Chapter

Starch Biodegradable Films Produced by Electrospraying

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Abstract

The use of particles obtained from biopolymers is of interest in fields such as bioengineering and nanotechnology, with applications in drug encapsulation, tissue engineering, and edible biofilms. A method used to obtain these particles is electrohydrodynamic atomization (EHDA), which can generate different structures depending on the process conditions and raw materials used, opening a wide range of research in the biopolymers field, where starch is considered an excellent material to produce edible and biodegradable films. This chapter is a compilation and analysis of the newest studies of this technique, using starch with or without modifications to prepare films or membranes and their potential applications. A systematic literature review, focused on starch, and EHDA was carried out, finding 158 articles that match these criteria. From these results, a search inside them, using the words edible and biodegradable was conducted, showing 93 articles with these key words. The information was analyzed observing the preference to use corn, potato, rice, and cassava starches, obtaining mainly scaffolds and fibers and, in much less proportion, films or capsules. This review shows a window of opportunity for the study of starchy materials by EHDA to produce films, coatings, and capsules at micro or nano levels.

Keywords: starch, electrospraying, electrospinning, edible films, biodegradable films

1. Introduction

Over the last decade, due to its multidisciplinary nature, the field of nanotechnology has seen a sharp increase in its applications in several areas, mainly on the "bottom-up" and "top-down" approaches. These terms refer to the synthesis processes used to produce new or modified materials, scaling up atom by atom to form a larger product structure or breaking apart larger particles into micro/nanomaterials, respectively [1]. One of the most reported of these methods, used in the food industry, tissue, and environmental engineering, is the electrohydrodynamic atomization technique (EHDA) [2–4], a "bottom-up" nanotechnology approach, which has been employed for the production of membranes, particles, encapsulation, and edible or biodegradable films.

When EHDA began to be used for the design of micro fibers, nano fibers, and membranes, many of the products were developed with synthetic polymers, which continue giving very good results to this day. However, as the need for greener technologies and more ecofriendly products increased, the use of biopolymers also rose. Thus, carbohydrates such as cellulose, pectin, chitosan, alginate, and starch, single or blended with other bio or synthetic polymers, have increasingly been proposed for the production of films, membranes, fibers, and encapsulates. Among these carbohydrates, starch represents a very good option, as it can be found in large quantities in nature, besides being an inexpensive biopolymer, normally found in leaves, stems, seeds, roots, and tubers or other sources such as algae and bacteria.

In this chapter, we present the basis of EHDA technology and summarize some of the data reported in the most recent studies for the production of fibers, films, and membranes using starch as raw material and analyzing the modifications required to be able to generate these starchy products.

2. Electrohydrodynamic atomization (EHDA)

EHD processess encompasses two methods called electrohydrodynamic spinning and electrohydrodynamic atomization, better known as electrospinning and electrospraying, respectively [5]. Electrospinning allows for the production of membranes from electrospun fibers, and electrospraying allows for the synthesis of materials such as core/shell, micro/nanoparticles, encapsulates, and films from fine droplets.

A typical EHDA device (**Figure 1**) consists of four parts: (1) a high-voltage power supply (typically ranging from 1 to 30 kV), (2) a syringe pump, (3) a capillary containing the conductive polymer solution (commonly a syringe with a stainless-steel

