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Antimicrobial and physical-mechanical properties of pectin/papaya puree/cinnamaldehyde nanoemulsion edible composite films

Caio G. Otoni [a,b,c], Márcia R. de Moura [b,d,*], Fauze A. Aouada [d], Geany P. Camilloto [c,e], Renato S. Cruz [c,e], Marcos V. Lorevice [a], Nilda de F.F. Soares [c], Luiz H.C. Mattoso [a,b]

[a] National Nanotechnology Laboratory for Agribusiness, EMBRAPA-CNPDIA – Rua XV de Novembro, 1452, São Carlos, SP, 13560-970, Brazil
[b] PPG-CEM, Department of Materials Engineering, Federal University of São Carlos – Rodovia Washington Luiz, km 235, São Carlos, SP, 13565-905, Brazil
[c] Laboratory of Food Packaging, Department of Food Technology, Federal University of Viçosa – Av. PH Rolfs, s/n, Viçosa, MG, 36570-000, Brazil
[d] Department of Physics and Chemistry, FEIS, São Paulo State University, Av. Brasil, 56, Ilha Solteira, SP, 15385-000, Brazil
[e] Technology Department, State University of Feira de Santana – Av. Transnordestina, s/n, Feira de Santana, BA, 44036-900, Brazil

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A B S T R A C T

The rising demand for bio-based materials to be used in food packaging has encouraged the development of novel, environmentally-friendly films. Fruit puree has the potential to be incorporated in the film-forming solution so that to produce edible films. The major components of plant essential oils (e.g., cinnamaldehyde) deliver antimicrobial properties against food pathogens and may be released by active films in an effort to replace synthetic preservatives. This work aimed at producing cinnamaldehyde nanoemulsions of different droplet sizes, as well as assessing the effect of papaya puree and cinnamaldehyde droplet diameter in the antimicrobial and physical-mechanical properties of high or low methylester pectin films. Increased stirring energies reduced droplet diameter. Papaya puree reduced films' resistance and rigidity while increased extensibility and water vapor permeability. Cinnamaldehyde nanoemulsions balanced the plasticizing effect of papaya puree by increasing rigidity and decreasing extensibility and permeability to water vapor of pectin films. Also, cinnamaldehyde provided antimicrobial properties against *Escherichia coli*, *Salmonella enterica*, *Listeria monocytogenes*, and *Staphylococcus aureus*. The reduction on droplet diameter did not influence the physical-mechanical properties of the films, but remarkably improved bacterial inhibition due to the higher delivery of active compounds having increased surface areas. Antimicrobial edible films from renewable sources were successfully produced here, and the improved bacterial inhibition provided by the same cinnamaldehyde content with smaller nanodroplets may play an important role in reducing preservative content as required by consumers.

1. Introduction

Polymers are used worldwide for many applications, including in food packaging massive production. Fossil fuels are the main source for commercial polymers, though there is an increasing environmental concern regarding their use. Bio-based materials have then been extensively researched to replace petroleum-based polymers. Renewable sources for biopolymers include polysaccharides such as pectin, a naturally occurring, hydrophilic polysaccharide found in plant cell walls which has good film-forming properties (Espitia, Du, Avena-Bustillos, Soares, & McHugh, 2014).

Traditional food packaging protects food from external conditions and provides consumers with information regarding the product it contains (Soares et al., 2009), but it is limited in increasing shelf-life of foods and in protecting consumers from foodborne outbreaks (Vermeiren, Devlieghere, van Beest, de Kruijf, & Debevere, 1999). Active packaging changes packaging conditions to extend shelf-life or to improve some properties of food products (Vermeiren et al., 1999), so that it denotes a feasible, innovative alternative for food processing and distribution. A way in which

* Corresponding author. Department of Physics and Chemistry, FEIS, São Paulo State University – Av. Brasil, 56, Ilha Solteira, SP, 15385-000, Brazil. Tel.: +55 18 3743 1195.

