7

BIOPLASTICS FROM AGRO-WASTES FOR FOOD PACKAGING APPLICATIONS

Isabel Gonçalves de Moura, Arsénio Vasconcelos de Sá, Ana Sofia Lemos Machado Abreu, Ana Vera Alves Machado

University of Minho, Institute of Polymers and Composites (IPC) and Institute of Nanostructures, Nanomodelling, and Nanofabrication, Guimarães, Portugal

1 Introduction

For many years, synthetic plastic materials produced from petrochemicals, have been used in a variety of applications in everyday life, such as, in packaging, automotive and health-care applications, and communication and electronic industries (Ohtake et al., 1998). They became essential due to their versatility, aesthetic qualities, durability, and low cost (Bayer et al., 2014). However, due to their excessive use, several drawbacks, such as, its resistance to decomposition, toxicity after incineration, and accumulation in the environment, induce negative ecological impact in landfills and water contamination. Moreover, the growing ecological responsiveness together with the novel environmental laws, are pushing the industries to search for more ecofriendly materials, specifically for food packaging, where the material has a very short lifetime (Ohtake et al., 1998; Scott, 2000).

Thus, minimizing their unfavorable ecological impact became a challenge. A possible solution to solve this problem could be to replace commodity-synthetic polymers by biodegradable ones, with good performance. The latter, after usage, would be prone to degradation and digestion by microorganisms, which would minimize their unfavorable ecological impact (Mohanty et al., 2000; Scott, 2000).

Simultaneously, the high amount of agro-wastes generated by the food industry has been a growing concern, which around 1.3 billion tons left-over, which becomes an environmental and financial issue (Bayer et al., 2014). Among these agro-wastes,

Food Packaging. http://dx.doi.org/10.1016/B978-0-12-804302-8.00007-8

food waste stands out, halum, and stems of vegetables/fruits, grains and seeds, from which it is possible to obtain natural polymers (Shah et al., 2008).

Thus, in this chapter the discussion is on how to directly extract natural polymers, namely cellulose, from vegetable agro-wastes by applying green chemistry methodology, and its modification in order to develop new biopolymers with potential application in food packaging.

2 Synthetic Plastics

During the past decades, petroleum-based synthetic polymers, commonly known as plastics, have gradually expanded and become one of the most appealing types of materials. The worldwide production is estimated to be around 140 million tons per year (Shah et al., 2008). This achievement is mostly associated with their properties, such as, low price, good processability, low density, good aesthetic qualities, and resistance to degradation.

The most widely-used plastics are polyethylene (PE, 29%), polypropylene (PP, 19%), polyvinyl chloride (PVC, 13%), polystyrene (PS, 7%), poly(ethylene terephthalate) (PET, 7%), polyurethane (PUR, 6%), and others (Fig. 7.1).

Polyolefins are the synthetic polymers with the highest commercial success, accounting for more than 47% of Western Europe's total consumption, 24.1 million tons per year. They present a combination of physical properties (flexibility, strength, lightness, stability, and impermeability) that are ideally suited to a wide variety of applications, such as food packaging (Simon et al., 1996).

Owing to the growing increase in the production of commodity plastics, as well as, the deposition rate in the past two decades of the 20th century, they are currently the most common and persistent pollutants worldwide. Once such material became part of the natural ecosystem, the negative effect of it is a long-lasting contribution to environmental contamination is depicted in Fig. 7.2 (Shah et al., 2008; Thompson et al., 2009). The growing ecological responsiveness, together with the new environmental laws, are pushing the industries to search for more ecofriendly plastics, specifically in applications where they have a very short lifetime (Moura et al., 2011).

Under natural conditions, the degradation of synthetic plastics is a very slow process that involves environmental factors, followed by the action of wild microorganisms (Albertsson et al., 1994; Cruz-Pinto et al., 1994). This has raised growing concern about the development of biodegradable polymers,

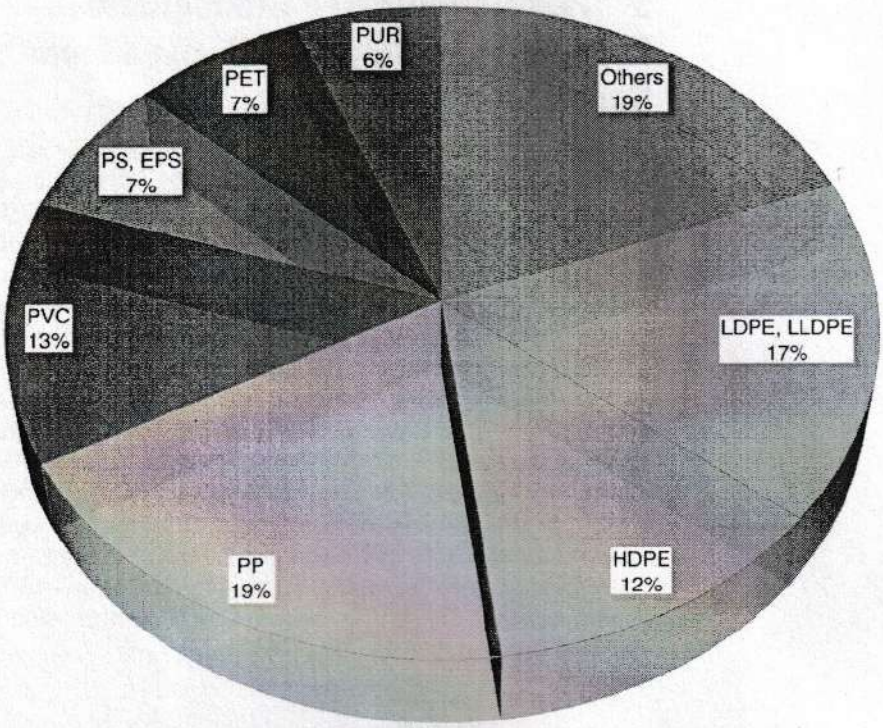


Figure 7.1. Global plastics market consumption.

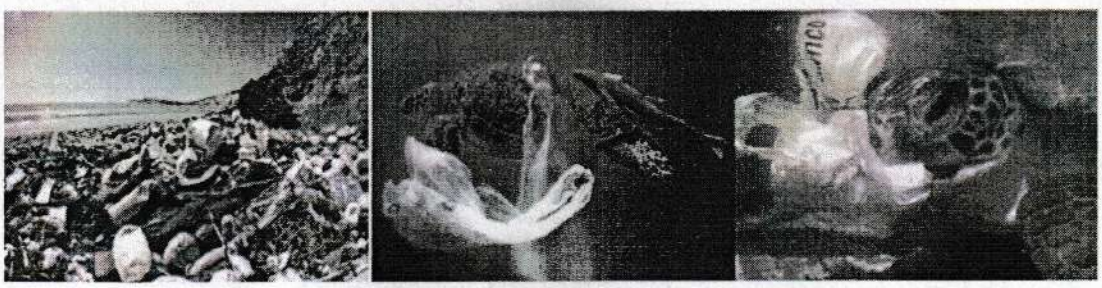


Figure 7.2. The negative impact of plastics waste disposal.

promoting research activity worldwide to either modify current products, in order to induce degradability, or to develop new alternatives that are biodegradable after use. The use of these materials, in applications with a short-life cycle, namely food packaging would be an ecological alternative to reduce the solid-plastic waste (Albertsson et al., 1994).

3 Petroleum-Based Biodegradable Polymers and Polymers Derived From Renewable Resources

Limited resources of petroleum-based polymers and increased environmental awareness on sustainability, has attracted a higher interest toward biodegradable polymers from renewable resources, for industrial application (Nabar et al., 2005). The use of these materials is an alternative to conventional nonbiodegradable plastics, which could be a more friendly solution for the environmental problem, induced by plastics wastes (Tserki et al., 2006).

The research and consumption of biodegradable polymers that are derived from renewable resources has increased in the past decades. The target market is mainly food packaging materials, hygiene products, and agricultural tools. Nevertheless, it is still a competition between commodity plastics and biodegradable ones, due the low cost of the former, functional properties, and processability (Gross and Kalra, 2002; Sudesh and Iwata, 2008).

Bioplastics can be made of biodegradable petroleum-based polymers, 100% renewable material, or a combination of renewable and fossil materials (Fig. 7.3).

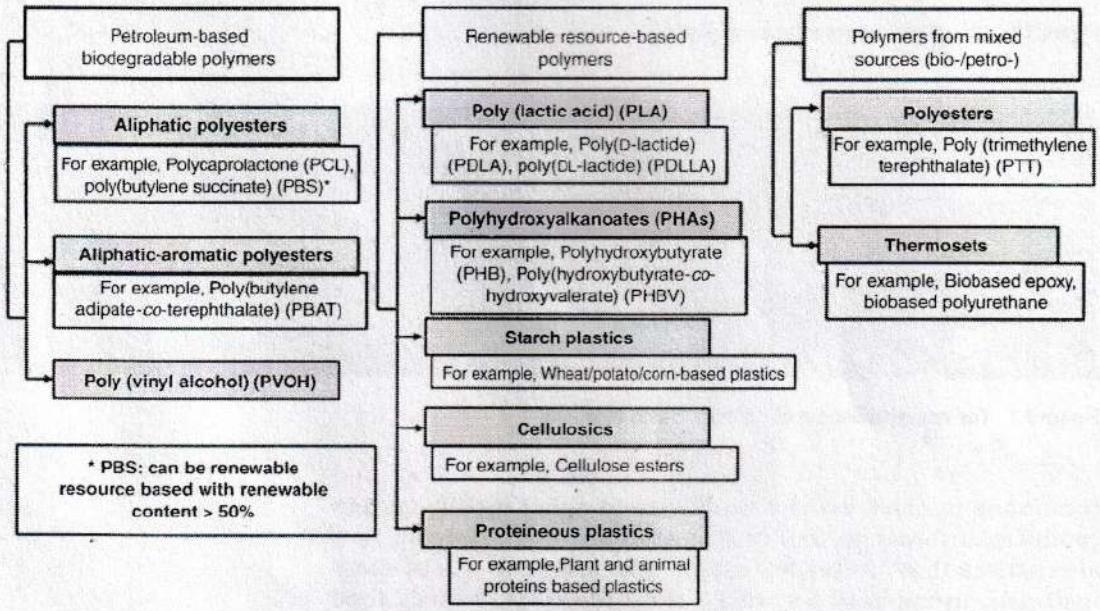


Figure 7.3. Resources of biodegradable polymers. From Reddy et al. (2013).

According to Reddy et al. (2012) biodegradable polymers can be divided as follows:

1. *Petroleum-based biodegradable polymers*: They are synthesized from petroleum resources that are biodegradable at the end of their functionality. Poly(ε-caprolactone) (PCL) and poly(butylene adipate-*co*-terephthalate) (PBAT) are some examples.
2. *Bioplastics from mixed sources (bio-/petro-)*: These biodegradable materials are developed from a combination of biobased and petroleum monomers; they include polymers as poly(trimethylene terephthalate) (PTT), biothermosets, and biobased blends.
3. *Renewable resource-based polymers*: These biopolymers are either synthesized naturally from plants and animals, or from renewable resources. Some of the most significant examples are polylactic acid (PLA), cellulose, starch, chitosan, lignin, and proteins.

This chapter focuses on bioplastics from renewable resources and their application in the food packaging industry. The current status of production and application of the renewable resource-based bioplastics, specifically PLA, starch, and cellulose (Table 7.1) and the new trends in obtaining biopolymers directly from agro-wastes, such as cellulose, using a green chemistry methodology.

3.1 Polyethylene-Based Polymers

Synthetic polymers similar to polyolefins are resistant to biodegradation by the action of microorganisms and have a long lifetime (Sastry et al., 1998). In its original form, PE does not degrade, which is related to the high molecular weight and also to the high hydrophobic character. Thus, the use of conventional PE in food packaging has a negative environmental impact. However, research studies concerning polyolefins' biodegradation have demonstrated that these polymers have short carbon chains and can be used by the microorganisms as a carbon source, which, therefore, makes them biodegradable (Yamada-Onodera et al., 2001). Accordingly, to turn PE biodegradable, it is essential to change its features, for instance, molecular weight and crystallinity level, which enhance the resistance to degradation. Studies related with the biodegradation of PE were carried out by Wang et al. (2004) and Bonhomme et al. (2003), and it was found that its degradation occurred in two distinct steps, hydrodegradation and oxo-biodegradation (Bonhomme et al., 2003). Other researchers also observed that the oxidation products of polyolefins are biodegradable (Smith, 2005). According to Albertsson et al. (1993), the biodegradation mechanism of PE occurs in different pathways. The first step is the oxidation process, in which the PE is oxidized,

Table 7.1 Current Applications of Plastics

Packaging Applications	Biopolymer
PLA	
Coffee and tea	Cardboard cups coated with PLA
Beverages	PLA cups
Fresh salads	PLA bowls
Carbonated water, fresh juices, and dairy drinks	PLA bottles
Freshly cut fruits, whole fruit vegetables, bakery goods, and salads	Rigid PLA trays and packs
Organic pretzels and potato chips	PLA bags
Yogurt	PLA jars
Frozen fries	PLA films (Bio-Flex)
Organic fruit and vegetables	PLA packaging
Pasta	PLA packaging
Herbs	PLA packaging
Prepared sandwiches and pasta salads	PLA bowls, packaging
Bread	Paper bags with PLA window
Organic poultry	PLA bowls and absorb pads
Starch-based	
Milk chocolates	Corn-starch trays
Organic tomatoes	Corn-based packaging
Cellulose	
Kiwi	Biobased trays wrapped with cellulose film
Potato chips	Metalized cellulose film
Organic pasta	Cellulose-based packaging
Sweets	Metalized cellulose film

From Peelman et al. (2013).

resulting in the formation of hydroxyl (—OH), carbonyl (—C=O), and carboxylic acid groups (—COOH), which leads to the decrease of the polymer chain molecular weight, followed by the biodegradation due the microbial action. The oxidation process plays a crucial role in the reduction of PE's molecular weight and consequently, the formation of compounds with reduced size, which can be subsequently be assimilated by the microorganisms. It has been shown that PE molecular fragments are easily degraded. Another

approach to increase the polyolefin biodegradation consists in blending them with native biodegradable polymers, such as, starch or even with other synthetic biodegradable polyesters like PLA, PCL, and poly(glycolic acid) (PGA). Iwamoto et al. (1994) evaluated the biodegradation of blends of low-density polyethylene (LDPE) and PCL and concluded that when samples are submitted to an enzymatic degradation they suffer a significant weight loss. Machado et al. (2007) evaluated the biodeterioration of high-density polyethylene (HDPE) blended with biodegradable polyesters, like Mater-Bi (thermoplastic starch with PLA or PCL), that is processed in a corotating twinscrew extruder. In a previous study, Albertsson et al. (1993) showed that starch, when blended with LDPE matrix, produces a material with higher susceptibility to biodegradation when compared with neat LDPE. Another alternative to the synthesized biodegradable PE consists is the graft copolymerization of a biodegradable polymer. Many research works reported the preparation of several grafted-polyethylene copolymers by chemical modification of natural polymers (eg, starch) for numerous potential applications, including food packaging. Maharana and Singh (2006) studied the graft copolymerization of starch onto LDPE, using an initiator. The soil-burial tests of PE-*g*-starch showed that by grafting, starch moieties onto synthetic PE, it is possible to enhance the percentage of biodegradation, which is correlated with the graft yield. Another study, carried out by Gautam (2010), reported the biodegradation of graft copolymers based on starch and PE. The biodegradability tests performed by soil-burial tests showed a growth in the number of microorganisms. Additionally, the products resulting from the biodegraded sample hydrolyze faster. Kaur et al. (2008) described the modification of polyethylene by the formation of graft copolymers based on gelatin (PE-*g*-gelatin). The biodegradation of these samples was monitored by soil-burial assays, by determining their weight loss. According to the analysis, it was observed that a growth in the number of microorganisms on the grafted material, as well as, an increase in the percentage weight loss occurs. Thus, the rational design of biodegradable polyolefins with the required features for a specific application, and with the capacity of being degradable/biodegradable after use, has been the subject of many works searching for valid alternatives to conventional nondegradable plastics.

