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# Biocomposites: Influence of Matrix Nature and Additives on the Properties and Biodegradation Behaviour

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Additional information is available at the end of the chapter

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## 1. Introduction

Composite materials are material systems which consist of one or more discontinuous phases embedded in a continuous phase. Thus, at least two distinct materials that are completely immiscible are combined to form a composite. The continuous phase are termed matrix and the discontinuous phase can be a reinforcement (reinforcing agent) or filler. Also, other additives as plasticizers, pigments, heat and light stabilizers are frequently added in order to provide certain properties. The type and reinforcement geometry impart strength to the matrix and the resultant composite shows optimized properties such as high specific strength, stiffness and hardness with respect to the specific components [1].

As conventional plastics are resistant to biodegradation, the concept of using biobased plastics (biodegradable polymers or biopolymers) as reinforced matrices for biocomposites is gaining more and more approval day by day [2]. A variety of natural and synthetic biodegradable polymers that can be used as biocomposite matrix are commercially available. These biocomposite materials are designed to have a better environmental impact than conventional plastics as well as to promote an improvement in their mechanical properties so that their applications can be expanded. By embedding natural fibers with renewable resource-based biopolymers such as cellulosic plastics; polylactides; starch plastics; polyhydroxyalkanoates (bacterial polyesters); soy-based plastics, the so-called green biocomposites could soon be the future [3].

Biocomposites are composites that present natural reinforcements (like vegetable fibers) in their composition and can be: (i) partial biodegradable with non-biodegradable polymers matrices such as thermoplastic polymers (e.g., polypropylene, polyethylene) and thermoset

polymers (e.g., epoxy, polyester) or (ii) fully biodegradable with biodegradable polymer matrices such as renewable biopolymer matrices (e.g., soy plastic, starch plastic, cellulosic plastic) and petrobased biodegradable polymer matrices (e.g., aliphatic co-polyester, polyest-eramides). The fully biodegradable ones are 100% biobased materials and show biodegradability and/or compostability properties [2, 4, 5]. For the purpose of this chapter, only fully biodegradable biocomposites are the subject considered.

Natural fiber reinforced plastics by using biodegradable polymers as matrices are the most environmental friendly materials which can be composted at the end of their life cycle. Unfortunately, the overall physical properties of those composites are far away from glass-fiber reinforced thermoplastics. Further, a balance between life performance and biodegradation has to be developed [6].

Hybrid composites are resulted from the incorporation of several types of reinforcing agents with the purpose of tailoring the properties of the obtained composite according to engineering requirements. A synergistic effect between the different kinds of reinforcements enhances the overall performance of the composite. Bionanocomposites are an emerging class of nanostructured biohybrid material which exhibit a singular combination of structural and functional properties together with biocompatibility and biodegradability that was not found in nature. These hybrid materials consist mainly in the assembly of biopolymers and silicates from clay mineral family that have shown extraordinary potential to be used in many applications [7].

In the present chapter, an overview of the current biodegradable polymer matrices and some of the most used reinforcements is described as well as the properties and applications of the obtained biocomposites are discussed.

## 2. Biodegradable polymer matrices

There are various ways that biodegradable polymers can be addressed. Depending on their origin, they may be divided as: natural, synthetic or microbial polymers.

### 2.1. Natural biodegradable polymers

Natural biodegradable polymers are polymers formed naturally during the growth cycle of living organisms. Their synthesis generally involves enzyme-catalyzed reactions and reactions of chain growth from activated monomers which are formed inside the cells by complex metabolic processes. Natural polymers such as proteins (collagen, silk and keratin), carbohydrates (starch, glycogen) are widely used materials for conventional and novel pharmaceutical dosage forms [8]. These materials are chemically inert, nontoxic, less expensive than the synthetic ones, eco-friendly and widely available [8,9]. The families of natural polymers are low-cost materials along with some disadvantages such as inferior thermal and mechanical properties. The natural polymers here described are from two groups, i.e., those obtained from vegetable and those from animal sources, as shown in Table 1.

Plant Source	Carbohydrates	Polysaccharides	Cellulose
			Starch
	Proteins	Pectin	
		Soy derivatives	
		Polypeptides	
Animal Source	Lignins	Proteins	Polyphenols
			Silk
	Polysaccharides	Wool	
		Polypeptides	
		Chitin	
			Chitosan
			Glycogen

**Table 1.** Classification of natural polymers based on their sources.

There are several types of carbohydrates: monosaccharides, disaccharides, oligosaccharides and polysaccharides. The latter ones, of particular interest, are comprised of hundreds or thousands of monosaccharides, commonly glucose, forming linear chains, such as cellulose, or branched chains, as in starch and glycogen. For this chapter, cellulose and its derivatives, starch and chitosan will be presented as natural biodegradable polymers [10].

### 2.1.1. Cellulose derivatives

Cellulose acetate (CA), universally recognized as the most important organic ester of cellulose because of its extensive applications in fibres, plastics and coatings, is prepared by reacting cellulose with acetic anhydride using acetic acid as a solvent and perchloric acid or sulphuric acid as a catalyst. CA is a carbohydrate composed of  $\beta$ -glucose molecules that are covalently linked through  $\beta$ -1,4-glycosidic bonds, widely found in nature in algae and land plants which has been valued as a functional material. CA comes to meeting the diverse needs of today's society including biodegradability characteristics, its hydrophilic behaviour and biocompatibility [11].

Several applications for cellulose and its derivatives have been shown, for example: in paints, textiles, pharmaceuticals and beauty, fibers, ionic liquids, construction technology and so on [12, 13]. Cellulose esters for coating applications are nearly always used as miscible blends with acrylics, polyesters and other polymers. This is possible because of their ability to form hydrogen bonds through the presence of hydroxyl groups and the carboxyl groups of the ester. An increase in ester molecular weight increases the toughness and melting point but decreases the compatibility and solubility, whereas hardness and density are unaffected. Compatibility, solubility and the maximum non-volatile content all decrease as the ester molecular weight increases. The hydroxyl group content inversely affects the moisture resistance and toughness [11].

Ignácio et al. [14] evaluated the production of cellulosic polymer membranes based on cellulose acetate and thus advanced technology was brought to be used in membranes for separation

processes (ultrafiltration, microfiltration, reverse osmosis, nanofiltration, gas separation, etc.). The use of these membranes has been shown to be effective for water treatment in chemical industries and pharmaceutical processes. Mulinari et al. [15] studied the preparation and characterization of a hybrid composite composed by bleached cellulose and hydrous zirconium oxide. Authors showed that these cellulose composites obtained by the crushed sugarcane combined with an inorganic material has intrinsic advantages such as low cost, biodegradability and simplicity in preparation and handling.

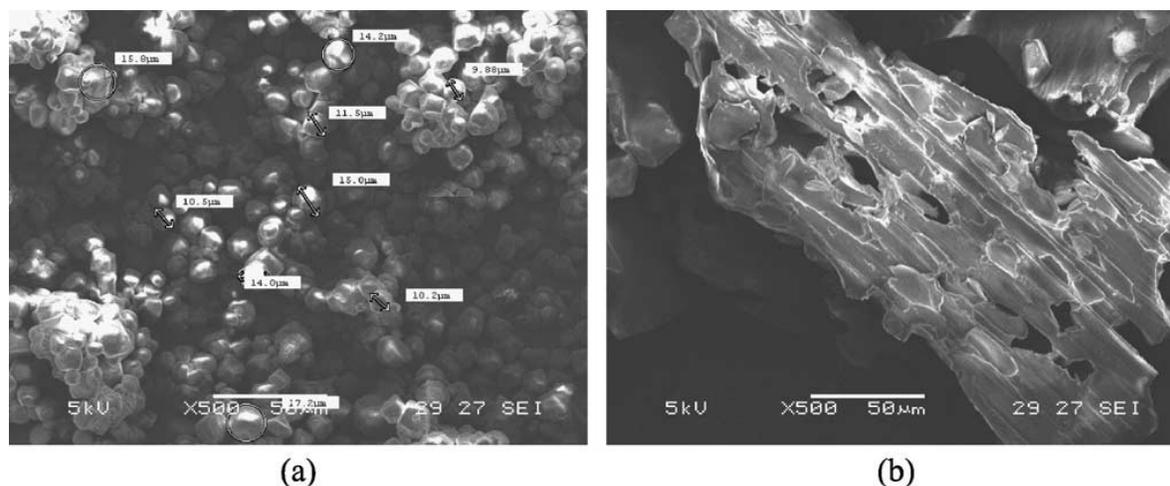
### 2.1.2. Starch

Starch, a low-cost biodegradable polymer, is abundant in plants, where it is stored in granule form and acts as an energy reserve [16]. Starch is composed of two polymers: amylose and amylopectin, both of which contain  $\alpha$ -D-glucose units. Amylose is mostly a linear molecule of  $\alpha(1\rightarrow4)$ -linked-D-glucopyranosyl units with the ring oxygen atoms all on the same side. Amylopectin is the major branched component of starch and presents a  $(1\rightarrow6)$  linkage that forms branch points. The hydrophilicity of these polymers is responsible for their incompatibility with most hydrophobic polymers [17]. When exposed to a soil environment, the starch component is easily consumed by microorganisms, leading to increase its porosity by void formation and the loss of integrity of the plastic matrix. The plastic matrix will be broken down into smaller particles.

Addition of a plasticizer like glycerin can further improve the ductility of starch, forming a polymer that is known as thermoplastic starch (TPS) which is capable of flowing easily. This plastifying agent lowers the glass transition temperature of starch as well as the melting temperature of the mixture by the introduction of mechanical and heat energy. The starch plastification is commonly carried out by extrusion at temperatures close to  $120^\circ\text{C}$ . The mixtures of TPS with other polymers have the potential to behave in a similar manner to more conventional polymer-polymer blends. This would allow greater control of the dispersed phase morphology since the TPS should undergo deformation, disintegration and coalescence [18].

The crystalline nature of starch granules reflects the organization of amylopectin molecules within the granules whereas amylose is the most constituent of the amorphous portion that is randomly distributed among the amylopectin clusters. The conversion of starch into a thermoplastic material by extrusion or by gel casting into films results in the loss of the natural organization of the chains [19]. Figure 1 shows granular starch (a) and pregelatinized starch (b).

Blends of starch with synthetic polymers such as ethylene-vinyl alcohol copolymer, starch/poly(ethylene-co-vinyl alcohol), copolymers of ethylene with vinyl acetate, vinyl alcohol, acrylic acid, cellulose derivatives and other natural polymers, recycled high density polyethylene (HDPE) and other polyethylenes (PE) as well as compounds with a mixture of glycerin as plasticizer have been studied. Among the environmentally friendly starch-synthetic polymer products currently marketed on a commercial scale are Mater-Bi TM (Novamont, Italy), Bioplast (Biotech, Germany), Biopar (Biop Biopolymer Technologies AG, Germany), and NovonTM (produced by Chisso in Japan and Warner Lambert in the USA [20]).



**Figure 1.** Scanning electron microscopy (SEM) photomicrographs of (a) granular starch and (b) pregelatinized starch. Reprinted from *Carbohydrate Polymers*, 59, Pedroso A. G. and Rosa D. S., Mechanical, thermal and morphological characterization of recycled LDPE/corn starch blends, 1–9, Copyright (2005) [19] with permission from Elsevier.

The blending of biodegradable starch with inert polymers, such as polyethylene (PE), has received considerable attention currently. The reasoning behind this approach is the possibility of disintegration and disappearing of the all plastic films in the waste disposal environment if the biodegradable component is present in sufficient amounts and can be removed by microorganisms.

Pedroso and Rosa [19] studied blends with recycled low density polyethylene (LDPE) and corn starch containing 30, 40 and 50 wt% starch. The blends were prepared by extrusion and characterized by the melt flow index (MFI), tensile test, dynamic mechanical thermal analysis (DMTA) and scanning electron microscopy (SEM). For comparison, virgin LDPE/corn starch blends were prepared and characterized under the same conditions. The addition of starch to LDPE reduced the MFI values, the tensile strength and the elongation at break whereas the modulus increased. The decreases in the MFI and tensile properties were most evident when 40 and 50 wt% were added. SEM images showed that the interfacial interaction was weak for blends containing virgin and recycled LDPE. Blends prepared with recycled LDPE showed the same behavior as those blends prepared with virgin LDPE, indicating that starch was the main factor that influenced the blend.

In other work [21], the same authors blended high density polyethylene (HDPE) and polypropylene (PP), both post-consumer polymers, with thermoplastic starch (TPS). Corn starch plastification was carried out by extrusion with glycerin addition. The processing, thermal and mechanical behaviours of the produced TPS were investigated as well as the morphology characterization of post-consumer HDPE/PP blends (100/0, 75/25, and 0/100 wt.%) in different proportions of TPS (30%, 40% and 50% wt.%). In conclusion, the addition of TPS to recycled PP reduces its melting flow index (MFI) whereas the MFI of HDPE and HDPE/PP blends increases. TPS also decreases the tensile strength and increases the rigidity of the polymers. The incorporation of TPS in polyolefin matrices results in the separation of phases and a disintegration of the starch granules.

### 2.1.3. Chitosan

Chitosan (CS) is a biopolymer (poly- $\beta$ -1,4-glucosamine) having immense structural possibilities for chemical and mechanical modifications to generate novel properties, functions and applications, especially in biomedical area. Chitosan is no longer just a waste by-product from the seafood processing industry. This material is now being utilized by industry to solve problems and to improve existing products as well as to create new ones. CS is composed by linear nitrogenous polysaccharides - a basic polysaccharide homopolymer from natural sources, biodegradable, biocompatible and non toxic. Chitosan is produced commercially by deacetylation of chitin, naturally occurring polysaccharides which is the structural element in the exoskeleton of crustaceans (crabs, shrimp, etc.). Due to its variable and incomplete deacetylation process, it acts as a copolymer of varying amounts of N-acetyl glucosamine and N-glucosamine repeated units. The presence of reactive primary amino groups renders special property that makes CS very useful in pharmaceutical applications [22].

CS has three types of reactive functional groups, an amino group as well as both primary and secondary hydroxyl groups. Chemical modifications of these groups have provided numerous useful materials in different fields of application. Chitosan oligomers as well as chitosan have been shown to inhibit growth of several fungi and bacteria, especially pathogens. Hirano and Nagao [23] have studied the relationship between the degree of polymerization of chitosan and the inhibition effect.

At room temperature, chitosan forms aldimines and ketimines with aldehydes and ketones, respectively. Reaction with ketoacids followed by reaction with sodium borohydride produces glucans carrying proteic and nonproteic amino groups. N-Carboxymethyl chitosan is obtained from glyoxylic acid and its potential uses are in chromatographic media and metal ion collection [24].

## 2.2. Biodegradable polymers of microbiological origin

Polymers of microbial origin are produced as intracellular reserve material for a variety of bacteria and have gained prominence due to their possible applications as well as their biodegradable and renewable characteristics.

