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Development and characterization of biodegradable antimicrobial packaging films based on polycaprolactone, starch and pomegranate rind hybrids

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ABSTRACT

Polycaprolactone (PCL)/starch/pomegranate rind (PR) hybrids were developed for antimicrobial packaging applications. PR was used, for the first time, as an antimicrobial compound and was incorporated directly in PCL matrix, without the extraction of any active compound from the fruit rind. The PCL-based antimicrobial films were fabricated using extrusion technique. It was observed that PCL/PR films demonstrated reasonably good antimicrobial activity at higher concentration of active compound. Addition of starch not only lowered the cost but also improved the rigidity of PCL matrix. Adding to this, starch enhanced the antimicrobial activity of PR, and provided a releasing channel for the delivery of polyphenols by attenuating the interactions between PCL and PR. Since all the materials used in this work are biodegradable and food contactable, it is expected that the developed material can be employed as food-grade antimicrobial packaging material.

1. Introduction

Antimicrobial packaging is a kind of active packaging in which active compound is incorporated within the packaging material to reduce the possibility of cross-contamination by suppressing the activities of targeted microorganisms (Ahmed et al., 2017; Appendini & Hotchkiss, 2002). Several organic and inorganic chemicals with antimicrobial properties have been utilized to develop active packaging materials. They mainly include organic acids (da Rocha, Loiko, Tondo, & Prentice, 2014; Ouattara, Simard, Piette, Begin, & Holley, 2000), bacteriocins (Jin, Liu, Zhang, & Hicks, 2009; Yuan, Lv, Yang, Chen, & Sun, 2015b), plant extracts (Adilah, Jamilah, & Hanani, 2018; Marcos et al., 2014; Wang & Rhim, 2016), natural polymers (Kurek, Galus, & Debeaufort, 2014; Pelissari, Grossmann, Yamashita, & Pineda, 2009; Schnell et al., 2017), enzymes (Ozer, Uz, Oymaci, & Altinkaya, 2016; Yener, Korel, & Yemenicioglu, 2009), nanoclays (Kanmani & Rhim, 2014) and metallic oxides (Shankar, Wang, & Rhim, 2017). Recently, the utilization of natural antimicrobial compounds such as essential oils (Hafsa et al., 2016; Wu et al., 2014; Zivanovic, Chi, & Draughon, 2005), spice extracts (Arfat, Ahmed, Ejaz, & Mullah, 2018; Nisar et al., 2017) and fruit extracts (Adilah et al., 2018; Emam-Djomeh, Moghaddam, & Yasini Ardakani, 2015; Uzunlu & Niranjan, 2017; Wang & Rhim, 2016) have attracted more attention due to their antimicrobial activity and safety. However, the high price and low decomposition temperature of such natural antimicrobial compounds makes them unsuitable for commercial applications, since the processing temperature of most of the biodegradable polymers (150–200 °C) is higher than the decomposition temperature of naturally occurring active compounds (~100 °C) (Scaffaro, Botta, Maio, & Gallo, 2016; Tawakkal, Cran, Miltz, & Bigger, 2014). Several approaches have been proposed till date to control the loss of antimicrobial activity of active compounds during processing, including but not limited to, plasticization of polymer (Liu, Jin, Coffin, & Hicks, 2009; Wang & Rhim, 2016), microencapsulation or formation of inclusion complexes (Abarca et al., 2017; Joo, Merkel, Auras, & Almenar, 2012), nanocomposites (Correa et al., 2017; Rhim, Hong, & Ha, 2009; Yahiaoui et al., 2015), etc. However, such techniques lack commercial success either due to high processing cost (for example, microencapsulation approach), safety issues (for example, nanocomposites) or migration phenomenon (for example, plasticized polymers) of packaging materials. In this regard, development of low-

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cost active packaging material will be highly beneficial for commercial applications.

Poly(caprolactone) (PCL), with its low melting (60 °C approximately) and glass transition (around −60 °C) temperature, offers an ideal biodegradable matrix for natural antimicrobial agents as it can be processed at low temperature and have the potential for use in commercial applications. Moreover, the toughness of PCL is superior than most of the biodegradable polymers (Averous, 2004). However, lower modulus and rigidity of PCL limit its many applications. Starch, being a natural polymer, is abundantly available and is blended with several bio-based polymers (Liu, Xie, Yu, Chen, & Li, 2009) with an objective to either reduce the cost or to control the hydrophobicity of the base polymer (Imre & Pukanszky, 2013). Starch have been widely used as reinforcing agent to improve modulus of various biodegradable polymeric materials (Khalid et al., 2017), since starch itself is also biodegradable (Imre & Pukanszky, 2013; Yu, Dean, & Li, 2006). Actually, PCL/starch composites have been reported previously, whereby starch was utilized as filler to optimize the mechanical properties and to control the cost of PCL matrix (Campos et al., 2013; Kong et al., 2017). Starch can also be used as a delivery vehicle for the transportation of embedded molecules from the matrix (Khalil, Galland, Cottaz, Joly, & Degraeve, 2014). By playing with the hydrophobicity of PCL matrix, the transportation of embedded antimicrobial compounds can be tailored for any specific application. PCL and starch, being immiscible polymers since the former is hydrophobic and the latter is hydrophilic, are ideal candidates for developing such kind of biodegradable polymers with controlled release properties.