3.2 Poly(ε-Caprolactone)

PCL is a biodegradable polyester, obtained from the ring-opening polymerization (ROP) of the corresponding monomer, ε-caprolactone (ε-CL). This thermoplastic is quite flexible, having low viscosity and a melting point around 58–60°C, presenting

good chemical resistance, and being easily processable (Calil et al., 2006). Nevertheless, it presents some disadvantages associated with the low mechanical performance and high price. Thus, it is necessary to blend it with other polymers to get biodegradable materials at lower cost for some applications. Many studies have been carried out to develop fully biodegradable polymer blends containing PCL (Koenig and Huang, 1995; Pranamuda et al., 1996). The research findings demonstrated that the mechanical performance of the resulting blends (PCL/starch) became poorer with increasing amount of starch. The results are attributed to the poor compatibility between both components, due to their distinct hydrophilic character, since PCL is hydrophobic and starch hydrophilic. Yang et al. (2001) prepared biodegradable composites based on PCL and chitosan by melt mixing. It was shown that increasing the amount of chitosan did not affect the melting temperature, which is explained by the immiscibility of the components. Other studies using PCL and biodegradable thermoplastic starch were performed in order to adjust the rheological behavior of the melt (Matzinos et al., 2002). They used several starch grades produced by Novamont and verified that the degradation of PCL was faster for higher starch content. Besides that, the mechanical behavior of PCL/starch blends was also evaluated. The increase in the amount of modified starch, induces a decrease in the elongation at break and tensile strength and an increase in the Young's modulus compared to neat PCL (Yavuz and Babaç, 2003). One approach to enhance the mechanical performance of PCL/starch blends is by using synthetic polymers, such as LDPE. Also, Bastioli et al. (1995) showed that the biodegradation of PCL can be significantly accelerated by the presence of starch.

Nevertheless, by simple bending PCL with other biodegradable polymers fails in several applications, owing to the incompatibility between the components. Thus, one possible way to overcome this issue is by the use of a compatibilizer, which induces an enhancement of the interfacial adhesion between both components. Choi et al. (1999), prepared PCL and starch blends using starch-*g*-PCL graft copolymer as compatibilizer. The mechanical performance of the resulting blends correlated with the effect of the compatibilizer addition. According to the reported results, it was observed that the starch-*g*-PCL graft copolymer induced a remarkable increase in the elongation and toughness.

3.3 Poly(Butylene Adipate-*co*-Terephthalate)

PBAT is a commercially well-known biodegradable copolymer, which is obtained by polycondensation of adipic acid,

1,4-butanediol, and dimethylterephthalate along with a catalyzer, for example, tetrabutylorthotitanate (Jiang et al., 2009). This polymer shows good mechanical properties (high flexibility, elasticity, and elongation at break) and suitable thermal properties for concentration of terephtalic acid above 35%. It has resistance to wear and fracture, good hydrophilic- and processing properties. Nevertheless, the high cost associated with its production, as well as, the fragile Young's modulus, circumscribe the application of this polymer. For values higher than 55% of terephalic acid, its biodegradability decreases (Witt et al., 2001). Several biodegradable copolyesters resulting from the modification of PET with different content of terephtalic acid were prepared (Mohanty et al., 2000). Nevertheless, PBAT is a polymer whose production is dependent on petroleum-based materials and is associated with a high production cost, limiting its application in industry. Thus, the development of blends based on PBAT and other biodegradable polymers can impart the properties of the blend components to the final polymer. Among the biodegradable polyesters, PLA is a strong candidate to be blended with PBAT, because it is possible to reduce the overall cost and enhance the mechanical performance of the final PLA/PBAT blend (Shahlari and Lee, 2012). Shahlari and Lee (2012) blended PBAT and PLA and achieved good elongation at break, an enhanced Young's modulus, and reduced the overall cost of the produced material. Additionally, Zarrinbakhsh et al. (2013) added inexpensive biomass in poly(hydroxybutyrate-*co*-valerate) (PHBV)/PBAT to develop biodegradable composites with improved mechanical properties. Remarkably, the incorporation of some types of stearic, caproic, and lauric saturated fatty acids enhanced the degree of crystallinity of the biodegradable polymers prepared with PBAT, starch, and glycerol. Also, agar biopolymer has been used to get reinforced PBAT. The resulting biodegradable composites developed by injection molding and extrusion were characterized in terms of their thermal, physicochemical, and morphological properties. Another approach consisted in the preparation of PBAT-biodegradable nanocomposites by using organically modified silicates . The results showed that by the incorporation of the nanofiller, the thermal stability, and stiffness of PBAT increased, producing a more sustainable polymeric material (Someya et al., 2005).

3.4 Polylactic Acid

PLA is a biodegradable thermoplastic polyester produced both from fossil and renewable resources, that is nowadays one of the most promising polymers for commercially replacing LDPE,

HDPE, PET, and PS (Peelman et al., 2013). The production of PLA presents advantages over other synthetic materials: (1) PLA can be obtained from the processing of renewable agricultural sources, like corn, or other carbohydrate sources, into dextrose, followed by a fermentation step, into lactic acid (LA); (2) its production consumes CO_2, providing significant energy savings; and (3) PLA is recyclable and compostable (Drumright et al., 2000; Whiteman, 2000; Massardier-Nageotte et al., 2006).

Early economic studies have shown that PLA is an economically feasible material that can be used as a packaging material (Datta et al., 1995). PLA properties are determined by both the polymer architecture (stereochemical makeup of the backbone) and the molecular weight, the latter being controlled by the addition of hydroxylic compounds. PLA can exist as a racemic mixture, denominated as dl, or as two stereoisomers, designated as L and D. While the DL form is optically inactive, L and D forms are active. Both, poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA) are semicrystalline, whereas poly(DL-lactic acid) (PDLLA) is completely amorphous (Vasanthan and Ly, 2009). The control of the polymer stereochemical architecture allows a precise control over the crystallization rate, the crystallinity degree, mechanical properties, and processing temperature (Auras et al., 2004). PLA is a biodegradable polyester with one of the highest melting temperatures, around 160–190°C.

Bacterial fermentation is used to produce LA from corn or cane sugar. However, LA cannot be polymerized as a useful product, because during the polymerization reaction, water molecules are generated, and its presence degrades the formed polymer chain. Thus, PLA of high molecular weight is produced by ring-open polymerization of LA using a catalyst, by solvent-free continuous process, and distillation method (Shah et al., 2008). This mechanism does not generate additional water, and thus, a wide range of molecular weights is achievable.

PLA is currently used in industrial packaging and biomedical applications, because the processing possibilities of this transparent material are very wide, ranging from injection molding to blow molding and thermoforming (Nair and Laurencin, 2006; Siracusa et al., 2008).

For commercial applications, due to the cost and brittleness of PLA, it is essential to blend it with other biodegradable polymers, to improve several properties and reduce its cost. Thus, some research studies were carried out on binary polymeric systems. As an example, Nijenhuis et al. (1996) blended PLA with up to 50% of polyethylene oxide (PEO), which results in blends with a single glass transition temperature (T_g), suggesting a compatibility of

both components in the amorphous phase. Similarly, by blending PLA with polyvinyl alcohol (PVA) a single Tg was observed, which indicates that the PLA/PVA system is compatible (Gajria et al., 1996). Other experiments performed by Sheth et al. (1997) have shown that by blending PLA with polyethylene glycol (PEG) it is possible to obtain PLA/PEG-miscible blends, at a defined concentration of PEG. The biodegradability results, achieved from an enzymatic degradation, indicate significant decrease in the weight loss when compared with neat PLA. For a PEG content of 30%, a lower weight loss of the samples is essentially due to the enzymatic degradation of the PLA. However, for a content above 30% of PEG, the weight loss is mainly due to the PEG dissolution. A combination of both, degradation of PLA and PEG dissolution, occurs for PLA/PEG blends up to 30% of PEG. Zhang et al. (1995) also studied the miscibility of PLA and PCL blends. They observed that to a certain extent of miscibility it is possible to get fine morphology and also fast hydrolysis. At the same time, some works devoted to the synthesis of PLA-based biodegradable copolymers have been carried out. Cohn and Younes (1988) synthesized block copolymers by using PLA and PEO aiming to develop bioadsorbable polymeric materials to overcome the mechanical limitations and degradation most of the biodegradable polymers. It was demonstrated that the incorporation of PEO into the PLA resulted in materials with a high hydrophilic character, suitable equilibrium water contents around 60%. Poly(lactic-*co*-glycolic) acid (PLGA) is also a PLA-based biodegradable copolymer that, due its biodegradability and biocompatibility, has been one of the most attractive polymers for tissue engineering and drug delivery applications.

3.5 Starch

Starch is a carbohydrate that consists of a large number of glucose units joined together by glyosidic bonds containing, usually, 20–25% amylose and 75–80% amylopectin. It occurs widely in plants, like rice, corn, cassava, and potatoes. In all of these plants, starch is produced in the form of granules, varying in size and in composition, according to the plant used. Starch granules are hydrophilic and the water content of starch varies with relative humidity. While the branched amylopectin component contains crystalline areas, the linear amylose is mostly amorphous. Starch granules can be gelatinized in water at lower temperatures in alkaline solution and can be used as a thickening, stiffening, and gluing agent, giving wheat paste (Postek and Brown, 2009).

There are several degradable plastics made from starch (Narayan, 1994; Chandra and Rustgi, 1998; Lawton, 1996). For

instance, a fully biodegradable starch-based polymer is prepared from corn or potato starch, along with smaller amounts of food-grade additives. The resin is suitable for manufacturing injection molded pieces, films, and starch-based loose-fill packaging material (Briassoulis, 2004). These pieces degrade in an active biological environment.

Starch has a wide variety of applications, including adhesives and industrial emulsions, construction, glass fiber, medical gloves, personal care, packaging, and in agriculture. The interest in this biopolymer has been recently renewed due to its abundance, low cost, availability, biodegradability, possibility of blending with conventional polymers, and the possibility to be processed using conventional polymer processing equipment, such as, extrusion and injection molding (Yew et al., 2005). However, starch by itself presents some limitations, owing to its hydrophilic character. In this context several studies have been carried out in order to associate thermoplastic starch with other biodegradable polymers to overcome the starch limitations. Among them, the most common are aliphatic polyesters, such as PLA, PCL, PHBV, poly(ester amide) (PEA), and poly(butylene succinate adipate) (PBSA), or even an aromatic polyester like PBAT (Schwach and Avérous, 2004). There are some starch-based blends, such as Mater-Bi (from Novamont, Italy), that are presently commercialized. The incorporation of the above biodegradable polymers improves the mechanical performance of plasticized starch. Even though blending is inexpensive and easier, its main disadvantage is the immiscibility of most of the polymers because of their distinct chemical structures. Therefore, another approach involves grafting other acrylic and vinyl monomers onto the starch polymer chain, increasing its hydrophilicity or hydrophobicity, depending on the conditions used.

Maharana and Singh (2006) have successfully prepared biodegradable PE by graft copolymerization of starch, and the biodegradability was evaluated. They proved that this approach allows high biodegradability, which increases with the amount of grafted starch. In other study Halley et al. (2001) synthesized starch-based biodegradable films based on starch-based biodegradable polymers mixed with high performance polyesters. The obtained films displayed excellent tensile strength and biodegradability. The biodegradation of the mentioned polymeric materials can occur by different pathways; when disposed in landfills, they undergo photodegradation by the action of catalysts, oxygen, water, microorganisms, sunlight, and enzymes of the soil (Saroja et al., 2000). Exceptional susceptibility to microorganisms' growth has been perceived in a humid environment for starch-graft copolymers. Thus, starch is a potential polymeric material that allows

development a wide variety of products. It can be integrated in the polymer, thermoplastic starch (TPS), graft copolymers, among others. Since it is an inexpensive material, ecofriendly, and biodegradable, starch is a good candidate to replace conventional petroleum-based nondegradable plastics.