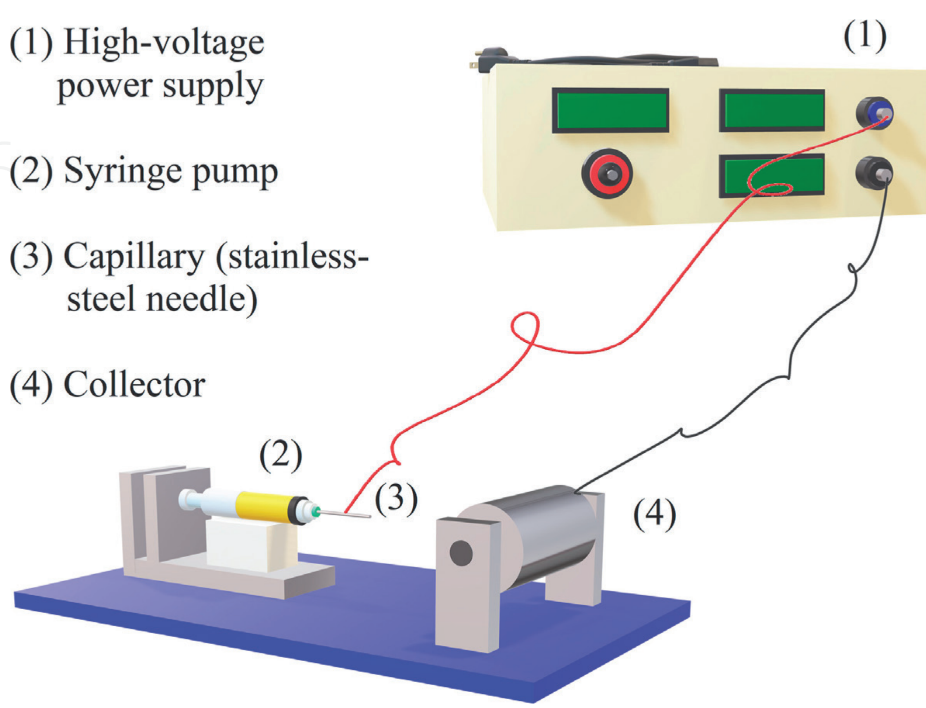

Figure 1.
Electrohydrodynamic equipment. Basic components.

needle), and (4) a collector (stainless-steel rotatory drum or static conductive plate) [2]. These components are present regardless of the method. Moreover, depending on the material to be synthesized, the equipment can be set in two standard configurations (**Figure 2**): horizontal (**Figure 2a**) or vertical (**Figure 2b**) [6], which have been used in the production of films formed by micro/nanoparticles [7] and encapsulates [8] in dry (**Figure 2c**) or wet (**Figure 2d**) configurations.

On the other hand, and in addition to the two standard configurations mentioned above, several modifications have been studied. These modifications have been done according to specific needs; for example, horizontal dry electrospinning (**Figure 2b**) is used to obtain membranes based on hydrolyzed collagen and polyvinyl alcohol with potential use for wound protection [9], and vertical wet spinning (**Figure 2c**) is used to synthesize membranes from polyvinyl alcohol and poly(ethyleneimine), to remove heavy metals from wastewater [10]. In these examples, the collector can be either immersed in a liquid, or dry, (**Figure 2d**).

Characteristics such as product morphology and size are affected by the properties of the solution (viscosity, polymer concentration, molecular weight of polymer, surface tension, conductivity), process variables (applied voltage, working-distance from needle to collector, flow rate), and environmental parameters (temperature, humidity, airflow) [11], resulting in products with different properties and intended uses.

