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Preparation of aqueous dispersions of coenzyme Q_{10} nanoparticles with amylomaize starch and its dextrin

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ABSTRACT

An aqueous dispersion of CoQ_{10} nanoparticles could be prepared by using amylomaize starch or its dextrin (average DP 311). CoQ_{10} (100 mg dry solids) was dispersed in aqueous starch or dextrin solution (500 mg/5 mL) at 60–80 °C for 3 days, and then the solids were isolated by centrifuging in the dispersion (25,000× *g*, 30 min). The isolated particles consisted of CoQ_{10} and starch at an approximate weight ratio of 2:1. The presence of V-amylose complex with CoQ_{10} was confirmed under differential scanning calorimetery (DSC), but most of the CoQ_{10} in the particles existed as crystalline aggregates. The isolated particles, initially ranged in micrometer, could be re-dispersed in water at nano-sizes by treating with a mild ultrasonication. The aqueous dispersions of CoQ_{10} nanoparticles (100 mg/100 g) exhibited zeta potentials of −33.9 and −51.1 mV, respectively for starch and dextrin dispersions, and remained homogeneous for more than 3 weeks without forming precipitates during an ambient storage.

1. Introduction

Coenzyme Q_{10} (CoQ_{10}) is a vitamin-like substance that plays an essential role in the mitochondrial respiratory chain as a carrier of electrons. It is responsible for the energy conversion from carbohydrates and fatty acids in metabolic pathway (Crane, 2001). It also has an antioxidant activity by scavenging or removing free radicals from body, and an ability to regenerate other radical scavengers such as α-tocopherol (Beal, 2002). In addition, beneficial effects of CoQ_{10} against various diseases such as cardiovascular, neurodegenerative and neuromuscular diseases have been reported (Beal, 2002; Overvad et al., 1999). CoQ_{10} is biosynthesized in healthy body of young generation, but the rate of synthesis gradually decreases with aging so that oral supplement becomes needed for the elders.

CoQ_{10} is a hydrophobic compound with a molecular weight of 863. The long isoprenoid side chain which is responsible for its water insolubility generates yellow color. Because of its hydrophobicity, application of CoQ_{10} in aqueous foods and drugs is limited and its bioavailability after intake is low (Kommuru, Gurley, Khan, & Reddy, 2001). There have been various approaches to improve water solubility of CoQ_{10}. Among those, emulsion formulations of CoQ_{10} using additives have been largely studied (Balakrishnan et al., 2009; Carli, Chiellini, Bellich, Macchiavelli, & Cadelli, 2005; Nepal, Han, & Choi, 2010; Shin et al., 2009; Siekmann & Westesen, 1995). However, most of the additives used for the formation of CoQ_{10} emulsions are chemically synthesized so that excess use of the additives often causes health concern and off-flavors of the host foods. Complex formation with cyclodextrin is also used to increase the solubility for CoQ_{10} in the aqueous foods and drugs (Fir, Smidovnik, Milivojevic, Zmitek, & Prosek, 2009; Terao et al., 2006). It was reported that the use of cyclodextrin increased the bioavailability by 420% compared to pure CoQ_{10} (Žmitek et al., 2008). However, complex with cyclodextrin often generates large aggregates which are unstable for an extended storage. It was reported that the average particle size and zeta-potential value of a CoQ_{10}-cyclodextrin complex were 2.4 μm and 0 mV, respectively (Hatanaka, Kimura, Lai-Fu, Onoue, & Yamada, 2008).

Starch, an agricultural biopolymer, is often used as a suspending aid for hydrophobic substances in aqueous dispersions. Amylose, the linear fraction of starch, is known for its ability of forming single helix complexes with hydrophobic molecules, although it is usually induced by the presence of hydrophobic compounds. The single helical configuration is often called as V-amylose in which the hydroxyl oxygens are located in exterior of helix providing water solubility to the entrapped the hydrophobic compounds (Eliasson, 2004). Various hydrophobic compounds such as iodine, lipids, linear alcohols, and aroma compounds have been used to form V-complexes with amylose (Bluhm & Zugenmaier, 1981; Gelders, Vanderstukken, Goesaert, & Delcour, 2004; Godet, Buléon, Tran, & Colonna, 1993; Helbert & Chanzy, 1994; Itthisoponkul, Mitchell, Taylor, & Farhat, 2007; Kim & Lim, 2009). V-amylose has been

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applied to form the complex with flavor compounds (Conde-Petit, Escher, & Nuessli, 2006) to improve the stability of flavors and to control the rate of flavor release (Escher, Nuessli, & Conde-Petit, 2000). Recently, genistein–amylose complex was introduced with improved aqueous solubility and bioavailability of genistein (Cohen, Orlova, Kovalev, Ungar, & Shimoni, 2008).

Starch is almost tasteless and odorless whereas emulsifiers used for water dissolution of hydrophobic compounds often cause off-taste. It can be utilized at much lower cost than cyclodextrin which is produced by enzymatic or fermentation process. In addition, amylose chains have a flexibility of cavity size for complex formation, readily adaptable to various guest compounds. Even if the single helix complex is not formed due to the structural inadaptability of hydrophobic compounds, starch itself has the ability of improving stability of the dispersed particles in aqueous media.