In the last three decades, the polymers, especially polysaccharides, have acquired great importance in a wide range of industrial processes [25]. Several species of fungi and yeasts produce polymers of commercial interest; however, polymers from bacterial origin are those with greater viability in terms of industrialization and commercialization since they present quality and constant supply. Among these polymers, we highlight the PHB and the PHBV which comprise the group of polyhydroxyalkanoates whose classification is presented in Table 2.

Polysaccharides	Polyhydroxyalkanoates	Poly(3-hydroxy-butyrate) - PHB
		Poly( $\beta$ -hydroxybutyrate-co-valerate) PHB-V

**Table 2.** Examples of polyhydroxyalkanoates.

The polyhydroxyalkanoates (PHAs) are thermoplastic polyesters which degrade completely into microbiologically active environments in addition to being biocompatible and may be biosynthesized by a large number of Gram negative and Gram positive bacteria, from different carbon sources or made from renewable and non-renewable genetically modified (GM) plants. Examples of pure cultures used for industrial production of PHAs include *Ralstonia eutropha*, *Alcaligenes lotus*, *Azotobacter vineland* and various *Pseudomonas* species [26-32].

Genetically modified plants, such as potatoes (*Solanum tuberosum*) and tobacco (*Nicotiana tabacum*) produce cereals such as sunflower and soybean that can provide other ways of producing PHAs. However, the yield (4% of the weight of the plant) is much less than the one obtained by bacteria which reduces the production of PHAs by this method [26-32].

### 2.2.1. Poly(3-Hydroxy-Butyrate) (PHB)

Poly(3-hydroxy-butyrate), PHB, which is a PHA produced by the *Alcaligenes eutrophorus* bacteria, is one of the most interesting biodegradable polymers because it is obtained by bacterial fermentation from renewable resources. PHB can also be synthesized by ring-opening polymerization of  $\beta$ -butyrolactone using distannoxane derivatives as catalysts, such as zinc and aluminium [33]. PHB is linear, homochiral, thermoplastic polyester produced by microorganisms as intracellular fat deposits in response to limited nutrient availability. PHB belongs to a polyhydroxyalkanoate class of shorter pendant groups that confers a high degree of cristalinity [34].

However, PHB presents some drawbacks like thermal instability at temperatures close to its melting point and a relatively low impact resistance [16]. PHB molar mass decreases proportionately with some processing parameters like time and temperature. In spite of its narrow processing window, PHB with high molar mass can be processed like other thermoplastics if adequate processing parameters are used.

Two main efforts have been used to change PHB properties: biosynthesis and blending. Since blends are a cheaper and faster method to improve polymer properties than synthesis, blends have often been used to improve mechanical properties and processability of PHB. [16, 35].

The biosynthesis of this polymer allows a cyclical process through sustainable renewable sources by replacing cutting edge technologies related to the production and use of synthetic polymeric materials. Among the microorganisms that produce PHB, bacteria like *Alcaligenes eutrophus*, *Azotobacter vinelandii* and *Ralstonia eutropha* can be detached. [36].

According to Lenz et al. [31], the chemical structure of the polyester is an important factor in determining its physical properties and determining the activity of the enzymes involved in their biosynthesis and biodegradation. PHB is a saturated linear polyester, behaving like conventional thermoplastic materials. It has high crystallinity and melting temperature of approximately 176°C. Its glass transition temperature ( $T_g$ ) is below 5°C and its properties resemble those of polypropylene (PP).

Comparing to polymer commodities, conventional PHB and its copolymers have the advantage of biodegradability and biocompatibility. In contrast, presents the disadvantage of having

a poor thermal stability and impact resistance relatively low. Its use spans several segments, such as applications in biomedical areas, agriculture, food packaging and pharmaceutical products, as well as the segments of packaging and agricultural films strongly highlighted. The combination of high temperature and crystallinity provides shine to the films, whereas the rigidity and low impact resistance presented by PHB hinder their use. PHB copolymers have better mechanical properties. The copolymer PHB-V, for example, provide an improvement in ductility and impact resistance, making it more interesting from the point of view of application and end products compared to PHB [30, 32, 37-40].

### 2.3. Synthetic biodegradable polymers

This class of polymers has been widely used in biomedical uses, such as controlled-release capsules of drugs in living organisms, fasteners surgery (sutures, implants for bone pins) and special packaging. Polymers of this class that have been studied more recently are poly(lactic acid) (PLA), polyglycolic acid (PGA), poly (glycolic acid-lactic acid) (PGLA) and poly( $\epsilon$ -caprolactone) (PCL) [35].

For greater understanding, synthetic biodegradable polymers are separated into classes. Table 3 shows the classification of non-natural synthetic biodegradable polymers.

	- PLA
Aliphatic	Poly(glycolic acid) - PGA
	Poly( $\epsilon$ -caprolactone) - PCL
	Polytrimethylene terephthalate - PTT
Aliphatic Aromatics (PAA)	Poly(butylene terephthalate) -PBT
	Poly (butylene succinate) - PBS

**Table 3.** Classification of non-natural synthetic biodegradable polymers.

The polyesters compete an important position among the group of biodegradable plastics and some biodegradable polyesters are already commercially available. The main biodegradable polyesters are those based on hydroxy-carbonic acids. The biodegradable polyesters still have high cost, but they have aroused great interest due to their accessible production by fermentation or synthetic routes [35].

During the last two decades, aliphatic polyesters such as poly( $\epsilon$ -caprolactone) (PCL) and poly(L-lactic acid) (PLLA) have been extensively studied due to their ability to undergo hydrolysis in the human body as well as in natural circumstances [37, 41, 42].

#### 2.3.1. Poly(Lactic Acid) (PLA)

Poly(lactic acid) (PLA) is a hydrolytically degradable aliphatic polyester which presents water vapor permeability that may have a significant influence on its rate of degradation. The poly(lactic acid) (PLA) is an aliphatic polyester obtained by polymerization of lactic acid. This

can be found in the form of two optical isomers: L- and D-lactide. PLA has potential for applications in the medical, pharmaceutical and packaging, mainly as implantable devices temporarily (sutures, staples, nano-reservoirs for drugs etc). Other applications involve the sectors of textiles and fibers, agriculture, electronics, appliances and housewares [43, 44, 45].

PLA presents some advantages like biocompatibility, has better thermal processibility compared to other biopolymers such as poly(hydroxyalkanoates) (PHAs), shows eco-friendly characteristics and requires 25–55% less energy to produce than petroleum-based polymers. Nevertheless, PLA is a very brittle material and chemically inert with no reactive side-chain groups making its surface and bulk modifications a challenging task. Besides, PLA shows low degradation rates and is hydrophobic [46].

Henry et al. [47] investigated systems including poly (lactic acid) (PLA). The thermal analysis showed that the glass transition temperature ( $T_g$ ) of the polymer is about 320 K. The  $\beta$  relaxation was observed between  $-150\text{ }^\circ\text{C}$  and  $-30\text{ }^\circ\text{C}$ , depending on the measurement frequency (1 Hz - 100 kHz) and was determined as secondary relaxation in the glassy state. The authors studied the changes that are associated with water penetration into the polymer which directly affect the relaxation process. Water molecules confined (outlined / permeated) and the polymer chains in polymer networks represent an important function in matrix degradation and, thus, the authors were able to observe the evolution of degradation for a few weeks in an environment with controlled humidity. It is accepted that water penetrates preferentially in amorphous areas, but also affects the crystalline regions. It is a clear evolution of the observed activation energy of relaxation during polymer degradation. The resulting dielectric relaxations are complemented with measures of molecular weight during degradation with time.

### 2.3.2. PCL

Poly ( $\epsilon$ -caprolactone) (PCL) is a synthetic aliphatic polyester made from ring opening polymerization. This biodegradable polyester presents good mechanical properties that is compatible with many types of polymers and is one of the most hydrophobic biodegradable polymers currently available. PCL has been widely studied for use in drug release systems [48]. Extracellular enzymes present in soil can cleave the extensive chains of PCL before assimilation of the polymer by microorganisms. However, the high cost of PCL has prevented its widespread industrial use. PCL has been thoroughly examined as a biodegradable medium and as a matrix in controlled drug-release systems [14, 49].

The main limitation of PCL is its low melting temperature ( $T_m\ 65^\circ\text{C}$ ) and also has some drawbacks, including a poor, long-term stability caused by water absorption, poor mechanical and processing properties. Some of these problems can be overcome by physical or chemical modifications, including the blending of these polymers. [49]

PCL/CA blends are generally incompatible, immiscible and show poor interpolymeric adhesion [14, 49]. Rosa et al. [11] reported miscibility between several CAs and aliphatic polyesters. The miscibility of the cellulose polymer with a polymeric plasticizer is important in order to maintain the already complex mixture as homogenous as possible. The use of coupling agents usually improves the elongation of composites, but frequently results in a

decrease in strength. One approach to improve the compatibility between the constituent polymers in PCL/CA mixtures is to incorporate a compatibilizer into the mixture. The chemical modification of aliphatic polyesters by grafting is another way of improving the compatibility between starch and aliphatic polyesters in polymeric blends. The effects of polyethylene grafted with maleic anhydride (PE-g-MA) on the thermal and mechanical properties, as well as on the morphology of blends of low-density polyethylene (LDPE) and corn starch have been studied using differential scanning calorimetry (DSC), tensile strength measurements and scanning electron microscopy [14, 49-53].

### 3. Natural reinforcement agents as additives for biocomposites

Polymer reinforcements are generally used in order to provide stiffness and strength to the polymer matrix resulting in improved mechanical properties for the obtained composites. Besides, properties like water and gas barrier as well as fire resistance and flame retardant properties and so on can be enhanced by the employ of reinforcements in polymer matrices [54-56].

The present review focuses on vegetable fibers (also reported as natural or plant fibers), nanofibers extracted from them and nanoclays in particular mineral silicates as reinforcement agents for biobased polymer matrices. Instead of being a natural non-renewable source, nanoclays are abundantly available and improve mechanical properties at lower loadings [57].

#### 3.1. Natural or vegetable fibers

The interest in the use of vegetable fibers as reinforcement agents in polymeric composites is growing currently owing to environmental regulations and ecological concerns of the actual society.

Vegetable fibers are abundantly available, fully and easily recyclable, non-toxic, biodegradable, non-abrasive to the molding machinery, easily colored as well as have lower cost, lower density and lower energy consumption in producing step with respect to synthetic fibers as glass and carbon fibers [58,59]. In addition to having lower processing energy requirements and more shatter resistant when compared with synthetic fibers, vegetable fibers have good sound abatement capability, non-brittle fracture on impact, high specific tensile modulus and tensile strength, low thermal expansion coefficient and low mold shrinkage [59].

There are thousands of different fibers in the world and a few of them have been studied. All vegetable fibers (wood or non-wood fibers) are constituted by cellulose; hemicellulose and lignin combined to some extent as major constituents [6]. In fact, the so-called lignocellulosic fibers have cellulose as the main fraction of the fibers. Cellulose is a semicrystalline polysaccharide made up of D-glucosidic bonds. A large amount of hydroxyl groups in cellulose (three in each repeating unit) imparts hydrophilic properties to the natural fibers [60]. Thus, they are hydrophilic in nature. Cellulose forms slender rodlike crystalline microfibrils that are embedded in a network of hemicellulose and lignin, i. e., the microfibrils are bonded together through an amorphous and complex lignin/hemicellulose matrix that acts as a cementing material.

Hemicellulose is a polysaccharide with lower molecular weight than cellulose. The main difference between cellulose and hemicellulose is that hemicellulose has much shorter chains and also has branches with short lateral chains consisting of different sugars while cellulose is a linear macromolecule [52]. Both are easily hydrolyzed by acids, but only hemicellulose is soluble in alkali solutions as well as lignin. Lignin is a hydrocarbon polymer with a complex composition that presents hydroxyl, methoxyl and carbonyl functional groups [4].

Lignocellulosic fibers may be found in different parts of the plant like leaf, bast, seed and fruit. Some fibers derived from leaf part - leaf fibers: abaca (Manila hemp), sisal, curauá, banana leaf fiber, pineapple leaf fiber (PALF) and henequen; fibers derived from the inner bark part - bast fibers: flax, ramie, kenaf/mesta, hemp, piaçava and jute; fibers derived from plant seed - seed fibers: cotton and kapok and fruit fibers: coconut husk, i.e., coir and luffa. Climatic conditions, age of plant and the digestion process influence not only the structure of fibers but also their chemical composition [56, 61]. Plant fibers from wheat straw, rice straw, oat straw, esparto, elephant grass, bamboo, bagasse (sugar cane) are classified as grass and reed fibers [56]. Some of these non-wood fibers were been studied as raw material source (pulp) for papermaking in many developing countries and for biocomposites manufacture whose composites can be applied mainly for food or non-food packaging, automobile parts and biomedical engineering in repairing or restoring tissues and implants as well as drug/gene delivery [62, 63].

Wood fibers have numerous types distributed in softwoods and hardwoods. Hardwoods are, in general, more complex and heterogeneous in structure than softwoods having a characteristic type of cell called vessel element (or pore) for water transport [64].

Table 4 shows the chemical composition of some non-wood vegetable fibers. The concentration of cellulose and other components of lignocellulosic fibers exhibit a considerable variation even for the same fiber. The references therein indicate concentration values all along the presented concentration range. The spiral angle of the cellulose microfibrils and the content of cellulose, determines generally the mechanical properties of the cellulose-based natural fibers [6]. For instance, these two structure parameters were used to calculate the Young's modulus of the fibers through models developed by Hearle et al [65] cited by Bledzski and Gassan [6].

As natural materials, vegetable fibers have nonuniformity such in dimensions as in mechanical properties when compared to synthetic fibers. Other drawbacks for the use of vegetable fibers in biocomposites are: (i) the lower processing temperature (limited to approximately 200°C) due to fiber degradation and/or volatile emissions; (ii) the high moisture absorption due to fiber hydrophilic nature and (iii) incompatibility with most hydrophobic polymers. These problems are well known and countless research has been developed to reduce them with reasonable success [66, 67]. Nevertheless, vegetable fibers (as fillers or reinforcements) are the latest growing type of polymer additives [68].

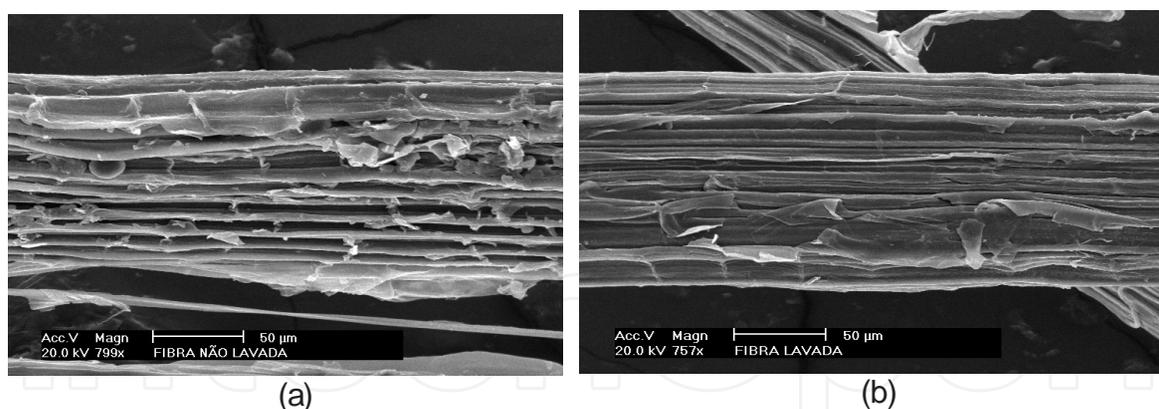
Because of the low interfacial properties between vegetable fiber and polymer matrix which often reduce their potential as reinforcing agents due to fiber hydrophilic nature, chemical modifications are considered to optimize the interface of fibers. Chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix [69].