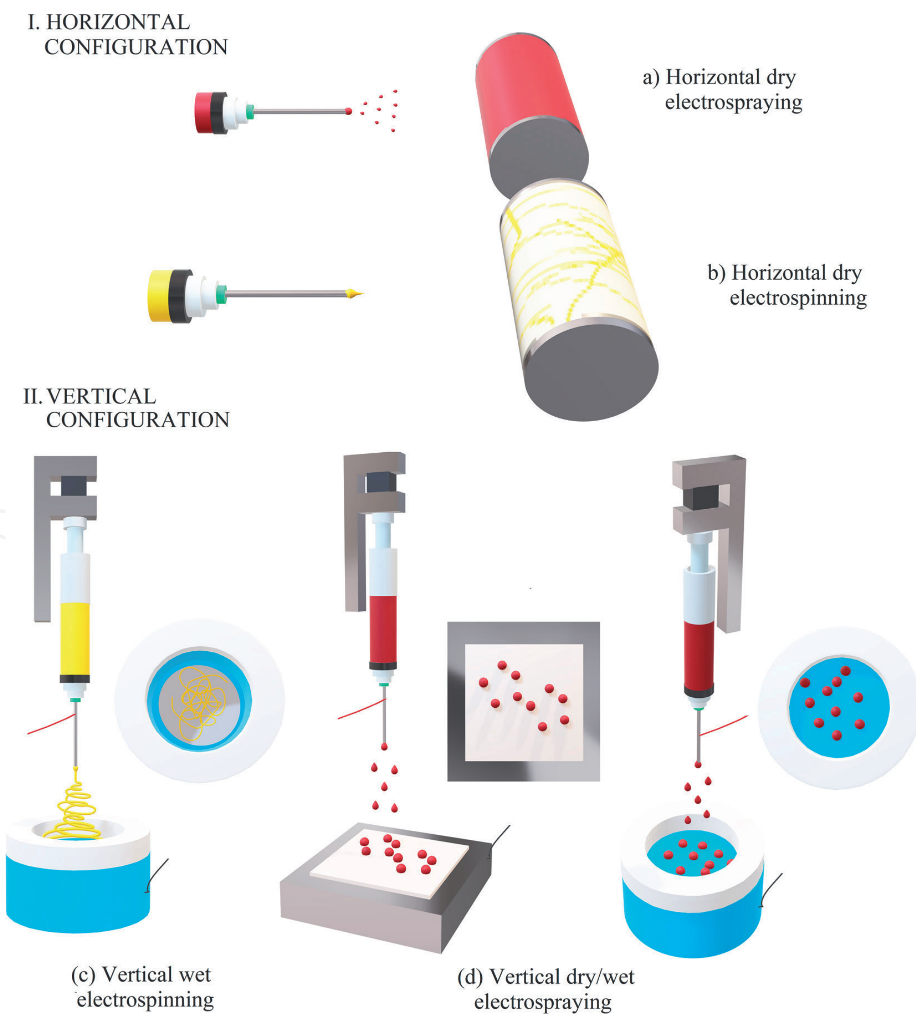

Figure 2.
Electrohydrodynamic configurations: (I) horizontal, (II) vertical. Electrohydrodynamic types: (a) horizontal dry electrospraying, (b) horizontal dry electrospinning, (c) vertical wet electrospinning, (d) vertical dry/wet electrospraying.

But, how are fibers or particles formed? In the case of fibers, when the electrical voltage is applied to the conductive polymer solution in the syringe, electrical charges accumulate on the surface of the liquid and, depending on the surface tension, the polymer solution remains within the capillary, not flowing. As the mutual repulsion of charges produces a force directly opposite to the surface tension and the intensity of the electric field increases, the solution reaches the end of the capillary, acquiring a conical shape, called a "Taylor cone." Consequently, when the electric field reaches a critical value, that is, when the repulsive electrical force exceeds the surface tension force, a jet of the polymer solution is produced at the tip of the cone. As the jet spreads through the air, the solvent in the solution evaporates, forming a polymeric micro or nanofiber. Finally, the fibers are deposited in the collector in the form of a nonwoven micro/nanofiber membrane [6–11].

Regarding the synthesis of films, micro/nanoparticles, and encapsulates, unlike membranes, these materials are formed from solutions of low polymer concentration, which allows the jet's destabilization and the formation of highly identically charged fine droplets that do not agglomerate. In other words, a polymeric solution in the capillary is sprayed from the nozzle into the collector under a high-voltage application due to electrostatic forces. Here, on the flight in time to the collector, the solvent evaporates and particles are produced [11, 12].

The fibers and the particles produced by these methodologies show a high surface area to volume ratio, good mechanical, electrical, and thermal properties, and smooth, homogenous, and variable morphologies, mainly as a result of the process parameters' manipulation, which in turn derives in the shape that the jet takes during the ejection process [13].

As mentioned earlier, the parameters that govern the EHDA process are properties of the solution, process conditions, and environmental parameters, all of which determine the morphology and diameter of the fibers or particles [11, 14].

EHDA products can be synthesized using a wide range of materials, including biopolymers from animals, plants, and algae, such as collagen, chitosan, gelatin, pectin, zein, cellulose, alginate, starch, and others, and synthetic polymers, such as polyethene oxide, polyvinyl alcohol, and polycaprolactone, among others [5, 6, 13]. However, due to their low molecular weight and mechanical properties, natural and synthetic polymers are commonly used in tandem. Furthermore, materials such as carbon-based nanomaterials, ceramics, and metallic nanoparticles have also been applied in combination with chitosan or casein nanofibers, to name a few [15, 16]. In general, since its invention, the application of the EHDA technique increased considerably, due to it being straightforward, inexpensive (low solution consumption), controllable, and reproducible [17], with starch being considered a potential raw material to be used in this technique.

3. Starch

Starch is found in all plants as a product of photosynthesis and is the main storage reserve carbohydrate of plants and the primary source of calories in the human diet. It is also a very important renewable and biodegradable raw material for the industry [18]. The main sources of starch are cereals (corn, wheat, rice, barley) and tubers or roots (potatoes, tapioca, cassava) [19], corn being the most important, followed by potato and cassava.

