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Starch films loaded with donut-shaped starch-quercetin microparticles: Characterization and release kinetics

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ABSTRACT

Starch films loaded with donut-shaped starch-quercetin microparticles were prepared from two different botanical origins. The quercetin release kinetics through the films were studied. The donut-shaped starch-quercetin microparticles were prepared by thermal aqueous-alcoholic treatment. The quercetin loading percentage and therefore the antioxidant activity were higher for the microparticles from legume than those of cereal origins. The starch-quercetin microparticles also showed higher thermal stability than the starch granules.
The starch films were produced using the solution casting method. The films with more microparticles content showed higher thermal stability. In-vitro release studies of the quercetin through the films were performed in aqueous-ethanolic medium. The quercetin released reached the equilibrium in 1 to 4 days for the films of cereal starch and in more than a week for the films of legume origin. The release data were fitted to Peppas–Sahlin model that suggests the release kinetics were controlled mainly by fickian diffusion. The produced biofilms can be utilized mainly for active food packaging applications.

1. Introduction

The scientific and the industrial communities are becoming more and more concerned about the environmental and the health issues caused by the petroleum derived plastics. For that, biopolymers are being extensively studied in the last years to evaluate their possible applications as replacement of the conventional plastics [1]. Biopolymers have found their ways to be applied in the fields of drug delivery, tissue engineering, biomedical scaffolds and stents and in the packaging industry [2–5]. However, more research is required to provide more characterization and improvement of their properties to adapt the desired applications.

Starch is the second most abundant carbohydrate polymer in nature after the cellulose. It is the polysaccharide most consumed by the human being. It is produced by most of the green plants to store energy [6]. The low cost and the wide availability of the starch make it one of the most interesting candidates as a biodegradable, biocompatible natural polymer. Starch is being widely used in food industries, paper making and as excipient in the pharmaceutical industry [7, 8]. In addition, starch is gaining an increasing attention in the packaging industry for its potential applications in the fields of food packaging, edible films and composting bags [9, 10].

The starch granules are formed mainly of two macromolecules: amylose and amylopectin. Both amylose and amylopectin are polymers of glucose units. The amylose is a helical α-(1–4)–linked D-glucose units while the amylopectin is a highly-branched macromolecule that consists of α-(1 → 4)-linked D-glucose units joined by frequent α-(1 → 6) branch points [11–13]. The starch composition varies depending on the botanical origin. The differences between starches of different origins include mainly the amylose/amylopectin ratio and the molecular weights of both macromolecules [14]. Those variations at the molecular and the supramolecular levels have their impacts on the physical properties of the different starch types and thus their processability and applications [15].

The starch films can be produced either by melt processing or by solution casting in the presence of water [16]. A suitable plasticizer must be added to the starch which normally improves the mechanical properties of the starch films [17, 18]. Different fillers can be added to modify the starch film properties such as nanoparticles and microparticles of biopolymers [19, 20]. Additional functional ingredients such as antimicrobials, antioxidants or other nutritional supplements can be added to the biofilms to obtain active packaging materials [21, 22]. The incorporation of an antioxidant in the packaging film provides a strategy to overcome the oxidation issue of the packed food and participate in the food preservation. However, the antioxidant must be non-toxic for the consumer and have no negative effect on the food quality [23]. Quercetin (3,3′,4′,5,7-pentahydroxyflavone) is a natural flavonoid which is

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found in many leaves, fruits and vegetables such as onions, apples and tea among other plants. It is known for its strong antioxidant activity and was reported to have anti-inflammatory and anti-cancer activities [24].

In this work, a combined strategy for modifying the starch films was applied. Donut-shaped starch microparticles from cereal and legume origins loaded with quercetin were produced by thermal aqueous-alcoholic treatment. The morphology, the thermal stability, the quercetin loading percentage and the antioxidant activity of the donut-shaped microparticles were analyzed. The quercetin loaded microparticles were introduced to films of starches of the same botanical origin in two different amounts. The thermal stability of the films was evaluated. The release kinetics of the quercetin from the starch films were evaluated and compared for films from both origins.

2. Materials and methods

2.1. Materials and reagents

Pea and corn starches were provided by Roquette Freres S. A. (France). The amylose content of the starches reported by the company was 35% and 25% respectively. Absolute ethanol was purchased from Scharlau (Spain). Quercetin (purity ≥95%), glycerol and DPPH (1,1-diphenyl-2-picrylhydrazyl) radical were purchased from Sigma Aldrich (Germany). Water was purified using a Milli-Q Ultrapure water-purification system (Millipore, France).