3.6 Cellulose

Cellulose is one of the most abundant polymer presents in nature, and is found as a structural component in the cell wall of plants and algae, and it can be also produced by various species of bacteria (Bishop, 2011). It is well known that cellulose is a very important and attractive biopolymer and an almost inexhaustible and renewable raw material, because it presents unique advantages and properties, including biodegradability, recyclability, renewability, biocompatibility, relatively high resistance, and stiffness (Dai et al., 2013). Even though wood is the most available raw source of natural cellulose, other sources have also been explored (eg, sisal, cotton, ramie) that can be used as raw materials for several products in a wide range of industries. These include coatings, laminates, optical films, and sorption media, additives to develop construction materials, composites, nanocomposites, and pharmaceuticals (Klemm et al., 2005; Moon et al., 2011).

The particular structure of cellulose provides interesting properties. The repeating units of glucose that constitute this macromolecule can be organized in different ways, resulting in its specificity, reactivity, and diversity of architectures (Moon et al., 2011). Its properties and specificity for a given reaction depend on several factors, such as, the process used to isolate the cellulose, chain lengths, its distribution, number of inter- and intramolecular hydrogen bonds, distribution of functional groups within the repeating units, crystallinity, and the degree of polymerization, which render cellulose as a unique material (Poletto et al., 2013; Åkerholm et al., 2004; Oh et al., 2005).

As an example, cellulose derived from wood pulp has molecules with 300–1700 repeating units, whereas cellulose from other plant fibers, cotton, as well as from bacteria, has polymer chains with 800–10,000-repeating units. Despite its hydrophilicity, the major drawback is related to its water-insolubility, as well as, in most of the organic solvents (Pingali et al., 2010; Onda et al., 2008; Nishiyama et al., 2002; Zhao et al., 2007). Only treatment with concentrated acids, at high temperatures, or even using Schweitzer reagents breaks down cellulose into its glucose units (Stenius, 2000). These solvents are used in the production of regenerated cellulose from dissolving pulp. Also, the dissolution process of cellulose can

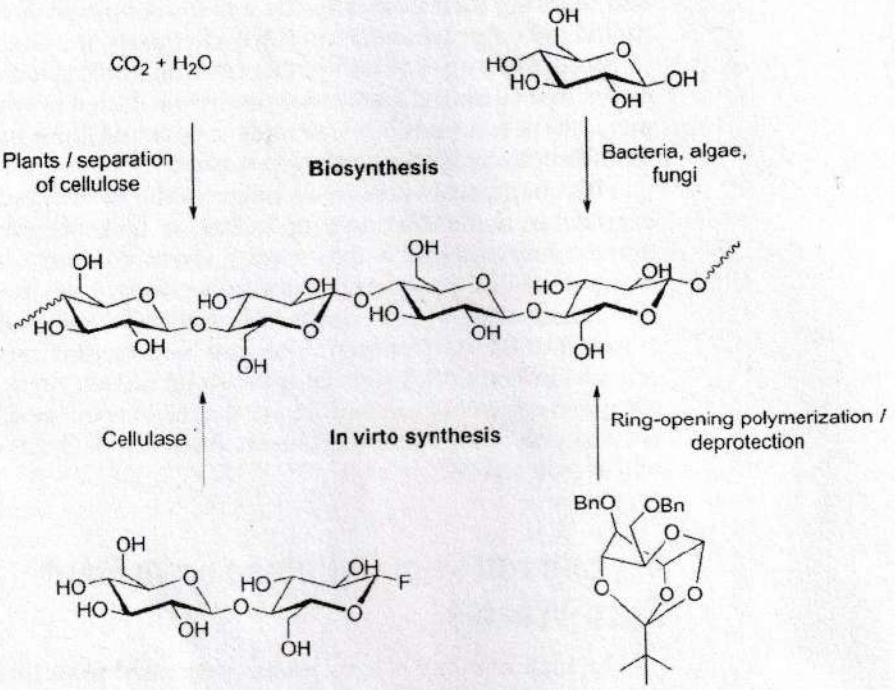
be significantly improved with many kinds of ionic liquids (Wang et al., 2012). For this reason, only a very small fraction of cellulose is used for the production of commodity materials and chemicals.

Cellulose can easily react with other synthetic polymers, because it has many hydroxyl groups. Examples of some studied cellulose-based blends are cellulose with PCL, which are partially compatible (Nishio and Manley, 1990), and blends of poly(4-vinylpyrrolidone) with cellulose in different ratios (Masson and Manley, 1991). Other authors reported the study of blends based on PVA and cellulose (Masson and Manley, 1991). The properties of resulting blends of cellulose and PE were also studied. It was demonstrated that the biodegradability ratio increases (Kaczmarek and Oldak, 2006). According to the results, it was concluded that the LDPE/cellulose blends are less biodegradable, due to the fact that the film's degradation occurs on the surface, under environmental conditions. Rogovina et al. (2013) developed LDPE/cellulose and LDPE/cellulose/PEO (or chitosan, chitin) binary and ternary blends, respectively. It was demonstrated that the incorporation of PEO or the polysaccharides (chitin or chitosan) as a third constituent enhances the biodegradability.

3.6.1 Cellulose From Plants and Bacterial Cellulose

Even though cellulose is the most abundant naturally occurring polymer of glucose, found as the main constituent of plants and natural fibers, it can be also synthesized by specific bacteria, such as, those of the genera *Gluconacetober*, *Agrobacterium*, *Aerobacter*, *Azotobacter*, *Rhizobium*, *Salmonella*, and *Acetobacterxylinum* (Ross et al., 1991). Both, bacterial cellulose (BC) and plant cellulose (PC) are chemically similar, though their macromolecular structure and physical properties are different (Czaja et al., 2007) (Scheme 7.1).

For both BC and PC, the units of glucose units are kept together by 1,4-β-glucosidic linkages, which determines the crystallinity degree of cellulose, being above 60% for BC and 40–60% for PC (Sannino et al., 2009) that contributes to its insolubility in common solvents and water, as previously referred. The fibers produced have reduced size when compared with BC are smaller than PC fibers and displays a fiber network with high tensile strength and water-retention capability compared to PC. Additionally, BC is purely contrasting with PC that is it is generally related with other components, including pectin and lignin (Keshk, 2014). Thus, while BC can be used without any further purification after synthesis by bacteria, PC requires additional modification and purification. Concerning its chemical modification, it is usually accomplished by etherification or esterification of the hydroxyl groups, aiming to



Scheme 7.1. Pathways to cellulose formation.

produce cellulose derivatives. These derivatives are more processable and find large applications at the industrial level due to the fact that cellulose and its derivatives are biodegradable and ecofriendly as are degraded by many microorganisms present in the environment (Tomšič et al., 2007). Several studies were carried out to evaluate their biodegradation. It was found that during this process a significant decrease in the molecular weight occurs, leading to the deterioration of the mechanical performance. Also, higher biodegradability of cellulose is confirmed by a decrease of the crystallinity degree and enhanced solubility in water (Miyamoto et al., 1989). Despite the advantages of BC compared to PC, it is well known that the latter has been used as a major source of raw materials and products.

3.6.2 Cellulose From Agro-Wastes

. Cellulose from vegetable agro-wastes is an example of plant-derived polymers that shall be exploited for new bioplastics production. These materials should have unique properties of considerable interest to replace conventional plastics. Herein, the direct synthesis of new bioplastics, from vegetable agro-wastes

and tailoring their properties by a grafting approach using controlled radical polymerization (CRP) chemistry, is a challenge.

Along with the environmental pressures and carbon footprints issues that surround traditional petroleum-based synthetic polymers, there is a possibility to replace some of these by biopolymers directly by synthesized agro-wastes.

This chapter provides an overview on the development of biodegradable materials based on cellulose, focusing on cellulose derived from vegetable agro-wastes. Green chemistry aspires to design chemical products that are fully effective, yet have little or no toxicity, which break down into innocuous substances if released into the environment after use, and/or that are based on renewable feedstocks, such as agricultural wastes. An overview of the green chemistry methodologies that have been used to extract natural polymers namely cellulose, from vegetable agro-wastes will be pointed out.

4 Extraction of Cellulose From Food Agro-Wastes

The high amount of agro-wastes generated from the food industry has been a growing concern, because it generates enormous amounts of inedible residues, originating from processed edible vegetables and cereals, all over the world. In Europe, more than 24 million tons of processed vegetable waste are generated and worldwide around 1.3 billion tons are left over per annum (Gaiker, 2004), which becomes an environmental and financial issue (Bayer et al., 2014).

Cellulose exhibits unique properties and can be produced from plants and agro-wastes, but its production with high purity from vegetable agro-wastes is still a challenge. Owing to its highly structured intermolecular hydrogen-bonding network, this polymer cannot be melted or dissolved by standard processes, such as thermoforming or dissolution (Pingali et al., 2010; Onda et al., 2008; Nishiyama et al., 2002; Zhao et al., 2007). For this reason, cellulose is mainly used in industrial applications in the form of cellulose derivatives, including cellulose esters or ethers. Conventional processing methods cannot be used, leaving industry to resort to cellulose derivatives, consuming extra time and costly chemical-purification steps to regenerate it (Kraemer, 1938). Trifluoroacetic acid (TFA), a natural organic acid with low toxicity, is biodegradable by microbial action and is capable for extraction of cellulose bioplastic (Kim et al., 2000). Bayer et al. (2014), used TFA as a unique solvent to cosolubilize cellulose with other

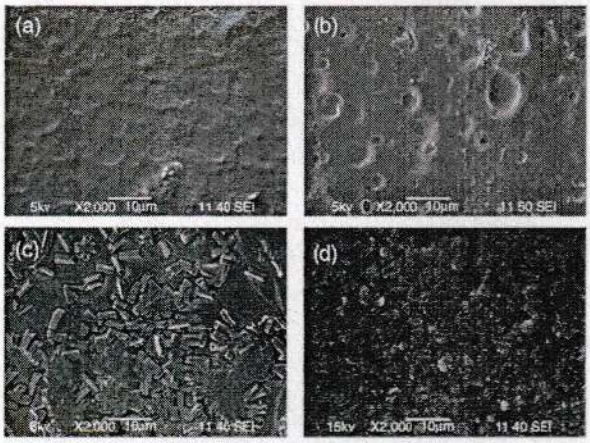


Figure 7.4. SEM images of the surfaces of (a) parsley, (b) rice, (c) spinach, and (d) cocoa samples, respectively. From Bayer et al. (2014).

organic-contained matter to obtain biopolymers from lignocellulosic biomass. Using this methodology, cellulose-based bioplastics from wastes of various edible vegetables and cereals (parsley and spinach stems, cocoa pod husks, and rice hulls) with diverse bioorigins, were prepared without requirement the of cellulose regeneration.

SEM images (Fig. 7.4) show different morphologies for all cereals thin films. For parsley and rice samples (Fig. 7.4a and b) small islands of inorganic aggregates are detected, while for spinach (Fig. 7.4c) film self-assembled embedded crystallites are evident. The new biopolymers exhibit broadly tunable-mechanical properties that are dependent on the biosource.

Bioplastic films, in comparison with commonly engineering polymers (Fig. 7.5), such as, PP, PE, polyester, elastomers (eg, silicone and PU elastomers), starch-based polymers, starch-polymer blends, and biodegradable polyesters (eg, PCL and PLA), have a mechanical performance between synthetic polymers and biopolymers.

Fig. 7.5b presents a comparison of ultimate tensile strength (UTS) versus Young's modulus. Amorphous neat cellulose films exhibit high UTS at high Young's moduli comparable to PET, while rice, spinach, and parsley biodegradable films have a similar behavior to elastomers and some thermoplastics, such as, LDPE. Bioplastics produced from cocoa-pod husk are comparable with petroleum-based thermoplastics, for instance, HDPE, and PP. The production of biopolymers with properties among those of PP and PET is also feasible. For example, blending microcrystalline

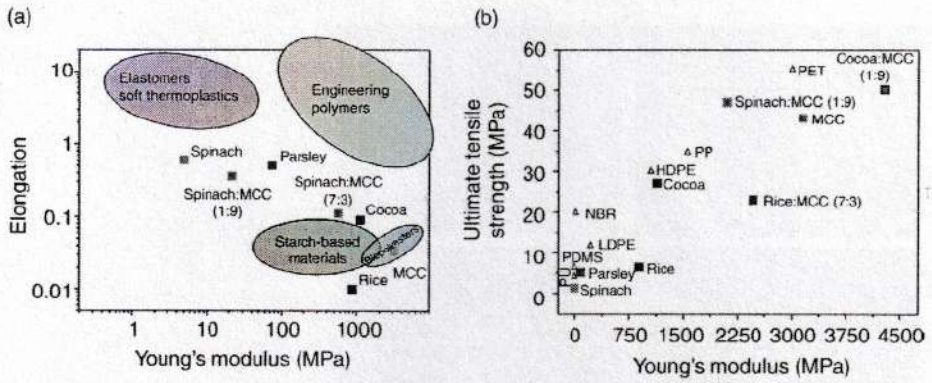


Figure 7.5. (a) Elongation versus Young's modulus data where the property domains of elastomers/soft thermoplastics (PU, rubbers, and silicone polymers), engineering polymers, (PP, PE, PS, polycarbonate, etc.), biopolyesters, and starch-based materials [PLA, poly(3-hydroxybutyrate), PCL, modified starches, etc.] are marked for comparisons, and (b) ultimate tensile strength versus Young's modulus data. From Bayer et al. (2014).

cellulose with spinach produces new materials with properties ranging between both components. This demonstrates that an extensive variety of materials with specific mechanical properties can be developed, by blending vegetable waste bioplastics that, most of the time, cannot be accomplished by solution- or even thermoform blending of conventional polymers, owing to its incompatibility.

Macedo et al. (2015) investigated the transformation of different agro-wastes, such as, raw parsley, carrot, and cabbage, by using TFA as a solvent to obtain biodegradable materials (Fig. 7.6).

