fibers composite materials are known to depend on (i) the intrinsic properties of the fiber used, including morphological characteristics such as aspect ratio and intrinsic mechanical properties,^{1,50} (ii) the fiber content,^{50,117} (iii) the dispersion state^{1,50} and orientation of fibers within the polymer matrix,¹ (iv) the surface properties of fibers and resulting fiber/matrix interphase,^{1,50,91} and (v) the modification of matrix intrinsic properties (crystallinity¹, molecular weight) induced by fibers introduction.¹¹⁶

As largely described in literature, the decrease in tensile properties induced by the presence of lignocellulosic fibers is mainly ascribed to a lack of adhesion between the hydrophobic matrix and hydrophilic fibers.^{50,88–90}

Young's modulus. In almost all publications dealing with short-fiber based biocomposites,^{50,59,88–90} the Young's modulus was found to increase with increasing fiber contents, mainly due to a simple rule of mixture. Indeed, in most of cited cases, the neat polymer matrix displayed a Young's modulus value in the range of 40–560 MPa, whereas the fiber Young's modulus varied from 5.5 up to 150 GPa according to the type of fibers (botanic origin, morphology, and surface treatment). The increase in Young's modulus can be even more pronounced for fiber contents higher than the fiber percolation threshold, this later decreasing with increasing fiber aspect ratio.⁵⁰

Ultimate tensile properties. It is known that tensile strength is mainly dependent on the compatibility between the filler and the matrix.⁹¹ This was confirmed in many studies, as tensile strength was degraded for increasing fiber content, authors observing a poor fiber/matrix adhesion. Lignocellulosic fibers being hydrophilic by nature, best compatibilities were observed

for hydrophilic matrices such as protein-based matrices.⁵⁹ There is a critical fiber length or aspect ratio below which stress transfer from matrix to fibers is not sufficient to reach the fiber fracture strength.⁹² They represent the minimal fiber length or aspect ratio required for load transmission from the continuous phase (matrix) to the dispersed reinforcing phase (fibers). If fiber length is lower than this critical fiber length, the fiber will be extracted from the matrix before being solicited. In the opposite case, if the fiber length is too important, the dispersion of fibers within the matrix becomes difficult because of favored fiber agglomeration phenomena. In the case of composites containing a distribution of fiber lengths, it is clear that only the fraction of fibers longer than the critical length can efficiently contribute to composite strength. In almost all cases, the strain at break was also degraded with increasing fiber content, which was ascribed to micro-defects induced by the presence of fibers.

Then, summarizing the general trends: stress and strain at break were shown to depend on filler content, particle surface properties, and fiber/matrix interfacial adhesion, while Young's Modulus was mainly affected by the intrinsic properties of each component as well as on the aspect ratio of fibers. Moisture storage conditions impact biocomposites mechanical properties, thus limiting their use as food packaging to dry products.

Impact of fiber moisture content on mechanical properties. Numerous studies have also been devoted to study the water damage on natural fiber composite materials.^{93–95} When fibers are exposed to mild humidity, water molecules can have a plasticizing effect, thus affecting the strength and the rigidity of fibers. Studied have also evidenced that moisture can seriously jeopardize the fiber–matrix adhesion, leading to the deterioration of the stress transfer efficiency from matrix to reinforcement.^{94,96} The degradation process starts with the swelling of the cellulose fibers, causing microcracking of the matrix around the swollen fibers.^{94,97} Nevertheless, few authors took interest in the influence of fiber moisture content at the moment of composites processing and its resultant impact on structure and properties.^{98,99} Main results displayed a decrease of flexural strength and modulus, in relation to a decrease of interfacial shear strength, which was attributed to the poor interfacial bonding formed at the high relative humidity conditions.^{98,99} It is worth noting that fiber treatments were widely and successfully experimented in order to reduce both the moisture level and the rate of absorption very significantly.^{10,44–48} Another possible impact of environmental moisture is the degradation of the polymer matrix, which has been notably studied in the case of PHBV.¹⁰⁰