Chemical Composition						
Fiber	Cellulose (wt%)	Lignin (wt%)	Hemicellulose (wt%)	Ash (wt%)	Microfibrillar/spiral angle (Deg.)	References
Abaca	56-63	7-13	15-25	5	-----	[2, 56, 68, 69]
Curauá	70.7-73.6	7.5-11.1	9.9	0.9	-----	[2, 66, 67]
Flax	64-71	2-5	18.6-20.6	5	5-10	[2, 56, 68, 69]
Hemp	57-77	3.7-13	14-22.4	-----	2-6.2	[2, 56, 68, 69]
Henequen	77.6	13.1	4-8	-----	-----	[68, 69]
Jute	45-72	12-26	12-21	0.5-2	8.0	[2, 6, 56, 68, 69]
Kenaf	31-72	8-21	22-24	2-5	-----	[2, 56, 68, 69]
PALF	70-82	5-12.7	-----	-----	14	[2, 68]
Ramie	68.6-91	0.6-0.7	5-16.7	-----	7.5	[2, 6, 56, 68, 69]
Sisal	47-78	8-13	10-24	0.6-1	10-22	[2, 6, 56, 68, 69]

**Table 4.** Chemical composition of some common vegetable fibers.

Over the last decade, many approaches towards enhancing interfacial adhesion have been pursued. Generally improvements can be accomplished, but there must be a critical cost-benefit evaluation of using the added interfacial agents or processing steps [63].

Alkaline treatment or mercerization is one of the most used chemical treatments of natural fiber. The important modification done is the disruption of hydrogen bonding in the fiber network structure, increasing surface roughness. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fiber cell wall, depolymerizes cellulose and exposes the short length crystallites [69, 70]. As a result; the adhesive characteristics of the fiber surface are enhanced [71]. Figure 2 shows the aspect of curauá vegetable fiber before and after treatment of NaOH solution.



**Figure 2.** SEM micrographs of curauá fiber: (a) as received (b) washed with 0.1 M NaOH solution 24 h at room temperature. Source: Authors

The efficiency of the alkali treatment depends on the type and concentration of the alkaline solution as well as time and temperature of the treatment. Different conditions for alkali treatment of vegetable fibers can be found in literature as well as combinations with other treatments [6, 72].

Authors reported that alkali concentration and reaction time of mercerization has a significant effect on the surface modification [73]. *C. indica* vegetable fibers were immersed firstly in 2% NaOH for the different time intervals at room temperature to optimize the mercerization time. Afterwards, the mercerization of *C. indica* fiber was also carried out in 4, 6, 8, 10, 12, and 14% NaOH solutions to study the effect of different concentrations of NaOH on the mercerization of the fibers. Maximum mercerization observed in terms of weight loss of fiber polymer backbone was observed at 210 min. With respect to the concentration of NaOH solution, the weight loss increases with the increase in alkali concentration and shows maximum weight loss at 10% alkali concentration. This happens due to the removal of lignin, hemicelluloses, pectin and other surface impurities with NaOH.

Campos et al. [74] reported the development of biocomposites of thermoplastic starch and polycaprolactone (PCL) with sisal fibers as reinforcement agent. Sisal fibers were treated with sodium hydroxide solution (NaOH 5% (w/v) at 90°C under agitation for 60 min. After that, sisal fibers were bleached with a blend solution of peroxide hydrogen (H<sub>2</sub>O<sub>2</sub> 16%) and sodium hydroxide (NaOH 5%) at 55 °C for 90 min. The authors observed strong adhesion fiber-matrix and interaction between carboxyl groups in PCL-starch and hydroxyl groups in sisal fibers.

Nevertheless, alkaline treatment or other chemical/physical treatment may damage vegetable fiber surface structure, reducing its strength [75, 76]. When a chemical treatment is applied on synthetic fibers like glass fibers only fiber surface is modified. On the contrary, chemical treatments applied on vegetable fibers can produce important chemical and structural changes not only at fiber surface but also on the interphase between elementary fibers [66]. Furthermore, the orientation of microfibrils of cellulose within each elementary fiber plays an important role because it changes the crystallinity of the natural fiber [77]. A different variety of chemical treatments applied on sisal fibers resulted in greater extensibility and lower

modulus. These phenomena must be related to the structural variation in the ultimate cells, that is, swelling and partial removal of lignin and hemicellulose [78].

Moraes et al. [76] showed the use of sodium borohydride ( $\text{NaBH}_4$ ) (1% wt/vol) as protective agent for vegetable sisal fibers under alkaline treatment with sodium hydroxide (NaOH). The authors reported that the effectiveness of hydride ions ( $\text{H}^-$ ) to protect the sisal fiber was more pronounced in moderate NaOH concentrations (5 wt/vol %) at room temperature or higher (10 wt/vol %) for shorter alkaline treatment times.

Acetylation of natural fibers is a well-known esterification method causing plasticization of cellulosic fibers. Acetylation reduces the hygroscopic nature of natural fibers and increases the dimensional stability of composites [54]. Acetylation is based on the reaction of cell wall hydroxyl groups of lignocellulosic materials with acetic or propionic anhydride at elevated temperature [70]. Other chemical treatments that have already used for fiber treatment are mainly benzoylation treatment, permanganate treatment, isocyanate treatment and peroxide treatment [69].

The use of coupling agents is also extensively used for chemical modification of synthetic and vegetable fibers. Organosilanes and maleic anhydride are both coupling agents that not only produce surface modification but also can produce grafting polymers [63, 79]. Acrylonitrile grafting has also been reported as fiber treatment for glass fibers as well as for vegetable fibers [69]. Coupling agents can be found inserted in polymer matrices (grafted polymer matrices) or in vegetable fibers or even introduced during reactive melt processing of the biocomposite.

In work of Chang et al. [80], kenaf fiber dust was added to a previous maleated polycaprolactone/thermoplastic sago starch blend used as biocomposite matrix. The addition of Kenaf fiber up to 30 phr decreased the water absorption capacity of the maleated treated biocomposites with respect to non-treated biocomposites. The decrease in water absorption was due to the enhanced adhesion between the Kenaf fiber dust and the matrix through grafting which led to decrease of voids between fiber/matrix interfaces. Besides, Kenaf fiber addition improved the mechanical properties of the maleated and non-maleated biocomposites. Nevertheless, tensile strength and modulus reached higher values for maleated biocomposites with higher Kenaf fiber loadings. The effective coupling mechanism of maleic anhydride between polymer matrix and Kenaf has been attributed to esterification reaction between the hydroxyl groups of the Kenaf and anhydride group to form ester linkages [69, 80].

Different authors have applied different methods for silane treatment and have studied the effect of silane treatment on surface morphological and hygroscopic character of the natural fibers. Most of the silane groups have the following formula:  $\text{R}_{(4-n)} - \text{Si} - (\text{R}'\text{X})_n$  ( $n = 1, 2$ ) where R is alkoxy, X represents an organofunctionality, and R' is an alkyl bridge connecting the silicon atom and the organofunctionality [81].

Some authors prepared bamboo fiber-reinforced polylactic acid (PLA) biocomposites using a film-stacking process [71]. Bamboo fibers were subjected to three different silane treatments: direct silane coupling, silane coupling after plasma treatment and silane coupling during UV irradiation. Biocomposites with silane coupling after plasma-treated fibers presented the highest increase in tensile strength with respect to biocomposites with untreated fibers and

among all tested fiber treatments, showing a close adhesion between the PLA matrix and fibers. Fiber surface modifications was related to the silane that should have two functional groups to effectively couple fiber and matrix: a hydrolyzable alkoxy group to condense with hydroxyls on the surface of bamboo fibers and an organofunctional group capable of interacting with the PLA matrix that can result in a copolymerization (grafting) and/or formation of a interpenetrating network.

Other works [81, 82] also reported that in general the interaction of the silane coupling agent with vegetable fibers involves four steps: (i) hydrolysis of silane monomers in presence of water to yield reactive silanol ( $-\text{Si}-\text{OH}$ ), (ii) self-condensation of silanol, (iii) The silanol monomers or oligomers are physically adsorbed to hydroxyl groups of fibers by hydrogen bonds on the fiber surfaces and/or in the cell walls. The free silanols also adsorb and may react with each other forming rigid polysiloxane structures linked with a stable  $-\text{Si}-\text{O}-\text{Si}-$  bond and (iv) grafting under heating conditions since the hydrogen bonds between the silanols and the hydroxyl groups of fibers can be converted into the covalent  $-\text{Si}-\text{O}-\text{C}-$  bonds and liberating water.

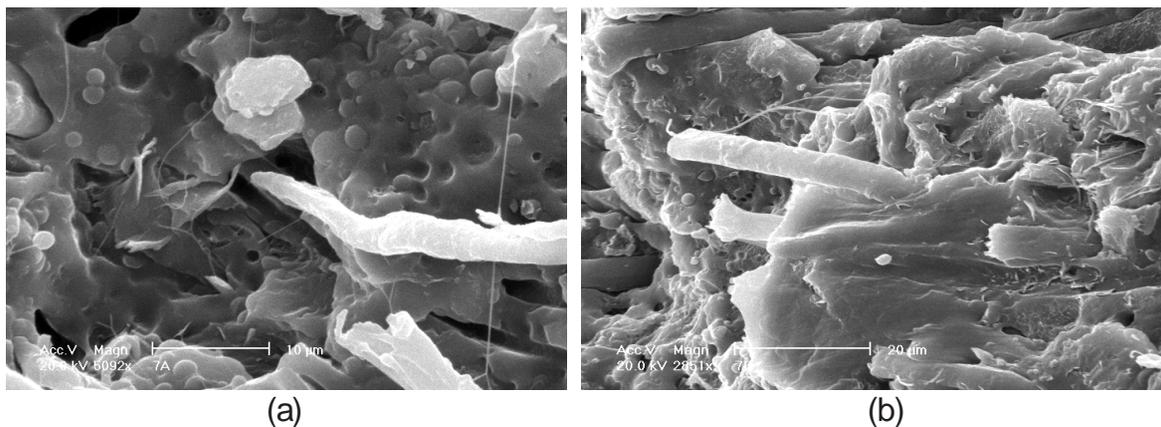
In order to enhance the behavior of Kenaf/PLA biocomposites, authors [43] treated kenaf fibers with sodium hydroxide and 3-aminopropyltriethoxysilane (APS) coupling agent. The authors described the hypothetical reaction of silanol and the fiber: the ethoxy groups of APS hydrolyze in water or a solvent producing a silanol and next the silanol reacts with the OH group of the kenaf fiber which forms stable covalent bonds to the cell wall that are chemisorbed onto the fiber surface. In other work [83], ramie fibers were treated with permanganate acetone solution and with permanganate acetone solution followed by silane acetone solution to produce biocomposites with poly(L-lactic acid) PLLA matrix by hot press molding. The fiber surface-treatment with permanganate acetone solution followed by silane acetone solution improved the interfacial adhesion with PLLA matrix. Both treatments accelerate the water permeation rate in PLLA biocomposites, which plays a critical role in the decline of interfacial adhesion strength.

Also, physical treatments have been used. These treatments change structural and surface properties of the fiber and thus influence the mechanical bonding with the polymer matrix. Some of these treatments involve fibrillation and electric discharge (Corona, cold plasma, sputtering) and so on [72]. Cold plasma treatment causes chemical implantation, etching, polymerization, free radical formation and crystallization whereas sputtering promotes physical changes such as fiber surface roughness that leads to fiber/matrix interface adhesion [71, 84].

Nevertheless, the hydrophilic character of natural (biobased) polymers has contributed to the successful development of environmentally friendly composites, as most natural fibers and nanoclays are also hydrophilic in nature [85]. Most of the published studies on biocomposites with biodegradable polymers are with polyester matrix, such PHA, due to its polar character that provides better adhesion to lignocellulosic fibers [86].

Authors [87] showed that curauá vegetable fibers have good interfacial adhesion to a polyester-based matrix even without coupling agent addition. In this work coupling agent was added

during reactive extrusion at the same time with the neat matrix and a masterbatch containing curauá fiber and the blend matrix. The authors reported the importance of the coupling agent addition, beside the NaOH treatment of the fiber, for improved interfacial fiber/matrix adhesion. Figure 3 shows SEM analysis of tensile fracture cross-section samples of polyester blend/curauá fiber biocomposite. Figure 3a revealed a weak fiber/matrix interface with numerous irregularly shaped microvoids and some de-bondings for composites in the absence of coupling agent, which could be responsible for deterioration of the stress transfer from the matrix to the fibers having an adverse effect on the mechanical properties. On the other hand, composites with coupling agent showed an improvement in polymer/fiber adhesion, avoiding fiber pull-out that leads to voids emerging. In this case, curauá fibers were broken under tension (Figure 3b).



**Figure 3.** SEM micrographs of fracture cross section of polyester blend/curauá fibers: (a) without coupling agent and (b) with coupling agent. Reprinted with kind permission from Springer Science and Business Media: *Journal of Polymers and the Environment Biodegradable Polyester-Based Blend Reinforced with Curauá Fiber: Thermal, Mechanical and Biodegradation Behaviour* 20, 2012, 237-244, Harnnecker F., Rosa, D. S., Lenz, D. M., Figure 3a and 3b [87].

### 3.2. Cellulose nanofibers from vegetable fibers

Cellulose is the most abundant renewable carbon resource on Earth. Thus, it can be obtained from many natural sources. Aside from occurring in wood, cotton and other plant-based materials derived from agricultural crops and by-products, cellulose is also produced by algae, some bacteria and tunics of marine animals – tunicates. [88, 89]. The main difference between cellulose obtained by plants and bacteria is that plant-synthesised cellulose usually also contains hemicellulose, lignin and pectin while cellulose produced by bacteria on the other hand, is pure cellulose without foreign substances [90]. Also, highly crystalline cellulose in the native state can be extracted from tunicates which shows high aspect ratio (length/diameter ratio) as well as allows better matrix-to-filler stress transfer [91].

Nanofibers are fibers that have at least one of its linear dimensions smaller than 100 nm. One of the more significant characteristics of nanofibers is the enormous availability of surface area per unit mass - 1 m<sup>2</sup> of them weighs only 0.1 - 1 gram [3, 92]. Cellulose nanofibers are one class of natural fibers that have resulted in structures with remarkable mechanical properties. These

nanofibers have received an increasing interest in the bio-based materials community since nanocellulose reinforced biopolymers will be less expensive than many common plastics derived from petroleum resources if processing costs can be kept to between \$0.20–\$0.25/lb [93]. However, the full reinforcing potential of nanofibers has yet to be realized partly because of issues related to scaling manufacturing processes [94].