Concerning the lignin component of the bioplastics, the FTIR spectra of the derived plastics from the earlier mentioned agro-wastes, indicates the existence of characteristic lignin bands in all cases, as shown in Fig. 7.7. The signal at 1740 cm^{-1} is attributed to C=O stretching of acetyl or carboxylic acid, which are also present in the structure of lignin (Dong et al., 2009). The signals at 1610–1595 cm^{-1} are attributed to the C=C aromatic stretching bands that are common to lignin. The peak that appears at 1465 cm^{-1} can be attributed

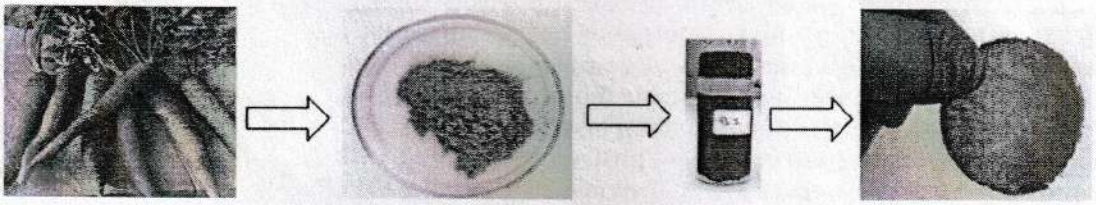


Figure 7.6. Biopolymer film production from raw of parsley wastes.

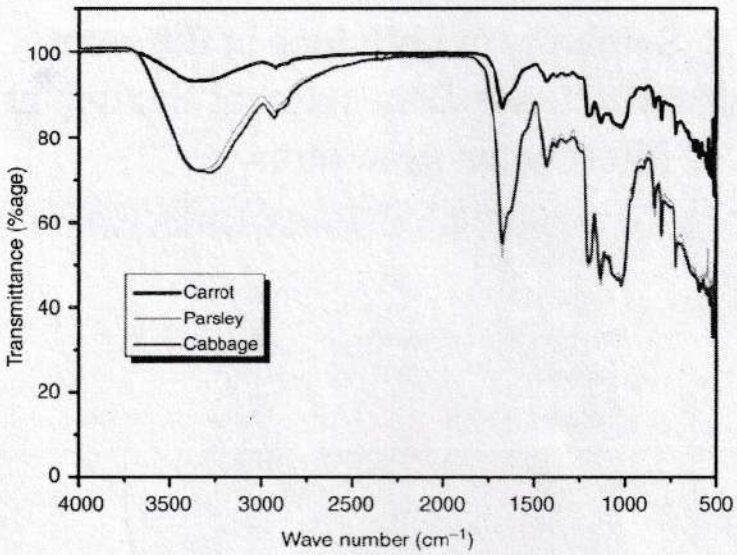


Figure 7.7. FTIR spectra of bioplastics after TFA digestion. From Macedo et al. (2015).

to the asymmetric bending of lignin CH_3 bonds. The results demonstrate that TFA can partially dissociate or break down lignin, which can be dispersed into the bioplastic matrix in its new forms.

The mechanical properties of the produced bioplastics were comparable to many synthetic polymers, in view of the substitution part of the latter, with degradable bioplastics having matching properties.

All of the earlier results indicate that agro-wastes rich in cellulose can be transformed into bioplastics by simply aging them in TFA solutions regardless of their bioorigin. Nevertheless, depending on the plant species, biopolymers were found to display diverse mechanical properties, ranging from brittle and rigid to soft and stretchable. Blending these vegetable waste solutions with TFA solutions of pure cellulose, all-natural plasticization of amorphous cellulose is achieved. These new bioplastics can replace many nondegradable plastics, preserving the environment.

Even though TFA demonstrated promising results, organic salts so-called ionic liquids (ILs), have received attention as promising green solvents for lignocellulose pretreatment or fractionation. If these solvents are efficiently recycled, the overall waste production of the process decreases, making this a green feature. However, some ILs are still synthesized using conventional organic solvents, which detracts from their overall green chemistry value. This is an issue that needs to be addressed in research. The

Table 7.2 Solubility of Cellulose in Different Ionic Liquids (ILs) Using Conventional Heating or Microwave Irradiation

Ionic Liquid	Heating Method	Solubility
[BMIM]Cl	Heating at 100°C	10%
[BMIM]Cl	Heating at 70°C	3%
[BMIM]Cl	Heating at 80°C and sonication	5%
[C6MIM]Cl	Heating at 100°C	5%
[C8MIM]Cl	Heating at 100°C	Poor
[BMIM]Cl	Microwave irradiation with pulses of 3–5 s	25%
[BMIM]Br	Microwave irradiation	5–7%
[BMIM]SCN	Microwave irradiation	5–7%
[BMIM]PF4	Microwave irradiation	None
[BMIM]PF6	Microwave irradiation	None

From Swatloski et al. (2002).

study by Swatloski et al. (2002) can be seen as a cornerstone for the dissolution of cellulose by ILs. They demonstrated that cellulose (Table 7.2) could be dissolved at high concentrations in imidazolium-based ILs.

Swatloski et al. (2002) suggested that the major contributor for the solubility of cellulose in 1-butyl-3-methyl-imidazolium chloride ([BMIM]Cl) over conventional solvents is the high chloride concentration that allows rapid and efficient dissolution, by breaking the prevailing hydrogen-bond network. When the length of the alkyl chain increases from C6 to C8, as in [C6MIM]Cl and [C8MIM]Cl, the solubility of cellulose decreased.

Most of the research studies covered in this chapter are concentrated purely on the synthesis of cellulose from plants using ILs. The first study on cellulose dissolution in ILs was published by Swatloski et al. (2002). ILs based on BMIM cation with diverse anions was tested as a suitable solvent for cellulose. The results showed higher efficiency of cellulose dissolution when chloride anion was present when compared with noncoordinating anions. Other studies regarding the solubility of cellulose using ILs, such [BMIM]Cl containing halide counter ions or even counter anions,

such as, acetate, formate, and acetate, have been described in the literature (Swatloski et al., 2002; Gericke et al., 2012). However, ILs containing halide counter anions present some drawbacks associated with their high viscosity, which reduces cellulose dissolution. Contrarily, ILs liquids with other anions, such as, phosphate, acetate, and formate show reduced viscosity compared to the former, which makes them more suitable to be used in several applications (Gericke et al., 2012).

Nowadays, commercial cellulose is produced using 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) IL, which exhibits reduced viscosity and enhanced cellulose dissolution capability. In several studies published on ILs, it was assumed that the anion used has a crucial role, being responsible for the cellulose dissolution, while the cation has a minor role. Nevertheless, other studies have demonstrated that the dissolution process is affected by both, the anion and cation structure. Accordingly, acidic protons present in the heterocyclic rings enhance the solubility considerably, which is explained by the formation of hydrogen bonds with cellulose, through its hydroxyl and ether oxygens (Andanson et al., 2014). Although ([EMIM]OAc) IL exhibited a solubility of 23 g mol^{-1} at 40°C, modifying its structure to 1-methoxyethyl-3-methylimidazolium resulted in a substantial decrease of the solubility (8 g mol^{-1}) at the same temperature. Currently, cellulose solubility has reached 14.5 wt.% using 1-allyl-3-methylimidazolium chloride at a temperature of 80°C (Zhang et al., 2005) and 16 wt.% applying 1-ethyl-3-methylimidazolium acetate IL at 90°C (Zavrel et al., 2009). However, the solubility can be improved till 25 wt.% by microwave heating. All these studies demonstrate that the effective cellulose dissolution using ionic liquids depends on both, that is, ILs should comprise cations including resilient acidic protons without atoms with high electronegativity and anions with resilient-hydrogen bond acceptability.

Wang et al. (2011) dedicated their study to the cellulose extraction from pine, poplar, Chinese parasol, and catalpa wood chips in an ionic liquid 1-allyl-3-methylimidazolium chloride ([AMIM]Cl). The results show that pine is the most suitable wood species for cellulose extraction with ILs, and the extraction rate reached 62% under optimized conditions and its cellulose content was 85% when DMSO/water was used as the precipitant (Wang et al., 2011). Teck Nam et al. (2011) studied the efficiency of ionic liquids in the dissolution of rice husk. They noticed that the ILs that dissolved cellulose provided an option to pretreat lignocellulosic biomass. The ionic liquids 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM] DEP), [BMIM]Cl, and [EMIM]OAc, were able to dissolve rice husk cellulose to varying extends, with the highest dissolution (36.7%)

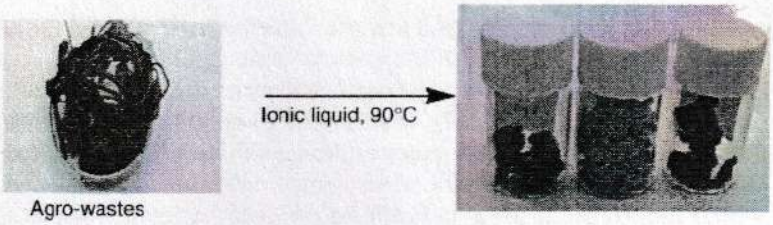


Figure 7.8. Cellulose (and other products) extracted from different food agro-residues: raw products of carrot, parsley, and cabbage. From Macedo et al. (2015).

given by [EMIM]OAc. It was observed that the regenerated cellulose was more amorphous when compared to untreated-rice husk.

Abushammala et al. (2015) reported the direct extraction of cellulose nanocrystals from wood by means of a [EMIM]OAc treatment. A native cellulosic product was recovered with 44% yield with respect to wood cellulose content. A cosolvent, DMSO, was also included to increase cellulose dissolution. It was demonstrated that the addition of an organic solvent increases the potential of the IL, reducing the time necessary for dissolution, independently of the used temperature (Andanson et al., 2014; Ries et al., 2014). Owing to the capabilities demonstrated by ILs to dissolve cellulose, several ILs have been studied not only to dissolve the cellulose but also to functionalize it.

As mentioned, ILs are used to make cellulose prone to hydrolysis (FitzPatrick et al., 2010), however, with exception of Macedo et al. (2015) no one has attempted to obtain biopolymers from lignocellulosic biomass from food agro-wastes through ILs reaction as illustrated in Fig. 7.8.

According SEM micrographs (Fig. 7.9), it is possible to observe the existence of different shapes and size distribution of the cellulose microfibers. Regarding Fig. 7.9b and d, cellulosic microfibers are clearly composed by multiple fibers. These results indicate that cellulose was successfully extracted from both, raw of carrot, parsley using [BMIM]Cl ionic liquid (Macedo et al., 2015), even though some contamination is caused by the ionic liquid inducing some agglomeration of the microfibers.

5 Cellulose Modification

5.1 Preparation of Blends of Cellulose and Biodegradable Polymers

As stated before, the most abundant biomacromolecule, cellulose, has attracted considerable attention in recent years due to

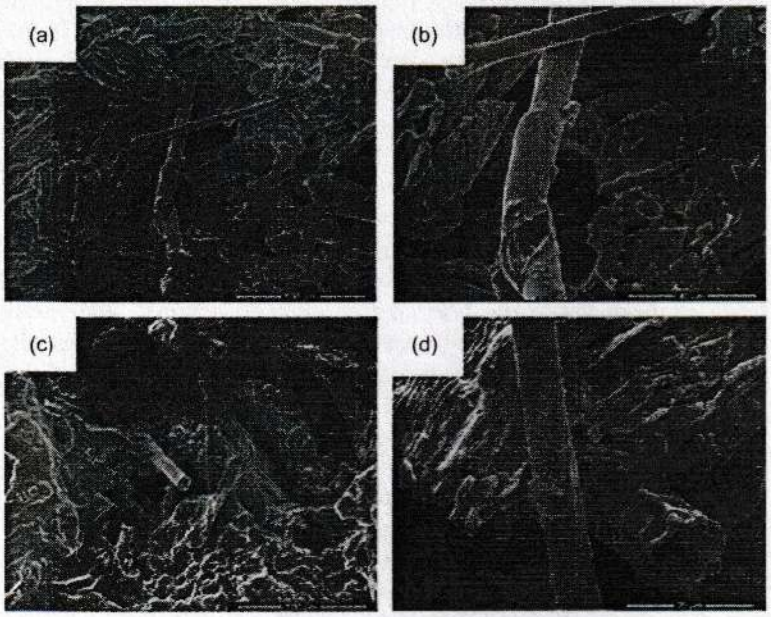


Figure 7.9. SEM micrographs of cellulose (and other products) extracted from (a) and (b) raw of carrot and (c,d) raw of parsley.

its biodegradability, biocompatibility, and renewable properties (Meng et al., 2009). Several studies reported the addition of cellulose into a biodegradable polymer matrix as a way to improve the final properties of the developed material. The most pronounced effect of this consists of the reduction of water vapor permeability, but also several mechanical properties, like tensile strength and Young's modulus, were significantly affected, mainly the elongation at break. Dias et al. (2011), observed that the addition of cellulose fibers were well covered in the plasticized starch-polymer matrix, which is attributed to the chemical resemblance between starch and natural fibers that provides a strong interaction (Avérous et al., 2001). The effect of the incorporation of cellulose fibers on the water permeability of starch films is related to the highly crystalline and hydrophobic character of the fibers. The addition of cellulose fibers decreases the water vapor transmission by increasing the diffusion path length through the film. However, this effect can be reversed by the addition of excess fiber, causing congregation (Dias et al., 2011). Müller et al. (2009) also found reinforcement of starch films lowered water vapor permeability after incorporation of cellulose fibers. Also, application of carboxymethyl cellulose (CMC) in starch-based films showed a decrease of the water vapor permeability with increasing CMC content

(Ghanbarzadeh et al., 2011). Gáspár et al. (2005) also tested the effect of different natural additives, such as, cellulose and hemicellulose, on the water resistance of a starch-based film (70% corn starch and 30% glycerol). Hemicellulose filled starch-based film showed better tensile strength and modulus than the pure film, but elongation of all four filled films was lower than the pure TPS. Water resistance of cellulose and hemicellulose films was better than pure TPS (Sanchez-Garcia et al., 2008). Authors have studied the effect of cellulose fibers in PHBV films. Water permeability decreased by 52% for 10 wt.% fiber content and by 71% for 1 wt.% fiber content. Petersson and Oksman (2006) devoted their work to the incorporation of microcrystalline cellulose. The results showed no reduction in the oxygen permeability of PLA. Conversely, Sanchez-Garcia and Lagaron (2010) found a 90% oxygen-permeability reduction for PLA after addition of 1, 2, 3, or 5 wt.% cellulose nanowhiskers. Thus, several studies on cellulose-based films showed that they could be used as an alternative for packaging several food products. Popa and Belc (2007) stated that paper and board, based on cellulose, are the most widely used renewable packaging materials nowadays.

