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An overview of starch-based biopolymers and their biodegradability

Una revisión sobre biopolímeros con base en almidón y su biodegradabilidad

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Abstract

Increasing interest in renewable feedstock and biopolymers has led to the development of several alternatives to traditional plastics. Starch has been explored as an interesting raw material; however, native starches exhibit poor mechanical properties and thermal stability. Numerous endeavors to develop blends of starch and biodegradable polymers to obtain materials with a wide range of application have been attempted. Starch blending with the most common biodegradable polymers is discussed. Additionally, tests of biodegradability applied to these blends have been reviewed. Several standardized tests, both aerobic and anaerobic, can be used to evaluate the biodegradability of biopolymeric blends. These tests attempt to using mass measurements, generated gases, visual observations, and various techniques through which changes in the structure of the materials can be determined. This review focuses on providing an overview of recent advancements in biopolymer production as well as to shows that in most cases the blends biodegrade considerably while a simultaneous decrease in their mechanical properties, especially with the increase of the amount of starch in the formulation.

Keywords: starch blends, thermoplastic starch, aerobic biodegradation, anaerobic biodegradation.

Resumen

El interés cada vez mayor en fuentes de alimentación renovables y biopolímeros ha llevado al desarrollo de varias alternativas para sustituir los plásticos tradicionales. El almidón aparece como una materia prima interesante; sin embargo, los almidones nativos presentan algunas limitaciones básicamente asociadas a malas propiedades mecánicas y de estabilidad térmica. Se han realizado numerosos esfuerzos para desarrollar mezclas de almidón/polímeros biodegradables para obtener materiales con una amplia gama de aplicación. Esta revisión se centra principalmente en presentar una visión general de los avances recientes en la producción de biopolímeros. Además, se ha revisado la literatura de varios ensayos de biodegradabilidad aplicados a estas mezclas. Se pueden aplicar varias pruebas estandarizadas, tanto aeróbicas como anaeróbicas para evaluar su biodegradabilidad. Se realizan mediciones de masa, gases generados, observación visual y técnicas analíticas que permitan determinar los cambios en la estructura de los materiales. De los resultados revisados, en la mayoría de los casos puede establecerse que dichas mezclas presentan un grado considerable de biodegradación pero al mismo tiempo una disminución de sus propiedades mecánicas, especialmente con el aumento de la cantidad de almidón en la formulación.

Palabras claves: mezclas con almidón, almidón termoplástico, degradación aerobia, degradación anaerobia.

1 Introduction

Plastic packaging materials perform an important role in the food industry due to their durability, lightness, and flexibility which ceramics and metals cannot provide (Kutz, 2012).However, the environmental consequences of additional plastics have prompted researchers to develop more environmentally-friendly materials(Vromany col., 2009),(Soroudiy col., 2013).Currently, the packaging industry is looking forward to introducing biodegradable polymers into the market, aiming to replace the petroleum-based materials and to help solve waste-disposal problems (Aliy col., 2013).

Biodegradable polymers are defined as polymers that can be transformed into carbon dioxide, water, methane, and other products withlow molecular weightthrough a degradation process. The chemical process of biodegradation is a series of reactions which occur through the presence of living organisms,e.g., bacteria, fungi, yeast, algae, and insects(Fliegery col., 2003) at specific conditions of light, temperature, oxygen (aerobic or anaerobic conditions), and other variable(Kopčilováy col., 2013, Guoy col., 2012, Wangy col., 2003).

The polymer microstructure also influences the degradation process (Vromany col., 2009).Furthermore, depending on the environmental conditions and the inherent molecular structure of the polymer, biodegradation can take from a few weeks to several months (Fliegery col., 2003).When these sorts of polymers degrade, production of harmful substances is reduced; instead, the residues produced can be incorporated into the natural geochemical cycle(Okada 2002,Wang y col., 2003).

Biobased and biodegradable polymers have an extensive range of applications such as pharmaceutical, biomedical, horticulture, agriculture, consumer electronics, automotive, textiles and packaging, the last being perhaps one of the most common applications(European Bioplastics, 2013). To date, many biodegradable polymers are available, namely, polylactic acid or polylactide (PLA), polycaprolactone (PCL), polybutylene adipate terephthalate (PBAT),polyhydroxybutyrate (PHB), polyhydroxyalkanoates (PHAs), and polyesteramide (PEA),(Soroudi y col., 2013).. Even so, in some cases,the high cost of producing biodegradable polymers prevents them from being used as substitutes for traditional polymers(Gironès y col., 2012).

An attractive alternative to the development of biopolymers is the use of natural raw materials such as starch, lignin, collagen, cellulose; moreover, starch offers a myriad of possibilities for producing environmentally-friendly materials with potential for mass commercial use (Gironès y col., 2012). Starch is a polysaccharide that comes from tubers, roots, and grains. Traditionally, starch has played an important role as a food ingredient ,but it is starting to be used in other applications, such as paper,pharmaceuticals, and textiles(Laycock y col., 2014).Native starchesexperiment high degradation rates, andmany shortcomings are associated with theirlimited mechanical properties and processability problems(Tang y col., 2008)(Xu y col., 2014)(Priya y col., 2014).Researchers have evaluated some methods of fulfilling all industry requirements in order to improve functional properties. Various processes including plasticization, physical, chemical, enzymatic and genetic modifications have been studied(Neelam y col., 2012), however, starch/biodegradable polymers blends seem to be the most promising way to enhance the mechanical and thermal properties of native starch(Marjadi, 2011, Cao y col., 2007). Consequently, the aim of this review is to analyze the current state of the art of starch blends with biodegradable polymers.