Cellulose nanofibers are nano-reinforcements from biomass that have been improved the biobased polymers properties such as thermal stability, mechanical toughness and barrier properties at much lower fiber fractions than those required in conventional vegetable fiber composites. Biocomposite materials have been showed potential to be used in packaging with PLA matrix [95] and medical applications using polyurethane - PU - matrix [96].

There are many different methods to obtain nanofibres from vegetable fibres. Cellulose nanocrystals, also reported in the literature as nanowhiskers (or just simply “whiskers”), nanofibers, cellulose crystallites or crystals, are the crystalline domains of cellulosic fibers, isolated mainly by acid hydrolysis [97].

Cellulosic materials intended for use as nano-reinforcements in biocomposites are usually subjected to hydrolysis by strong acids such as sulfuric or hydrochloric acid, yielding in a selective degradation of amorphous regions of cellulose and, consequently, the splitting of micro-fibril beams. As a result of cellulose hydrolysis, the disintegration of its hierarchical structure takes place to form crystalline nanofibers [89]. Usually the acid hydrolysis is combined with sonication [88]. The source of cellulose and hydrolysis conditions (acid concentration, acid to cellulose ratio, temperature and reaction time directly affect the morphology of the nanocrystals [89, 98]. The length of the so-produced nanocrystals generally ranges between 100 and 300 nm and width of 5-20 nm [88, 99]. Invariably these nanocrystals from plant fibers present a rod-like structure [91].

Cellulose nanoparticles are obtained as stable aqueous suspensions and thus the processing of cellulose nanocomposites was first limited to using hydrosoluble (or at least hydrodispersible) or latex-form polymers as nanocomposite matrices. After dissolution of the hydrosoluble (or hydrodispersible) polymer, the aqueous solution was mixed with the aqueous suspension of cellulosic nanoparticles to form a mixture that was cast and evaporated to obtain a solid nanocomposite film. The use of the extrusion processing technique was hampered due to the hydrophilic nature of cellulose which causes irreversible agglomeration of the nanofibers in polymer matrices [3]. The development of newer industrially viable processing techniques as melt compounding is the focus currently. PLA nanocomposites reinforced by cellulose nanofibers separated from kenaf pulp were obtained using a two-step process: masterbatch preparation using a solvent mixture of acetone and chloroform followed by extrusion process and injection molding. The tensile modulus and the tensile strength of the PLA nanocomposite using 5 wt% of nanofiber showed an increase of 24% and 21%, respectively [100].

Cellulose nanocrystals can also be produced by submitting vegetable fibres to high mechanical shearing forces, disintegration of the fibres occurs, leading to a material called microfibrillated cellulose (MFC) [88, 101]. However, depending upon the raw material and the degree of processing, chemical treatments (alkaline, enzymatic or oxidation treatments) may be applied

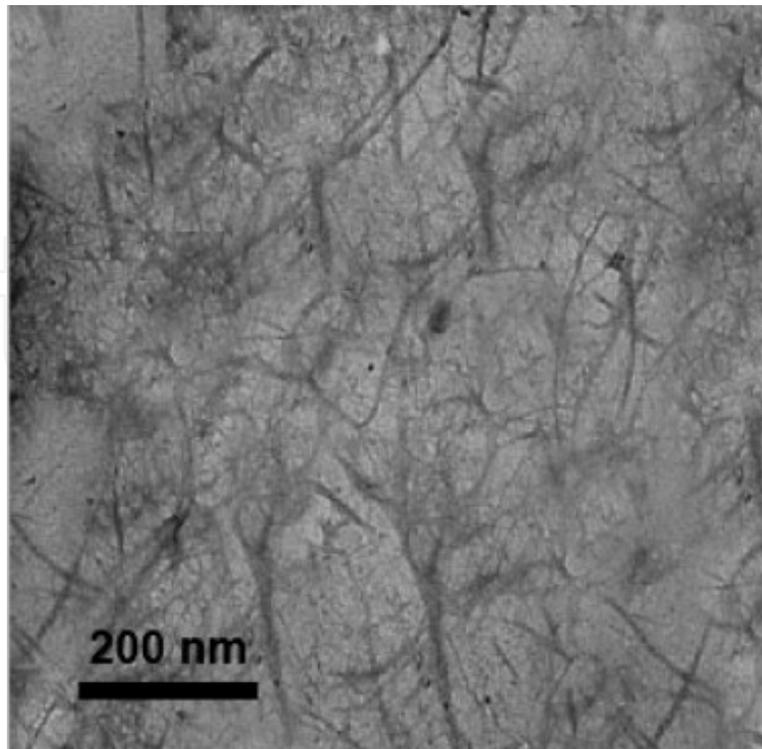
prior to mechanical fibrillation which aim to produce purified cellulose, such as bleached cellulose pulp, which can then be further processed [101]. These nanofibrils ideally consist of individual nanoparticles with a lateral dimension around 5 nm, but MFC generally consists of nanofibril aggregates, whose lateral dimensions range between 10 and 30 nm or more [88].

The major obstacle when producing cellulose based nanocomposites is to disperse the hydrophilic reinforcement in the hydrophobic polymer matrix without degradation of the biopolymer or the reinforcing phase. This can be addressed by improving the interaction between cellulose nanofibers and the matrix and/or by using suitable processing methods [102]. Jute nanofibers submitted to alkali, dimethyl sulfoxide (DMSO) and acid hydrolysis treatments were incorporated into the biocopolyester matrix by melt mixing in varying weight percentages ranging from 0% to 15%. The enhancement in properties was highest for 10 wt % jute nanofiber loaded composites, indicating the most uniform dispersion in this material [103]. In work of Wang and Drzal [104], the solvent evaporation technique (commonly used for drug microencapsulation) was employed to suspend PLA in water as microparticles. The suspension of the PLA microparticles was mixed with high pressure homogenized cellulose nanofibers, producing nanocomposites with good fiber dispersion after water removal by membrane filtration followed by compression molding. Tensile modulus and strength increased up to 58% and 210%, respectively, with respect to neat PLA.

In other work, a hybrid multi-scale biocomposite composed by microfibrillated cellulose (MFC) and bamboo fiber bundles in a polylactic acid (PLA) matrix were successfully processed by extrusion using a surfactant which favoured the dispersion of nanowhiskers in PLA matrix [105]. A hierarchy structure of reinforcement was created with bamboo fiber as the primary reinforcement and cellulose creates an interphase in the PLA matrix around the bamboo fiber that prevents sudden crack growth.

In work of Cherian et al. [106], the nanodimensional cellulose embedded in pineapple fibers was extracted applying acid coupled steam treatment. This treatment was found to be effective in the depolymerization and defibrillation of the fiber to produce nanofibrils of these fibers. Figure 4 shows the cellulose nanofibers extracted through this treatment. These nanofibrils were used to reinforce the polyurethane (PU) by compression moulding [96]. The addition of 5 wt% of cellulose nanofibrils to PU increased the strength nearly 300% and the stiffness by 2600%. The developed composites were utilized to fabricate various versatile medical implants.

A new type of modification of vegetable fibers which consists in the deposition of a nanosized cellulose coating onto natural fibers or the dispersion of nanosized cellulose in natural fiber reinforced composites has been studied in order to develop hierarchical structures. This fiber modification has great potential to improve the fiber-matrix interface and the overall mechanical performances of such composites. Nevertheless, the aspect ratio and alignment of the cellulose nanofiller need optimization as well as novel processing techniques need to be developed to take advantage of the potential use of cellulose nanocrystals [107].



**Figure 4.** Transmission electron micrograph of cellulose nanofibers from pineapple fibers. Reprinted from Carbohydrate Polymers, 81, Bibin Mathew Cherian, Alcides Lopes Leão, Sivoney Ferreira de Souza, Sabu Thomas, Laly A. Pothan, M. Kottaisamy Isolation of nanocellulose from pineapple leaf fibers by steam explosion, 720–725, Copyright (2010) [106] with permission from Elsevier.

### 3.3. Nanoclays

Various inorganic nano-particles have been recognized as possible additives to enhance the polymer performance such as polymer nanofibers, the cellulose whiskers and the carbon nanotube. Among these, up to now only the layered inorganic solids like nanoclay have attracted some attention by the packaging industry. This is not only due to their availability and low cost but also due to their relative simple processability and significant improvements in some properties of the resulting polymer composites that include [108, 109]:

- Mechanical properties;
- Decreased permeability to gases, water and hydrocarbons;
- Thermal stability and heat distortion temperature;
- Flame retardancy and reduced smoke emissions;
- Chemical resistance;
- Surface appearance;
- Electrical and thermal conductivity;
- Optical clarity in comparison to conventionally filled polymers.

Most of synthetic bionanocomposites result from the assembly of biopolymers and silicates belonging to the clay mineral family. The effect of nanoclay minerals on polymer properties is mainly attributed to their high surface area and high aspect ratio as well as the combination of singular properties such as chemical inertness, low or null toxicity, good biocompatibility with high adsorption ability and cation exchange capacity [110]. Nanoreinforcement of biobased polymers with nanoclays can thus create new value-added applications of “green” polymers in the materials world [111].

Montmorillonite (MMT) clays, part of the smectite family clays, are the clay minerals most used as fillers in polymer nanocomposites due to environmental and economic criteria [112]. The chemical structure of MMT clays consist of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either magnesium or aluminum hydroxide establishing a nanometer scale platelets of magnesium aluminum silicate [113]. Each platelet of MMT is about 1 nm in thickness and varies in lateral dimension from 50 nm to several micrometers, showing high aspect ratio. Also, the platelet has a negative charge arising from isomorphous substitution in the lattice structure, which is compensated by naturally occurring cations that are located within the gallery (or interlayer) regions between the platelets [8]. Clay structure is formed by hundreds of layered platelets stacked into particles or tactoids of approximately 8 to 10  $\mu\text{m}$  in diameter [114, 115].

MMT clays have hydrophilic nature due to the presence of inorganic cations on the basal planar surface of montmorillonite layer [116]. The hydrophilicity of the surface of MMT clays makes their dispersion in organic matrices difficult [117]. Thus, MMT clays must be submitted to treatments which play an important role in the preparation of nanocomposites since it can affect their final properties. The most widely used treatments are the diverse functionalizations of clay by various organic cations through ion exchange where the inorganic cations are replaced by organic cations intercalated into the silicate layers. Its hydrophilic nature and ionic exchange capacity allow the silicate mineral to be intercalated by organic cations, which in most cases are alkylammonium ions, to make the clay organophilic and compatible with polymer matrices, preferably with polymers with polar groups which exhibit a higher affinity towards the alkylammonium ion-modified clays [118]. Functionalization of MMT clay by means of the silylation reaction with 3-aminopropyltriethoxysilane and *N*-[3-(trimethoxysilyl)propyl]ethylene-diamine was also reported [119].

There are three possible morphologies for polymer-clay nanocomposites that include: (i) immiscible, (ii) intercalated and (iii) exfoliated structures [115, 120]. In the immiscible structure the polymer does not penetrate between the clay platelets and the interlayer space of the clay gallery does not expand due to its poor affinity with the polymer, so this structure is also known as phase separated morphology or tactoid morphology. Intercalation is attained when polymer chains slightly penetrate within the gallery space and induce moderate expansion of the clay platelets. Exfoliation is characterized by a random distribution of the clay platelets due to extensive penetration of the polymer chains, resulting in the delamination of the clay platelets and the loss of the crystalline structure of the clay. This is due to a high affinity between polymer and clay.

There are three main processing routes for the development of well dispersed clay/biobased nanocomposites [108, 121]: (i) the solvent route which consists in swelling the layered silicates in a polymer solvent, (ii) the *in-situ* polymerization route for which the layered silicates are swollen in the monomer or monomer solution so as the polymer formation can occur between the intercalated sheets and (iii) the melt processing route which is based on polymer processing in the molten state (extrusion, injection molding, etc) which is highly preferred in the context of sustainable development since it avoids the use of organic solvents.

#### **4. Biocomposites of biobased polymers and natural reinforcement agents: Properties and applications**

The development of biocomposites started in the late 1980s and most of the biodegradable polymers which are now available in the market do not yet satisfy each of the requirements for bio-composites. Although promising results were obtained, development of biocomposites is still in its preliminary stage. More data on properties of biocomposites are required to establish confidence in their use [122]. Nanotechnologies promise many stimulating changes in composite materials in order to enhance health, wealth and quality of life, while reducing the environmental impact [108]. Thus, many researches in the biocomposite area can be found in literature. Some of them are reported in the following items.

##### **4.1. PLA based biocomposites**

One of the most studied biocomposites is PLA (polylactide) based biocomposite since PLA was the first commodity plastic produced from annually renewable resources [123]. Lactid acid based polymers (polylactides) are polyesters made from lactic acid. PLLA (poly-L-lactide) is a polymer built with only repeating units of L-stereoisomer configuration. The general term PLA (polylactide) is used for polymers without isomer specification.

PLA is brittle, so it needs modification for practical applications. Bledzki and Jaszkiwicz [124] reported that one of the main drawbacks concerning technical applications of biodegradable polymers, especially for PLA polymers, is their low impact strength. Most research on PLA biocomposite ultimately seeks to improve the mechanical properties to a level that satisfies a particular application [125]. The mechanical properties of biocomposites depend on a number of parameters such as percentage of fiber content, interfacial characteristics between fiber and matrix, fiber aspect ratio, surface modification of fibers and addition of various additives (coupling agents) to enhance the compatibility between fiber and matrix [126].

Huda et al. [82] studied the addition of alkali and/or silane treated Kenaf fibers in PLA matrix through compression molding using the film-stacking method with a fiber content of 40 wt%. Although the introduction of treated kenaf fibers significantly improves flexural modulus compared to the neat PLA matrix, the flexural strength of the PLA composites decreases with the addition of Kenaf fibers. The composite with silane-treated fibers showed an increase of 69% in modulus than that of alkali treated fibers. The notched Izod impact strength of surface-

treated composites was higher than those of the neat PLA. The impact strength of neat PLA improved almost 45% with the addition of 40 wt% untreated fiber and 90% with alkali treated Kenaf fibers with the same content. The high toughness of this natural fiber laminated biocomposite places it in the category of tough engineering materials. Other authors [63] used a carding process that provided a uniform blend of PLA fiber and Kenaf fiber that was followed by needle punching, pre-pressing and further hot-pressing in presence of silane coupling agent to form the biocomposite material. The flexural modulus and flexural strength of the treated fiber biocomposites increased with respect to neat PLA and untreated fiber biocomposites.

In other work, tensile strength and Charpy notched strength were evaluated for PLA biocomposites with a variety of types of natural fiber: abaca fibers, man-made cellulose, jute and flax fibers. Authors observed that increasing the content of fibers up to 30 wt% the composite's stiffness significantly increases as well as tensile and impact strengths with respect to neat PLA [127]. The same improvement in mechanical properties was reported by Choie and Lee [128] using ramie fibers and PLA resin as matrix.

