Agroindustrial residues as cellulose source for food packaging applications

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Abstract

Food packaging materials available in the market are mainly made of synthetic plastic derived from fossil resources. However, growing economic and environmental threats related to their life cycle have fostered the search for alternative sustainable raw-materials to produce biodegradable products. In this sense, cellulose extracted from agroindustrial residues, as an available, renewable and low-cost polymer, is a suitable feedstock to produce bio-based packaging. Although research in this field is still limited, cellulose in the form of nanostructures, regenerated products, derivatives and fibers have shown potential to produce packaging components with enhanced properties. This review summarizes the up-to-date developments/applications of cellulosic materials obtained from agroindustrial residues in bio-based packaging, including some prospective applications resulting from the introduction of smart and active functionalities.

INTRODUCTION

Polymer-based packaging play an essential role throughout the food distribution and storage chain. In addition to ensuring food safety and quality, packaging must prevent environmental degradation. In 2015, almost 115 million tons of synthetic polymers, predominantly consisting of polyolefins, were used for packaging (Geyer et al. 2017). Despite the versatile properties of polyolefins there are growing concerns over economic and environmental issues related to them. Namely oil market price fluctuations, finiteness of fossil raw materials and pollution of earth's compartments have become nucleation supports for new sustainable thoughts on polymers' life cycle. At the research level, great efforts are currently being focused on the search for alternative renewable resources to produce nonpersistent plastic packaging.

In this scenario, agroindustrial residues have emerged as a source of low-cost raw material, widely available and suitable to produce bio-based and biodegradable plastics as they are composed almost entirely of natural polymers. Their valorization not only avoids the disposal of huge amounts of residues but also does not generate competition with food production. Within the natural polymers, cellulose stands out due to its wide availability and properties, including renewability, low cost, biodegradability, as well as its ability to form derivatives. Recently, cellulose fibers, cellulose derivatives, regenerated cellulose and nanocellulose obtained from agroindustrial residues have been successfully applied to produce food packaging materials with remarkable properties. Besides that, some improvements and multifunctionality have been achieved by introducing additives to the cellulose-based packaging. As far as we know, few reviews and book chapters have covered the use of agroindustrial residues as cellulose source for food packaging applications. Therefore, this review concentrates in summarizing the up-to-date developments/applications on this field and briefly discuss related topics, namely agroindustrial residues, cellulose structure and properties and fractionation techniques.

AGROINDUSTRIAL RESIDUES: SOURCE, COMPOSITION AND PRETREATMENT

The term agroindustrial residues spans over two main categories, depending on the generation source: (1) crop residues and (2) industry processing residues. The crop residues are generated during the harvesting phase and comprise straw, branches, stover, leaves, stalks, roots, trimmings and pruning. On the other hand, crops such as sugarcane, grape, orange, potato, coffee, cocoa and coconut are particularly interesting to obtain processed products. From processing food industry, residues in the form of bagasse, pomace, husk, hull and peels are commonly generated.

The attractiveness of agroindustrial residues as a promising sustainable source of biomaterials comes from their availability and chemical composition. They are mainly composed by cellulose (50%), hemicellulose ($20-40\%$) and lignin ($10-40\%$) linked together by covalent crosslinks, which results in their recalcitrant property (Hassan et al. 2018). In a recent publication, Araújo et al. (2018) provided the chemical composition and availability of various crop and industry processing residues. Cellulose, a high molecular weight homopolymer generated from repeating D-glucopyranose ring units linked by $\beta-1$,4-glycosidic bonds (cellobiose unit), stands out as the most abundant renewable resource in nature (Habibi et al. 2010). The drawback of cellulose high hydrophilicity and low thermoplasticity can be solved by its modification in the form of derivatives, nanoparticles, regenerated products, or blending with other materials. However, when sourced from agroindustrial residues, cellulosic fibers must be extracted through fractionation techniques prior to their processing.

The fractionation techniques, also named as pretreatment methods, are carried out to disrupt the compact structure of biomass and fractionate it into its main components. They can be classified basically into physical, chemical, physicochemical or biological treatments. Currently, the pretreatment step is considered one of the main bottlenecks to the cost-effective valorization of agroindustrial residues. Its application may demand high energy and material consumption and generate hazardous wastes (Bhutto et al. 2017). Hence, recently, the use and development of green pretreatments and fine-tuned green solvents, such as ionic liquid, deep eutectic solvents, liquid hot water, steam explosion and biological have been increasingly encouraged (Farrán et al. 2015; Yoo et al. 2017; Hassan et al. 2018).