2 Types of biodegradable polymers

Biodegradable polymers are classified in two important groups according to their origin: biologically derived or natural polymers and synthetics polymers (Nair y col., 2007). Natural biopolymers come from living organisms, which means that they are available in large quantities from renewable sources. On the other hand, synthetic polymers are produced from non-renewable sources like petroleum, coal, and natural gas(Vroman y col., 2009)(Marrazo y col., 2007). However, no clear-cut line separates these groups, e.g.,polyglycol acid could be obtained from oil-derived materials using a synthetic process or by fermentation mechanisms (Zhang y col., 2014).

2.1 Natural polymers

2.1.1 Biodegradable polymers obtained through fermentation

Biodegradable polymers obtained through fermentation are related to polyesters and neutral polysaccharides produced by microorganisms with access to a feed reserve of carbon and to an energy source (Flieger y col., 2003). The market presents an important advance in the research of PHAs, which is a group of ydroxybutyric and hydroxyvaleric acids. PHAs are high molecular weight polymers with n-alkyl substitutions in the main chain. Usually, these polymers exhibit a rate of biodegradability on the order of years (Zhang y col., 2014). Within this group, poly(3-hydroxyburtyrate) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) have been proposed as alternative materials for different industrial applications(Vroman y col., 2009).The latest research in PHB production opens the possibility of obtaining it from water hyacinth, one of the most notorious aquatic weeds, thus it is easily available and inexpensive. One of the most important advantages of this biopolymeris its heat tolerance; with a melting point around 175°C(Laxmana Reddy y col., 2013).

2.1.2 Biodegradable polymers made from chemically modified natural products

Biodegradable polymers made from chemically modified natural materials include polymers like polysaccharides, polymers formed by many glucose and fructose units(Zhang y col., 2014). Cellulose and starch have been studied the most because of their perceived potential for replacing the oil-based polymers on a large scale and at a low cost (Moad, 2011, Schwach y col., 2004).

Starch is inexpensive and biodegradable, thus it has generated increasing interest as a component of plastic.However, the poor mechanical properties and water solubility of starches have led to the development of proposed techniques such as plasticization or blends to produce competitive commercial commodities (Schwach y col., 2004).

2.2 Synthetic polymers

Synthetic polymers materials come mainly from petroleum sources; however these materials are able to decompose, which is evaluated by standardized tests such asISO 1708, ASTM D6400,ASTM D6868, ASTM D5338, and CSN EN 13432(Remar, 2011).In general,these types of biopolymers, are biologically inert and have predictable properties(Nair y col., 2007, Okada, 2002).

Polyesters are the most representative polymers of this group. They are classified in aliphatic and aromatic. Corresponding to the aliphatic polyestersgroup can be mentioned for example PCL, PLA, poly(butylene succinate) (PBS),poly(butylene succinate-co-butyleneadipate) (PBSA), poly(glycolic acid) (PGA), and poly(vinylalcohol) (PVA).The main problem associated with these materials is that their melting point is around 60°C, which excludes them from some applications (Remar 2011).

Because of its high biodegradability, biocompatibility, good process-ability, and relatively low cost, PLA is one of the most studied biopolymers(Kazem y col., 2013).Synthesis of PLAstarts with the production of lactic acid through bacterial fermentation and the follows the polymerization(Laxmana Reddy y col., 2013). Recently, an innovative process consisting of the ring-opening polymerization of pre-polymer lactide dimers is used to obtain high molecular weight of PLA (Babu y col., 2013). In order to improve the properties of PLA, it is blended with several hydrophilic polymers likePCL, PVA, poly(ethylene glycol) (PEG), poly(propylene oxide), hyaluronicacid, and poly(vinyl acetate) (PVAc) (Liao y col., 2009).

PVA has excellent gas barrier properties, high strength, tear, adhesive, flexibility, water absorption, and bondingcharacteristics (Priya y col., 2014). Industrially, PVAis usedin themanufacturing of biodegradable films as well as adhesives and paper coatings (Flieger y col., 2003).

3 Starch blending

Native starches exhibit some limitations mostly related tomechanical integrity, thermal stability, and humidity absorption (Tang y col., 2011, Teixeira y col., 2012, Schwach y col., 2004).Because of these limitations, starches are often blended with other materials to enhance their properties. Blending starches aims to reduce the production cost; to improve barrier properties and dimensional stability; to decrease the hydrophilic character of starch; and increase its biodegradability(Schwach y col., 2004, Tang y col., 2011). In order to optimize theoverall properties of such blends, starche sare blended with low molecular mass plasticizers such as glycerol, glucose, sorbitol, urea and ethylene glycol(Priya y col., 2014, Teixeira y col., 2012, Schwach y col., 2004). The addition of plasticizers conduct to thermoplastic starch (TPS), (Tang y col., 2011, Soares y col., 2014), which is characterized by the spontaneous destructuration of the semi-crystalline structure of starch and the formation of hydrogen bonds between the plasticizer and the starch (Bendaoud y col., 2013)(Fabunmi y col., 2004).