E-mail addresses: caiogomide@gmail.com (C.G. Otoni), marciadqi@gmail.com (M.R.de Moura), faouada@yahoo.com.br (F.A. Aouada), geanyperuch@yahoo.com.br (G.P. Camilloto), cruz.rs@gmail.com (R.S. Cruz), marcos.lorevice@gmail.com (M.V. Lorevice), nfsoares@ufv.br (N. de F.F. Soares), luiz.mattoso@embrapa.br (L.H.C. Mattoso).

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active packaging interacts with food is by gradually releasing antimicrobials from packaging material instead of adding them into food matrix (Appendini & Hotchkiss, 2002; Moura, Mattoso, & Zucolotto, 2012; Otoni, Soares, Silva, Medeiros, & Baffa Junior, 2014).

Numerous studies have found plant essential oils (EOs)—including cinnamon (*Cinnamomum zeylanicum*) EO—to inhibit or delay the growth of pathogenic microorganisms (Burt, 2004; Friedman, Henika, & Mandrell, 2002; Hammer, Carson, & Riley, 1999; Karapinar & Aktug, 1987; Passarinho et al., 2014; Raybaudi-Massilia, Mosqueda-Melgar, & Martín-Belloso, 2006; Rojas-Graü et al., 2007). Cinnamon EO is included in many food formulations, thus it fits desirable sensory characteristics (Friedman, Kozukue, & Harden, 2000). This EO is listed as generally recognized as safe (GRAS) for human consumption (Adams et al., 2004). Antimicrobially effective EOs contain certain oil compounds (OCs) in higher proportions, which are themselves known to exhibit pronounced antimicrobial properties, such as cinnamaldehyde in cinnamon EO (Pauli & Schilcher, 2010).

As a food-grade polymer, pectin may serve as matrix for the production of biodegradable and environmentally friendly edible films (Tharanathan, 2003). Pectin may be combined with fruits and vegetables in an effort to provide nutritional value to edible films and to exploit fruit processing wastes. There is an increasing trend in using underutilized food processing byproducts and wastes for edible film production (Otoni et al., 2012). Mango puree was used as the matrix for edible film production not only due to its high polysaccharide content, but also because of its color, flavor and potential in replacing synthetic polymers for film-forming purposes (Azeredo et al., 2009). Lorevice, Moura, Aouada, and Mattoso (2012) developed edible films based on guava puree for the same reasons, in addition to the vitamins and minerals that this guava provides. Edible films may carry several food additives, including antimicrobials (Cagri, Uspunol, & Ryser, 2004). EOs from allspice, garlic, lemongrass, cinnamon, clove bud, and oregano, when incorporated in edible films, exhibited antimicrobial activity against food pathogens (Du et al., 2008a, 2008b, 2009a, 2009b; Ravishankar et al., 2012). Apple-based edible films lessened growth of pathogenic bacteria (e.g., *Escherichia coli*) when combined with oregano, lemongrass, or cinnamon EO, even though their major constituents (carvacrol, citral, and cinnamaldehyde, respectively) delivered higher antimicrobial properties (Rojas-Graü et al., 2006, 2007). Pectin/apple-based edible films containing carvacrol or cinnamaldehyde lessened growth of *E. coli*, *Salmonella enterica*, and *Listeria monocytogenes* (Ravishankar, Zhu, Olsen, McHugh, & Friedman, 2009). Besides antimicrobial properties, EO- or OC-containing edible films may have improved barrier (Mancini & McHugh, 2000), antioxidative, sensory (Bakkali, Averbeck, Averbeck, & Idaomar, 2008; De Rovira, 2008), and mechanical properties (Du et al., 2008b).