Nanotechnology that is widely applied in many industrial fields is also applied in food and pharmaceutical sciences. Reduction of particle size to nanometer ranges results in increasing of surface area per mass and thus substantial increases in the functionality of the particles (Lee, Kim, Ahn, & Lee, 2010). For hydrophobic drugs, as the dissolution rate increases by reducing the particle size, bioavailability of drugs in body is also improved (Liversidge & Cundy, 1995; Rasenack & Müller, 2002). In addition, particles in the nanometer range showed higher dispersion stability (Ribeiro, Chu, Ichikawa, & Nakajima, 2008; Yuan, Gao, Zhao, & Mao, 2008), which is beneficial for the preparation of aqueous foods containing various hydrophobic compounds.

In this study, CoQ_{10} was dispersed in aqueous solutions of a maize starch containing high amount of amylose (70 g amylose/100 g starch), and its dextrin prepared by acidic hydrolysis. Simple processes of aqueous blending under mild heat were applied for the preparation of the dispersion, and the complex formation between CoQ_{10} and starch chains were analyzed. Effects of various physical conditions for the dispersion formation and post-treatment such as ultrasonication on the particle size and stability of the dispersed CoQ_{10} were investigated.

2. Materials and methods

2.1. Materials

High amylase maize starch (HylonVII, 70 g amylose/100 g starch) was a gift from National Starch and Chemical Company (Bridgewater, NJ). A dextrin (average degree of polymerization 311) was prepared by hydrolyzing the starch following the method of (Kim, Yoon, & Lim, 2009). Prior to dispersion formation, the starch and dextrin were purified by dissolving in a boiling dimethylsulfoxide solution (90 mL/100 mL), and precipitating in ethanol. CoQ_{10} (purity: 99.4 g/100 g) was provided by Daewoong Co. (Seoul, Korea).

2.2. Dispersion formation

The starch or dextrin (500 mg) was dissolved in a NaOH solution (1.0 mol/L, 5 mL), and the solution was diluted by adding 40 mL of distilled water and neutralized by adding a HCl solution (1.0 mol/L, 5 mL). For complete dissolution, the starch or dextrin solution was autoclaved at 121 °C for 20 min. Dry powder of CoQ_{10} (100 mg) was dispersed in the solution and then the dispersion was continuously stirred (550 rpm) at 60–80 °C for up to 3 days to provide a sufficient period for any possible interactions between starch and CoQ_{10}. After 6 h of stirring, a mild ultrasonication for 3 min (200 W/cm^2, JAC-2010, Jinwoo Engineering, Seoul, Korea) was applied once to improve the reaction. The CoQ_{10} dispersion, after 1–3 days of stirring, was transferred in a styrofoam box and allowed to cool slowly to room temperature while stirring for 12 h. The dispersion was centrifuged at 25,000× g for 30 min at 40 °C, and the precipitates were freeze-dried for the structural and compositional analyses. For comparison, pure CoQ_{10} and starch were also treated in the same process (Control 1 and 2).

2.3. Ultrasonication for re-dispersion

The CoQ_{10} particles isolated by centrifugation of the dispersions in starch and dextrin solutions were re-dispersed (100 mg/100 mL). Ultrasonication (750 W/cm^2, VCX 750, Sonics & Materials Inc., Newtown, CT) was applied to the re-dispersed solution for 3–7 min in ice bath, and its effect on the dispersion stability and the particle size were examined. The amplitude was 80% of the maximum and pulsed on and off for 5 s each.

2.4. CoQ_{10} and starch contents

The re-dispersion of the centrifuged residue (100 mg/100 mL) was autoclaved (121 °C, 20 min) to disrupt any linkages between CoQ_{10} and starch. Isopropyl ether (5 mL) was added in the dispersion with a vigorous vortexing. The amount of CoQ_{10} in the upper isopropyl ether layer was measured using a spectrophotometer at 275 nm (Ultraspec 2000, Pharmacia Biotech., UK). The amount of starch in the aqueous bottom layer was quantified by using the phenol-sulfuric acid method (DuBois, Gilles, Hamilton, Rebers, & Smith, 1956).

2.5. Zeta potential of CoQ_{10} nano-dispersion

Zeta potential value of the particles re-dispersed in distilled water was measured using a Zeta-sizer (3000HS Advance Malvern Instruments Ltd., UK) for the stability analysis of CoQ_{10} nano-dispersions. It measures distribution of electrophoretic mobility and zeta potential of the particles using Laser Doppler Velocimetry. The measurement was carried out at a temperature of 25 °C and pH 4.4.

2.6. Differential scanning calorimetry (DSC)

Thermal transition property of the CoQ_{10} and starch complexes was measured by using a differential scanning calorimeter (DSC 6100, Seiko instrument, Chiba, Japan). Freeze-dried complex (1.5 mg) was transferred into an aluminum DSC pan and distilled water (3.0 mg) was added into the DSC pan. The sealed pan was equilibrated in a cold chamber (4 °C, 12 h) and then analyzed by heating from 25 °C to 125 °C at a rate of 5 °C/min. Empty pan was used as a reference, and physical mixture of equal ratio of CoQ_{10} and starch was analyzed as a control.

2.7. X-ray diffraction

The crystallinity of the freeze-dried complex was determined by an X-ray diffractometer (MO3XHF22, MAC Science Co., Japan) at a target voltage and a current of 30 kV and 40 mA, respectively. The scanning range and speed were 3–30° (2θ) and 1.0 °/min, respectively. Physical mixture of CoQ_{10} and starch was also tested for comparison.

2.8. Particle size distribution

Hydrodynamic particle size distribution was measured by using a dynamic light scattering detector (Dynamic Titan, Wyatt Technology, Santa Barbara, CA). The particles isolated by centrifugation were re-dispersed in water for the measurement. The refractive index and the viscosity of water were 1.333 and 1.00 cP at 20 °C, respectively.