CELLULOSE IN FOOD PACKAGING APPLICATIONS

The development of cost-effective and sustainable methods to produce cellulose food packaging from residues is still challenging and the most innovative products released in the market are based on high-quality cellulose from wood pulp or cotton. The production of new bio-based materials has to meet market requirements and keep up with innovative trends on food packaging, that appears as the enhancement of properties by the introduction of smart, intelligent and active functionalities, obtained via the intentional embedment of supplementary components including inorganic and organic materials/nanomaterials (Ghoshal 2018; Huang et al. 2018). Recent developments and applications on this field are presented in the following subsections, which are themed into the main application forms of cellulose. It's worth to emphasize that we only covered applications that used cellulose emerged from agroindustrial residues. Moreover, it is not the propose of this paper to make fundamental explanations on design, synthesis, preparation methods or concepts regarding cellulose-based materials/derivatives, but rather to present the latest applications.

Regenerated cellulose in packaging applications

Regenerated cellulose refers to a class of materials prepared directly via the dissolution of cellulose into a solution, followed by its shaping and regeneration process (Wang et al. 2016). By changing the regeneration parameters (e.g. coagulating anti-solvent, time and temperature), regenerated cellulose with different shapes (such as powder, fibers, films, hydrogels, aerogels and spheres) and properties can be obtained (Wang et al. 2016). Many green solvents have been used to prepare regenerated cellulose, including N,N-dimethylacetamide/lithium chloride (DMAc/LiCl), ionic liquids (ILs) and NaOH /urea aqueous solution (Wang et al. 2016; Li et al. 2018). Regenerated films with mechanical and barrier properties comparable with those of conventional films were also prepared by simple dissolution in IL and regeneration of pretreated sugarcane bagasse (Vanitjinda et al. 2019) and borassus fruit fibers (Reddy et al. 2017).

A fairly new concept of materials, the so-called all-cellulose composite (ACC), have been developed from the application of cellulose regeneration techniques and have shown potential application in food packaging (Li et al. 2018). A homogeneous and transparent ACC film, with tensile strength (TS) reaching 67 MPa , was produced in an IL medium by using corn husk as the regenerated matrix and partially dissolved cellulose microcrystalline (MCC) as filler (Zhang et al. 2017). Using an opposite approach, Wei et al. (2016) employed an alkali-treated straw as the reinforcing phase in a MCC regenerated matrix and produce an ultra-higher tensile strength (568 MPa) ACC.

Currently, hydrogels and aerogels are an attractive subject of research in food packaging, mainly due to their liquid absorption capacity (Batista et al. 2019; Oliveira et al. 2019). However, the development of regenerated cellulose-based hydrogels and aerogels from agroindustrial residues are still limited, and their application in food packaging has not been reported yet. Notwithstanding, some published works present results of great interest to the concerned application.

Hydrogels are three-dimensional networks of polymeric chains, randomly crosslinked by physical or chemical bonds, characterized by the ability to absorb large amounts of fluids (Batista et al. 2019). Hydrogels with high water absorption were obtained by homogenization of aqueous dispersion of PVA and cellulosic samples extracted from rice and oat husk, followed by freezing and thawing (Oliveira et al. 2017). Liu et al. (2017) added graphene oxide on a tea residue cellulose/1-allyl-3-methylimidazolium chloride solution, and by coagulation in distilled water produced composite hydrogels with enhanced thermal stability and textural properties.

In opposite to hydrogels, aerogels are highly porous solids that contain gas instead of a liquid phase within their pores. They are typically made through a solvent exchange and freeze-drying process of hydrogels, in a way that its three-dimensional polymeric network remains intact (Gan et al. 2017). Highly porous lignocellulose aerogels, with great water adsorption and swelling properties, were synthesized by dissolving ethylenediamine-pretreated soybean straw in LiCl/DMSO, followed by coagulation, solvent replacing and freeze-drying (Liu et al. 2019). Wheat straw (Li et al. 2016) and cotton stalk (Mussana et al. 2018) were also used as a cellulose source to produce aerogels with high specific surface area and absorption capacity.

Nanocellulose in packaging applications

In recent years, nanostructured cellulose has attracted research attention due to its potential to maximize mechanical, structural, thermal and barriers properties of plastic-based packaging (Azeredo et al. 2017). Depending on how the nanocellulose is extracted from biomass, two main nanostructures can be obtained: cellulose nanocrystals (CNCs) or nanofibrils (CNFs). The nanocellulose is generally applied as a reinforcement filler for food packaging applications, and improvements of composite properties (namely mechanical and barriers) are intrinsically related to the source and characteristics of nanostructures (Silvério et al. 2013; Rhim et al. 2015; Oun and Rhim 2016; Asad et al. 2018). Nanocellulose extracted from corn cob (Silvério et al. 2013), onion skin (Rhim et al. 2015), wheat straw, rice straw and barley straw (Oun and Rhim, 2016) have already been applied in bio-based packaging.