Depending on the type of the plasticizer blended with the starch, the final properties of the TPSdiffer. In general, plasticizers produce anincrease in flexibility, extensibility, and fluidity by reducing the strong intermolecular chain interactions. Additionally,TPS remains a very hydrophilic material (Schwach y col., 2004).Recent advances in starch blending include blending TPS with biodegradable polymers is one of the most recent advancements mainly in food packaging applications (Lu y col., 2009).

3.1 Starch/PVA

PVA is a synthetic biodegradable polymer that has the advantages of good film forming, strong conglutination, high thermal stability, and gas barriers properties (Priya y col., 2014)(Parvin y col., 2010). The presence of PVA in a blend increases the mechanical strength, water resistance, and weather resistance of the blend (Wang y col., 2014). Gelatinization is the most common method of blending starch with PVA; other methods might not be useful because of the gap between the thermo-degradation temperature and the melting temperature (Wang y col., 2014). The compatibility of the PVA and starch enables them to form a continuous phase at blending (Lu y col., 2009)even though the properties of the blends deteriorate as starch content rises, causing phase separation during blend preparation. To improve the compatibility between PVA and starch, the addition of suitable plasticizers, cross-linking agents, fillers, and compatibilizers has been studied (Priya y col., 2014). Some common plasticizers used in this blend are glycerol and water (Tang y col., 2011). Both PVA and starch can be plasticized into a thermoplastic material, regularly using the casting method and glycerol in an aqueous medium (Zhou y col., 2009).

Both starch and PVA are biodegradable in several microbial environments; however, the biodegradability of PVA depends on its degree of hydrolysis and its molecular weight (Lu y col., 2009, Azahari y col., 2011).

3.2 Starch/PLA

Due to its biodegradable and hydrophobic characteristics, PLA has received considerable attention in the research of biomedical and packaging applications. Commercial PLA grades are usually copolymers of poly(L-lactic acid) and poly(D, L-lactic acid) (Martin y col., 2001, Soares y col., 2014), Murariu y col., 2016).

Some of the disadvantages of PLA are low flexibility, ductility, and impact résistance. To improve PLA's flexibility and impact resistance, numerous plasticizers have been incorporated such as poly (ethylene glycol), glycerol, glucose monoesters, citrate esters, and oligomers. However, TPS as a blend component for PLA offers important advantages in terms of cost, properties, and biodegradability (Soares y col., 2014, Martin y col., 2001, Murariu y col., 2016).

The hydrophilic properties of starch and the hydrophobic ones of PLA, cause low miscibility between the two compounds; for this reason, good melt-blending techniques and the addition of compatibilizers are required to increase successful interaction, i.e., amphiphilic molecules or coupling agents (Brito y col., 2013)(Teixeira y col., 2012). Poly (hydroxyester ether), methylenediphenyldiisocyanate (MDI), PLA-graft-(maleic anhydride), PLA-graft-(acrylic acid) and PLA-graft-starch and poly(vinyl alcohol) have been used as compatibilizers in this blend (Wang y col., 2007).

3.3 Starch/PCL

Poly(ε-caprolactone)is a linear,semi-crystalline, aliphaticpolyester that is prepared by ring-opening polymerization of ε-caprolactone. It is hydrophobic with alow melting point (60-65□C), which could be overcome bytreating it with a radiation cross-linking process or blending it with other polymers (Singh y col., 2003)(Tokiwa y col., 2009)(Ortega-Toro y col., 2016).The degradation rate of PCL homopolymersis relatedtotheir molecular weight and degree of crystallinity. Thus, copolymerization of PCL with other aliphatic polyesters can improve its biodegradable ability. (Singh y col., 2003). On the other hand, the presence of starch increases the rate of biodegradation of PCL because it intensifies hydrolysis reactions (Vikman y col., 1999).

Because PCL is a hydrophobic polymer, blends of PCL and starch exhibit an undesirable phase separation (Sugih y col., 2009). In order to increase the compatibility between the two materials, the addition of an interfacial agent or compatibilizer is necessary. Sugihy col. Assessed the behavior of two interfacial agents, PCL-g-glycidyl methacrylate (PCL-g-GMA) and PCL-g-diethyl maleate (PCL-g-DEM) in a PCL-starch blend(Sugih y col., 2009); meanwhile, Singh y col. Mentioned introducing poly(ethylene glycol) (PEG) to PCL to improve interfacial properties(Singh y col., 2003).

Adding PCL to starch overcome the weaknesses of pure TPS and starch and at the same time, crystallinity reduction of PCL favored the enzymatic degradation (Rosa y col., 2005b), (Avérous y col., 2000). Blends of starch and PCL have been extensively studied during the last decade, although both high production cost and properties variation have limited its applications (Singh y col., 2003).

3.4 Starch/PHB-HV

Reis et al. evaluateblends of polyhydroxybutyrate-hydroxyvalerate with cornstarch at different concentrations prepared by casting, nonetheless,these blends show a lack of interfacial adhesion among the starch, thePHB-HV,and heterogeneous dispersion of starch granules over the PHB-HV matrix(Reis y col., 2008). With adequate formulation and processing techniques,can be reduced the shortcoming of adhesion between starch and PHB-HV(Wang y col., 2003).

3.5 Starch/PBSandstarch/PBSA

PBS is commercially available as a thermoplastic polymer. Its high degree of crystallinityproduces low degradation rates which provide interesting properties such as excellent impact strength, high thermal stability, and good chemical resistance(Suchao-in y col., 2013).The addition of starch to PBS improves its flexibility and increases its biodegradation time.This way expanding its applications in packaging and flushable hygiene products is possible(Wang y col., 2003), (Babu y col., 2013).