Similarly, a lot of cellulose derivatives are produced commercially, on which cellulose acetate (CA) is the most commonly used for food packaging (fresh produce, baked goods). Makino and Hirata (1997), found that a laminate of chitosan–cellulose and PCL had a similar film permeability as LDPE, which makes this laminate a possible material for packaging for fresh produce. Popa and Belc (2007) found that coating of cellophane with nitrocellulose or PVDC (polyvinylidine chloride) improved barrier properties and this film could be used for packaging of candies, processed meat, cheese, and baked goods. Furthermore, Rhim and Kim (2009) stated that paperboard coated with PLA could be used as a substitute for PE-coated paperboard in the manufacture of paper cups or containers for high moisture foods (beverage cartons and ice cream containers).

Although many studies reported the development of cellulose derivatives and their potential applications, more research is required to explore more environmentally friendly methodologies to extract cellulose from renewable sources and to overcome the inherent difficulty in the modification of its properties associated with the reduced availability of common solvents to dissolve cellulose (Swatloski et al., 2003). Traditional cellulose-dissolution processes are often expensive and require the use of unusual solvents, typically with high ionic strength and relatively harsh conditions (Wu et al., 2004). Moreover, these processes sometimes cause severe environmental problems because they cannot be

recovered and reused (Zhang et al., 2005). In recent years, the rational green-comprehensive utilization of cellulose resources has received great attention (Shengdong et al., 2005). The common methodologies used for cellulose extraction and dissolution processes are fronting challenges due to energy and environmental problems (Shengdong et al., 2005; Zhu et al., 2005). Therefore, to make cellulose resources useful, it is necessary to develop green cellulose extraction, suitable cellulose dissolution approaches, and novel modification methodologies.

5.2 Cellulose Modification Using Ionic Liquids

Cellulose-based materials are currently a large renewable resource to reduce society's dependence on nonrenewable petroleum-based feedstocks (Zhu et al., 2006a). Therefore, to improve the properties of biodegradable/biobased materials, the addition of cellulose has been the focus of many research studies. The most investigated effect was the development of plastics with lower water vapor permeability, as well as, the enhancement of mechanical properties of the industrialized materials.

Homogeneous-cellulose derivatizations have been successfully obtained by using common solvent systems, such as reaction media, which are used to process cellulose at an industrial scale (Barthel and Heinze, 2006; Heinze et al., 2005; Köhler et al., 2008; Edgar et al., 1995; Liebert and Heinze, 2001; Heinze and Schaller, 2000; Regiani et al., 1999). However, due to their toxicity, together with the partial recovery, they have limited the use of conventional solvents for this purpose. Owing to their complex structure, to use cellulose as a green material, many research efforts have been made (Zhu et al., 2006b). As previously mentioned, cellulose can be dissolved in ILs and it can be easily also be regenerated from them. Because they are chemically and thermally stable, nonflammable, and have low vapor pressure, they are called green solvents. This has been providing a new platform for the green-comprehensive utilization of cellulose resources. Thus, the dissolution of cellulose with ILs is reviewed.

Besides cellulose dissolution, ILs can also be used for cellulose functionalization and its chemical modification. Though specific attention has been given to the acetylation of cellulose due to its wide variety of applications, other functionalizations to produce other cellulose derivatives (cellulose butyrate, cellulose phthalate, and cellulose benzoate) have been performed (Liu et al., 2007; Zhang et al., 2009; Schenzel et al., 2014).

In addition to esterification and etherification reactions, cellulose derivatization with various functional groups, including

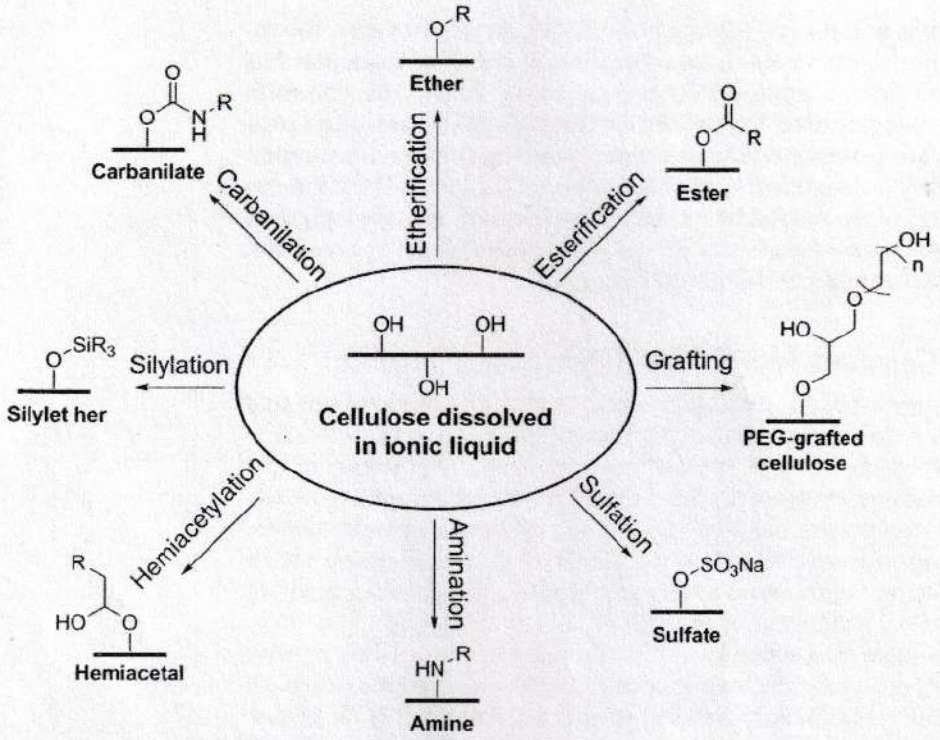


Figure 7.10. Chemical modifications of cellulose using ILs. From Isik et al. (2014).

amines, silylates, sulfonates, sulfates, and carbanilates has been also effectively accomplished by modification of cellulose hydroxyl groups (Fig. 7.10) (Erdmenger et al., 2007; Köhler et al., 2008; Liebert et al., 2006; Song et al., 2008). Tome et al. (2011) used te tradecyltrihexylphosphoniumbis(trifluoromethylsulfonyl)imide ([TDTHP][NTF_2]) to solubilize and functionalize cellulose with anhydrides. Using this IL, they were able to catalyze the esterification reaction. As a result, depending on the anhydride applied in the modification process the grafted fibers showed greater surface hydrophobicity. Moreover, the grafted-fibers characterization demonstrated that the esterification occurs at the fibers' peripheral layers, corroborating that the ultrastructure was not affected during the process.

5.3 Cellulose Modification Using by Grafting via Controlled Living Radical Polymerization

Another fascinating way to modify cellulose consists in the grafting of polymers by branching into cellulose, in order to impart

new properties, retaining its intrinsic properties (Semsarilar et al., 2010). Grafting reactions of cellulose and its derivatives has been widely studied to develop new materials, allowing the combination of properties of one or more polymers in one new material. Thus, it is possible to attain properties, such as, temperature responsiveness (Chauhan et al., 2000), hydrophobicity and oleophobicity, flexibility (Guo et al., 2013), sorbancy (Chauhan et al., 2000; Gupta and Khandekar, 2003; Waly et al., 1998; El-Salmawi et al., 2001), ion-exchange capability (Waly et al., 1998), and polarization (O-Rak et al., 2013). These materials are promising candidates to replace the conventional petroleum-based materials that are currently available in the market. Some examples of their applications include their use in drug delivery, as sorption agents, in coatings, and in membranes (Nishio, 2006).

Several methodologies are used for graft copolymerization of several monomers on the cellulose backbone, including free radical polymerization (ROP), nitroxide-mediated polymerization, reversible addition–fragmentation chain transfer (RAFT) polymerization, and atom transfer radical polymerization (ATRP) (Meng et al., 2009).

Cellulose was chemically modified by ROP. Usually, cyclic monomers (eg, epoxides, lactones, and anhydrides) are used along with cellulose, which are dissolved in an appropriate IL. The hydroxyl groups of cellulose are subsequently used to accomplish ROP of the monomers to graft polymers onto the cellulose polymer chains (Guo et al., 2013). Hufendiek et al. (2014) converted cellulose into a macro-RAFT agent in [BMIM]Cl. Cellulose-*g*-polyacrylamide copolymers with temperature-responsive properties was prepared using the previous marco-RAFT and polyacrylamide. ATRP was also used to graft, by polymerization of vinyl monomers onto cellulose and cellulose derivatives in a living/controllable way. Synthesis of cellulose-based graft copolymers by ATRP has been carried out in either heterogeneous- or homogenous-reaction medium. The heterogeneous ATRP was mainly used for surface modification of solid-cellulose materials, such as, paper or film (Carlmark and Malmström, 2002; Lindqvist and Malmström, 2006; Lee et al., 2004; Nystrom et al., 2006), fibers (Carlmark and Malmström, 2003; Plackett et al., 2005), and particles (Lindqvist and Malmström, 2006; Coskun and Temüz, 2005). The homogenous reactions, graft polymerization via ATRP, were mostly performed on cellulose derivatives (Chang et al., 2008; Shen and Huang, 2004), such as CA (Vlček et al., 2006), ethyl cellulose (EC) (Tang et al., 2007), and hydroxypropyl cellulose (HPC) (Östmark et al., 2007). However, a few studies were also found on homogeneous graft polymerization via ATRP on underivatized cellulose backbone without any

protection of the reactive groups. Direct grafting of polymers, for example, synthetic ones, on the underivatized-cellulose backbone, in a homogenous reaction medium, is expected to generate a new kind of polymer that combines the advantages of natural- and synthetic-polymers properties. Graft polymerization via ATRP in homogenous reaction media requires the synthesis of macroinitiator based on cellulose. Nevertheless, for underivatized cellulose this has been restricted by the lack of effective solvents. Bontempo et al. (2006) have reported a versatile ATRP method for polysaccharide grafting, in homogeneous conditions, without using protecting group chemistry. *N,N*-dimethylformamide (DMF) was used as a reaction medium for the synthesis of polysaccharide-based macroinitiators and water/DMF mixtures with different compositions as the polymerization medium for ATRP. However, this method cannot be directly applied for underivatized cellulose because it is insoluble in this solvent system and other common solvents. Wu et al. (2004) found out that the IL, [AMIM]Cl, at room temperature, was a powerful nonderivatizing solvent for cellulose and it was found as a desirable medium for the cellulose acylation. Meng et al. (2009) synthesized a macroinitiator, cellulose 2-bromoisobutyrylate, through homogeneous acylation of underivatized cellulose with 2-bromoisobutyryl bromide in ionic liquid [AMIM]Cl. Then, the cellulose-based macroinitiators were used for graft copolymerization of methyl methacrylate (MMA) and styrene.

Morphological studies of cellulose-*g*-PMMA copolymer (Fig. 7.11) show that the average diameters of sphere-like particulates were roughly 50 nm. Using this new method for graft modification of cellulose directly onto its backbone under a homogeneous condition has been successfully carried out. The

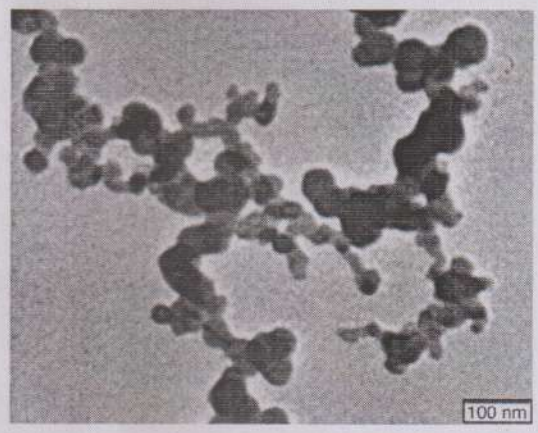


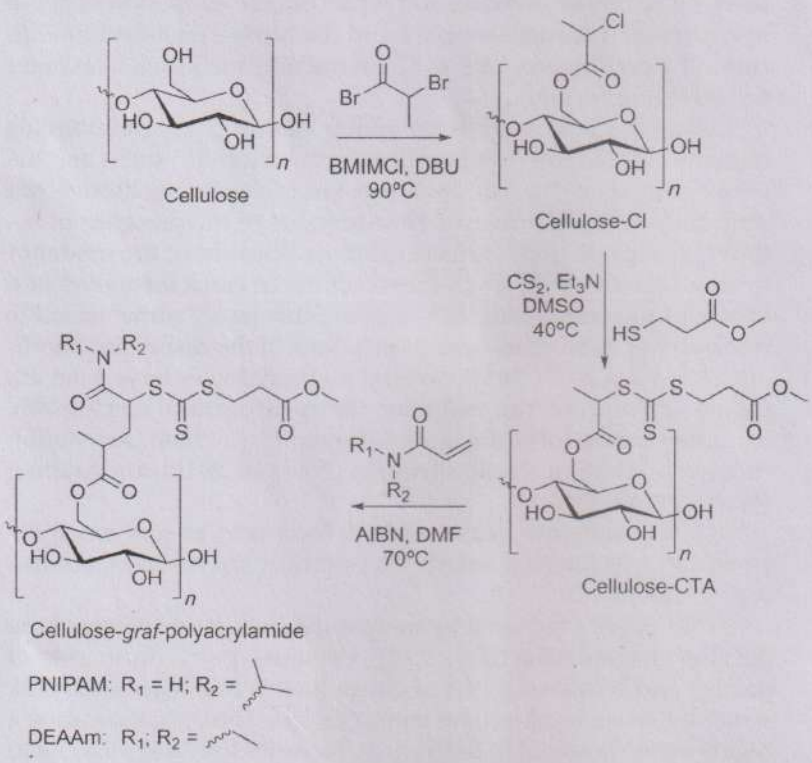
Figure 7.11. TEM pictures for cellulose-*g*-PMMA. From Meng et al. (2009).

macroinitiator for ATRP was synthesized by direct homogenous acylation of cellulose in [AMIM]Cl.