Starch is a polysaccharide composed of α-glucose polymer molecules: a linear one called amylose and a branched one known as amylopectin. The proportion of these molecules varies depending on the source, with the most common being an amylose content of 13–30%. However, it is possible to find amylopectin-only materials [20, 21], mainly cereals, referred to as waxy cereal varieties (corn, sorghum, rice). These differences in starch composition result in diverse physicochemical properties, affecting properties such as gelatinization temperature, solubility, and final viscosity of starch slurries.

Starch can be extracted by different methods, most of them being classified as dry or wet, and in both cases looking to maintain its functional properties at the highest possible yields and purity [22] and without damaging the crystalline phase or promoting depolymerization [23] of the materials. One of these methods is dry milling, which consists of the grinding of the samples and an air classification [24]. This method simplifies the handling of large amounts of liquid in comparison to wet milling [22] but increases the proportion of damaged starch [25], resulting in a lower quality product [26].

Conversely, wet milling is used to extract starch from flour by producing an aqueous slurry, which is filtrated and washed at least two times [27]; the starch obtained in this process has a higher purity than dry milling [28]. In most wet extraction processes, a reactant, such as sodium bisulfite [29], metabisulfite [30], sodium hydroxide [31], oxalic acid/ammonium oxalate [32], or low concentrations of citric acid [33], is added, mainly to facilitate protein separation. Other techniques, such as sonication [34] or freezing, to assist the extraction process to increase the starch yields have been reported as well.

3.1 Starch sources

Starch is organized into tiny particles called grains or starch granules, and their size and shape are characteristic of each botanical species (**Table 1**). It is known that the granule size is decisive in its processability, which affects the solubility (in a plasticizer medium) and the swelling power, facilitating the release of soluble polymer chains for the formation of a single coherent amorphous phase [47–49].

The size of the starch granule varies from a very small size (4 μm or less), such as that found in amaranth, jicama, or rice, up to 100 μm from potato granules [21]. Most of the materials do not present a unique size and, in some cases, have very different shapes. As an example, in barley starch, there are two populations of granules: small

Type	Amylopectin (%)	Amylose (%)	Gelatinization temperature (°C)	Granule size (microns)	References
Corn	66.19	33.81	70–80	5–25	[21, 35–37]
Corn rich in amylose	20–45	55–80	67–80	5–25	[21]
Potato	79	21	58.5	5–100	[21, 38, 39]
Rice	83	17	68.4–73.95	2–5	[21, 36, 37]
Tapioca	21.4–35.4	24.3	64.1	5–20	[21, 40, 41]
Wax corn	99–100	1–2	64.3–68	5–25	[21, 42]
Wax sorghum	99–100	7.9–12.1	67–74	4–35	[43, 44]
Wheat	76	1.5–39.5	56.1	11–41	[21, 40, 45]
Jicama	73.8	26.4	66.6	3–21	[46]

Table 1.
Some starch characteristics.

2–5 micron-long spheres and large 15–25 micron-long lenticular granules [49]. In the case of rice, corn, and waxy corn starches, they have a polyhedral shape, while the granules of potato starch are ovoid. Cassava follows a similar behavior; starch granules are not uniform, are round with truncated terminals, have a well-defined nucleus, and their size varies between 4 and 35 μm with an average of 20 μm [50, 51]. These differences in size, as well as in amylose and amylopectin content, promote the various functional properties of the starch, such as gelatinization temperatures and thus lead to different industrial applications.

3.2 Modified starches

Starch has many applications in food and nonfood industries based on its physicochemical and functional properties; for example, it is used in the pharmaceutical industry as a raw material for the production of dextrose and serum, as an excipient in the manufacture of tablets and pills, and as capsules [52]. It has been also used as an adhesive, binder, thickener, and co-builder; in gelling, complexing, and flocculating agents; and in the paper and corrugating industry. Another application is in the preparation of edible and biodegradable films, due to barrier characteristics (O_2 and CO_2). However, most of these applications are carried out employing modified starches [21, 52–54].

Starches have functional properties that can be related to their final use and vary depending on the granule secondary and tertiary structures and if the starch has been modified or remains native. These differences influence the gelatinization temperature, type of diffraction patterns, crystallinity degree, solubility, clarity, viscosity, water-retention capacity, and swelling capacity, which help to explain the stability of the biopolymer, and therefore suggest its proper application [55, 56].