Tensile strength, Young's modulus and impact strength of short hemp fibre reinforced PLA biocomposites increased with increased fibre content (10–30 wt.%) as well as with the application of surface fiber treatments like alkali and silane treatments. It was found that PLA could be reinforced with a maximum of 30 wt.% fibres using conventional injection moulding, but could not be processed at higher fibre contents due to poor melt flow of the compounded materials [123]. In Table 5 the best results of each reference for some mechanical properties of PLA biocomposites with vegetable fiber are summarized.

As shown in Table 5, PLA biocomposites have shown different mechanical properties. Kenaf and hemp fiber PLA biocomposites showed a significantly increase in tensile strength and Young's modulus while a decrease in impact strength with respect to neat PLA was also reported [129]. In this work, neat PLA showed a tensile strength of 30.1 MPa, Young Modulus of 3.6 GPa and 24.4 kJ/m<sup>2</sup> for unnotched Charpy impact strength. The same observation was achieved by Oksman et al. [130] for unnotched Charpy impact strength of PLA biocomposite (12 kJ/m<sup>2</sup>) with respect to neat PLA (15 kJ/m<sup>2</sup>). Different values for neat PLA mechanical properties were reported and they depend mainly on inherent PLA properties (average molar mass, density, etc.) as well as the manufacturing process. Nevertheless, some authors have already observed an increase from a notched impact test for PLA biocomposites [82, 123, 124, 131] for different types of vegetable fibers.

Biodegradable composites have showed insufficient impact strength, preventing a broader field of application of these materials in automotive sector and in electronic devices. However, PLA reinforced with a man-made cellulose (Cordenka<sup>®</sup>) produced a biocomposite which have met performance requirements, especially for impact properties (72 kJ/m<sup>2</sup> for unnotched Charpy impact strength), that can be used in automotive and electronic industry [132]. Authors [129] also reported PLA biocomposites with man-made cellulose that have shown good tensile and impact properties and they can be used in different fields of application like household appliances and in bumpers in the automobile industry.

Fiber and Content (wt%)	Interface Treatment	Manufacturing Process	Tensile strength (MPa)	Young's modulus, (GPa)	Impact strength (kJ/m <sup>2</sup> )	Reference
Abaca (30)	Untreated fibers	Extrusion followed by injection molding	74.0	8.0	5.0 (notched Charpy)	124
Bamboo (20)	Plasma and silane coupling	a filmstacking procedure	90	1.8	-	71
Flax (30)	Enzyme retting of fiber	Extrusion followed by compression molding	53	8.3	12 (unnotched Charpy)	130
Hemp (30)	Mercerized fiber	Extrusion followed by injection molding	75.5	8.2	2.64 (notched Charpy)	123
Hemp (40)	Untreated fibers	Roller carding with PLA followed by compression molding	57.5	8	9.5 (unnotched Charpy)	129
Jute (30)	Untreated fibers	Extrusion followed by injection molding	81.9	9.6	4.8 (notched Charpy)	124
Kenaf (40)	Untreated fibers	Roller carding with PLA followed by compression molding	52.9	7.1	9.0 (unnotched Charpy)	129
Kenaf (30)	5 wt% Coupling agent (maleic anhydride grafted PLA)	Internal mixing followed by compression molding	-	-	3.46 ± 0.13 (notched Charpy)	131
Man-made cellulose (Lyocell) (40)	Untreated fibers	Roller carding with PLA followed by compression molding	81.8	6.8	39.7 (unnotched Charpy)	129
Man-made cellulose (30)	Untreated fibers	Extrusion followed by injection molding	92	5.8	8.0 (notched Charpy)	124

**Table 5.** Tensile strength, Young's modulus and impact strength (room temperature) of PLA-based biocomposites with vegetable fibers.

Biocomposites that show high tensile strength and stiffness as well as low impact strength could be used in manufacture of furniture, boardings or holders for grinding discs and so on

which are not subjected to high impact stress. Biocomposites that show the combination of properties as low tensile strength with high impact strength leads to application of these materials in interior parts in cars or safety helmets [129]. Also, kenaf fiber-reinforced PLA matrix biocomposites which the processing is based on injection molding have been used for spare tire covers and circuit boards [133] and these biocomposites were proposed to be used in an automotive headliner made from a 50/50 PLA/Kenaf fiber using a carding process [63].

The mechanical properties are thus among the most widely tested properties of natural fiber reinforced composites [2]. Compared with widespread research on mechanical properties of biocomposites, there are few reports on flame retardancy of biopolymers and biocomposites [134, 135]. The flame retardancy of ramie fiber reinforced PLA biocomposites was tested using halogen-free ammonium polyphosphate (APP). PLA biocomposites using flame-retardant treatment of ramie fibers have demonstrated a certain flame retardancy but cannot be classified by UL94 testing (Test for flammability of plastic materials for parts in devices and appliances) because of low APP loading (4.5 wt%). When PLA matrix is mixed in a extruded with APP, biocomposites with treated or non-treated ramie fibers and having the same APP loading (10.5 wt%) achieved V-0 rating (short burning time, no dripping; self-extinguishing). Low loading of APP does not adversely affect the mechanical performance of PLA/ramie biocomposites [136]. Other authors [137] also studied PLA biocomposites using plasma-treated coconut fiber and prepared using the commingled yarn method. As expected, plasma-treated coconut fibers improved mechanical properties like tensile strength and modulus of biocomposites compared to neat PLA, but no significant changes on the fire retardant properties was achieved for the biocomposites with respect to neat PLA, according to the limiting oxygen index (LOI) value: around 25 for neat PLA and 10 wt% treated coconut fiber biocomposite. Generally, when the LOI value is greater than 26, materials can be considered to have flame retardancy [134].

Nanoreinforcements were also tested in fully biodegradable biocomposites of PLA matrix. These biocomposites help to provide new food packaging materials with improved mechanical, barrier, antioxidant and antimicrobial properties [138]. The addition of cellulose nanowhiskers to PLA matrix reduced the water permeability by up to 82% and the oxygen permeability by up to 90% with only 3 wt% of nanofiller content [139]. Moreover, the incorporation of organomodified mica-based clay to PLA matrix enhanced barrier properties to UV light; besides other barrier properties. This property is highly important for food packaging as protection against light which is a basic requirement to preserve the quality of many food products [140].

In previous research, PLA matrix was reinforced by 5wt% microcrystalline cellulose or 5wt% commercial organically modified bentonite (layered silicate) [141]. The bionanocomposite reinforced by bentonite showed great improvements in tensile modulus and strength as well as a decrease in oxygen permeability whereas the bionanocomposite reinforced with microcrystalline cellulose only showed a tendency to improve strength as well as a reduction in elongation at break. No changes for oxygen permeability were observed. This was attributed to the larger surface area of bentonite that allows interaction with a larger amount of PLA chains.

In other work, the presence of a surfactant favoured the dispersion of cellulose nanocrystals in the PLA matrix, yielding bionanocomposites with higher tensile modulus and strength. The addition of silver nanoparticles to the bionanocomposite did not enhance these mechanical properties. Besides, an antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* cells was detected for ternary systems, indicating that these bionanocomposites have great potential to be applied in food packaging when an antibacterial effect is required [95].

Poly lactides and their copolymers were been widely reported to be used in the fields of orthopedic and reconstructive surgery due to its biodegradability and better features for use in the human body (nontoxicity) [142, 143]. According to Walker et al. [144], poly lactides degrade in vivo by hydrolytic mechanisms of the ester bonds into lactic acid which is processed through metabolic pathways and is eliminated from the body through the renal and/or respiratory mechanisms. PLLA constructs have a longer degradation time when compared to other polymers, having shown to be present at 3 years after implantation. Its structural characteristics have proven useful for the construction of orthopedic hardware.

Bionanocomposites of hydroxyapatite (HPA) nanospheres which is the main inorganic constituent of natural bone and PLLA microspheres were tested for biomedical application to produce scaffolds using a laser sintering process [145]. HPA particles can reinforce polymer matrices and decrease the degradation rate of PLA [146]. Also, other work showed that PLA/organoclay bionanocomposites have enhanced their thermomechanical properties and gas barrier properties with respect to neat PLA and their biodegradation rate depends on the organoclay nature, organoclay content, organoclay dispersion as well as the organic modifier used to treat the nanoclay [147]. The relative hydrophilicity of the clay layers has been shown to play a key role in the hydrolytic degradation of the PLA chains [148].

Biodegradability of flax fiber reinforced PLA based biocomposites in presence of amphiphilic additives like benzoic acid, mandelic acid, dicumyl peroxide (DCP) and zein protein was investigated by soil burial test with farmland soil. Authors reported that neat PLA films degraded rapidly compared to natural fiber reinforced biocomposites. But, regarding the use of amphiphilic additives, the higher loss in weight is obtained for flax reinforced PLA biocomposites in the presence of mandelic acid. In the presence of DCP, the biodegradability of the biocomposites was comparatively delayed. Depending on the end-uses of the biocomposites, suitable amphiphilic additives can be used as triggers for inducing controlled biodegradation [149].

The aerobic biodegradation of biocomposites of PLA, thermoplastic starch (TPS) and a blend of 75 wt% of PLA and 25 wt% of TPS with short natural fiber (coir) with and without the addition of maleic anhydride (MA) coupling agent were investigated under controlled composting conditions. TPS showed higher biodegradation rates than PLA, probably due to the TPS domains preferentially attacked by microorganisms. Besides, authors ascertained that coir fibers probably have no influence in the biodegradation process due to the slight differences in carbon dioxide produced for neat polymers and their biocomposites with coir fiber. Also, the presence of coupling agent decreased the percentage of evolved CO<sub>2</sub> compared to biocomposites without coupling agent [150].

In other work, bacterial (*Burkholderia cepacia* bacteria) biodegradation studies were performed for biocomposites of PLA and mercerized banana fiber (BF) produced by melt blending followed by compression molding. Banana fibers were also treated with various silanes to improve their compatibility with PLA matrix. Authors reported improvements in tensile and impact strength of the biocomposites with respect to neat PLA. Weight loss experiments showed that PLA had 60% of degradation within a period of 25 days and all biocomposites showed higher degradation rates (80–100%). While biocomposites with untreated and alkaline-treated BF degraded almost completely, silane-treated biocomposites degraded at lower rates. Water absorption studies supported this evidence [151, 152].

#### 4.2. PHBV biocomposites

Poly(hydroxy-alkanoates) (PHAs) are a family of bacterial polyesters which poly(hydroxybutyrate) (PHB) and its copolymer poly(3-hydroxybutyrate-co-3-valerate) (PHBV) make part. According to Bledzki and Jaszkiwicz [124], PHBV has been technologically developed to improve the known weaknesses of PHB like brittleness and poor processability.

Biocomposites of PHBV with wood and bamboo fibers were fabricated using extrusion followed by injection molding. Tensile and flexural modulus increased with fiber loading for biocomposites with the two kinds of fiber and no appreciable difference among the two fiber loadings (30 and 40 wt% fiber) was noticed. However, notch impact strength of PHBV decreased with the fiber addition and the reduction was greater in case of bamboo fiber biocomposites [153]. However, in other work biocomposites of PHBV and bamboo pulp fibers which were prepared by melt compounding and injection molding showed substantially increase of the impact strength by the addition of bamboo pulp fiber as well as increased tensile strength and modulus and flexural strength and modulus. The maleic anhydride grafted PHBV used as coupling agent improved polymer/fiber interactions and therefore resulted in increased strength and modulus. However, the toughness of the composites was substantially reduced due to the hindrance to fiber pullout [154]. Also, authors [124] reported an increase of the impact strength for PHBV biocomposites using 30 wt% of man-made cellulose, abaca and jute fibers at 23°C and also at -30 °C. The most pronounced results were obtained with man-made cellulose. PHBV was blended with 27.6 wt% of poly(butylene adipate-co-butylene terephthalate) (PBAT) and 2.4 wt% of processing aids. Moreover, tensile strength and modulus were increased.

In recent work, PHBV was blended with PBAT using extrusion (in a twin-screw extruder) followed by injection molding. Biocomposites were performed with 20–40wt% switchgrass and the compatibilizer pMDI. With the addition of 25wt% switchgrass the tensile and flexural strengths of the biocomposite have improved. On increasing the fiber content to 30wt% and further to 40wt%, both tensile and flexural strength dropped but the modulus of the composites increased progressively with increasing fiber content. With regard to uncompatibilized composites, impact strength of 53 J/m was achieved for composites with 25wt% switchgrass because of the proper wetting achieved between the fiber and the matrix. Impact strength reduced with increase in fiber content. The use of the pMDI compatibilizer in biocomposites

with 30 wt% switchgrass promoted interfacial interactions between the matrix and the fiber and significantly improved the mechanical properties of the biocomposites. The addition of pMDI significantly increased the impact strength of the composites. The notched impact strength increased 80% compared to the uncompatibilized composite owing to the enhanced interfacial adhesion [155]. Also, by incorporation of biomass fiber reinforcement like corn straw, soy stalk and wheat straw into the PHBV by melt mixing technique, authors showed that the alkali treatment of wheat straw fibers enhanced strain, break and impact strength of PHBV composites by 35%, hardly increasing strength and modulus compared to their untreated counterparts. Authors also showed that the tensile and storage modulus of PHBV were improved by maximum 256% and 308%, respectively, with 30 wt% of the biomass and these values were much higher than the corresponding polypropylene (PP) composites [156].

Nanoparticles also have already been incorporated into PHBV matrix. Well-dispersed cellulose nanocrystals into PHBV matrix were obtained with simultaneous enhancements on the mechanical property and thermal stability of PHBV. Compared to neat PHBV, a 149% improvement in tensile strength and 250% increase in Young's modulus were obtained for the resulting nanocomposites with 10 wt% of cellulose nanocrystals [157]. Lower concentrations of cellulose nanowhiskers (0–4.6 wt%) were used to prepare PHBV bionanocomposites by solution casting [158]. The mechanical properties of the films increased with increasing cellulose nanowhiskers content until the content reached 2.3 wt %. Real permittivity of the composites also peaked at 2.3 wt % cellulose nanowhiskers over a wide spectrum of frequencies (0.01–10<sup>6</sup> Hz). These property transitions at 2.3% cellulose nanowhiskers content were due to the transition of cellulose nanowhiskers dispersion from homogeneous dispersion to agglomeration. Nevertheless, rheological results of the bionanocomposites indicated a transition point lower than 2.3% due to the formation of a biopolymer-fiber network in the composite melt.