Pectin is a water-soluble compound that polymerizes into films by casting and drying a film-forming solution (Espitia et al., 2014). The addition of hydrophobic substances (e.g., EOs and OCs) to an aqueous film-forming solution leads to a continuous (aqueous) and a dispersed (oil) phase. Although the stability of an emulsion system is favored by the low surface area of nanoemulsion droplets, there is still the risk of aggregation of the nanodroplets. This is undesirable for film-forming purposes due to the reduced homogeneity of the final film. A surfactant is added to produce thermodynamically stable oil-in-water emulsions. Depending upon the energy input during emulsification, different droplet size distributions are achieved. Nanoemulsions have extremely small droplets ranging in diameter from 20 to 500 nm (Solans, Izquierdo, Nolla, Azemar, & Garcia-Celma, 2005) and are much more stable than regular emulsions (Huang, Yu, & Ru, 2010). Due to their increased surface area, nanoemulsions provided improved delivery of active ingredients when compared to emulsions having bigger droplets (Huang et al., 2010; Tadros, Izquierdo, Esquena, & Solans, 2004; Yang, Marshall-Breton, Leser, Sher, & McClements, 2012).

In an effort to develop novel bio-based, edible, and environmentally friendly films to be used as active food packaging, the present study aimed at producing cinnamaldehyde nanoemulsions, as well as evaluating how papaya puree and cinnamaldehyde droplet diameter affect the antimicrobial and physical-mechanical properties of pectin films. To the best of our knowledge, this is the first report of nanoemulsion incorporation into fruit-based edible films and of the evaluation of their antimicrobial properties as affected by droplet size.

2. Materials and methods

2.1. Materials

Polyoxyethylene (20) sorbitan monooleate (Tween 80) was bought from Synth (Diadema, Brazil) and used as surfactant. Ultrapure water was used in all emulsions and solutions. Cinnamaldehyde (>93% pure) was purchased from Petite Marie (Itaquaquecetuba, Brazil). Low (LMP; with a degree esterification (DE) lower than 50%) and high methylester pectins (HMP; DE > 50%) were kindly provided by CP Kelco (Atlanta, GA). Papaya puree was acquired at the local trade of São Carlos, Brazil.

2.2. Emulsification

Direct oil-in-water (O/W) emulsions were prepared by adding 2% (wt.) of cinnamaldehyde and 1.5% (wt.) of Tween 80 to ultrapure water, followed by mixing in a T25 Ultra-Turrax (IKA Werke GmbH & Co, Staufen, Germany) at 7000, 12,000, or 16,000 rpm for 4 min to obtain different droplet sizes, relying on preliminary unpublished experiments.

2.3. Particle size, size distribution, and short-term stability

The average particle size and size distributions of emulsion droplets were determined by dynamic light scattering in a Zetasizer Nano Series (Malvern Instruments Inc., Worcestershire, U.K.) 1 h and 48 h after emulsification. Ultrapure water was used as dispersant to avoid multiple scattering effects and interdroplet interactions. The cumulant mean (z-average) diameter and the polydispersity index (PdI) were used to describe droplet size and size distribution, respectively.

2.4. Film preparation

Solutions (3% wt.) of either LMP or HMP were prepared by dissolving powdered pectin in ultrapure water and mixing at 1500 rpm until complete solubilization. These solutions were diluted (1:1) in ultrapure water to produce the control films (LP and HP). The solutions were also incorporated with 6% (wt.) of papaya puree and were diluted (1:1) either likewise to produce the control films added by papaya puree (LPP and HPP) or in the previously formed emulsions, producing LPP7, LPP12, and LPP16 for LMP, as well as HPP7, HPP12, and HPP16 for HMP. The compositions of the film-forming solutions are addressed in Table 1. The solutions were rested for 4 h to bubble elimination before casting over level overhead transparencies and drying at 25 ± 2 °C for 48 h. Dried films were cut and stored air-tight and under refrigeration until used for testing. Four films were produced for each treatment.

Du et al. (2009a) evaluated the antimicrobial properties of apple-based edible films containing different concentrations of