PBSA is an aliphatic thermoplastic copolymer synthesized by polycondensation of 1,4-butanediol with succinic and aliphatic acids. It has melt processability, good mechanical properties, biodegradability, and boththermal and chemical resistance (Jbilou y col., 2013)(Maubane y col., 2017). Maubane y col. evaluated the morphology and properties of melt-processed butyl-etherified starch/PBSA blends and found that highly-branched amylopectin structures in starches permit better chemical interactions with the PBSA matrix compared to linear amylose structures (Maubane y col., 2017).

3.6 Ternary Blends

Liao y col. studied ternary blends between PCL, PLA, and starch with acrylic acid grafted PLA70PCL30 as compatibilizer in an attempt to overcome the shortcomings of brittle and processing properties as well as to reduce the overall cost of production. Polymer literature reports that the addition of PCL increased the ductility of TPS/PLA blends(Liao y col., 2009). Other researchers have used poly(butylene adipate –co-terephthalate) (PBAT) instead of PCL because PBAT is a flexible copolyester with a high level of degradability (Ren y col., 2009).

In recent years, interest has been focused on ternary blends of PHB, EVA, and starch. The compatibility between PHB and EVA is enhanced by the vinyl acetate content. Thus, EVA copolymer can be an important modifier for PHB/starch blends (Ma y col., 2014).

3.7 Application s of and perspectives of starch blending

The developingof starch blending tend to be more interesting while potential applications are extensive, and they can be able to substitute an older material that exhibits the same properties. Some important applications of starch-based biopolymers are summarized in Table 1.

Table 1. Applications of starch-synthetic polymer blends

Blend	Applications	References
Starch/PVA	• Replacement of LDPE films in applications where barrier properties are not critical. • Water-soluble laundry bags • Biomedical and clinical field • Replacement of polystyrene foams as loose fill packaging material • Packaging applications	(Tang y col., 2011), (Azahari y col., 2011)
Starch/PLA	• Food packaging, electronic devices, membrane material (chemical and automotive industries), textile industry (as PLA fibers), and medical applications • Packaging material	(Babu y col., 2013), (Martin y col., 2001)
Starch/PBSA	• Antimicrobial packaging materials	(Khalil y col., 2014)
Starch/ PHB	• Biomaterial in medical applications	(Godbole y col., 2003)

3.7 Nanocomposites: fillers in starch matrix

The addition of nanocomposites to reinforce starch blends is one of the latest advances; these nanocomposites can bemade using inorganic or natural materials with a charge between 2 and 8% of nanoscale inclusions (Almasi y col., 2010).Nanofillerscan be presented in different ways: spherical or polyhedral nanoparticles, nanotubes, and nanolayers. In all cases, these nanomaterials exhibit a large superficial area that improves adhesion between the composites of the polymer blend (Ahmed y col., 2012).

Xiey col .present a complete review of different types of nano-fillers in plasticized starch-based matrixes, the mainly are phyllosilicates (montmorillonite, hectorite, sepiolite), polysaccharide (nanowhiskers/nanoparticles from cellulose, starch, chitin, chitosan), carbonaceous nanofillers(carbon nanotubes, graphite oxide, carbon black), and so on.Phyllosilicatesare the nanofillers employed most often due to their availability, low price, and high aspect ratio. However ,polysaccharidenanofillers require acid hydrolysis during preparation, making their use not ecologically friendly(Xie y col., 2013).The principal effects of the addition of nanofillers in starch-based materials are:thermo-mechanical stability improvement,biodegradation increase ment and hydrophilicity reduction(Xie y col., 2013)(Belibi y col., 2013).

3.8 Starch-based nanocrystals

Starch-based nanocrystals are formulated from native starch granules under hydrolysis reactions of the amorphous regions, thereby releasing the crystalline lamellae (Wittaya, 2012). This type of nanofiller involves low cost production, renewability, and environmentally-friendly characteristics (Wittaya, 2012).

The use of starch-based nanocrystals to reinforceelastomer-based matrixes shows a positive reinforcing effect evidenced by the increase of both stresses at thebreak and relaxed storage modulus (Dufresne y col., 2013). The main aspects that highlight by the addition of starch-based nano-biocomposites are the increase of values of strength at break and glass transition temperature, but also their disadvantages associated are related with the increment of water absorption and decomposition temperature (Xie y col., 2013). Tang and Alavi also mention the possibility of incorporating starch/PVA nanocomposites in starch/PVA blends to improve the physical properties as an application(Tang y col., 2011).

4 Environmental biodegradability of biopolymers

During recent decades, the production and use of plastics has grown exponentially. Those plastic materials take an average of 100 years to break down in the environment (Villa y col., 2009). Some waste-management options available for plastics at the end of their useful life include recycling, incineration, and disposing of them in a landfill. In all cases, plastics cause a significant negative impact on the environment through the generation of pollutant gases and toxic substances such as dioxins, furans (Wagner, 2009), and endocrine disruptors (Katami y col., 2002) and the production of leachate which contains heavy metals that pollutes water and soil. In addition, the accumulation of plastics in landfills due to their low biodegradability represents an important impact (Merchán y col., 2009).