Usually physical and chemical surface treatments are necessary to disperse the cellulose nanostructures in polymeric matrix. For example, 4-acetamido-TEMPO/NaBr/NaCLO and ultrasonic treatment were employed to promote concurrently the isolation and oxidation of cellulose nanocrystals from oil palm empty fruit bunches. Composite films were produced and the oxidized CNCs presented better dispersibility in the polyvinyl alcohol (PVA) matrix (Asad et al. 2018).

Recently, kiwi pruning residues were used as precursors for the extraction of CNCs through a standard treatment (Luzi et al. 2017). The nanostructures were used as a reinforcement element in a PVA matrix blended with chitosan and carvacrol. The addition of CNCs increased the mechanical properties of composite and their combination with carvacrol improved the shelf-life of perishable food products, by maintaining low moisture migration and bacterial activity.

Another relatively new application in food packaging is the use of nanocellulose-based aerogels and hydrogels. In Ooi et al. (2016), CNCs extracted from rice husk were simply mixed with gelatin and by an evaporative concentration method a pH -responsive CNC - gelatin hydrogel, with potential to be applied in active food packaging, was produced. Similar to regenerated cellulose-based aerogels, nanocellulose-aerogels are prepared via freeze-drying or critical point drying of hydrogels. In Oliveira et al. (2019), an aqueous suspension of CNCs extracted from rice and oat husk was homogenized with PVA and freeze-thawing to form hydrogels. Aerogels with high water absorption capacity (maximum WAC of 402.8 % for oat husk CNC-aerogel) were produced by freeze-drying the hydrogel. Shamskar et al. (2016) produced CNC-only aerogels with high specific surface area and mesoporous structure using cotton stalk as nanocellulose precursor.

Cellulosic fibers and derivatives in packaging applications

Similar to the nanostructured cellulose, the cellulosic fibers are usually applied as fillers in polymeric matrix, mainly due to their non-thermoplastic property. In Safont et al. (2018), mechanically ground almond shell (AS) was submitted to a standard purification (alkali and bleach treatment) and blended with poly(3-hydroxybutyrate) (PHB) to produce a fully compostable biocomposite packaging. Compared to the neat PHB, the mechanical properties of the produced composite were enhanced and its total disintegration under composting conditions occurred after 35 days. Using a different and greener approach, Asgher et al. (2017) applied a bacterial cellulose-assisted method to delignify and modify wheat straw fibers and applied them in a PVA matrix. The obtained fibers showed a bacterial cellulose integration with the cellulose microfibrils leading to a significant improvement in the mechanical and water absorption properties of the composite.

Interesting biodegradable biocomposite films made up of carrot processing waste, hydroxypropyl methylcellulose and high pressure microfluidized cellulose fibers were produced without any pretreatment other than mechanical ground (Otoni et al. 2018). The authors extended the production of biocomposites to a pilot scale through continuous casting approach and were able to process $1.56\ m^2$ of biocomposite film per hour. Recently, by applying an easy and industrial suitable approach, Bilo et al. (2018) produced a cellulose-based bioplastic from rice straw with promising dual-shaping memory.

While natural cellulosic fibers cannot be processed directly into plastic packaging, their chemical modification may result into derivatives that are able to be used in thermoplastic processing. Among the most important derivatizing techniques are etherification and esterification, particularly because they can result in high value-added products. Due to its broad range of applications and easy processability, the modification of cellulosic biomass into cellulose acetate (CA) has been the most commonly explored approach, and current research focuses mainly on the development of more sustainable processing methods (Daud and Djuned 2015; Camiscia et al. 2018). Recently, a fully bio-based and transparent ACC film was fabricated by the simple aqueous blending of water-soluble CA synthesized from waste cotton fabrics (WCFs) and nanocelluloses (Cao et al. 2016a). The same research group (Cao et al. 2016b) used the synthesized water-soluble

CA to produce Ag Nps@CA nanohybrid films with good antibacterial property. Great focus has also been devoted to carboxymethyl cellulose (CMC) as it is currently also finding an increasing number of applications. Sugar beet residues and sugarcane bagasse were used as cellulosic fiber sources and carboxymethylated to produce high strength and stiffness film (Šimkovic et al. 2017). Other residues such as corn husk and rice stubble have also been applied as a cellulose source to produce CMC (Mondal et al. 2015; Rodsamran and Sothornit 2017).

CONCLUSIONS

Cellulose-based packaging materials emerged from agroindustrial residues are a promising alternative to replace the conventional polymers. Besides to present suitable physicochemical properties, they are biodegradable and can be produced on a large scale due to the raw material availability. Recently, the embedment of natural additives and nanoparticles has been shown to be effective in bringing out functionalities capable to enhance the expected performance of packaging. Notwithstanding, the valorization of agroindustrial residues towards an innovative, acceptable and commercial packaging is still inching and their use must be increasingly encouraged.

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