Starch can be modified by different procedures, either physical or chemical, reaching different final properties and characteristics. The most common physical modifications include heating starch slurries in boiling water or autoclaving at 121°C, thus promoting gelatinization (low and high temperatures) and as a consequence an increase in its solubilization capacity [56]. Other common physical procedures include ultrasonication [57] and ball milling [58]. Regarding chemical modifications, these procedures change the starch structure, by excising the molecule during a hydrolysis process or by introducing new components as a result of oxidation, esterification, or etherification [53], increasing in most of the cases its solubility and a loss of crystallinity [51, 54].

4. EHDA starch films

Many studies have been carried out regarding electrohydrodynamic atomization, with the first publications about this technique using biopolymers, and specifically starch, coming out in 2003. Many of these documents report on fibers and capsules of different sizes (micro or nano). These were studied alone or as part of scaffolds, membranes, or films—with one or more layers—and built from different polymeric materials besides starch, either of biological or of chemical origin.

Starch is a common material widely distributed in nature, with EHDA products being mainly built from commercial sources, such as corn and maize starch are the ones that have different amylose/amylopectin content [59–67], or others such as potato [66, 68–73], rice [74], and cassava or tapioca starches [75–79].

The use of chemically modified starches, such as cationic starch prepared from hydroxyethylated starch [80], hydroxypropyl starch [81], or octenylsuccinylated starch [82], is also a common practice, while the study of noncommercial biopolymers sources is less frequent [66, 74, 83].

Another normal practice observed for the elaboration of EHDA starch products is combining starch with other polymers, being PVA (polyvinyl alcohol), PCL (polycaprolactone), and PLA (polylactic acid) widely employed [61, 68, 76, 78, 80, 84, 85]. The use of PEO (polyethylene oxide), PMMA (polymethyl methacrylate), and TPU (thermoplastic polyurethane) has also been reported, although in fewer amounts [81, 86].

Starch in its native form is seldom used for the elaboration of EHDA starch products due to its poor solubility and hydrophobicity. This is the reason why it is used in combination with other polymers or modified by physical or chemical procedures.

In this regard, heating by conventional techniques, which render gelatinized starch, is one of the most common procedures. More recently, microwave heating has been reported [74], with both methods increasing the solubility of this polysaccharide. The temperatures reported in these studies use to promote the starch solubilization varied from 70°C up to 140°C, and the heating duration from 10 min to 720 min, with differences seeming to be mostly related to the temperatures used [59–61, 67, 73, 74, 77, 81, 83, 87, 88]. Ultrasonic starch disruption has also been cited [59, 70], along with aqueous DMSO solution to improve starch dissolution [62, 63, 66, 67, 75, 76, 83, 84, 86].

When preparing polysaccharide solutions for electrospinning, the [63] concentrations of native starch [63] are low, ranging from 0.5% [74] to 15%. Higher concentrations of these materials have been reported for commercial soluble (50%) and cassava (66%) starches [71, 87]. In most cases, the solvents added correspond to water [59, 62, 68, 78, 80, 88] or DMSO solutions [63, 70, 75, 76, 83, 87] and in lower amounts to acetic acid, formic acid, ethanol, chloroform, DCM and DMF solutions [71, 79, 84, 85, 89]. **Figure 3** summarized the main steps to prepare starch solutions for electrospraying.

Once the starch solution is obtained, it is fed to the EHDA equipment, and the flow rate, voltage, and distance to collector are set. Most authors reported using