Moreover, RAFT polymerization has been employed to prepare cellulose-*g*-copolymers using (soluble) cellulose derivatives (eg, hydroxyisopropylcellulose and ethyl hydroxylethyl cellulose), which are commercially available, for subsequent modification with variable polymer side chains [eg, PS, poly(vinyl acetate), poly(ethyl acrylate), PNIPAM, polyacrylamide] using RAFT polymerization (Stenzel et al., 2003; Hernández-Guerrero et al., 2005; Fleet et al., 2008; Hiltunen et al., 2009).

Recently Hufendiek et al. (2014) synthesized well-defined temperature responsive cellulose-*g*-polyacrylamide copolymers in a grafting RAFT approach in an IL (Scheme 7.2).

The method of synthesis of cellulose-*g*-polyacrylamides, employing RAFT polymerization, takes place in a controlled fashion and may be transferred to the synthesis of a variety of other



Scheme 7.2. Synthetic pathway for cellulose-*g*-polyacrylamide copolymers via RAFT-polymerization. DBU, 1,8-Diazabicycloundec-7-ene; AIBN, Azobisisobutyronitrile; PNIPAM, Poly(*N*-isopropylacrylamide); CS2, Carbon disulfide; Et3N, Triethylamine. From Hufendiek et al. (2014).

cellulose-g-copolymers. The result provides a benign and efficient access route to produce cellulose-hybrid materials, introducing a synthetic-platform technology that may be exploited for the employment of cellulose materials in applications where a stimuli–response is of importance.

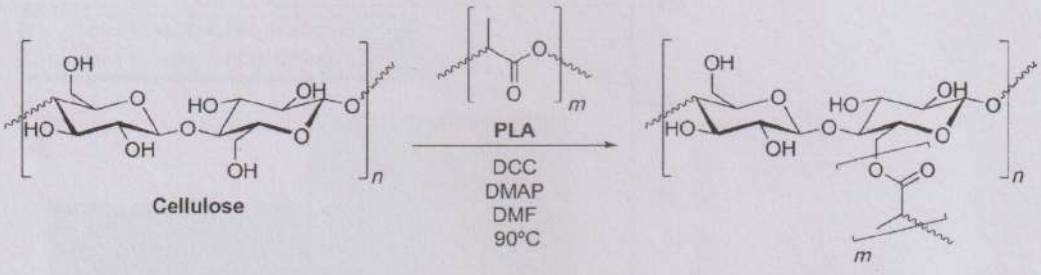
These new copolymers developed using different routes are at this time new candidates for a wide field of applications, such as drug delivery. Moreover, from the mentioned examples, the dissolution of cellulose with an IL in moderate conditions enables the accomplishment of homogeneous reactions, resulting in different materials with several properties, applying a green-chemistry methodology.

Agriculture crops have been used as alternative sources of biodegradable polymers, but the agricultural potential of Earth is limited, therefore, attention is necessary to avoid competition with food crops. In this context, agro-food waste industry appears as a sustainable and continuous source of bioplastics. Nevertheless, there no scientific investigation reporting the extraction of cellulose from agro-wastes using ILs and the further chemical modification by grafting via CRP in ILs extraction mediums to achieve cellulose biopolymers.

Cellulose fibers have been much explored as a reinforcing material in biopolymer-based matrix material, such as PLA (Siqueira et al., 2010). The challenge lies in dispersing these fibers uniformly in the PLA matrix. However, due to the presence of hydroxyl groups on their surface, cellulose fibers have the tendency to stick together or agglomerate resulting in crack formation and failure of the composite. To overcome this issue, some scientific research has been made using variations of the dispersion methods (Eichhorn et al., 2010). Several methodologies have been explored to improve the cellulose fibers-dispersion mechanism, including the use of surfactants (Oksman et al., 2006), acetylation (Braun and Dorgan, 2009), silylation (Pei et al., 2010), and grafting (Pracella et al., 2010).

Recently, cellulose extracted from food agro-wastes was grafted into PLA as the base matrix via esterification reaction, according to Scheme 7.3.

SEM images were used to analyze the bulk morphology of the developed bioplastics (Fig. 7.12). Cellulose-g-PLA from raw of parsley and cellulose-g-PLA of carrot have a heterogeneous bulk structure, whereas films have some cracks in the bulk, indicating a highly brittle material in both cases. Nevertheless, it is possible to observe that the fibers of parsley and raw of carrot residues are entangled in a PLA matrix. In addition, a noncompact structure can be observed, suggesting that the reactions were not complete.



Scheme 7.3. Esterification reaction between cellulose extracted from food agro-wastes and polylactic acid (PLA). DCC, *N,N'*-Dicyclohexylcarbodiimide; DMAP, *N,N*-Dimethylpyridin-4-amine. From Macedo et al. (2015).

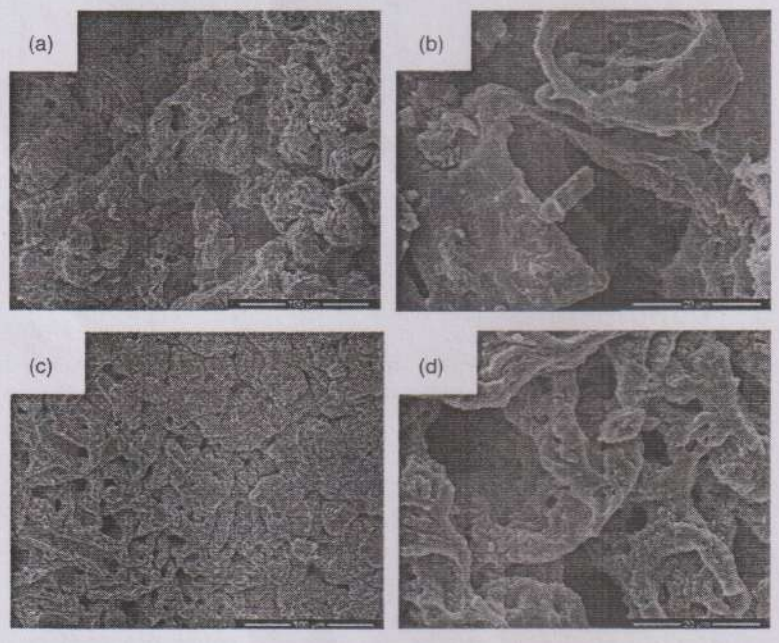


Figure 7.12. SEM micrographs resulting from the esterification reaction between cellulose extracted from (a, b) raw of parsley (c, d) raw of carrot and PLA. From Macedo et al. (2015).

Thus, even the similarity among both films, depending on the batch of waste used, different forms of self-assembled crystal structures emerged, similar to the naturally synthesized minerals of plant leaves (Ball, 2012).

Moreover, the samples prepared by transesterification-reaction polymerization show differences in biodegradability behavior, cellulose-*g*-PLA from raw of carrot being the more biodegradable sample (Fig. 7.13).

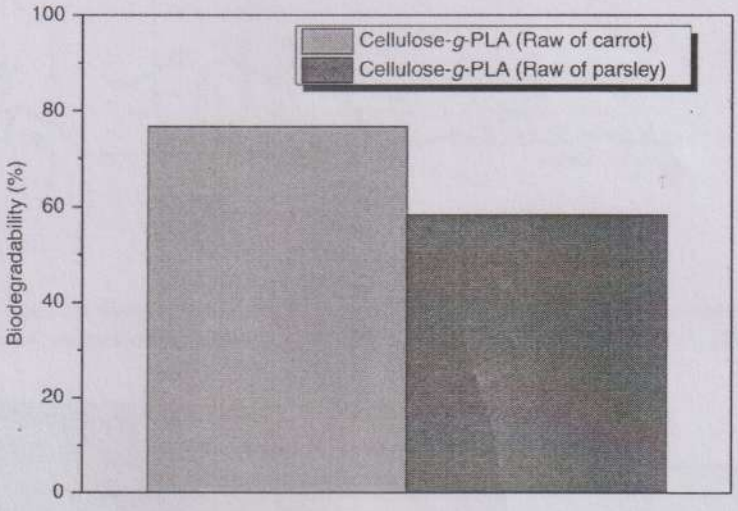


Figure 7.13. Biodegradability of food agro-waste residues according to ISO 14851(1999).

6 Conclusions

This chapter focused on the cellulose derived from food agro-wastes dissolution, using ILs to build up a new platform to get green cellulose and to improve the cellulose-bioplastics properties, by grafting via CRP in TFA and ILs extraction mediums. It is possible to adapt the chemistry, by the right selection of the IL and the cellulose resource from food agro-wastes, as well as, the synthesis parameters to use CRP methodologies for (1) innovation in production from lignocellulosic materials and reduce society's dependence on nonrenewable petroleum-based feed-stocks, in order to solve the environmental and energy issues keeping social sustainable developments; and (2) providing the possibility to develop various advanced materials, including cellulose derivatives and new cellulose composites, to replace conventional polymers with a slow biodegradation rate, mainly for products with short life times, as food packaging.

There is no doubt that the examples presented in this chapter are only some illustrations of the huge potential of the synthesis of cellulose bioplastics by a direct digesting and valorization of vegetable agro-wastes, including its regeneration and tailoring of properties by chemical modification.

Acknowledgments

The authors would like acknowledge the n-STeP—Nanostructured systems for Tailored Performance, with reference NORTE-07-0124-FEDER-000039, supported by the Programa Operacional Regional do Norte (ON.2), PEst-C/CTM/LA0025/2013 (Strategic Project—LA 25—2013-2014).

References

Abushammala, H., Krossing, I. Laborie, M.P., 2015. Ionic liquid-mediated technology to produce cellulose nanocrystals directly from wood. Carbohydr. Polym. 134, 609–616.

Åkerholm, M., Hinterstoisser, B., Salmén, L., 2004. Characterization of the crystalline structure of cellulose using static and dynamic FT-IR spectroscopy. Carbohydr. Res. 339, 569–578.

Albertsson, A.A., Barenstedt, C., Karlsson, S., 1993. Increased biodegradation of a low-density polyethylene (LDPE) matrix in starch-filled LDPE materials. J. Environ. Polym. Degrad. 1, 241–245.

Albertsson, A.C., Barenstedt, C., Karlsson, S., 1994. Degradation of enhanced environmentally degradable polyethylene in biological aqueous media: mechanisms during the first stages. J. Appl. Polym. Sci. 51, 1097–1105.

Andanson, J.M., Bordes, E., Devemy, J., Leroux, F., Padua, A.A.H., Gomes, M.F.C., 2014. Understanding the role of co-solvents in the dissolution of cellulose in ionic liquids. Green Chem. 16, 2528–2538.

Auras, R., Harte, B., Selke, S., 2004. An overview of polylactides as packaging materials. Macromol. Biosci. 4, 835–864.

Avérous, L., Fringant, C., Moro, L., 2001. Plasticized starch—cellulose interactions in polysaccharide composites. Polymer 42, 6565–6572.

Ball, P., 2012. Material witness: why leaves have stones. Nat. Mater. 11, 271–1271.

Barthel, S., Heinze, T., 2006. Acylation and carbanilation of cellulose in ionic liquids. Green Chem. 8, 301–306.

Bastioli, C., Cerutti, A., Guanella, I., Romano, G.C., Tosin, M., 1995. Physical state and biodegradation behavior of starch-polycaprolactone systems. J. Environ. Polym. Degrad. 3, 81–95.

Bayer, I.S., Guzman-Puyol, S., Heredia-Guerrero, J.A., Ceseracciu, L., Pignatelli, F., Ruffilli, R., Cingolani, R., Athanassiou, A., 2014. Direct transformation of edible vegetable waste into bioplastics. Macromolecules 47, 5135–5143.

Bishop, C.A., 2011. Vacuum Deposition onto Webs, Films and Foils, second ed. William Andrew Publishing, Oxford.

Bonhomme, S., Cuer, A., Delort, A.M., Lemaire, J., Sancelme, M., Scott, G., 2003. Environmental biodegradation of polyethylene. Polym. Degrad. Stabil. 81, 441–452.

Bontempo, D., Masci, G., De Leonardis, P., Mannina, L., Capitani, D., Crescenzi, V., 2006. Versatile grafting of polysaccharides in homogeous mikle conditions by using atom transfer radical polymerization. Biomacromolecules 7, 2154–2161.

Braun, B., Dorgan, J.R., 2009. Single-step method for the isolation and surface functionalization of cellulosic nanowhiskers. Biomacromolecules 10, 334–341.

Briassoulis, D., 2004. An overview on the mechanical behaviour of biodegradable agricultural films. J. Polym. Environ. 12, 65–81.

Calil, M.R., Gaboardi, F., Guedes, C.G.F., Rosa, D.S., 2006. Comparison of the biodegradation of poly(ε-caprolactone), cellulose acetate and their blends by the Sturm test and selected cultured fungi. Polym. Test. 25, 597–604.

