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Microencapsulation by pectin for multi-components carriers bearing both hydrophobic and hydrophilic active agents

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ABSTRACT

Oil/water microencapsulation by microfluidic systems has been a prominent delivery method to prepare functional microcapsules in the food, cosmetic, and pharmaceutical industries because it is an easy way to control the shape and size of structures and functionalities. We prepared biocompatible and multi-component microcapsules using the precipitation and ionic crosslinking of pectin in a poor solubility environment and with multivalent cations, respectively. When the aqueous solution (including calcium ions and ethanol) in a sheath flow met the flow of a pectin aqueous solution containing oil droplets, ethanol-gelation and ionic cross-linking occurred, enclosing the inner oil phase droplets by solidified pectin shells. Furthermore, the resulting microcapsules stabilized by pectin shells exhibited functionalities using a hydrophobic agent and nanoparticles of a hydrophilic species that were dissolved and dispersed, respectively, in the oil phase.

1. Introduction

Microcapsule technology has been attracting a lot of attention as a promising method for fabricating delivery systems. Microcapsules can prevent internal active substances from degrading and losing their activities due to external environmental factors, such as air, moisture, or ultraviolet (UV) light (Kim et al., 2014; Lee et al., 2016; Ogonczyk, Siek, & Garstecki, 2011). This advantage allows microencapsulation technology to be applicable in many industries, such as the pharmaceutical industry for drug delivery systems (Decher, 1997), bioengineering for cell microencapsulation (Wan, 2012), and the food industry for sustaining taste or flavor (Koo, Cha, Song, Chung, & Pan, 2014; Ziani, Fang, & McClements, 2012). In particular, the microencapsulation method is an effective technique to protect the most active agents that are chemically unstable and easily oxidized by external conditions.

In the cosmetic application as well as above-mentioned industries, biocompatibility is one of the most important properties of the chosen materials. Therefore, polysaccharides have been used for decades because they show excellent biocompatibility and are cheaper than other biopolymers. In particular, pectin, a polysaccharide natural polymer, can potentially form biocompatible microcapsules because of its gelation property by forming an “egg box” via electrostatic interactions between the carboxylate anions in pectin and calcium cations (Deng, He, Wu, & Yang, 2008; Jonassen, Treves, Kjoniksen, Smistad, & Hiorth, 2013). “Egg-box gelation” helps pectin form a solid hydrogel in an aqueous solution without any hazardous substance. In addition, pectin is a suitable material for cosmetic agent delivery capsules because of its anti-oxidative effect and hydrogel performance, which provides moisture retention to supply and maintain moisture, and its biocompatibility and biodegradability. Research has shown that pectin can maximize the stability of some active agents because of its anti-oxidative effect and improve skin penetration (Ro et al., 2015). These merits suggest the potential for using pectin in functional microcapsule formulations for cosmeceutical multimeric active agent carriers by gelation upon electrostatic crosslinking.

Microcapsules have been prepared by spray-drying (Ré, 1998; Reis et al., 2009; Koo et al., 2014), layer-by-layer (Decher, 1997), sol-gel (Wang, Tsai, & Yang, 2006), coacervation (Deasy, 1984), and microfluidic (Zhang et al., 2006) methods. In particular, microfluidic routes have the advantage of preparing mono-dispersed polymer capsules of various sizes and shapes by controlling the micro-scale flows, compared to other encapsulation methods. However, there are still some limitations to the microfluidic method. Firstly, the inner flow liquid only contains one type of active substance among the hydrophobic or hydrophilic materials corresponding to the inner flow. Therefore, hydrophilic fluids can only convey hydrophilic active agents and hydrophobic

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liquids can only include hydrophobic active agents. This makes it difficult to deliver multi-component active agents. Another limitation is that this method must have a solidification process because of the flow-based system. Generally, there are two methods for solidification: 1) covalent bonding by photo-polymerization or cross-linking by UV light and 2) non-covalent bonding, including precipitation by solvent diffusion or ionic cross-linking. In the former case, initiators or UV cross-linkers should be used during the polymerization or crosslinking process. However, they are generally harmful to the human body and unsuitable for cosmetic applications (Zhao et al., 2011). The latter solvent diffusion precipitation generally uses a variety of polymers, including natural polymers, polysaccharides (cellulose, arginine, agarose, and chitosan), proteins (collagen, gelatin), and synthetic polymers (poly(ethylene glycol) and poly(vinyl alcohol)) (Kim et al., 2014). In this process, the polymers must flow into certain solvents, such as ionic liquids for cellulose, chloroform or toluene for synthetic polymers, but most of these solvents are dangerous for bio-applications (Liu et al., 2009).