All of these aspects have led to concern about plastics in the last few years and have made clear the need for biodegradable plastics and understanding of how they biodegrade (Gironès y col., 2012).Some studies have been conducted to investigate new materials that employ biodegradable polymers instead of conventional ones (Soroudi y col., 2013). In 2017, the world production of bioplastics is expected to exceed six million tons(European Bioplastics, 2013).

In order to evaluate the biodegradability of these biodegradable polymers, institutions such as the American Society for Testing and Materials (ASTM), the European Committee for Standardization and the International Standards Organization (ISO) have established some standard test (Kyrikou, 2007)(Pagga, 1999).

Two basic methods are used in biodegradation assays: aerobic and anaerobic digestion. The activity of certain microorganisms decomposes biodegradable polymers into environmentally friendly components, e.g., carbon dioxide, methane, water, inorganic elements such as sodium, potassium, phosphorous, and calcium and biomass (Leja, 2010). Another type of biodegradation assay is to test the ecotoxicity using plant and animal species such as cress and earthworms (Kyrikou, 2007). Some other non-standard tests based on the use of material exposure to specific microorganisms also exist (Jayasekara, 2005). In general, most of the methods include the measurement of molecular weight, molecular weight distribution, carbon dioxide and/or methane, and weight loss of the material as well as visual observations of changes in the samples after the assay (Kyrikou, 2007). Tensile properties evaluated after a biodegradability assay are tensile strain, tensile strength, elongation, and tensile modulus. A number of analytic techniques are also used: Fourier transform infrared spectroscopy, differential scanning colorimetry, nuclear magnetic resonance spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy, and X-ray diffraction (Jayasekara, 2005).

4.1 Biodegradation of starch/PVA

PVA and starch are biodegradable in some microbial environments; they are compatible and their blends present good film properties. Starch/PVA blends are some of the most common biodegradable plastics used in packaging and agricultural applications (Leja, 2010).

A number of studies have been conducted to determine the biodegradability of these blends, here some of them are highlighted. Several wheat starch/PVA/glycerol blends prepared using a solution casting technique under ISO 14855 were examined by composting for 45 days. Starch and glycerol were totally degraded while PVA appeared practically intact. The blend characteristics were enhanced by surface modification with chitosan, which did not interfere with the biodegradation of the starch (Jayasekara y col., 2003). In another study, the biodegradation of PVA and the effect of its molecular weight on the biodegradation of PVA/starch blends with various amounts of cross-linked starch (CLS) compared to PVA blends with acid-modified starches (AMS) were evaluated in a 180 days assay. The blends with PVA with higher molecular weights demonstrated higher biodegradability, while the biodegradability of some PVA/AMS blends increased with increasing percentages of AMS. Overall, PVA/AMS samples showed higher biodegradation than those of PVA/CLS (Chai y col., 2012).

Other studies have been carried out in aqueous anaerobic environments with digested activated sludge from municipal wastewater treatment plants. The degradation of blow-molded films made of commercial PVA and starch was examined. The degradation of PVA after being blended with native or plasticized starches increased in approximately the same amount even at a low starch level of approximately 5 %wt.(Pšeja y col., 2006). When the quantity of starch in the starch-modified PVA blend increased from 21% to 42%, a higher degree of biodegradation – about 60% – was achieved, and mechanical properties of modified PVA were diminished when the biodegradability of blends composed of PVA, glycerol-plasticized and biopolymer such as starch, gellan and xanthan was evaluated (Hrnčiřík y col., 2010).

The behavior of some blends in soil environments has been also analyzed. The biodegradability of starch/PVA films was evaluated in a 6-month soil burial test in which the weight loss over time was measured. Degradation of the citric acid-added films was better than of those with glycerol added. In all cases, degradation of films of about 80% occurred in the initial 70 days, after which the rate of degradation was slow (Yun, 2010). In a 30 day study of the biodegradability of starch/PVA blends with glacial acetic acid as crosslinking agent, researchers found that the biodegradability of starch/PVA blend films is especially relevant in moist soils. In dry soils, biodegradation time increased from 10 to 14 days with increasing molecular weight of the PVA from $31x10^3$ to $205x10^3$ g/mole, while the degradation of the same blend films in a moist soil environment occurred within three days (Negim y col., 2014). The effect of starch content on the biodegradability starch/PVA blend films prepared using the melting technique was determined by the weight loss of specimens buried in soil for 30 days was investigated. Weight loss increased with increasing starch content and burial time. The films with the highest percentage of starch had the highest values of weight loss (Râpă y col., 2014). For some starch/PVA blends buried in soil for a testing period of 45 days, biodegradation of 28 to 38% was observed in blends of 0 to 30 % of starch. Thus, researchers concluded that as the starch content increases, the biodegradation rate also increases in most cases (Tanase y col., 2016). A study of the biodegradability by burial in soil and compost of corn starch/PVA blend films prepared using the solution-casting method showed that films with corn starch were highly biodegraded by enzymes both in soil and compost. As the percentage of corn starch increased, the strength of the blends decreased. The biodegradability increased up to 85% as the burial time increased in both soil and compost in 8 weeks (Azahari y col., 2011).

Microorganisms from different sources have been found to degrade starch/PVA blends. Specifically, bacteria and fungi isolated from the activated sludge of a municipal sewage plant and from a landfill biodegraded blends containing starch, PVA, and glycerol; the microorganisms consumed the starch, the amorphous region of PVA and the plasticizer (Jayasekara, 2005). Additionally, two fungi, *Penicilliumdaleae* and *Apergillusflavus*, isolated from an aerobic compost environment degraded PVA/starch films. A weight loss of nearly 71% was measured after 300 days when these two fungi were working separately, significantly higher degradation than the 60% observed in the actual compost over the same period (Maiti y col., 2013).