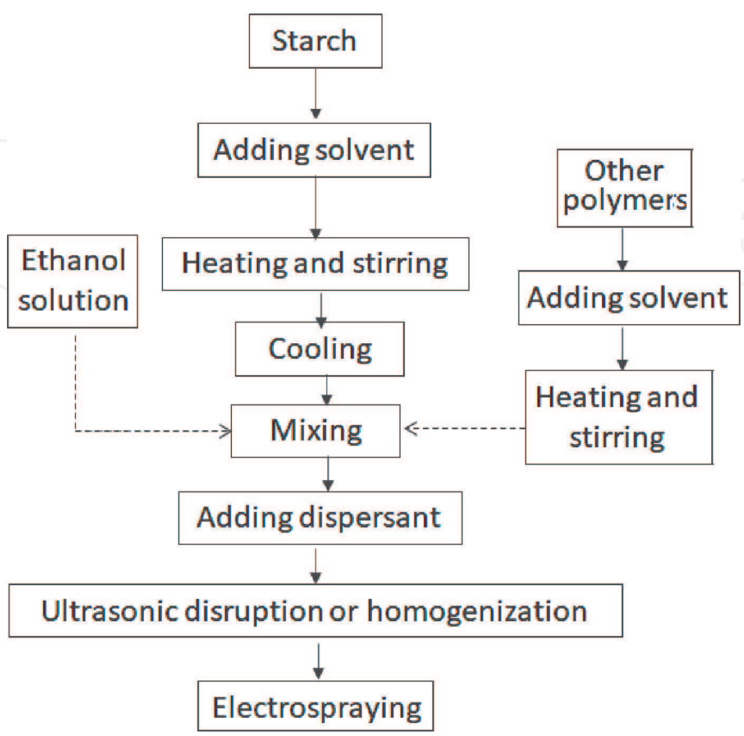

Figure 3.
General method to prepare starch solutions for electrospraying. Dotted lines indicate alternative methodologies.

	EHDA conditions					
Starch source	**DC* (cm)**	**V* (kV)**	**FR* (mL/h)**	**SND* (mm)**	**Product & reference**	
Maize starch (10–20 μm, 27% amylose, 73% amylopectin ratio	2	4.1–7	0.18	0.25	Films	[59]
Cationic starch-PVA	11–14	40–70	NR	NR	Nanofibers	[80]
Starch-PCL	20	9.5	1.0	0.50	Scaffolds	[83]
Corn starch-chitosan-PET	15	20	NR	NR	Fibers	[60]
Cassava Starch-PLA	20	20	0.6	0.55*	Fibers	[75]
Oxidized corn starch-PVA	12	11	NR	0.41	Fibers	[61]
Corn starch of different amylose content-Ming bean starch	5–10	0–15	0.1–0.4	0.60	Fiber entanglements	[83]
Hydroxypropyl starch-PEO	30	11–14	0.02–0.04	0.84	Fiber mats	[81]
Tapioca Starch	15	20	10	0.9	fibers	[77]
Fibersol-guar gum	9-11	10	0.15	NR	Micro/nano capsules	[78]
Potato starch-TPU	24	35	0.75	0.51	Nanofibrous bandages	[84]
Rice starch-Carob flour-PEO	30	12	0.8	NR	Fiber membranes	[74]
Potato starch	20	25	0.6	0.8	Ultrafine fibers	[79]

**Outer diameter.*
DC: distance to collector; V: voltage; FT: flow rate; SND: syringe needle inner diameter. NR: no reported. PVA: polyvinyl alcohol; PCL: polycaprolactone; PET; polyethylene terephthalate; PLA: polylactic acid; PEO: polyethylene oxide; TPU: thermoplastic polyurethane.

Table 2.
Process conditions employed to develop EHDA starch products. Some examples.

voltages between 0 and 20 kV (66%), flow rates smaller than or equal to 1.0 mL/h (81%), and highly variable distances to collector (5–30 cm); in most of these cases, micro and nanofibers or mats were developed, with the exception of two works reporting capsules [86, 87] and two reporting films [59, 67]. However, in some cases, more than one method to prepare mats or films is used, combining, for example, both electrospraying and casting or others [85]. **Table 2** shows some examples of specific process conditions used to obtain the different EHDA starch products.

5. Conclusions

It is of notice that even though starch electrospraying has been studied for many years, most of this research has been focused exclusively into an electrospinning field, with very few works having been published related to the production of edible or biodegradable films, coatings, or microcapsules.

This observation shows a window of opportunity, for the study of new starchy materials and to better understand this technique and its intricacies. Some examples include the effects of different assay parameters, such as syringe inner diameter or the size of starch granules and their relationship to film properties, factors that have not been reported yet. Several studies with other biopolymers [88, 90–92], as well as starch, can serve as a basis for the development of new and improved ecological coating materials.

Acknowledgements

Verónica Cuellar Sánchez, Marcela González Vázquez and Alitzel B. García-Hernández would like to thank CONACyT and BEIFI-IPN for the scholarships provided and the financial support for this work. This research was funded through the projects: 20195500, 20201679, 20201695, 20210624, and 20211381 from the Instituto Politécnico Nacional (IPN, Mexico) and 1668 from CONACyT.

Conflict of interest

The authors declare no conflict of interest.

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