Some authors [159] showed that the incorporation of low concentrations of nanoclays (5 wt%) and cellulose nanowhiskers (3 wt%) into PHBV matrix and other biodegradable matrices like PLA and polycaprolactone (PCL) resulted in improvements in oxygen permeability that can be very useful for food packaging. With respect to water permeability, authors showed that PHBV films with 1 wt% alpha cellulose fiber content had a water permeability drop of 71% compared to the unfilled material, whereas PHBV films with a fiber content of 10 wt% showed a water permeability reduction of around 52% due to fiber agglomeration. However, the lowest water and limonene permeability coefficient values were obtained for the bionanocomposites containing 5 wt% of clay due to the good morphology for these nanocomposites. The same work also reported that mica-based nanoclays exerted certain UV/visible light blocking action in PLA and PHBV matrices. The blocking effect of PHBV in the UV-Vis region was higher than that of PLA since PHBV is a translucent material. Moreover, greater reductions in vapour permeability were attained for PHBV bionanocomposites with clay contents of 1 wt% [94]. Furthermore, the PHBV processing behavior could be improved with addition of montmorillonite nanoclay since the processing temperature range enlarged by lowering melting temperature with the increasing clay content. The tensile properties of the corresponding materials were improved by incorporation of 3wt% of clay [160].

Thus, in general many properties have been improved with the incorporation of fibers and mainly nanofibers and nanoclays into PHBV which are helpful to overcome many obstacles and enhance the efficiency in a diverse number of applications. In this way, it is found that nanofibers can induce fast regeneration of many tissues/organs in medical applications and improve the efficiency of many chemical and electronic applications [161].

PHA's family was related to be used in numerous biomedical applications, such as sutures, cardiovascular patches, wound dressings, scaffolds in tissue engineering, tissue repair/regeneration devices, drug carriers and so on, but much deep studies [162]. PHBV bionanocomposites were manufactured with various calcium phosphate-reinforcing phases for bone tissue regeneration while inducing a minimal inflammatory response. Authors showed that the addition of a mineral nano-sized reinforcing phase to PHBV reduced the proinflammatory response and also improved osteogenic properties with respect to pure PHBV [163].

With respect to biodegradation behaviour, biocomposites of PHBV matrix and 10, 20 and 25 wt% of peach palm particles were investigated [164]. Soil biodegradation tests were carried out according to ASTM G160-98 with test exposures of up to 5 months. The addition of peach palm particles reduced the maximum strength but improved the Young's modulus and also soil biodegradation tests indicated that the biocomposites degraded faster than the neat polymer due to the presence of cavities that resulted from introduction of the peach palm particles and that degradation increased with increasing particles content. These voids allowed for enhanced water adsorption and greater internal access to the soil-borne degrader microorganisms. Similarly, other authors found that biocomposites with PHBV and wood fiber have higher degradation rates than the neat polymer [165]. On the other hand, some authors reported no significant difference between the degradability of PHBV and its composite with wheat straw using either Sturm tests or soil burial tests [166].

## 5. Conclusion

Due to the high demand for environmental sustainable products, researchers continue to seek materials derived from renewable resources that can be applied in a wide range of applications. This overview provided a survey of some of the current researches on the biocomposites area. Within this context, this chapter showed that there have been many attempts to produce biocomposites using natural reinforcements and biobased polymers since improvements in their mechanical, barrier and other properties can be accomplished through the use of reinforcement agents like vegetable fibers and nanoparticles (cellulose nanofiber or nanoclays). Vegetable fibers are generally submitted to chemical treatments, mostly alkaline and acid treatments in order to favour interfacial adhesion between polymer matrices and the fiber. Also, the use of coupling agents enhance adhesion by surface modification as well as they can produce grafting reactions between matrix and fiber. Moreover, the presence of polar groups in most biobased polymers contributes to better affinity to cellulosic groups of vegetable fibers. All these issues dramatically influence the mechanical properties of the biocomposites. With respect to nanoreinforcements, cellulose nanofibers and organic functionalized clays (organoclays) are the most used as fillers in bionanocomposites.

PLA based biocomposites are one of the most studied biocomposites and some researches showed that the use of vegetable fiber can improve the impact strength of the PLA matrix, but insufficient strength values were found to enable their application in automotive sector and in electronic devices. PLA biocomposites with a man-made cellulose fiber that fulfill the requirements for mechanical properties were already reported and their use can be extended to different fields of application. The use of nanoreinforcements in PLA matrices produced bionanocomposites with remarkable mechanical, thermal, barrier, antioxidant and antimicrobial properties, presenting a new material with potential for food packaging application. The biodegradability of PLA biocomposites with vegetable fibers showed to be sensitive to the additives used in biocomposite processing. The presence of coupling agents provides lower degradation times than neat PLA. Also, depending on the nature of the amphiphilic additives, they may speed up or delay the biodegradation process. Researches with organoclay in bionanocomposites showed that their biodegradation rate depends on the nature, the content and the dispersion level of organoclay in the bionanocomposite as well as the nature of organic modifier of the clay.

PHBV based biocomposites also showed an increase in mechanical properties in presence of treated vegetable fibers and coupling agents. However, the incorporation of cellulose nanofibers and organoclays in PHBV matrix promoted greater improvements not only in mechanical properties but also in oxygen and water permeability. The bionanocomposites produced can be used in medical applications due to the faster regeneration of many tissues/organs and in many chemical and electronic applications. The specific use of organoclays also produced UV-Vis blocking effects and greater reductions in vapour permeability as well as processing behaviour improvements. The biodegradability of these bionanocomposites showed to be similar or faster than the neat PHBV matrix.

Therefore, bionanocomposites arise as a promising area that can overcome some of the drawbacks of biobased polymers and their biocomposites since the use of nanoparticles generally promotes greater improvements in many properties with respect to biocomposites. However developments must be performed on processing techniques and key research challenges like nanoparticles dispersion into biopolymers. Thus, the construction of a biocomposite/bionanocomposite is not a simple process and it needs the knowledge of the real contribution of each composite phase for property tuning. Moreover, biocomposites/bionanocomposites will be only attractive if material and process costs are competitive compared to conventional composites which use petrochemical resources.

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## References

- [1] Chand, N and Fahim, M Tribology of natural fiber polymer composites. Chapter 1, 1-58, Woodhead Publishing and CRC Press (2008).
- [2] Faruk, O, Andrzej, K, Bledzki, H-P, Fink, M S Biocomposites reinforced with natural fibers: 2000–2010. *Progress in Polymer Science*, 37(11)1552-1596 (2012).
- [3] Kalia, S, Dufresne, A, Cherian, B M, Kaith, B S, Avérous, L, Njuguna, J, Nassiopoulou, E Cellulose-Based Bio- and nanocomposites: a review. *International Journal of Polymer Science* (2011) Article ID 837875, 35 pages doi:10.1155/2011/837875.
- [4] John, M J, Thomas, S Biofibres and biocomposites. *Carbohydrate Polymers*, 71: 343-364 (2008).
- [5] Fowler, P A, Hughes, J M, Elias, R M Review Biocomposites: technology, environmental credentials and market forces. *Journal of the Science of Food and Agriculture*, 86(12):1781-1789 (2006).
- [6] Bledzki, A K, Gassan, J Composites reinforced with cellulose-based fibres, *Progress in Polymer Science*, 24(2): 221-274 (1999).
- [7] Ruiz-Hitzky, E, Darder, M, Aranda, P Progress in bionanocomposite materials. In: *Annual Review Nano Research Volume 3*, Chapter 3, 149-189, Guozhong Cao, Qifeng Zhang and C. Jeffrey Brinker(Ed) World Scientific Publishing, Singapore (2010).
- [8] Malviya, R, Srivastava, P, Bansal, V and Sharma, P K Formulation, evaluation and comparison of sustained release matrix tablets of diclofenac sodium using natural polymers as release modifier, *International Journal of Pharma and Biosciences*,1(2): 1-8 (2010).
- [9] Malviya, R, Srivastava, P, Bansal M and Sharma P K Preparation and evaluation of disintegrating properties of Cucurbita maxima pulp powder. *International J. Pharmaceutical Sci.*, 2(1):395-399 (2010).
- [10] Šimkovic, I What could be greener than composites made from polysaccharides? *Carbohydrate Polymers*, 74 (4): 759-762 (2008).

- [11] Rosa, D S, Guedes, C G F, Casarin, F, Braganca, F C The effect of the Mw of PEG in PCL/CA blends. *Polymer Testing*, 24(5): 542–548 (2005).
- [12] Klemm, D , Heublein, B, Fink, H-P, Bohn, A Cellulose: fascinating biopolymer and sustainable raw material *Angewandte Chemie International Edition*, 44 (22): 3358-3393 (2005).
- [13] Edgar, K J , Buchanan, C M, Debenham, J S, Rundquist, P A, Seiler, B D, Shelton, M C, Tindall, D Advances in cellulose ester performance and application *Progress in Polymer Science*, 26 (9):1605-1688 (2001).
- [14] Ignácio C and Barros D M Membranas celulósicas – efeitos da concentração de polímero-solvente-não solvente na morfologia da membrana. 8º Brazillian Polymer Congress, Águas de Lindóia, 624-625 (2005).
- [15] Mulinari, D R, Silva M L C P, Silva G L J P Preparação e caracterização dos compósitos celulose branqueada/ZrO<sub>2</sub>nH<sub>2</sub>O preparados pelos métodos da precipitação convencional e precipitação em solução homogênea. 8º Brazillian Polymer Congress, Águas de Lindóia, 245-246 (2005).
- [16] Vroman, I and Tighzert, L *Biodegradable Polymers, Materials*, 2: 307-344 (2009) doi: 10.3390/ma2020307.
- [17] Rosa D S, Carvalho C L, Gaboardi, M L F, Rezende, M I, Tavares B, Petro M S M, Calil M R Evaluation of enzymatic degradation based on the quantification of glucose in thermoplastic starch and its characterization by mechanical and morphological properties and NMR measurements. *Polymer Testing*, 27(7): 827-834 (2008).
- [18] Rosa, D S, Guedes, C G F, Carvalho C L Processing and thermal, mechanical and morphological characterization of post-consumer polyolefins/thermoplastic starch blends. *Journal of Materials Science*, 42(2): 551–557 (2007).
- [19] Pedroso, A G and Rosa, D S Mechanical, thermal and morphological characterization of recycled LDPE/corn starch blends. *Carbohydrate Polymers*, 59 (1): 1-9 (2005).
- [20] Rosa, D S, Guedes, C G F, Volponi, J E Biodegradation and dynamic mechanical properties of starch gelatinization in poly(-caprolactone)/corn starch blends. *Journal of Applied Polymer Science*, 102 (1): 825-832 (2006).
- [21] Rosa, D S, Guedes C G F, Carvalho, C L Processing and thermal, mechanical and morphological characterization of post-consumer polyolefins/thermoplastic starch blends. *Journal of Materials Science*, 42(2): 551–557 (2007).
- [22] Furusaki E., Ueno Y., Sakairi N., Nishi N. and Tokura, S. Facile Preparation and inclusion ability of a chitosan derivative bearing carboxymethyl- $\beta$ -cyclodextrin. *Carbohydrate Polymers*, 9: 29-34 (1996),

- [23] Hirano, S and Nagano, N Effects of chitosan, pectic acid, lysozyme and chitinase on the growth of several phytopathogens. *Agricultural and Biological Chemistry*, 53: 3065-3066 (1989).
- [24] Kumar, M N V R A review of chitin and chitosan applications. *Reactive & Functional Polymers*, 46 (1): 1-27 (2000).
- [25] Piermaria, J A, Pinotti, A, Garcia, M A, Abraham, A G Films based on kefir, an exopolysaccharide obtained from kefir grain: development and characterization. *Food Hydrocoll.*, 23: 684-690 (2009).
- [26] Chandra, R, Rustgi, R Biodegradable polymers. *Progress in Polymer Science*, 23: 1273-1335 (1998).
- [27] Andrade, C T, Lopes, L Polímeros de origem microbiana: polissacarídeos bacterianos. *Revista de Química Industrial*, 703:19-23 (1995).
- [28] Serafim S L, Lemos P C, Reis, M A M Produção de bioplásticos por culturas microbianas mistas. *Boletim de Biotecnologia*, 76:15-20 (2003).
- [29] Pradella, J G C Biopolímeros e intermediários químicos. Technical Report nº 84396-205, Centro de Tecnologia de Processos e Produtos, Laboratório de Biotecnologia Industrial – LBI/CTPP (2006).
- [30] Coutinho, B C, Miranda, G B, Sampaio, G R, Souza, L B S, Santana, W J, Coutinho, H D M A importância e as vantagens do polihidroxibutirato (plástico biodegradável). *Holos* 3: 76-81 (2004).
- [31] Lenz, R W, Marchessault, R H Bacterial polyesters: biosynthesis, biodegradable plastics and biotechnology. *Biomacromolecules* 6 (1):1-8 (2005).
- [32] Rosa, D S, Penteado, D F, Calil, M R Propriedades térmicas e biodegradabilidade de PCL e PHB em um pool de fungos. *Revista Ciência & Tecnologia*, 15: 75-80 (2000).
- [33] Corrêa, M C S, Rezende, M L, Rosa, D S, Agnelli, J A M, Nascente, P A P Surface composition and morphology of poly(3-hydroxybutyrate) exposed to biodegradation. *Polymer Testing* 27 (4): 447-452, 2008.
- [34] Quental, A C, de Carvalho, F P, Rezende, M I, Rosa, D S, Felisberti M I Aromatic/aliphatic polyester blends. *Journal of Polymers and the Environment*, 18 (3): 308-317 (2010).
- [35] Luckachan, G. E., Pillai C. K. S. Biodegradable polymers- a review on recent trends and emerging perspectives *Journal of Polymers and the Environment* , 19: 637-676 (2011).
- [36] Keshavarz, T and Roy, I Polyhydroxyalkanoates: bioplastics with a green agenda *Current Opinion in Microbiology*, 13:321-326 (2010).

- [37] Rosa, D S and Pântano Filho, R Biodegradação: um ensaio com polímeros. Moara (Ed.), Itatiba, S.P; Editora Universitária São Francisco (Ed.), Bragança Paulista, S.P. (2003).
- [38] Lotto, N T Dimensionamento da degradação dos polímeros PHB e PHB-V através da variação da rugosidade. (Master Dissertation), 78 p. Universidade São Francisco, S. P., Brazil (2003).
- [39] Rosa, D S, Franco, B L M, Calil, M R Biodegradabilidade e propriedades mecânicas de novas misturas poliméricas. *Polímeros: Ciência e Tecnologia*, 2 (11): 82-88 (2001).
- [40] Lotto, N T, Calil, M R, Guedes. C G F, Rosa, D S The effect of temperature on the biodegradation test. *Materials Science and Engineering: C*, 24(5): 659-662 (2004).
- [41] Vogelsanger, N, Formolo, M C, Pezzin, A P T, Schneider, A L S, Furlan, A A, Bernardo, H P, Pezzin S H, Pires, A T N, Duek, E A R Blendas biodegradáveis de poli(3-hidroxi-butirato)/poli(-caprolactona): obtenção e estudo da miscibilidade. *Materials Research*, 6 (3):359-365 (2003).
- [42] Raghavan, A D Characterization of Biodegradable Plastics. *Polymer-Plastics Technology and Engineering*, 34(1): 41-63 (1995).
- [43] Zenkiewicz, M, Richert, J, Rózański, A Effect of blow moulding ratio on barrier properties of polylactide nanocomposite films. *Polymer Testing*, 29(2): 251-257 (2010).
- [44] Bhatia, A, Gupta, R, Bhattacharya, S, Choi, H. Effect of clay on thermal, mechanical and gas barrier properties of biodegradable poly(lactic acid)/poly(butylene succinate) (PLA/PBS) nanocomposites. *International Polymer Processing*, 25 (1):5-14 (2010).
- [45] Martino, V P, Ruseckaite, R A, Jiménez, A, Averous, L Correlation between composition, structure and properties of poly(lactic acid)/polyadipate-based nano-Biocomposites. *Macromolecular Materials and Engineering*, 295(6): 551-558 (2010).
- [46] Rasala, R M, Janorkarc, A V, Hirta, D E Poly(lactic acid) modifications Progress in *Polymer Science*, 35:338-356 (2010).
- [47] Henry, F, Costa, L C, Devassine, M The evolution of poly(lactic acid) degradability by dielectric spectroscopy measurements *European Polymer Journal*, 41(9): 2122-2126 (2005).
- [48] Ulery, B D, Nair, L S, Laurencin, C T Biomedical applications of biodegradable polymers *Journal of Polymer Science Part B: Polymer Physics*, 49: 832-864 (2011).
- [49] Bragança, F C and Rosa, D S Thermal, mechanical and morphological analysis of poly(3-caprolactone), cellulose acetate and their blends, *Polymers for Advances Technology* 14(10):669-675 (2003).
- [50] Landry, C J T, Lum, K K, O'Reilly, J M Physical aging of blends of cellulose acetate polymers with dyes and plasticizers, *Polymer*, 42 (13):5781-5792 (2001).