The biodegradability of PVA/starch blends that have been modified with other materials has been also studied. Composite films of PVA and lignocellulosic fibers from orange waste, with and without cornstarch, biodegraded within 30 days in soil with about 80% mineralization. Starch and lignocellulosic fiber degraded much more rapidly than PVA, and the addition of fiber enhanced the PVA degradation (Imam y col., 2005). The biodegradability of nano-SiO_2 reinforced starch/PVA nanocomposite films was evaluated. The compounds reached a weight loss of about 60%, similar to that obtained without nanoparticles, leading to the conclusion that nanoparticles had no significant effect on the biodegradability of the films tested. However, other studies concluded that biodegradation of films of clay/starch/PVA depends on the type and content of the specific nanoparticles used in the composites (Tang y col., 2011).

In contrast, some studies indicate that starch/PVA blends are not easily biodegradable in environmental conditions. However, a certain degree of biodegradation was achieved in one study when starch/PVA films cast by the solvent method were exposed to soil containing manure. The results showed an increase in the rate of biodegradation as the starch content increased. The ultimate weight loss did not exceed 40% over a period of 3 months, allowing the authors to affirm that this starch/PVA blend plastic film may not degrade easily in natural conditions (Raj, 2004). On the other hand, a study based on the China National Standards 14432 also showed that the degradability increased with the addition of starch. In this study, the biodegradability of starch/PVA blends was analyzed by bio-reactivity kinetic models. The growth rate of the microorganisms in the model increased with the increase in starch content in the first-order reaction kinetics. Applying this model, the decomposition rate of the starch/PVA reached only 36.66% after 180 days. These results add support to the conclusion that starch/PVA blends do not completely biodegrade in a short period of time in natural environments (Chai y col., 2009).

4.2 Biodegradation of starch/PLA

A number of studies exploring the biodegradability of starch-PLA blends in a variety of environments have been conducted. The biodegradation of co-extruded starch/PLA films was studied in liquid, inert solid, and composting media using experimental ISO methods. The percentage of mineralization in the compounds was higher than the minimum required 60% that allows a compound to be classified as biodegradable. Researchers found that the addition of starch enhanced biodegradation of the PLA component, especially in liquid media (Gattin y col., 2002). These results are similar to those obtained in a two-stage study of the behavior of agricultural mulch co-extruded starch/PLA films, in the first stage, the films were treated with ultraviolet light at 315 nm. For the second stage, the standard procedures described in ASTM D 5209–92 and 5338–92 and ISO/CEN 14852 and 14855 were used to measure the biodegradability of films. Regardless of the procedure applied in stage 2, the percentage of biodegradation was higher in the liquid medium than in the inert medium, 92.4–93.4% compared to 80–83% respectively. Weight loss was about 74% after 30 days of treatment (Copinet y col, 2003). The effects of starch and wood flour on the degradation of PLA-based blends were investigated by composting under ISO 14855 standard. The biodegradation rates of starch/PLA blends and PLA/wood flour blends were found to be higher than those of pure PLA. The biodegradation rate increased about 80% when the starch content increased to 40% after 80 days (Petinakis y col., 2010). The compostability of PLA alone compared to starch/PLA blends with different amounts of starch has also been evaluated. After 30 days, all of the samples tested were completely biodegraded, and no residuals were observed in visual inspection. An ecotoxicity test in which the rate of germination and plant growth of monocotyledon and dicotyledon species on the resulting compost were not significantly affected when compared to blank compost showed that both PLA by itself as well as starch/PLA blends appeared to be safe for the ecosystem (Rudeekit y col., 2012). In another study, PLA was blended with chemically modified TPS (CMPS) in a twin-screw extruder. The biodegradability and rate of biodegradation of the blends were investigated in a controlled environment using cellulose as control material. The biodegradability of the blends increased with increasing CMPS content because the CMPS degraded fully, which occurred within 42 days (Shin y col., 2011). A study of the degradation of PLA and it blends with TPS submitted to degradation by tert-butyl hydroperoxide, myoglobin, and peroxide-activated myoglobin in simulated soil showed that TPS favored degradation of the material in all cases (Rodrigues y col., 2015).

Studies using PLA, starch, and several compatibilizers or other substances have been conducted. The study of injection molded tensile bars indicated that weight loss increased with increasing starch and poly(hydroxyester-ether) (PHEE) contents. The blends were composed of various combinations of native cornstarch, PLA, and PHEE, and the bars were buried in soil for one year to determine the effects of the starch and PHEE on the rate of biodegradation (Shogren y col., 2003). The properties of a PLA/starch blend were compared to those of a PLA/acrylic acid (AA) grafted starch composite (PLA-g-AA/starch). The starch in the composite degraded almost completely in a soil environment within three months. The mechanical properties of the blends presented a reduction with regard to tensile strength at breakpoint especially in those with a higher starch content. PLA-g-AA was shown to be resistant to degradation as only a small decrease in weight was seen and only in weeks 7 to 12 (Wu, 2005). The biodegradation of PLA/starch blends using maleic anhydride (MA) as reactive compatibilizerwas evaluated. MA compatibilized blends showed higher biodegradability than starch/PLA blends at the same PLA-starch concentrations. The biodegradability increased with increasing starch content, and MA compatibilized blends showed higher biodegradability compared to those of blends without MA (Jang y col., 2007). The biodegradability of PLA alone and corn starch/PLA composites with and without lysine di-isocyanate was evaluated by enzymatic degradation tests using Proteinase K and burial tests. All composites gradually degraded over time except pure PLA. The degradation rate increased as corn starch content increased (Ohkita, 2006). The effects of the addition of PEG to PLA/TPS blends on the biodegradation properties of the blends were investigated using a 5-month soil burial test. Results indicate that adding PEG causes the blends to degrade faster with considerable weight loss and loss of mechanical properties. The degradation of the blends improved as TPS content increased. The samples containing PEG showed greater weight loss than the samples. The addition of PEG also enhances the degradation rate of TPS/PLA blends (Wang y col., 2003).