In this study, we produced polysaccharide microcapsules that can simultaneously carrying hydrophilic and hydrophobic functional components by using precipitation and ionic crosslinking of pectin on oil droplet templates in a simple microfluidic system. Mono-dispersed oil droplets were continuously generated by hydrodynamic flow-focusing in an aqueous pectin solution within the oil-templates channel of our microfluidic device (Fig. 1A). The aqueous pectin solution containing the oil droplets and a mixed solution of water, ethanol, and calcium ions were acted as a core and a sheath flows in the output microchannel, respectively. Pectin microcapsules were created based on the precipitating properties of pectin in ethanol and the ionic crosslinking of carboxylic acid groups in pectin with calcium ions, as illustrated in Fig. 1B. Ethanol is a biologically harmless solvent and does not require additional solvent removal steps (as for other organic solvents). Pectin can be immediately precipitated and become an alcohol-gel when a pectin-aqueous solution contacts with ethanol (Veronovski, Tkalec, Knez, & Novak, 2014). Previous research reported one of coacervate methods in emulsion to use both ionic cross-linking and alcohol precipitation using carboxymethyl cellulose and gelatin (Huei, Muniyandy, Sathasivam, Veeramachineni, & Janarthanan, 2016). In our approach, pectin in the aqueous core flow can be solidified on the surface of oil droplets by such ethanol-gelation as well as ionic crosslinking in the microchannel. The ionic crosslinking requires a long time for gelation using calcium ions but provides a stronger gelation than ethanol. In contrast, the ethanol-gelation is immediate but weak. The strong and fast gelation of pectin can be accomplished by a synergetic effect of both alcohol-gelation and ionic crosslinking.

To incorporate multi-components into oil droplet-templated microcapsules with pectin shells, we selected retinyl palmitate (RP) as a hydrophobic agent and quercetin as a hydrophilic agent (Fig. 1C). RP is an ester form of retinol (vitamin A), one of the most common and effective anti-wrinkle agents (Hubinger, 2009). Like many other cosmetic agents, retinol can be easily degraded by heat and must be protected from degradation factors (UV, oxygen, and moisture). RP is more stable than retinol, but it is still chemically unstable with respect to UV radiation and oxidation. One method to improve the stability of RP is to absorb RP into pectin microparticles that allow RP to preserve its unstable chemical structure for a longer period because of the antioxidant property of pectin (Ro et al., 2015). Using our encapsulation approach, RP could be stable when dissolved in the oil phase followed by encapsulating the oil phase by pectin shells because the internal oil phase and the external pectin shell could protect RP from the oxidation by oxygen and water. As for the hydrophilic agent, quercetin is an antioxidant, skin-soothing agent, and restorative ingredient. This hydrophilic species can be dispersed as nanoparticles in the oil phase; the nanoparticles can be formed using a nano-precipitation process. As our expectation, the pectin microcapsules bearing both of quercetin nanoparticles and RP in the oil-droplet core were successfully realized using the microfluidic platform. The optimal flow conditions to produce the pectin microcapsules and control the capsule size were investigated. The existence of RP and quercetin nanoparticles together with pectin shells was confirmed by absorption spectroscopy and imaging techniques. The resulting pectin microcapsules bear multi-components with anti-oxidizing properties from pectin, anti-wrinkling properties from RP, and a whitening effect from quercetin, which should be useful for cosmetic applications.

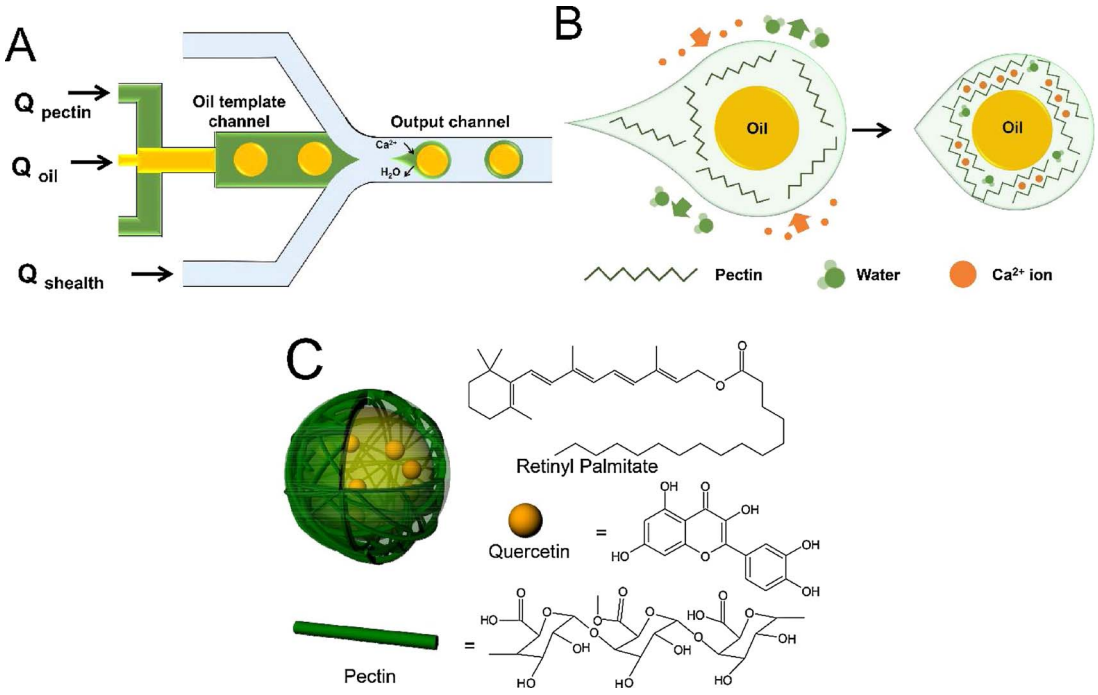

Fig. 1. Schematic illustration of (A) the microfluidic device and the generation of pectin microcapsules, (B) fabrication of pectin microcapsules in the micro-fluidic channel, and (C) pectin microcapsules carrying retinyl palmitate-quercetin particle active agents.