- [51] Wang, Z, Qu, B, Fan, W, Hu, Y, Shen, X Effects of PE-g-DBM as a compatibilizer on mechanical properties and crystallization behaviors of magnesium hydroxide- based LLDPE blends. *Polymer Degradation and Stability*, 76(1): 123-128 (2002).
- [52] Kim, C-H, Cho, K Y, Park, J-K Grafting of glycidil methacrylate onto polycaprolactone: preparation and characterization. *Polymer*, 42(12): 5135-5142 (2001).
- [53] Liu, W, Wang, Y L, Sun, Z Effects of polyethylene-grafted maleic anhydride (PE-g-MA) on thermal properties, morphology, and tensile properties of low-density polyethylene (LDPE) and corn starch blends, *Journal of Applied Polymer Science*, 88 (13): 2904–2911 (2003),.
- [54] Mucci, V, Pérez, J, Vallo, C I Preparation and characterization of light-cured methacrylate/montmorillonite nanocomposites *Polymer International*, 60 (2): 247-254 (2011).
- [55] Sreekumar, P A and Thomas, S Matrices for natural-fibre reinforced composites. In: *Properties and performance of natural-fibre composites*. Chapter 2, 67-126, Kim L. Pickering (Ed) Woodhead Publishing Limited and CRC Press (2008).
- [56] Kozłowski, R and Władyska-Przybylak, M Uses of natural fiber reinforced plastics. In: *Natural Fibers, Plastics and Composites*. Chapter 14, 249-271, Wallenberger FT, Weston NE (Ed). Kluwer Academic Publishers: Dordrecht (2004).
- [57] Yang, L, Hu, Y, Lu, H, Song, L Morphology, thermal, and mechanical properties of flame-retardant silicone rubber/montmorillonite nanocomposites. *Journal of Applied Polymer Science*, 99(6): 3275–3280 (2006).
- [58] Duhovic, M, Peterson, S, Jayaraman, K Natural-fibre-biodegradable polymer composites for packaging In: *Properties and performance of natural-fibre composites*. Chapter 9, 301-329, Kim L. Pickering (Ed), Woodhead Publishing Limited and CRC Press (2008).
- [59] Satyanarayana, K G, Arizaga, G G C, Wypych, F Biodegradable composites based on lignocellulosic fibers- an overview. *Progress in Polymer Science*, 34(9): 982-1021 (2009),.
- [60] Spinacé, M A S, Lambert, C S, Feroselli, K K G, De Paoli, M-A. Characterization of lignocellulosic curaua fibres. *Carbohydrate Polymers*, 77(1): 47-53 (2009).
- [61]
- [62] Sánchez, C Lignocellulosic residues: Biodegradation and bioconversion by fungi. *Biotechnology Advances*, 27(2):185-194 (2009).
- [63] Pilla, S Engineering applications of bioplastics and biocomposites – an overview. In: *Handbook of Bioplastics and Biocomposites - Engineering Applications*, chapter 1, 1-14, Srikanth Pilla (Ed), Scrivener Publishing LCC and John Wiley & Sons, Massachusetts and New Jersey (2011).

- [64] Lee, B-H, Kim, H-S, Lee, S, Kim, H-J, Dorgan, J R Bio-composites of kenaf fibers in polylactide: Role of improved interfacial adhesion in the carding process. *Composites Science and Technology*, 69(15-16): 2573–2579 (2009).
- [65] Stelte, W, Sanadi, R A Preparation and characterization of cellulose nanofibers from two commercial hardwood and softwood pulps. *Industrial and Engineering Chemical Research*, 48 (24):11211–11219 (2009).
- [66] Hearle, J W S and Sparrow, J T Mechanics of the extension of cotton fibers. I. Experimental studies of the effect of convolutions. *Journal of Applied Polymer Science*, 24 (6): 1465-1477 (1979).
- [67] Silva, R V and Aquino, E M F Curaua Fiber: a new alternative to polymeric composites *Journal of Reinforced Plastics and Composites*, 27(1): 103-112 (2008).
- [68] Santos, P A, Spinacé, M A S, Fermoselli, K K G, De Paoli, M.-A Polyamide-6/vegetable fiber composite prepared by extrusion and injection molding. *Composites Part A: Applied Science and Manufacturing* , 38 (12): 2404–2411 (2007).
- [69] Bismark, A, Mishra, S, Lampke,, T. Plant Fibers as reinforcement for green composites. In: *Natural fibers, biopolymers and biocomposites*, Chapter 2, 37-108, A. K. Mohanty, M. Misra and L. T. Drzal (Eds) Taylor & Francis, CRC Press (2005).
- [70] Li, X, Tabil, L G, Panigrahi, A S Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review. *Journal of Polymer and the Environment*, 15 (1): 25–33 (2007).
- [71] Kalia, S, Kaith, B S, Kaur, I. Pretreatments of natural fibers and their application as reinforcing material in polymer composites—a review. *Polymer Engineering & Science*, 49 (7): 1253–1272 (2009).
- [72] Ma, H and Joo, C W Influence of surface treatments on structural and mechanical properties of bamboo fiber-reinforced poly(lactic acid) biocomposites. *Journal of Composite Materials*, 45(23): 2455-2463 (2011).
- [73] Franco, P J H, Valadez-González, A Fiber-matrix adhesion in natural fiber composites In: *Natural fibers, biopolymers and biocomposites*, Chapter 6, 177-230, A. K. Mohanty, M. Misra and L. T. Drzal (Eds) Taylor & Francis, CRC Press (2005).
- [74] Singha, A S and Rana, A K Effect of silane treatment on physicochemical properties of lignocellulosic *C. indica* fiber *Journal of Applied Polymer Science*, 124(3): 2473–2484 (2012).
- [75] Campos, A, Marconcini, J M, Martins-Franchetti, S M, Mattoso, L H C The influence of UV-C irradiation on the properties of thermoplastic starch and polycaprolactone biocomposite with sisal bleached fibers. *Polymer Degradation and Stability*, 97 (10): 1948-1955 (2012).
- [76] Stocchi, A, Bernal, C, Vazquez, A, Biagotti, J, Kenny, J A silicone treatment compared to traditional natural fiber treatments: effect on the mechanical and viscoelastic prop-

- erties of jute–vinylester laminates. *Journal of Composite Materials*, 41 (16): 2005-2024 (2007).
- [77] Moraes, A G O, Sierakowski, M R, Amico, S C The novel use of sodium borohydride as a protective agent for the chemical treatment of vegetable fibers *Fibers and Polymers*. 13 (5): 641-646 (2012) DOI: 10.1007/s12221-012-0641-7.
- [78] Mukherjee, A, Ganguly P K, Sur, D J Structural mechanics of jute: the effects of hemi-cellulose or lignin removal. *Journal of the Textile Institute*. 84 (3):348-353 (1993).
- [79] Rong, M Z, Zhang, M Q, Liu, Y., Yang, G C, Zeng, H M The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. *Composites Science and Technology*, 61 (10): 1437–1447 (2001).
- [80] Kim, H-S, Lee, B-H, Choi, S-W, Kim, S, Kim, H-J The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled polypropylene composites. *Composites: Part A*, 38 (6): 1473–1482 (2007).
- [81] Chang, S Y, Ismail, H, Ashan, Q Effect of maleic anhydride on kenaf dust filled polycaprolactone/ thermoplastic sago starch composites. *Bioresources*, 7(2):1594-1616 (2012).
- [82] Xie, Y, Hill, C A S, Xiao, Z, Militz, H, Carsten, M Silane coupling agents used for natural fiber/polymer composites: A review. *Composites: Part A* 41(7): 806–819 (2010),.
- [83] Huda, M S, Drzal, L T, Mohanty, A K, Misra, M Effect of fiber surface-treatments on the properties of laminated biocomposites from poly(lactic acid) (PLA) and kenaf fibers. *Composites Science and Technology* 68 (2): 424–432 (2008)..
- [84] Chen, D, Li, J, Ren, J Influence of fiber surface-treatment on interfacial property of poly(l-lactic acid)/ramie fabric biocomposites under UV-irradiation hydrothermal aging. *Materials Chemistry and Physics*, 126 (3): 524–531 (2011).
- [85] Jayamol, G, Sreekala, M S, Thomas, S A review on interface modification and characterization of natural fiber reinforced plastic composites. *Polymer Engineering & Science* 41 (9): 1471–1485 (2001)..
- [86] Yu, L, Dean, K, Li, L Polymer blends and composites from renewable resources. *Progress in Polymer Science* 31(6): 576–602 (2006).
- [87] Avérous, L Biocomposites based on biodegradable thermoplastic polyester and lignocellulose fibers In: *Cellulose Fibers: Bio- and Nano-Polymer Composites: Green Chemistry and Technology*. Chapter 17,453- 478, Susheel Kalia, B. S. Kaith, Inderjeet Kaur(Eds), Springer, Heidelberg (2011).
- [88] Harnnecker, F, Rosa, D S, Lenz, D M Biodegradable Polyester-Based Blend Reinforced with Curaua Fiber: Thermal, Mechanical and Biodegradation Behaviour *Journal of Polymers and the Environment*, 20(1): 237-244 (2012).
- [89] Eichhorn, S J, Dufresne, A, Aranguren, M, Marcovich, N E, Capadona, J R, Rowan, S J, Weder, C, Thielemans, W, Roman, M, Rennecker, S, Gindl, W, Veigel, S, Keckes, J,

- Yano, H, Abe, K, Nogi, M, Nakagaito, A N, Mangalam, A, Simonsen, J, Benight, A S, Bismarck, A, Berglund, L A, Peijs, T Review: current international research into cellulose nanofibres and nanocomposites *Journal of Materials Science*, 45(1):1–33 (2010).
- [90] Szczesna-Antczak, M, Kazimierczak, J, Antczak, T Nanotechnology - Methods of Manufacturing Cellulose Nanofibres. *Fibers & Textiles in Eastern Europe*, 20, 2(91): 8-12 (2012).
- [91] Iguchi, M, Yamanaka S, Budhiono A Bacterial cellulose - a masterpiece of nature's arts. *Journal of Materials Science*, 35(2):261-270 (2000).
- [92] Rusli R., Shanmuganathan K., Rowan S. J., Weder C, Eichhorn S J. Stress Transfer in Cellulose Nanowhisker Composites - Influence of Whisker Aspect Ratio and Surface Charge. *Nature* 472: 334-337 (2011).
- [93] European Commission, Nanotechnology Research needs on nanoparticles. Proceedings of the workshop held in Brussels, 25-26.01.2005.
- [94] Halley, P J and Dorgan, J R Next-generation biopolymers: Advanced functionality and improved sustainability *MRS Bulletin*, 36: 687-691 (2011).
- [95] Masoodi, R, Hajjar, R E, Pillai, K M, Sabo, R Mechanical characterization of cellulose nanofiber and bio-based epoxy composite. *Materials and Design*, 36: 570-576 (2011).
- [96] Fortunati, E, Armentano, I, Zhou, Q, Iannoni, A, Saino, E, Visai, L, Berglund, L A, Kenny, J M Multifunctional bionanocomposite films of poly(lactic acid), cellulose nanocrystals and silver nanoparticles. *Carbohydrate Polymers*, 87(2): 1596–1605 (2012).
- [97] Cherian, B M, Leão, A L, de Souza, S F, Costa, L M M, Olyveira, G M, Kottaisamy, M, Nagarajan, E R, Thomas, S Cellulose nanocomposites with nanofibers isolated from pineapple leaf fibers for medical applications *Carbohydrate Polymers*, 86(4): 1790–1798 (2011).
- [98] Souza Lima, M M and Borsali, R. Rodlike Cellulose Microcrystals: Structure, Properties, and Applications. *Macromolecular Rapid Communications*, 25 (7): 771-787 (2004).
- [99] Habibi, Y, Lucia, L A, Rojas, O J Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications *Chemical Reviews*, 110: 3479–3500 (2010).
- [100] George, J, Ramana, K V, Bawa, A S and Siddaramaiah. Bacterial cellulose nanocrystals exhibiting high thermal stability and their polymer nanocomposites. *International Journal of Biological Macromolecules*, 48(1): 50-57 (2011).
- [101] Jonoobi, M, Harun, J, Mathew, A P, Oksman, K Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion, *Composites Science and Technology*, 70(12): 1742-1747 (2010).