Carlmark, A., Malmström, E., 2002. Atom transfer radical polymerization from cellulose fibers at ambient temperature. J. Am. Chem. Soc. 124, 900–901.
Carlmark, A., Malmström, E.E., 2003. ATRP grafting from cellulose fibers to create block-copolymer grafts. Biomacromolecules 4, 1740–1745.
Chandra, R., Rustgi, R., 1998. Biodegradable polymers. Prog. Polym. Sci. 23, 1273–1335.
Chang, F., Yamabuki, K., Onimura, K., Oishi, T., 2008. Modification of cellulose by using atom transfer radical polymerization and ring-opening polymerization. Polym. J. 40, 1170–1179.
Chauhan, G.S., Mahajan, S., Guleria, L.K., 2000. Polymers from renewable resources: sorption of Cu^{2}+ ions by cellulose graft copolymers. Desalination 130, 85–88.
Choi, E.J., Kim, C.H., Park, J.K., 1999. Structure–property relationship in PCL/starch blend compatibilized with starch-g-PCL copolymer. J. Polym. Sci. Part B 37, 2430–2438.
Cohn, D., Younes, H., 1988. Biodegradable PEO/PLA block copolymers. J. Biomed. Mater. Res. 22, 993–1009.
Coskun, M., Temüz, M.M., 2005. Grafting studies onto cellulose by atom-transfer radical polymerization. Polym. Int. 54, 342–347.
Cruz-Pinto, J.J.C., Carvalho, M.E.S., Ferreira, J.F.A., 1994. The kinetics and mechanism of polyethylene photo-oxidation. Die Angew. Makromol. Chem. 216, 113–133.
Czaja, W.K., Young, D.J., Kawecki, M., Brown, R.M., 2007. The future prospects of microbial cellulose in biomedical applications. Biomacromolecules 8, 1–12.
Dai, D., Fan, M., Collins, P., 2013. Fabrication of nanocelluloses from hemp fibers and their application for the reinforcement of hemp fibers. Ind. Crop. Prod. 44, 192–199.
Datta, R., Tsai, S.P., Bonsignore, P., Moon, S.H., Frank, J.R., 1995. Technological and economic potential of poly(lactic acid) and lactic acid derivatives. FEMS Microbiol. Rev. 16, 221–231.
Dias, A.B., Müller, C.M.O., Larotonda, F.D.S., Laurindo, J.B., 2011. Mechanical and barrier properties of composite films based on rice flour and cellulose fibers. LWT Food Sci. Technol. 44, 535–542.
Dong, D., Sun, J., Huang, F., Gao, Q., Wang, Y., Li, R., 2009. Using trifluoroacetic acid to pretreat lignocellulosic biomass. Biomass Bioenerg. 33, 1719–1723.
Drumright, R.E., Gruber, P.R., Henton, D.E., 2000. Polylactic acid technology. Adv. Mater. 12, 1841–1846.
Edgar, K.J., Arnold, K.M., Blount, W.W., Lawniczak, J.E., Lowman, D.W., 1995. Synthesis and properties of cellulose acetoacetates. Macromolecules 28, 4122–4128.
Eichhorn, S.J., Dufresne, A., Aranguren, M., Marcovich, N.E., Capadona, J.R., Rowan, S.J., Weder, C., Thielemans, W., Roman, M., Renneckar, 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., 2010. Review: current international research into cellulose nanofibres and nanocomposites. J. Mater. Sci. 45, 1–33.
El-Salmawi, K.M., Zaid, M.M.A., Ibraheim, S.M., El-Naggar, A.M., Zahran, A.H., 2001. Sorption of dye wastes by poly(vinyl alcohol)/poly(carboxymethyl cellulose) blend grafted through a radiation method. J. Appl. Polym. Sci. 82, 136–142.
Erdmenger, T., Haensch, C., Hoogenboom, R., Schubert, U.S., 2007. Homogeneous tritylation of cellulose in 1-butyl-3-methylimidazolium chloride. Macromol. Biosci. 7, 440–445.
FitzPatrick, M., Champagne, P., Cunningham, M.F., Whitney, R.A., 2010. A biorefinery processing perspective: treatment of lignocellulosic materials for the production of value-added products. Bioresour. Technol. 101, 8915–8922.

Fleet, R., Mcleary, J.B., Grumel, V., Weber, W.G., Matahwa, H., Sanderson, R.D., 2008. RAFT mediated polysaccharide copolymers. Eur. Polym. J. 44, 2899–2911.
Gaiker, C.T., 2004. Handbook for the Prevention and Minimization of Waste and Valorisation of By-Products in European Agro-Food Industries. AWARENET, Beirut, Lebanon.
Gajria, A.M., Davé, V., Gross, R.A., Mccarthy, P.S., 1996. Miscibility and biodegradability of blends of poly(lactic acid) and poly(vinyl acetate). Polymer 37, 437–444.
Gáspár, M., Benkő, Z., Dogossy, G., Réczey, K., Czigány, T., 2005. Reducing water absorption in compostable starch-based plastics. Polym. Degrad. Stabil. 90, 563–569.
Gautam, I.K.A.N., 2010. Starch grafted polyethylene evincing biodegradation behaviour. Malay. Polym. J. 5, 26–38.
Gericke, M., Fardim, P., Heinze, T., 2012. Ionic liquids—promising but challenging solvents for homogeneous derivatization of cellulose. Molecules 17, 7458.
Ghanbarzadeh, B., Almasi, H., Entezami, A.A., 2011. Improving the barrier and mechanical properties of corn starch-based edible films: effect of citric acid and carboxymethyl cellulose. Ind. Crop. Prod. 33, 229–235.
Gross, R.A., Kalra, B., 2002. Biodegradable polymers for the environment. Science 297, 803–807.
Guo, Y., Wang, X., Shen, Z., Shu, X., Sun, R., 2013. Preparation of cellulose-graft-poly(ε-caprolactone) nanomicelles by homogeneous ROP in ionic liquid. Carbohydr. Polym. 92, 77–83.
Gupta, K.C., Khandekar, K., 2003. Temperature-responsive cellulose by ceric(iv) ion-initiated graft copolymerization of n-isopropylacrylamide. Biomacromolecules 4, 758–765.
Halley, P., Rutgers, R., Coombs, S., Kettels, J., Gralton, J., Christie, G., Jenkins, M., Beh, H., Griffin, K., Jayasekara, R., Lonergan, G., 2001. Developing biodegradable mulch films from starch-based polymers. Starch Stärke 53, 362–367.
Heinze, T., Schaller, J., 2000. New water soluble cellulose esters synthesized by an effective acylation procedure. Macromol. Chem. Phys. 201, 1214–1218.
Heinze, T., Schwikal, K., Barthel, S., 2005. Ionic liquids as reaction medium in cellulose functionalization. Macromol. Biosci. 5, 520–525.
Hernández-Guerrero, M., Davis, T.P., Barner-Kowollik, C., Stenzel, M.H., 2005. Polystyrene comb polymers built on cellulose or poly(styrene-*co*-2-hydroxyethylmethacrylate) backbones as substrates for the preparation of structured honeycomb films. Eur. Polym. J. 41, 2264–2277.
Hiltunen, M., Riihelä, S., Maunu, S.L., 2009. New associative EHEC-g-PAam copolymers: their syntheses, characterization, and rheological behavior. J. Polym. Sci. Part B 47, 1869–1879.
Hufendiek, A., Trouillet, V., Meier, M.A.R., Barner-Kowollik, C., 2014. Temperature responsive cellulose-graft-copolymers via cellulose functionalization in an ionic liquid and RAFT polymerization. Biomacromolecules 15, 2563–2572.
Isik, M., Sardon, H., Mecerreyes, D., 2014. Ionic liquids and cellulose: dissolution, chemical modification and preparation of new cellulosic materials. Int. J. Mol. Sci. 15, 11922.
Jiang, L., Liu, B., Zhang, J., 2009. Properties of poly(lactic acid)/poly(butylene adipate-*co*-terephthalate)/nanoparticle ternary composites. Ind. Eng. Chem. Res. 48, 7594–7602.
Kaczmarek, H., Ołdak, D., 2006. The effect of UV-irradiation on composting of polyethylene modified by cellulose. Polym. Degrad. Stabil. 91, 2282–2291.
Kaur, I., Bhalla, T.C., Deepika, N., Gautam, N., 2008. Biodegradation and swelling studies of gelatin-grafted polyethylene. J. Appl. Polym. Sci. 107, 3878–3884.
Keshk, S.M.A.S., 2014. Bacterial cellulose production and its industrial applications. J. Bioprocess. Biotech. 4, 2.

Kim, B.R., Suidan, M.T., Wallington, T.J., Du, X., 2000. Biodegradability of trifluoroacetic acid. Environ. Eng. Sci. 17, 337–342.
Klemm, D., Heublein, B., Fink, H.P., Bohn, A., 2005. Cellulose: fascinating biopolymer and sustainable raw material. Angew. Chem. Int. Ed. Engl. 44, 3358–3393.
Koenig, M.F., Huang, S.J., 1995. Biodegradable blends and composites of polycaprolactone and starch derivatives. Polymer 36, 1877–1882.
Köhler, S., Liebert, T., Heinze, T., 2008. Interactions of ionic liquids with polysaccharides. VI. Pure cellulose nanoparticles from trimethylsilyl cellulose synthesized in ionic liquids. J. Polym. Sci. Part A 46, 4070–4080.
Kraemer, E.O., 1938. Molecular weights of celluloses and cellulose derivates. Ind. Eng. Chem. 30, 1200–1203.
Lawton, J.W., 1996. Effect of starch type on the properties of starch containing films. Carbohydr. Polym. 29, 203–208.
Lee, S.B., Koepsel, R.R., Morley, S.W., Matyjaszewski, K., Sun, Y., Russell, A.J., 2004. Permanent, nonleaching antibacterial surfaces. 1. Synthesis by atom transfer radical polymerization. Biomacromolecules 5, 877–882.
Liebert, T.F., Heinze, T.J., 2001. Exploitation of reactivity and selectivity in cellulose functionalization using unconventional media for the design of products showing new superstructures. Biomacromolecules 2, 1124–1132.
Liebert, T., Hänsch, C., Heinze, T., 2006. Click chemistry with polysaccharides. Macromol. Rapid Commun. 27, 208–213.
Lindqvist, J., Malmström, E., 2006. Surface modification of natural substrates by atom transfer radical polymerization. J. Appl. Polym. Sci. 100, 4155–4162.
Liu, C.F., Sun, R.C., Zhang, A.P., Ren, J.L., 2007. Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium. Carbohydr. Polym. 68, 17–25.
Macedo, M.J., Moura, I., Oliveira, M., Machado, A.V., 2015. Development of bioplastics from agro-wastes. Abstract in MATERIAIS 2015. Porto, Portugal.
Machado, A.V., Moura, I., Duarte, E.M., Botelho, G., Nogueira, R., Brito, A.G., 2007. Evaluation of properties and biodeterioration potential of polyethylene and aliphatic polyester blends. Int. Polym. Process. 22, 512–518.
Maharana, T., Singh, B.C., 2006. Synthesis and characterization of biodegradable polyethylene by graft copolymerization of starch using glucose–Ce(IV) redox system. J. Appl. Polym. Sci. 100, 3229–3239.
Iwamoto, A., Tokiwa, Y., 1994. Environmentally degradable polymers enzymatic degradation of plastics containing polycaprolactone. Polym. Degrad. Stab. 45, 205–213.
Makino, Y., Hirata, T., 1997. Modified atmosphere packaging of fresh produce with a biodegradable laminate of chitosan-cellulose and polycaprolactone. Postharvest Biol. Technol. 10, 247–254.
Massardier-Nageotte, V., Pestre, C., Cruard-Pradet, T., Bayard, R., 2006. Aerobic and anaerobic biodegradability of polymer films and physico-chemical characterization. Polym. Degrad. Stabil. 91, 620–627.
Masson, J.F., Manley, R.S.J., 1991. Cellulose/poly(4-vinylpyridine) blends. Macromolecules 24, 5914–5921.
Matzinos, P., Tserki, V., Kontoyiannis, A., Panayiotou, C., 2002. Processing and characterization of starch/polycaprolactone products. Polym. Degrad. Stabil. 77, 17–24.
Meng, T., Gao, X., Zhang, J., Yuan, J., Zhang, Y., He, J., 2009. Graft copolymers prepared by atom transfer radical polymerization (ATRP) from cellulose. Polymer 50, 447–454.
Miyamoto, T., Takahashi, S.I., Ito, H., Inagaki, H., Noishiki, Y., 1989. Tissue biocompatibility of cellulose and its derivatives. J. Biomed. Mater. Res. 23, 125–133.

Mohanty, A.K., Misra, M., Hinrichsen, G., 2000. Biofibres, biodegradable polymers and biocomposites: an overview. Macromol. Mater. Eng. 276-277, 1–24.
Moon, R.J., Martini, A., Nairn, J., Simonsen, J., Youngblood, J., 2011. Cellulose nanomaterials review: structure, properties and nanocomposites. Chem. Soc. Rev. 40, 3941–3994.
Moura, I., Machado, A.V., Duarte, E.M., Nogueira, R., 2011. Biodegradability assessment of aliphatic polyesters-based blends using standard methods. J. Appl. Polym. Sci. 119, 3338–3346.
Müller, C.M.O., Laurindo, J.B., Yamashita, F., 2009. Effect of cellulose fibers addition on the mechanical properties and water vapor barrier of starch-based films. Food Hydrocoll. 23, 1328–1333.
Nabar, Y., Raquez, J.M., Dubois, P., Narayan, R., 2005. Production of starch foams by twin-screw extrusion: effect of maleated poly(butylene adipate-co-terephthalate) as a compatibilizer. Biomacromolecules 6, 807–817.
Nair, L.S., Laurencin, C.T., 2006. Polymers as biomaterials for tissue engineering and controlled drug delivery. Adv. Biochem. Eng. Biotechnol. 102, 47–90.
Narayan, R., 1994. Impact of governmental policies, regulations, and standards activities on an emerging plastics industry. In: Doi, Y., Fukuda, K. (Eds.), Biodegradable Plastics and Polymers. Elsevier, Amsterdam, Netherlands.
Nijenhuis, A.J., Colstee, E., Grijpma, D.W., Pennings, A.J., 1996. High molecular weight poly(L-lactide) and poly(ethylene oxide) blends: thermal characterization and physical properties. Polymer 37, 5849–5857.
Nishio, Y., 2006. Material functionalization of cellulose and related polysaccharides via diverse microcompositions. Adv. Polym. Sci. 205, 97–151.
Nishio, Y., Manley, R.S.J., 1990. Blends of cellulose with nylon 6 and poly(epsillon-caprolactone) prepared by a solution-coagulation method. Polym. Eng. Sci. 30, 71–82.
Nishiyama, Y., Langan, P., Chanzy, H., 2002. Crystal structure and hydrogen-bonding system in cellulose from synchrotron x-ray and neutron fiber diffraction. J. Am. Chem. Soc. 124, 9074–9082.
Nystrom, D., Lindqvist, J., Ostmark, E., Hult, A., Malmstrom, E., 2006. Superhydrophobic bio-fibre surfaces via tailored grafting architecture. Chem. Commun., 3594–3596.
Oh, S.Y., Yoo, D.I., Shin, Y., Kim, H.C., Kim, H.Y., Chung, Y.S., Park, W.H., Youk, J.H., 2005. Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. Carbohydr. Res. 340, 2376–2391.
Ohtake, Y., Kobayashi, T., Asabe, H., Murakami, N., 1998. Studies on biodegradation of LDPE—observation of LDPE films scattered in agricultural fields or in garden soil. Polym. Degrad. Stabil. 60, 79–84.
Oksman, K., Mathew, A.P., Bondeson, D., Kvien, I., 2006. Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. Compos. Sci. Technol. 66, 2776–2784.
Onda, A., Ochi, T., Yanagisawa, K., 2008. Selective hydrolysis of cellulose into glucose over solid acid catalysts. Green Chem. 10, 1033–1037.
O-Rak, K., Ummartyotin, S., Sain, M., Manuspiya, H., 2013. Covalently grafted carbon nanotube on bacterial cellulose composite for flexible touch screen application. Mater. Lett. 107, 247–250.
Östmark, E., Harrisson, S., Wooley, K.L., Malmström, E.E., 2007. Comb polymers prepared by ATRP from hydroxypropyl cellulose. Biomacromolecules 8, 1138–1148.
Peelman, N., Ragaert, P., De Meulenaer, B., Adons, D., Peeters, R., Cardon, L., Van Impe, F., Devlieghere, F., 2013. Application of bioplastics for food packaging. Trends Food Sci. Technol. 32, 128–141.

