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Optimized and scaled-up production of cellulose-reinforced biodegradable composite films made up of carrot processing waste

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ABSTRACT

The ever-growing environmental concern arising from the unrestricted exploitation of fossil sources for the massive production of non-biodegradable materials encourages research on alternative renewable resources. We herein pave the route for the production of biodegradable biocomposites made up of carrot minimal processing waste (CMPW) by optimizing its combination with hydroxypropyl methylcellulose (HPMC) and high-pressure microfluidized cellulose fibers, which played ligand and mechanical reinforcement roles, respectively. Ternary mixture designs established mathematical models aimed at structure-composition-property correlations, allowing their mechanical performances to be innovatively predicted without the need for further experiments. The optimized formulation comprised 33 wt.% CPMW and led to biodegradable biocomposites featuring *ca.* 30 MPa of tensile strength, *ca.* 3% elongation at break, and *ca.* 2 GPa of Young's modulus, properties which are suitable for food packaging applications. Finally, the film-forming protocol was successfully scaled-up through a continuous casting approach, allowing the production of 1.56 m^2 of biodegradable biocomposite in each hour. While scaling up did not affect film's barrier to moisture, it did impair its mechanical behavior.

1. Introduction

Globalization and industrialization are increasingly demanding more complex food distribution systems. This scenario leads to longer transportation and storage periods, during which food products are susceptible to microbial spoilage as well as sensory and nutritional losses, in addition to increased packaging requirements in terms of production and properties. Among properties, the mechanical and water barrier denote the most relevant for commercial food packaging applications (Hosseini et al., 2015; Souza et al., 2017). Polymers obtained through petrochemical routes are traditionally the most exploited due to their advantageous cost-benefit ratios as well as suitable properties (Ferrer et al., 2017). However, the forthcoming limitation of fuel sources and the growing environmental concern regarding the disposal of non-biodegradable materials motivate the use of polymers that are biodegradable and/or obtained from renewable raw materials (Otoni et al., 2017; Souza et al., 2017).

A further environmentally friendly approach of producing bio-based packaging materials without competing with commercial applications (*e.g.*, food *versus* feed paradigm) relies on the use of underutilized natural resources as well as of the by-products, residues or wastes resulting from their processing operations (Graichen et al., 2017). In this context, researchers have been taking advantage of overripe fruit and vegetable processing waste to produce edible and/or biodegradable bioplastics (Andrade et al., 2016; de Moraes Crizel et al., 2016; Otoni et al., 2017). This strategy is interesting because it combines the unique sensory and nutritional aspects of such plant materials with their film-forming components. Studies on the formulation of edible and/or biodegradable bioplastics primarily based on underutilized portions of fruits and vegetables are however scarce, making this topic worthy of further exploitation.

Carrot (*Daucus carota* L.) is a widely grown, non-seasonal vegetable

Abbreviations: ANOVA, analysis of variance; CMPW, carrot minimum processing waste; EVOH, ethylene vinyl alcohol copolymer; FFF, film-forming formulation; HDPE, high-density polyethylene; HPMC, hydroxypropyl methylcellulose; LDPE, low-density polyethylene; PCL, poly(ε-caprolactone); PET, poly(ethylene terephthalate); PP, polypropylene; PS, polystyrene; PVC, polyvinylchloride; PVDC, poly(vinylidene chloride); RH, relative humidity; TPS, thermoplastic starch; WVP, water vapor permeability

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featuring pleasant flavor and rich in phenolic compounds, carotenoids (*e.g.*, β-carotene), vitamins, minerals, and dietary fiber (Alasalvar et al., 2001; Hiranvarachat and Devahastin, 2014). Approximately 70–75% of harvested carrots are marketed after minimal processing into Baby Carrots™, carrot chips and sticks, and chopped, shredded, and sliced carrots (Du et al., 2012). Nevertheless, minimal processing yields are typically low: *ca.* 40% of the initial carrot weight is discarded after peeling, shaping, polishing, and sorting (Silva et al., 2008). Carrot minimal processing waste (CMPW), which is often thrown away or used as animal feed (Iahnke et al., 2015), contains high content of organic matter – which implies difficult disposal – and presents great potential of use, mainly due to its nutritional properties.

Iahnke et al. (2015) combined fibers from carrot processing residue with bovine gelatin waste – resulting from the production of linseed oil capsules − to produce films through bench casting. Both components were necessary because, in most cases, the film-forming constituents naturally present in fruits and vegetables are not able to form cohesive layers that are detachable from the casting substrate (Otoni et al., 2017). Several binding agents have been used to create self-standing edible and/or biodegradable bioplastics, including cellulose derivatives, as this raw material is the most abundant biopolymer on earth (Kanmani et al., 2017). Hydroxypropyl methylcellulose (HPMC) is a cellulose ether with widely reported film-forming ability (Otoni et al., 2018). It has been combined with other fruit and vegetable purees to produce bioplastics (Lorevice et al., 2014, 2012).