4.3 Biodegradation of starch/PCL blends

Scientists have evaluated the biodegradation of starch/PCL blends. The biodegradation of two PCL blends, one with dried granulated sago starch and the second with undried thermoplastic sago starch (TPSS), was evaluated by the determination of weight loss and the amount of adipic acid liberated from PCL in one study. Dried granulated sago starch presented an advantage in both the mechanical properties and biodegradation of the blend. The biodegradation increased as the content of both forms of sago starch increased. The presence of granulated sago starch coincided with higher weight loss compared to weight loss in blends containing the thermoplastic sago starch. The increased amount of adipic acid liberated from PCL indicated that the addition of granulated sago starch enhanced the degradability of PCL and TPSS appeared to decrease the biodegradability (Ishiaku y col., 2002). Another study investigated the biodegradation of three different types of films in different aerobic environments. The three types of films are 100% PCL; a blend of 50% modified starch and 50% polycaprolactone; and a blend of 50% nonmodified starch and 50% polycaprolactone blend, and the aerobic environments in the study were the presence of *Pseudomonas putida*, activated sludge, and compost. *P. putida* was observed to have no effect on degradation over a 90 day period, while considerable deformation of all films was observed even in the first 7 days of degradation with the activated sludge. In the compost environment, degradation was faster, and none of the films were detectable after 15 days (Yavuz, 2003). The biodegradability of blends of PCL with various types of starches in an anaerobic aqueous environment of mesophilic sludge from a municipal wastewater treatment plant was also investigated. For blend preparation, native starch from corn, starch from a genetically modified type of corn, a gelatinized corn starch and an amaranth starch were used. Additional starch/PCL blends were prepared with glycerol using the same basic blends. Blends with glycerol exhibited improved mechanical properties and higher degrees of biodegradation. The biodegradability of the starches ranges from 70% for the maize starch to 81% for the amaranth starch, but the biodegradation of PCL was very low and reached only 2% (Hubackova y col., 2013).

Some studies investigated the biodegradation of multiple PCL/starch blends combined with other substances using composting and soil burial tests. The results of the composting tests were as follows: PCL/high amylose starch compatibilized using pyromellitic anhydride blends indicated that the presence of cellulose acetate butyrate reduced the biodegradability of the blends subjected to a modification of the ASTM D5338 procedure of controlled composting. Neat PCL exhibited a lower rate of degradation than all of the PCL/starch blends. Ten percent modified PCL in blends did not affect theirbiodegradability.(Avella y col., 2000). The evaluation of biodegradation of PCL blends with wood flour and lignin with maleic anhydride-grafted PCL used as compatibilizers showed that the addition of lignin slows biodegradation(Nitz y col., 2001). The biodegradation of blends of PCL/starch and maleic anhydride (MAH)-grafted-polycaprolactone/starch (PCL-g-MAH/starch) was evaluated by soil burial tests. Weight loss of blends indicated that both were biodegradable, at high levels of starch substitution. The mechanical properties of both blends, such as tensile strength and elongation at break, were diminished. As seen in other studies, as the starch content increased, the weight loss of both the PCL/starch and the PCL-g-MAH/starch blends increased (Wu, 2003). Modified PCL was synthesized by melt reaction of PCL with glycidyl methacrylate (GMA) and benzoyl peroxide. The biodegradability of these blends was investigated using the composting method. Over a period of 8 weeks, the PCL in this PCL/GMA blend did not degrade significantly. The blends with the higher GMA content degraded more slowly than the blends with lower GMA content (Kim y col., 2004). The effects of adding azodicarbonomide (ADC) as an expansor on the biodegradability of blends of PCL with cornstarch were evaluated in simulated soil. Different proportions of ADC were added to pure PCL and to PCL/cornstarch (50/50) blends. The 50/50 PCL/cornstarch blends biodegraded faster than PCL alone, and ADC showed no influence on the biodegradation of the blends but did inhibit the biodegradation of PCL alone. PCL and its blends showed no significant weight loss after 75 days in the presence of ADC; however, after 100 days, degradation became measurable (Rosa y col., 2005a). Three different blends of PCL, high amylose starch and CAB were studied to estimate their rates of degradation. The specimens were buried inside mature compost made from autoclaved municipal solid waste using a seed mixture of compost made from garden waste. The degradation decreased with the decreasing of starch content (Ali, 2014). The biodegradability of a PCL/corn starch nanocompositeobtained by the melt-blending method using fatty hydroxamic acid to modify sodium montmorillonite (Na-MMT) was studied by ASTM D5338-92. The nanocomposite shows higher weight loss in comparison with the PCL/CS blend, especially after 60 days (Al-Mulla, 2014). The biodegradation of blends of TPS/PCL and PCL modified with MA as the compatibilizer in a soil environment showed that pure TPS was completely degraded after 21 days and that the degradation rate of the blends increased as the TPS content increased. The blends containing 5 wt. % of PCL-MA showed the slowest biodegradation rates, independent of the TPS content (Guarás y col., 2015).