Pei, A., Zhou, Q., Berglund, L.A., 2010. Functionalized cellulose nanocrystals as biobased nucleation agents in poly(L-lactide) (PLLA) – Crystallization and mechanical property effects. Compos. Sci. Technol. 70, 815–821.
Petersson, L., Oksman, K., 2006. Biopolymer based nanocomposites: comparing layered silicates and microcrystalline cellulose as nanoreinforcement. Compos. Sci. Technol. 66, 2187–2196.
Pingali, S.V., Urban, V.S., Heller, W.T., Mcgaughey, J., O'neill, H., Foston, M., Myles, D.A., Ragauskas, A., Evans, B.R., 2010. Breakdown of cell wall nanostructure in dilute acid pretreated biomass. Biomacromolecules 11, 2329–2335.
Plackett, D., Jankova, K., Egsgaard, H., Hvilsted, S., 2005. Modification of jute fibers with polystyrene via atom transfer radical polymerization. Biomacromolecules 6, 2474–2484.
Poletto, M., Zattera, A.J., Pistor, V., 2013. Structural characteristics and thermal properties of native cellulose. In: van de Van, T., Godbout, L. (Eds.), Cellulose Fundamental Aspects. InTech.
Popa, M., Belc, N., 2007. Packaging. In: McElhatton, A., Marshall, R. (Eds.). Food Safety: A Practical and Case Study Approach. Springer, New York.
Postek, M., Brown, E., 2009. Sustainable, renewable nanomaterials may replace carbon nanotubes. SPIE Newsroom 17.
Pracella, M., Haque, M.M.-U., Alvarez, V., 2010. Functionalization, compatibilization and properties of polyolefin composites with natural fibers. Polymers 2, 554.
Pranamuda, H., Tokiwa, Y., Tanaka, H., 1996. Physical properties and biodegradability of blends containing poly(ε-caprolactone) and tropical starches. J. Environ. Polym. Degrad. 4, 1–7.
Reddy, M.M., Misra, M., Mohanty, A.K., 2012. Bio-based materials in the new bio-economy. Chem. Eng. Prog. 108, 37–42.
Reddy, M.M., Vivekanandhan, S., Misra, M., Bhatia, S.K., Mohanty, A.K., 2013. Biobased plastics and bionanocomposites: current status and future opportunities. Prog. Polym. Sci. 38, 1653–1689.
Regiani, A.M., Frollini, E., Marson, G.A., Arantes, G.M., El Seoud, O.A., 1999. Some aspectsof acylation of cellulose under homogeneous solution conditions. J. Polym. Sci. Part A 37, 1357–1363.
Rhim, J.W., Kim, J.H., 2009. Properties of poly(lactide)-coated paperboard for the use of 1-way paper cup. J. Food Sci. 74, E105–E111.
Ries, M.E., Radhi, A., Keating, A.S., Parker, O., Budtova, T., 2014. Diffusion of L-ethyl-3-methyl-imidazolium acetate in glucose, cellobiose, and cellulose solutions. Biomacromolecules 15, 609–617.
Rogovina, S., Aleksanyan, K., Prut, E., Gorenberg, A., 2013. Biodegradable blends of cellulose with synthetic polymers and some other polysaccharides. Eur. Polym. J. 49, 194–202.
Ross, P., Mayer, R., Benziman, M., 1991. Cellulose biosynthesis and function in bacteria. Microbiol. Rev. 55, 35–58.
Sanchez-Garcia, M., Lagaron, J., 2010. On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. Cellulose 17, 987–1004.
Sanchez-Garcia, M.D., Gimenez, E., Lagaron, J.M., 2008. Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. Carbohydr. Polym. 71, 235–244.
Sannino, A., Demitri, C., Madaghiele, M., 2009. Biodegradable cellulose-based hydrogels: design and applications. Materials 2, 353–373.
Saroja, N., Gowda, L.R., Tharanathan, R.N., 2000. Chromatographic determination of residual monomers in starch-g-polyacrylonitrile and starch-g-polyacrylate. Chromatographia 51, 345–348.
Sastry, P.K., Satyanarayana, D., Mohan Rao, D.V., 1998. Accelerated and environmental weathering studies on polyethylene–starch blend films. J. Appl. Polym. Sci. 70, 2251–2257.

Schenzel, A., Hufendiek, A., Barner-Kowollik, C., Meier, M.A.R., 2014. Catalytic transesterification of cellulose in ionic liquids: sustainable access to cellulose esters. Green Chem. 16, 3266–3271.
Schwach, E., Avérous, L., 2004. Starch-based biodegradable blends: morphology and interface properties. Polym. Int. 53, 2115–2124.
Scott, G., 2000. "Green" polymers. Polym. Degrad. Stabil. 68, 1–7.
Semsarilar, M., Ladmiral, V., Perrier, S., 2010. Synthesis of a cellulose supported chain transfer agent and its application to RAFT polymerization. J. Polym. Sci. Part A 48, 4361–4365.
Shah, A.A., Hasan, F., Hameed, A., Ahmed, S., 2008. Biological degradation of plastics: a comprehensive review. Biotechnol. Adv. 26, 246–265.
Shahlari, M., Lee, S., 2012. Mechanical and morphological properties of poly(butylene adipate-*co*-terephthalate) and poly(lactic acid) blended with organically modified silicate layers. Polym. Eng. Sci. 52, 1420–1428.
Shen, D., Huang, Y., 2004. The synthesis of CDA-g-PMMA copolymers through atom transfer radical polymerization. Polymer 45, 7091–7097.
Shengdong, Z., Ziniu, Y., Yuanxin, W., Xia, Z., Hui, L., Ming, G., 2005. Enhancing enzymatic hydrolysis of rice straw by microwave pretreatment. Chem. Eng. Commun. 192, 1559–1566.
Sheth, M., Kumar, R.A., Davé, V., Gross, R.A., Mccarthy, S.P., 1997. Biodegradable polymer blends of poly(lactic acid) and poly(ethylene glycol). J. Appl. Polym. Sci. 66, 1495–1505.
Simon, C.M., Kaminsky, W., Schlesselmann, B., 1996. Pyrolysis of polyolefins with steam to yield olefins. J. Anal. Appl. Pyrol. 38, 75–87.
Siqueira, G., Bras, J., Dufresne, A., 2010. Cellulosic bionanocomposites: a review of preparation. Polymers 2, 728–765.
Siracusa, V., Rocculi, P., Romani, S., Rosa, M.D., 2008. Biodegradable polymers for food packaging: a review. Trends Food Sci. Technol. 19, 634–643.
Smith, R., 2005. Biodegradable Polymers for Industrial Applications. CRC Press, New York.
Someya, Y., Sugahara, Y., Shibata, M., 2005. Nanocomposites based on poly(butylene adipate-*co*-terephthalate) and montmorillonite. J. Appl. Polym. Sci. 95, 386–392.
Song, Y., Sun, Y., Zhang, X., Zhou, J., Zhang, L., 2008. Homogeneous quaternization of cellulose in NaOH/urea aqueous solutions as gene carriers. Biomacromolecules 9, 2259–2264.
Stenius, P., 2000. Papermaking Science and Technology: Forest Products Chemistry Book 3. Fapet, Helsinki, Finland.
Stenzel, M.H., Davis, T.P., Fane, A.G., 2003. Honeycomb structured porous films prepared from carbohydrate based polymers synthesized via the RAFT process. J. Mater. Chem. 13, 2090–2097.
Sudesh, K., Iwata, T., 2008. Sustainability of biobased and biodegradable plastics. Clean Soil Air Water 36, 433–442.
Swatloski, R.P., Spear, S.K., Holbrey, J.D., Rogers, R.D., 2002. Dissolution of cellulose with ionic liquids. J. Am. Chem. Soc. 124, 4974–4975.
Swatloski, R.P., Holbrey, J.D., Rogers, R.D., 2003. Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. Green Chem. 5 (4), 361–363.
Tang, X., Gao, L., Fan, X., Zhou, Q., 2007. Controlled grafting of ethyl cellulose with azobenzene-containing polymethacrylates via atom transfer radical polymerization. J. Polym. Sci. Part A 45, 1653–1660.
Teck Nam, A., Yoon, L.W., Lee, K.M., Ngoh, G.C., Chua, A.S.M., Lee, M.G., 2011. Efficiency of ionic liquids in the dissolution of rice husk. Bioresources 6, 4790–4800.
Thompson, R.C., Moore, C.J., Vom Saal, F.S., Swan, S.H., 2009. Plastics, the environment and human health: current consensus and future trends. Phil. Trans. R. Soc. B 1, 1–14.

Tome, L.C., Freire, M.G., Rebelo, L.P.N., Silvestre, A.J.D., Pascoal Neto, C., Marrucho, I.M., Freire, C.S.R., 2011. Surface hydrophobization of bacterial and vegetable cellulose fibers using ionic liquids as solvent media and catalysts. Green Chem. 13, 2464–2470.

Tomšič, B., Simončič, B., Orel, B., Vilčnik, A., Spreizer, H., 2007. Biodegradability of cellulose fabric modified by imidazolidinone. Carbohydr. Polym. 69, 478–488.

Tserki, V., Matzinos, P., Pavlidou, E., Vachliotis, D., Panayiotou, C., 2006. Biodegradable aliphatic polyesters. Part I. Properties and biodegradation of poly(butylene succinate-*co*-butylene adipate). Polym. Degrad. Stabil. 91, 367–376.

Vasanthan, N., Ly, O., 2009. Effect of microstructure on hydrolytic degradation studies of poly (L-lactic acid) by FTIR spectroscopy and differential scanning calorimetry. Polym. Degrad. Stabil. 94, 1364–1372.

Vlček, P., Janata, M., Látalová, P., Kříž, J., Čadová, E., Toman, L., 2006. Controlled grafting of cellulose diacetate. Polymer 47, 2587–2595.

Waly, A., Abdel-Mohdy, F.A., Aly, A.S., Hebeish, A., 1998. Synthesis and characterization of cellulose ion exchanger. II. Pilot scale and utilization in dye heavy metal removal. J. Appl. Polym. Sci. 68, 2151–2157.

Wang, Y.-Z., Yang, K.-K., Wang, X.-L., Zhou, Q., Zheng, C.-Y., Chen, Z.-F., 2004. Agricultural application and environmental degradation of photo-biodegradable polyethylene mulching films. J. Polym. Environ. 12, 7–10.

Wang, X., Li, H., Cao, Y., Tang, Q., 2011. Cellulose extraction from wood chip in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). Bioresource Technol. 102, 7959–7965.

Wang, H., Gurau, G., Rogers, R.D., 2012. Ionic liquid processing of cellulose. Chem. Soc. Rev. 41, 1519–1537.

Whiteman, N.F., 2000. New packaging thermoplastic, polylactide. Polymers, Laminations and Coatings Conference, Chicago, USA.

Witt, U., Einig, T., Yamamoto, M., Kleeberg, I., Deckwer, W.D., Müller, R.J., 2001. Biodegradation of aliphatic–aromatic copolyesters: evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. Chemosphere 44, 289–299.

Wu, J., Zhang, J., Zhang, H., He, J., Ren, Q., Guo, M., 2004. Homogeneous acetylation of cellulose in a new ionic liquid. Biomacromolecules 5, 266–268.

Yamada-Onodera, K., Mukumoto, H., Katsuyaya, Y., Saiganji, A., Tani, Y., 2001. Degradation of polyethylene by a fungus, *Penicillium simplicissimum*. Polym. Degrad. Stabil. 72, 323–327.

Yang, A., Wu, R., Zhu, P., 2001. Thermal analysis and miscibility of chitin/polycaprolactone blends. J. Appl. Polym. Sci. 81, 3117–3123.

Yavuz, H., Babaç, C., 2003. Preparation and biodegradation of starch/polycaprolactone films. J. Polym. Environ. 11, 107–113.

Yew, G.H., Yusof, A.M.M., Ishak, Z.A.M., Ishiaku, U.S., 2005. Natural weathering effects on mechanical properties of polylactic acid/rice starch composites. 8th Polymers for Advanced Technologies International Symposium, Budapest, Hungary.

Zarrinbakhsh, N., Mohanty, A., Misra, M., 2013. Improving the interfacial adhesion in a new renewable resource-based biocomposites from biofuel coproduct and biodegradable plastic. J. Mater. Sci. 48, 6025–6038.

Zavrel, M., Bross, D., Funke, M., Büchs, J., Spiess, A.C., 2009. High-throughput screening for ionic liquids dissolving (ligno-)cellulose. Bioresour. Technol. 100, 2580–2587.

Zhang, L., Xiong, C., Deng, X., 1995. Biodegradable polyester blends for biomedical application. J. Appl. Polym. Sci. 56, 103–112.