Even if they are detachable from the casting surface, edible and/or biodegradable films often present poorer mechanical and water barrier properties than those based on petroleum-derived polymers (Otoni et al., 2017), requiring the addition of another component to act as a reinforcement filler (Azeredo, 2009). Lignocellulosic fibers have been widely exploited in this context (Azeredo et al., 2017; Ferrer et al., 2017). Cellulose fibers/crystals were previously combined with HPMC (Bilbao-Sáinz et al., 2010; Bilbao-Sainz et al., 2011; de Moura et al., 2011; Dogan and McHugh, 2007; George et al., 2014) or fruit puree (Azeredo et al., 2009; Azeredo et al., 2012). However, to the best of our knowledge, cellulose fibers, HPMC, and fruit/vegetable purees have never been combined into biocomposite films.

In line with the environmental concerns raised above as well as with the trend towards the maximum use of natural resources, this contribution set out to produce biodegradable − the biodegradability was actually determined −biocomposites based on CMPW in combination with HPMC and cellulose fibers. Understanding the role that each component played in the physical-mechanical performances of the resulting materials was another aim of this research in order to allow correlations between structures, compositions, and properties. Ternary mixture design was used to optimize the properties of the biocomposites, which were then scaled up from a laboratory to a pilot scale. Finally, the influence of the film-forming protocols − bench and continuous casting − on their properties was investigated.

2. Material and methods

2.1. Materials

Freshly harvested carrots (length: 26 ± 2 cm; diameter: 4.2 ± 0.6 cm) were provided by a local grower in São Carlos, Brazil. HPMC Methocel® E4 M [CAS No. 9004-65-3; weight average molecular weight: *ca.* 350,000 g mol^{-1} (Otoni et al., 2018); viscosity (2% dispersion in water, at 0.1 s^{-1} and 20 °C): *ca.* 4000 mPa s^{-1} (Otoni et al., 2018); substitution degree: 1.9] was kindly supplied by The Dow Chemical Company (Brazil) and used as received. Microcrystalline cellulose (Sigmacell® Type 50) was provided by Sigma-Aldrich Brazil Ltda. (Brazil), suspended in deionized water at 1% (w v^{-1}), and submitted to seven cycles of high-pressure microfluidization (Microfluidizer® model M-110P, Microfluidics Corp., USA) at 138 MPa, relying upon preliminary experiments (data not shown). Ultrapure, deionized water (Barnstead Nanopure Diamond, USA) was used in all experiments.

2.2. Carrot minimal processing

Fresh carrots were minimally processed according to Moretti and Mattoso (2007). First, 100 mL of a 50% benzalkonium chloride solution was diluted in 20 L of water. This solution was used for sanitizing the cold room and food-contacting surfaces and utensils. Carrots were sanitized in 200 ppm sodium hypochlorite solution for 10 min at 4 ± 1 °C and pH *ca.* 7.5. The tops of the sanitized roots were removed prior to peeling and cutting into *ca.* 1-cm-sided cubes. The remainder − tops and other visually impaired portions − were discarded, while the other portions were kept for another 10 min in the same sanitizing solution before being centrifuged. CMPW − *i.e.*, scrapings and non-uniform pieces that would not be marketed as minimally processed products − was freeze-dried and ground into powder in a ball mill.

2.3. Effect of CMPW on the mechanical and water barrier properties of HPMC films

2.3.1. Film production via bench casting

CMPW and HPMC Methocel® E4 M were combined at different weight ratios (Table 1) in water upon mechanical stirring at 1500 rpm for 30 min under vacuum (–500 mmHg), at 25 ± 2 °C.

The film-forming formulations (FFF) were allowed to rest under vacuum for another 30 min before being spread with uniform thickness onto a poly(ethylene terephthalate) (PET) sheet. FFF were allowed to dry on the bench at 25 ± 2 °C and 50 ± 10% relative humidity (RH) for 24 h. Dried films were peeled from the casting surface and equilibrated at 50% RH for 48 h in a desiccator containing saturated magnesium nitrate solution prior to testing.

2.3.2. Mechanical properties

Films samples were shaped into at least six test specimens per treatment according to ASTM D882–12 (ASTM, 2012c) and submitted to uniaxial tensile assay on a universal testing machine (model DL3000, EMIC Equipamentos e Sistemas de Ensaio Ltda., Brazil) equipped with a 10-kgf load cell. Film specimens − initial length (L_0): 100 mm − were uniaxially stretched at 10 mm min^{-1} to calculate tensile strength (σ_T), Young's modulus (E), and elongation at break (ε_B) using Eq. (1)–(3), respectively.

$$\sigma_T = F/A_0 \quad (1)$$

$$E = \lim_{L \to 0} \sigma/L \quad (2)$$

$$\varepsilon_B = [(L - L_0)/L_0] \cdot 100 \quad (3)$$

Wherein F is the maximum load, L is the ultimate specimen extension prior to breakage, and A_0 is the initial specimen cross-sectional area. Thickness was previously measured to the nearest 0.001 mm with a digital micrometer (Mitutoyo Corp., Japan) at three random positions throughout.

Table 1
Film-forming formulations (FFF). Compositions of aqueous FFF containing different contents of carrot minimal processing waste (CMPW) and hydroxypropyl methylcellulose (HPMC).

HPMC:CMPW (wt. ratio)	HPMC (g)	CMPW (g)	Water (mL)
1:0	1.6	–	80
2:1	1.1	0.5	80
1:1	0.8	0.8	80
2:3	0.6	1.0	80
0:1	–	1.6	80