However, since huge changes of atmosphere relative humidity can occur in a single day, a week, a season, a year and over a number of years, up-scaling the preparation of biocomposites from lab scale to industrial scale should also take this aspect into account, especially in the case of moisture sensitive polymers, such as PHBV. To our knowledge, no paper has been yet devoted to study the impact of fiber moisture content, at the moment of processing, on the relationships between the structure and the mechanical properties of PHBV-based biocomposites. A forthcoming paper¹⁰¹ aims at studying the impact of initial moisture content on the structure/mechanical properties relationships of PHBV/wheat

straw fibers biocomposites. It is shown that fiber/matrix adhesion was visually not affected by the initial fiber moisture content, while PHBV molecular weight decreased with increasing fiber moisture content, which was attributed to hydrolysis reactions induced by residual water molecules, inducing an increase in the overall material crystallinity. In spite of structural differences, tensile properties were similar for all composites, leading to the conclusion that the initial fiber moisture content was not a predominant factor for controlling the mechanical properties of PHBV/wheat straw fibers composites. Since no impact on fiber/matrix adhesion was spotted, such a stability in mechanical properties toward fiber moisture content could be explained either by the fact that structural changes were not sufficient to alter the bulk mechanical properties, or by the occurrence of competitive phenomena. Such assumptions should be deepened and may be system dependant. Similar studies should be conducted by selecting a polymer matrix that would be less sensitive to moisture, e.g., a polyolefin.¹⁰⁴

CONCLUSIONS AND PERSPECTIVES

Gaining increasing attention, full-biocomposites were widely studied over the last decade. Numerous systems were thus developed, composed of bioplastics as matrices, presenting original mechanical and barrier properties, combined to lignocellulosic fibers, either aiming a reinforcing effect or new functionality, a decrease of the overall material cost or exploring the potential valorization of biomass by-products. To sum up, the specific stakes to keep in mind when developing full-biocomposites that should be used in a viable way for food packaging applications are the following ones.

A reduced overall environmental impact. This can be reached by using full-bioplastics as matrices, by favoring the use of agricultural wastes or food industries by-products as raw materials to avoid competition with food usages, but also by designing the packaging material in such a way to reduce degradation reactions of packed food, and thus food waste and losses. Today, it is worth noting that based on the available tools (such as life cycle analysis), it not yet proven that the use of full-biocomposites will allow to reduce the environmental impact, save energy and water and/or reduce food losses.

Optimized functionalities. Packaging has to ensure its fundamental role of container and protection of food toward physical damage, by displaying adequate mechanical properties, but also to be designed in such a way to limit food degradation reactions, by controlling mass transfer properties. It was evidenced that lignocellulosic fibers often act as defects, which impact both mechanical and permeability properties, degrading the firsts and increasing the seconds. Increasing material permeability by choosing the appropriate formulation seems to be a valuable approach, especially for the packaging of respiring products such as fruits and vegetable. Mechanical properties were widely explored and reported, for multiple combinations of bioplastics and lignocellulosic fibers. However, despite the importance of mass transfer properties, the state of the knowledge on this theme remains very poor. It clearly emerges from this context a need of fundamental research turned toward full-

biocomposites, by developing understanding and modeling approaches able to consider the whole complexity of such systems. The current bottlenecks are the lack of knowledge on the intrinsic mass transfer properties of vegetal fibers and on the role of the filler/matrix interphase. Due to the high complexity of vegetal fibers and to their sensitivity toward environmental conditions (e.g., humidity, temperature), the evaluation of quantitative structural parameters that could be further used in models still remains a challenging issue. Finally, it is to be noticed that we are faced to a multitude of systems and composite structures due to the large variety, heterogeneity and complexity of raw constituents. The overall performance of full-biocomposites is thus very system-dependant, what makes difficult the design of packaging materials using a reverse engineering approach. To resolve this bottleneck, it appears necessary to identify a few main parameters displaying key effects of overall functional properties.

Production at industrial scale. For a sustainable use of full-biocomposites, such materials have to be produced using processes commonly used in plastics industry (compounding using extrusion, injection molding, and thermoforming) by achieving the similar production rates as conventional plastics.

Economical competitiveness. Given the low-added value of the majority of food products, full-biocomposites should be economically competitive. Currently, the consumer willingness to pay more for a biodegradable and bio-sourced food packaging is still uncertain. In this context, it is necessary to pursue efforts to decrease the overall cost of full-biocomposites. It is worth noting that cost reduction is strongly dependent on the industrial implementation of low cost and eco-efficient production of bioplastics (e.g., PHAs), but also on the availability all over the year of low cost lignocellulosic fibers with reproducible intrinsic properties. The use of lignocellulosic biomass from agricultural wastes or food industry by-products should also be favored.

Food safety. Full-biocomposites, if used as food packaging materials, should comply with the regulations on food contact materials and guaranty the health of the consumer. This could become very challenging when using lignocellulosic fibers, especially from agricultural wastes and food by-products, due to the potential presence of toxicological substances able to migrate from packaging toward food. A special attention should be thus paid to evaluate the inertness of developed materials, but also on the decontamination efficiency of the respective extraction and production processes.

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