PCL/starch blends reinforced with fibers has also been explored. The biodegradation of starch/PCL and sisal fiber-reinforced PCL/starch blends was evaluated during 9 months in soil burial tests. The addition of the fibers to PCL/starch blends increases the rate of degradation in soil burial tests (Di Franco y col., 2004). In another study, TPS/PCL were extruded in a twin-screw extruder with 5% and 10% of sisal fibers. The addition of fibers to the blends slowed the degradation of the blends while higher proportions of TPS promoted the biodegradation of PCL (Campos y col., 2012). Researchers also investigated the biodegradation of coextruded TPS and TPS/PCL matrices of sisal whisker contents of 5 and 10 wt. %. The addition of the whiskers increased the biodegradability of the TPS and of the TPS/PCL matrices. In contrast, the addition of PCL to TPS in TPS/PCL blends retards the biodegradation of the TPS (Campos y col., 2013). In some cases, the sisal fibers sped up the biodegradation, and in others, the fibers slowed it, which indicates that the addition of fibers should be carefully considered depending on the application of the blends.

4.4 Biodegradation of starch/PHB-V

The biodegradation of starch/PHB-V blends have not been studied extensively; however, several studies have been conducted. In one such study, corn starch was blended with poly(3-hydroxybutyrate)-co-poly(3- hydroxyvalerate) (PHB-V) or PCL by extrusion in different proportions, and the biodegradability of the blends in soil compost was assessed after thermal aging at different temperatures between 100°C and 140°C for 192, 425 and 600 hours for each temperature. PHB-V blends exhibited higher biodegradability in 10 months than PCL blends; the biodegradation of the PHB-V with 25 % of starch blend was the only one affected by thermal aging. For PHB-V, the addition of 50% of starch increased the biodegradability of the blend causing it to degrade in about 50% of the time required for PHB-V blends not containing starch. (Rosa y col., 2003). The behavior of three types of TPS: potato starch, corn starch, and water soluble potato starch, with two different degrees of gelatinization blended with poly(hydroxy butyrate) was evaluated in a soil burial test. Weight loss increased with increasing time and increased glycerol content, but decreased with increasing PHB. The amount of weight loss generally decreased with increasing PHB (Lai y col., 2006). In a soil burial biodegradation test for melt blending of 1:1 PHB-V and glycerol-TPS in the presence of an organically-modified montmorillonite, the mechanical properties of the blends improved in relation to TPS alone and a faster biodegradation rate than PHB-V alone. The biodegradation blends occurred faster as the amount of organically-modified montmorillonite incorporated in the blend increased, reaching a 90% of biodegradation. (Magalhães 2013).

4.5 Biodegradation of starch/PBS and starch/PBSA

In the published literature about the biodegradation of starch/PBS and starch/PBSA blends, only a couple of studies can be mentioned here. First, a study of the biodegrade ability by aerobic and anaerobic assays of plasticized corn flour/PBSA blends indicate that PBSA caused a decrease in the biodegradability of blends (Jbilou y col., 2013). In a different study, the biodegradation rates of PBS/starch, PBS, and PLA were studied by burying powdered bioplastics in soil. PBS/starch showed the highest degradability; the structures of PBS and PBS/starch were considerably more degraded than that of PLA for the same time interval. The degradation rates of PBS and PBS-starch are faster than that of PLA (Adhikari y col., 2016).

4.6 Biodegradation of ternary blends

As with blends of starch and PBS or PBSA, very little research has been published about biodegradation of ternary blends. However, the biodegradability of ternary blends composed of PLA, PCL, and starch was studied. The blends were prepared with the addition of acrylic acid grafted by a melt blending method. Buried in soil, the blends degraded rapidly in the first 8 weeks (Liao y col., 2009). The biodegradability of binary and ternary blends composed of PLA, TPS, and glycidyl methacrylate grafted poly(etylene octane) was evaluated by compost testing under ISO 14855 standard. The samples with 40 % starch content achieved more than 80% biodegradation in 10 weeks, while the samples with lower levels -10 to 20%- of starch had only degraded 40% in the same time. The blends with GPOE had higher biodegradation rates than the blends without GPOE(Shi y col., 2011).

5 Final comments

Blending starch with other biopolymers is outlined as a viable alternative to overcome the shortcomings of native starch. The degree of compatibility between starch and other biopolymers differs extensively depending on the specific biopolymer. At present, the mixing of TPS and PLA offers significant advantages related to cost, properties, and biodegradability. However, good meltblending techniques and the addition of compatibilizers are required to enhance miscibility.

In terms of biodegradability, it is important to take into account that although starch/biodegradable blends are a good option for solving environmental problems, their mechanical properties often have an inverse relationship to their degradability. Thus, optimization of their mechanical properties needs further study. Numerous studies on starch/PLA or starch/PVA blends can be found, but the research about mixtures as starch/PBS starch/PBH-V, and ternary mixtures is limited.

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