Pomegranate (*Punicagranatum* L.) rind (PR) is obtained as a by-product during processing of pomegranate juice. PR is rich in tannins and polyphenols, that demonstrate remarkable antimicrobial activity (Al-Zoreky, 2009). However, the extraction of tannins or polyphenols from the rind is an expensive step that makes it unsuitable for general applications. In this study, PR powder was used as an antimicrobial compound, and was incorporated directly in the matrix without extracting any active compound from the fruit rind. PCL-based films were prepared using extrusion technique to check the stability of active compound in actual processing conditions. Both starch and PR were also used to decrease the cost of PCL. It is expected that this study will be beneficial in designing biodegradable materials filled with naturally occurring antimicrobial compounds and can also be employed to design any other kind of active packaging material.

2. Materials and methods

2.1. Materials

Polycaprolactone (MW: 37000; & MFI: 24) was obtained from Taisu Plastic Industrial Ningbo Co Ltd (Ningbo, China). Cornstarch (amylose/amylopectin ratio was 26/74) was obtained from Foshan Nanhai Suiyang Food material Co Ltd (Foshan, China). Stearic acid, with a melting point of 67–70 °C, was procured from Shanghai Lingfeng Chemical Reagen t Co (Shanghai, China). Pomegranate rind powder (bulk density: 52 g/100 mL) was obtained from Shaanxi Honghao Biotech Co Ltd (Xian, China). Both culture media (brain heart infusion-BHI agar, HCM105; and lactose broth-LB agar, HCM055) and microbial culture (*Staphylococcus aureus*: ATCC 29213; and *Eschericia coli*: ATCC 25922) were procured from Guangdong Huankai Microbial Sci & Tech Co Ltd (Guangzhou, China). Sodium carbonate (MW = 105.99), gallic acid (MW = 170.12; purity = 99%) and Folin-Ciocalteu's phenol reagent (2 M Acid) were procured from Guangzhou Chemical Reagent Factory (Guangzhou, China), Guangzhou Topwork Chemical Co Ltd (Guangzhou, China) and Sinopharm Chemical Reagent Co Ltd (Ningbo, China), respectively.

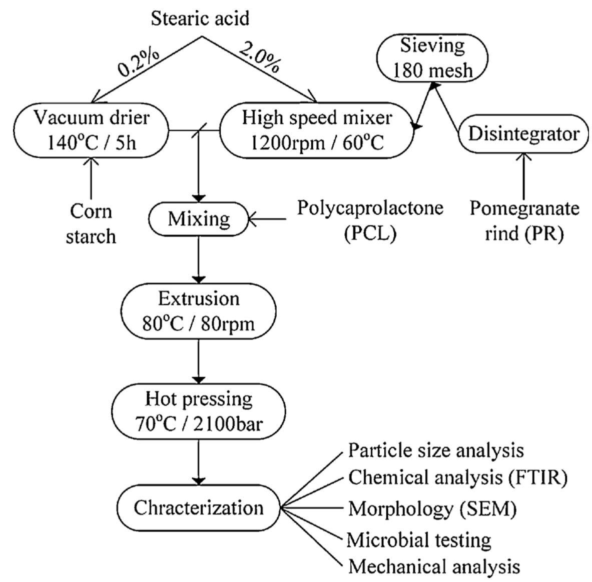

Fig. 1. Flow line of sample preparation.

2.2. Sample preparation

Fig. 1 shows the step-by-step guide that was followed to prepare samples. Initially, starch was dried in a vacuum drier (Yingkou Liaohe pharmaceutical & chemical equipment Co Ltd, Yingkou, China) at a speed of 90 rpm, −0.1 MPa of vacuum, 140 °C temperature for 4 h, followed by the addition of stearic acid (0.2% concentration on w/w basis); vacuum drier was run again to coat the surface of starch granules with stearic acid at 140 °C for 1 h at a speed of 110 rpm without creating any vacuum pressure. Pomegranate rind was ground using herbal medicine disintegrator (FW177, Tianjin Taisite Instrument Co Ltd, Tianjin, China) and was then passed through 180 mesh sieve size. Sieved PR was then dried at 37 °C for 10–12 h in air drier (DHG 9145 A, Shanghai Right Instrument Co Ltd, Shanghai, China). PR was then surface treated with stearic acid in a lab scale high speed mixer (SRL W10/25) at 1200 rpm for 3 min. All the samples were hermetically sealed and were stored in air-tight container under controlled conditions of temperature and humidity to avoid any probability of moisture uptake.

2.3. Processing

2.3.1. Extrusion

PCL/starch/PR composites were prepared using twin screw extruder (Rheomex PTW 24/40p, Ø30, screw diameter $D = 24$ mm, screw length $L = 28D$) with 150 mm wide sheet die. PCL, starch and PR were mixed manually, and the composition of each specimen is given in Table 1. Samples were fed through hopper using 80 rpm screw speed. There were eight temperature controlling zones along the barrel of extruder and the maximum temperature of barrel was set as 80 °C while the temperature of die was set as 75 °C A separate hauling device was used to collect the extruded sheets from the die.

2.3.2. Hot pressing

Samples were pressed using hot-plate machine (Guangzhou Shunchuang Rubber Machinery Factory, Guangzhou, China) with an objective to control the thickness and to flatten the extruded specimens. All the samples were covered with fiber coated Teflon sheets prior processing them in hot plate machine in order to avoid thermal degradation of the material. Temperature and pressure of 70 °C and 2100 bar, respectively, was used while the thickness of all the samples was adjusted to around 0.300 mm. All the samples were stored in room