2.2. Preparation of starch-quercetin microparticles

Starch microparticles were prepared by thermal aqueous-alcoholic treatment under the following procedure [25]. An amount of 8 g of starch was added to 150 mL of Milli-Q water. The mixture was heated at 66 °C under constant stirring at 500 rpm during 1 h. Then, 150 mL of 12 mg/mL quercetin solution in absolute ethanol were added during 75 min (2 mL/min) using a diaphragm pump (SIMDOS 02, KNF Neuberger, Switzerland) to the starch slurry under the same stirring conditions without heating. When the starch microparticles suspension was cooled to room temperature, another 150 mL of 12 mg/mL quercetin solution in absolute ethanol were added dropwise under constant stirring at a flow rate 3 mL/min. Finally, the suspension was centrifuged for 20 min at 4400 rpm, and washed with ethanol to remove water and the excess quercetin. After washing, the microparticles were dried in a forced air oven at 50 °C. The microparticles were prepared in triplicate.

2.3. Preparation of starch films loaded with donut-shaped starch-quercetin microparticles

The films of corn and pea starches that contain starch donut-shaped microparticles loaded with quercetin were prepared using the solution casting method [15]. Native starches were suspended in 60 mL of glycerol and water solution. The suspensions were mixed and then heated in a microwave oven for 150 s. The suspensions were withdrawn each 30 s for mixing and then returned to the microwave oven. The gelatinized starch solutions were then stirred at 800 rpm using magnetic stirring till cooling down. The starch-quercetin microparticles were added to the starch solution and homogenized using a T 25 digital ULTRA-TURRAX homogenizer at 5000 rpm for 10 min. The obtained suspensions were sonicated for degassing and then poured in a 20 cm diameter flat bottom petri dishes lined with Teflon sheets. The petri dishes were dried in a forced air oven for 30 h at 30° C. The obtained films were reconditioned in a climate chamber at room temperature and at 40% relative humidity to insure the equilibration of the water in the films.

The total weight of dry starch (i.e. native starch weight + donut-shaped starch-quercetin microparticles weight) was kept at 2.1 g. The starch-quercetin microparticles were added in a percentage of 10% and 15% of the total dry starch content. The ratio between the native starch weight and the glycerol weight was 7:3. The different formulations used for the preparation of the different TPS films were detailed in Table 1.

2.4. Scanning electron microscopy

The morphology of the starch-quercetin microparticles was characterized using a Carl Zeiss ultra plus field emission scanning electron microscope (FESEM) operated at 3 kV (Carl Zeiss, Germany). The particles were previously sputter-coated with iridium using QUORUM Q150T-S turbo-pumped sputter coater (Quorum Technologies Ltd., UK). The size of the microparticles was measured directly from the SEM micrographs using ImageJ software [26].

2.5. Determination of quercetin loading percentage

2 mg of the dried starch-quercetin microparticles were accurately measured and suspended in 1.5 mL of methanol. The suspensions were shaken and left overnight to allow the complete release of the loaded quercetin. Afterwards, the suspensions were centrifuged at 14500 rpm for 5 min and the absorbance of the quercetin in the supernatant was determined using an UV–vis spectrophotometer SPECORD 200 PLUS (Analytikjena, Germany) at a wavelength of 372 nm. A series of standard solutions of quercetin in methanol were used for obtaining the calibration curve. The absorbance of the quercetin in the supernatants was measured after further dilution and then compared to the corresponding calibration curve. The measurements were performed in triplicate.

The loading of quercetin was calculated according to Eq. (1) [27].

$$\text{Drug loading } (\%) = \frac{\text{weight of drug released}}{\text{weight of microparticles}} \times 100 \quad (1)$$

2.6. Antioxidant activity

The antioxidant activities of the starch-quercetin microparticles were determined by the DPPH method [28]. This experiment is based on measuring the scavenging capacity of the antioxidant toward the stable DPPH radical. The freeze-dried starch-quercetin microparticles were suspended in methanol in a concentration of 1 mg/mL. The suspensions

Table 1
Formulations of different TPS films.

TPS film	Total dry starch (2.10 g)		Glycerol + water (60 mL)	
	Native starch (g)	Starch microparticles (g)	Glycerol (mL)	Water (mL)
Corn TPS	2.10	0	0.90	59.10
Corn TPS + 10% microparticles	1.89	0.21	0.81	59.19
Corn TPS + 15% microparticles	1.79	0.31	0.77	59.23
Pea TPS	2.10	0	0.90	59.10
Pea TPS + 10% microparticles	1.89	0.21	0.81	59.19
Pea TPS + 15% microparticles	1.79	0.31	0.77	59.23

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