- [102] Siró, I and Plackett, D Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose*, 17 (3): 459–494 (2010).
- [103] Oksman, K, Mathew, A P, Sain, M Novel bionanocomposites: processing, properties and potential applications. *Plastics, Rubber and Composites*, 38(9-10): 396-405 (2009).
- [104] Das, K, Ray, D, Banerjee, C, Bandyopadhyay, N R, Sahoo, S, Mohanty, A K, Misra, M Physicomechanical and Thermal Properties of Jute-Nanofiber-Reinforced Biopolyester Composites. *Industrial & Engineering Chemical Research*, 49(6): 2775–2782 (2010).
- [105] Wang, T and Drzal, L T Cellulose-nanofiber-reinforced poly(lactic acid) composites prepared by a water-based approach. *Applied Materials & Interfaces*, 4(10): 5079–5085 (2012).
- [106] Okubo, K, Fujii, T, Thostenson, E T Multi-scale hybrid biocomposite: processing and mechanical characterization of bamboo fiber reinforced PLA with microfibrillated cellulose *Composites Part A*, 40(4): 469-475 (2009).
- [107] Cherian, B M, Leão, A L, de Souza, S F, Thomas, S, Pothan, L A, Kottaisamy, M Isolation of nanocellulose from pineapple leaf fibers by steam explosion. *Carbohydrate Polymers*, 81(3): 720–725, (2010).
- [108] Blaker, J J, Lee, K-Y, Bismarck, A. Hierarchical Composites Made Entirely from Renewable Resources *Journal of Biobased. Materials and Bioenergy*, 5(1): 1-16 (2011).
- [109] Sorrentino, A, Gorrasi, G, Vittoria, V Potential Perspectives of Bio-Nanocomposites for Food Packaging Applications, *Trends in Food Science & Technology*, 18(2): 84-95 (2007).
- [110] Chrissafis, K and Bikiaris, D Can nanoparticles really enhance thermal stability of polymers? Part I: An overview on thermal decomposition of addition polymers. *Thermochimica Acta*, 523(1): 1–24 (2011).
- [111] Choy, J H, Choi, S J, Oh, J M, Park, T Clay minerals and layered double hydroxides for novel biological applications. *Applied Clay Science*, 35(1-3): 122-132 (2007).
- [112] Liu, Z and Erhan, S Z “Green” composites and nanocomposites from soybean oil. *Materials Science and Engineering A*, 483–484: 708–711 (2008).
- [113] Annabi-Bergaya, F Layered clay minerals. Basic research and innovative composite applications. *Microporous and Mesoporous Materials*, 107(1-2): 141–148 (2008).
- [114] Fu, H-K, Huang. C-F, Huang, J-M, Chang, F-C Studies on thermal properties of PS nanocomposites for the effect of intercalated agent with side groups. *Polymer*, 49(5): 1305-1311 (2008).
- [115] Rodriguez, F, Sepulveda, H M, Bruna, J, Guarda, A, Galotto, M J Development of Cellulose Eco-nanocomposites with Antimicrobial Properties Oriented for Food

- Packaging. *Packaging Technology and Science*, 2012 DOI: 10.1002/pts.1980. <http://onlinelibrary.wiley.com/doi/10.1002/pts.1980/full> (accessed 20 July 2012).
- [116] Arora, A and Padua, G W Review: Nanocomposites in Food Packaging *Journal of Food Science*, 75(1): R43–R49 (2010).
- [117] Rajkiran, R, Tiwari, K C, Khilar, U N Synthesis and characterization of novel organo-montmorillonites. *Applied Clay Science*, 38(3–4): 203–208 (2008).
- [118] Kim, J-T, Lee, D-Y, Oh, T-S, Lee, D-H Characteristics of nitrile–butadiene rubber layered silicate nanocomposites with silane coupling agent *Journal of Applied Polymer Science*, 89(10): 2633–2640 (2003).
- [119] Panagiotis, I, Xidas, K, Triantafyllidis, S Effect of the type of alkylammonium ion clay modifier on the structure and thermal/mechanical properties of glassy and rubbery epoxy–clay nanocomposites *European Polymer Journal*, 46(3): 404–417 (2010).
- [120] Piscitelli, F, Scamardella, A M, Valentina, R, Lavorgna, M, Barra, G, Amendola, E Epoxy composites based on amino-silylated MMT: The role of interfaces and clay morphology *Journal of Applied Polymer Science*, 124(1): 616–628 (2012).
- [121] Tjong, S C Structural and mechanical properties of polymer nanocomposites, *Materials Science and Engineering: R: Reports*, 53(3–4): 73–197 (2006).
- [122] Bordes, P, Pollet, E, Avérous, L Nano-biocomposites: Biodegradable polyester/nanoclay systems *Progress in Polymer Science*, 34(2): 125–155 (2009)
- [123] Kumar, K A A, Sreekala, M S, Arun, S Studies on Properties of Bio-Composites from Ecoflex/Ramie Fabric-Mechanical and Barrier Properties *Journal of Biomaterials and Nanobiotechnology*, 3: 396-404 (2012).
- [124] Sawpan, M A, Pickering, K L, Fernyhough, A Improvement of mechanical performance of industrial hemp fiber reinforced polylactide biocomposites. *Composites Part A: Applied Science and Manufacturing*, 42(3): 310-319 (2011).
- [125] Bledzki, A K, Jaszkiwicz, A Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibres – A comparative study to PP. *Composites Science and Technology*, 70 (12): 1687–1696 (2010).
- [126] Huda, M S, Drzal, L T, Mohanty, A K, Misra, M. Chopped glass and recycled newspaper as reinforcement fibers in injection molded poly(lactic acid) (PLA) composites: A comparative study. *Composites Science and Technology*, 66 (11–12): 1813–1824 (2006).
- [127] Bajpai, P K, Singh, I, Madaan, J Development and characterization of PLA-based green composites: A review. *Journal of Thermoplastic Composite Materials* 2012, 1–30, DOI: 10.1177/0892705712439571, <http://jtc.sagepub.com/content/early/2012/03/21/0892705712439571.full.pdf+html> (accessed 10 August 2012).
- [128] Bledzki, A K, Jaszkiwicz, A, Murr, M, Sperber, V E, Lützkendorf, R, Reußmann, T Processing techniques for natural and wood–fibre composites. In: *Properties and per-*

formance of natural-fiber composites. Chapter 4, 163–92, Pickering KL (Ed) Cambridge, UK: Woodhead Publishing (2008).

- [129] Choi, H-Y and Lee, J- S Effects of surface treatment of ramie fibers in a ramie/poly(lactic acid) composite. *Fibers and Polymers*, 13(2): 217-223 (2012).
- [130] Graupner, N, Herrmann, A S, Müssig, J Natural and man-made cellulose fibre-reinforced poly(lactic acid) (PLA) composites: An overview about mechanical characteristics and application areas. *Composites: Part A*, 40(6-7): 810–821 (2009).
- [131] Oksman, K, Skrifvars, M, Selin, J F. Natural fibres as reinforcement in polylactic acid (PLA) composites. *Composites Science and Technology*, 63(9):1317–24 (2003).
- [132] Avella, M, Bogoeva-Gaceva, G, Buzarovska, A, Errico, M E, Gentile, G, Grozdanov, A. Poly(lactic acid)-based biocomposites reinforced with Kenaf fibers. *Journal of Applied Polymer Science*, 108(6): 3542–3551 (2008).
- [133] Bax, B and Mussig, J. Impact and tensile properties of PLA/cordenka and PLA/flax composites. *Composites Science and Technology*, 68(7-8): 1601–1607 (2008).
- [134] Nakamura, R, Goda, K, Noda, J, Ohgi, J High temperature tensile properties and deep drawing of fully green composites. *Express Polymer Letters*; 3(1): 19–24 (2009).
- [135] Matkó Sz., Toldy, A, Keszei, S, Anna, P, Bertalan, Gy, Marosi, Gy. Flame retardancy of biodegradable polymers and bio-composites. *Polymer Degradation and Stability*, 88(1): 138–145 (2005).
- [136] Bourbigot, S, Fontaine, G, Duquesne, S, Delobe, R. PLA nanocomposites: quantification of clay nanodispersion and reaction to fire. *International Journal of Nanotechnology*, 5(6-8): 683-692 (2008).
- [137] Shumao, L, Jie, R, Hua, Y, Tao, Y, Weizhong, Y. Influence of ammonium polyphosphate on the flame retardancy and mechanical properties of ramie fiber-reinforced poly(lactic acid) biocomposites *Polymer International*, 59(2): 242–248 (2010).
- [138] Jangm, J Y, Jeong, T K , Oh, H J, Youn, J R, Song, Y S. Thermal stability and flammability of coconut fiber reinforced poly(lactic acid) composites. *Composites Part B: Engineering* , 43(5): 2434–2438 (2012).
- [139] Jiménez, A and Ruseckaite, R A. Nano-Biocomposites for Food Packaging In: *Environmental Silicate Nano-Biocomposites Green Energy and Technology*, Chapter 15, 393-408, L. Avérous and E. Pollet (Eds) Springer-Verlag, London (2012).
- [140] Sanchez-Garcia, M D and Lagaron, J M. On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. *Cellulose*, 17(5): 987-1004 (2010).
- [141] Sanchez-Garcia, M D and Lagaron, J M Novel clay-based nanobiocomposites of biopolyesters with synergistic barrier to UV light, gas and vapour. *Journal of Applied Polymer Science*, 118(1): 188-199 (2010).

- [142] Petersson, L and Oksman, K. Biopolymer based nanocomposites: Comparing layered silicates and microcrystalline cellulose as nanoreinforcement. *Composites Science and Technology*, 66 (13): 2187-2196 (2006).
- [143] Lasprilla, A J R, Martinez, G A R, Lunelli, B H, Jardini, A L, Maciel Filho, R. Polylactic acid synthesis for application in biomedical devices - A review. *Biotechnology Advances*, 30(1): 321-328 (2012).
- [144] Chen, L, Yang, J, Wang, K, Chen, F, Fu, Q. Largely improved tensile extensibility of poly(L-lactic acid) by adding poly ( $\epsilon$ -caprolactone). *Polymer International*, 59(8): 1154-1161 (2010).
- [145] Walker, P A, Aroom, K R, Jimenez, F, Shah, S K, Harting, M T, Gill, B S, Cox Jr, C S. Advances in progenitor cell therapy using scaffolding constructs for central nervous system injury *Stem Cell Reviews and Reports*, 5(3): 283-300 (2009).
- [146] Zhou, W Y, Lee, S H, Wang, M, Cheung, W L, Ip, W Y. Selective laser sintering of porous tissue engineering scaffolds from poly (L-lactide)/carbonated hydroxyapatite nanocomposite microspheres *Journal of Materials Science-Materials in Medicine*, 19: 2535-2540 (2008).
- [147] Hong, Z K, Qiu, XY, Sun, J R, Deng, M X, Chen, X S, Jing, X B. Grafting polymerization of l-lactide on the surface of hydroxyapatite nano-crystals. *Polymer*, 45(19): 6699-6706 (2004).
- [148] Ray, S S and Okamoto, M. Biodegradable Polylactide and Its Nanocomposites: Opening a new dimension for plastics and composites. *Macromolecular Rapid Communications*, 24(14): 815-840 (2003).
- [149] Paul, M-A, Delcourt, C, Alexandre, M, Degée, Ph., Monteverde, F, Dubois, Ph. Polylactide/montmorillonite nanocomposites: study of the hydrolytic degradation *Polymer Degradation and Stability*, 87(3): 535-542 (2005).
- [150] Kumar, R, Yakubu, M K, Anandjiwala, R D. Biodegradation of flax fiber reinforced poly lactic acid. *Polymer Letters*, 4(7): 423-430 (2010).
- [151] Iovino, R, Zullo, R, Rao, M A, Cassar, L, Gianfreda, L. Biodegradation of poly(lactic acid)/starch/coir biocomposites under controlled composting conditions. *Polymer Degradation and Stability*, 93(1): 147-157 (2008).
- [152] Jandas, P J, Mohanty, S, Nayak, S K, Srivastava, H. Effect of surface treatments of banana fiber on mechanical, thermal, and biodegradability properties of PLA/banana fiber biocomposites. *Polymer Composites*, 32(11): 1689-1700 (2011).
- [153] Jandas, P J, Mohanty S, Nayak S K. Renewable Resource-Based Biocomposites of various surface treated banana fiber and poly lactic acid: Characterization and Biodegradability. *Journal of Polymers and the Environment*, 20(2): 583-595 (2012).

- [154] Singh, S, Mohanty, A K, Sugie, T, Takai, Y, Hamada, H. Renewable resource based biocomposites from natural fiber and polyhydroxybutyrate-co-valerate (PHBV) bioplastic. *Composites: Part A*, 39(5): 875–886 (2008).
- [155] Jiang, L, Huang, J, Qian, J, Chen, F, Zhang, J, Wolcott, M P, Zhu, Y. Study of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/bamboo pulp fiber composites: Effects of nucleation agent and compatibilizer. *Journal of Polymers and the Environment*, 16(2): 83-93 (2008).
- [156] Nagarajan, V, Misra, M, Mohanty, A K New engineered biocomposites from poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/poly(butylene adipate-co-terephthalate) (PBAT) blends and switchgrass: Fabrication and performance evaluation. *Industrial Crops and Products*, 42: 461–468 (2013)
- [157] Ahankari, S S, Mohanty, A K, Misra, M. Mechanical behaviour of agro-residue reinforced poly(3-hydroxybutyrate-co-3-hydroxyvalerate), (PHBV) green composites: A comparison with traditional polypropylene composites. *Composites Science and Technology*, 71(5): 653–657 (2011).
- [158] Yu, H-Y, Qin, Z-Y, Liu, Y-N, Chen, L, Liu, N, Zhou, Z. Simultaneous improvement of mechanical properties and thermal stability of bacterial polyester by cellulose nanocrystals *Carbohydrate Polymers*, 89(3): 971–978 (2012).
- [159] Ten, E, Bahr, D F, Li, B, Jiang, L, Wolcott, M P. Effects of Cellulose Nanowhiskers on mechanical, dielectric and rheological properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhisiker. *Composites Industrial & Engineering Chemical Research*, 51 (7): 2941–2951 (2012).
- [160] Sanchez-Garcia, M D, Lopez-Rubio, A, Lagaron, J M. Natural micro and nanobiocomposites with enhanced barrier properties and novel functionalities for food biopackaging applications. *Trends in Food Science & Technology*, 21(11): 528-536 (2010).
- [161] Chen, G X, Hao, G J, Guo, T Y, Song, M D, Zhang, B H. Structure and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/clay nanocomposites. *Journal of Materials Science Letters*, 21(20):1587–1589 (2002).
- [162] Nguyen L. T. H., Chen S., Elumalai N. K., Prabhakaran M. P., Zong Y., Vijila C., Al-lakhverdiev S. I., Ramakrishna S. Biological, chemical, and electronic applications of nanofibers. *Macromolecular Materials and Engineering*, 297(11): 1035–1123 (2012).
- [163] Hazer, D B, Kılıçay, E, Hazer, B. Poly(3-hydroxyalkanoate)s: Diversification and biomedical applications. A state of the art review. *Materials Science and Engineering C*, 32(4): 637–647 (2012).
- [164] Cool, S M, Kenny, B, Wu, A, Nurcombe V., Trau M., Cassady A. I., Grøndahl L. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) composite biomaterials for bone tissue regeneration: In vitro performance assessed by osteoblast proliferation, osteoclast

adhesion and resorption and macrophage proinflammatory response. *Journal of Biomedical Materials Research Part A*, 82: 599-610 (2007).

- [165] Batista, K C, Silva, D A K, Coelho, L A F, Pezzin, S H, Pezzin, A P T. Soil biodegradation of PHBV/peach palm particles biocomposites *Journal of Polymers and the Environment*, 18(3): 346-354 (2010).
- [166] Petersson, S, Jayaraman, K, Bhattacharyya, D. Forming performance and biodegradability of wood-fibre Biopol™ composites. *Composites Part A*, 33: 1123-1134 (2002).
- [167] Avella, M, La Rota, G, Martuscelli, E, Raimo, M, Sadocco, P, Elegir, G, Riva, R. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and wheat straw fibre composites: thermal, mechanical properties and biodegradation behaviour. *Journal of Materials Science*, 35(4): 829-836 (2000).

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