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Ascorbyl palmitate-β-cyclodextrin inclusion complex as an oxygen scavenging microparticle

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ABSTRACT

An ascorbyl palmitate-β-cyclodextrin inclusion complex (IC) was produced and evaluated as a possible oxygen scavenger. The X-ray diffraction profiles of ascrobyl palmitate (AP), β-cyclodextrin (β-CD), and the IC were characterized by wide angle X-ray diffraction (WAXD). The formation of inclusion complex induced large shifts in the WAXD signals. Surface morphology images from scanning electron microscopy showed that the IC had a rod shape. TGA analysis demonstrated that the IC had better thermal stability than the AP. The off-flavor profiles of the AP and the IC were analyzed by GC/MS. The IC had less off-flavor byproducts than the AP during oxygen scavenging reaction. The oxygen scavenging capability of the IC was compared with other oxygen scavengers, the AP and iron powder (IP), at two different storage temperatures, 4 and 23 °C. The IC had higher oxygen scavenging capability than the AP and the IP at both storage temperatures. The effect of thermal processing on oxygen scavenging capability was also investigated. Only the IC maintained good oxygen scavenging capability after thermal processing. Results demonstrated that the IC can be used as an effective oxygen scavenger.

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1. Introduction

Residual oxygen in the package headspace can cause the oxidation of packaged food and the growth of aerobic bacteria or proliferation of molds (Brown & Williams, 2003). To eliminate these undesirable changes, various oxygen scavengers have been investigated over the last 30 years (Brody, Strpinsky, & Kline, 2001). Utilizing natural compounds as the basis for oxygen scavengers has received considerable interest from the food packaging industry. Recently, a new oxygen scavenging system which utilizing α-Tocopherol and iron chloride(II) has been developed (Byun, Darby, Cooksey, Dawson, & Whiteside, 2011). However, it had low oxygen scavenging capacity compared with iron powder. Therefore, natural oxygen scavenging compounds which have better oxygen scavenging rate and capacity need to be developed.

Another issue placed on oxygen scavenging technology is utilizing UV light as an activator for oxygen scavenging film. Many patents have been issued for UV light activated oxygen scavengers (Albert & Rooney, 2004; Speer et al., 1994). However, the UV activation step reduces packaging line speed and resulting in reduced profitability. Recently, a nanoencapsulation technique has been adopted for the application of a different activation system (Byun, Hwang, et al., 2011; Byun, Whiteside, Cooksey, Darby, & Dawson, 2011). However, this oxygen scavenging nanoparticle had low oxygen scavenging capacity and rate due to its excellent stability. Therefore, there is demand for new scavenging nano or microparticles which have higher oxygen scavenging capabilities.

Cyclodextrin inclusion complex is one microencapsulation technique that has a significant potential for oxygen scavenging technology. Cyclodextrins (CDs) are cyclic oligosaccharides with a hydrophilic exterior and a hydrophobic central cavity. Its molecular dimensions allow total or partial inclusion of guest compounds. Among conventional microencapsulation methods, β-cyclodextrin inclusion is the most effective for protecting flavors. It also has been reported that cyclodextrin inclusion complex can reduce off-flavors (Byun, Desai, Kim, & Park, 2010, chap. 12). Both oxygen scavenging sachets and films have a common problem with the production of off-flavor byproducts from the oxygen scavenging reaction (Vermeiren, Heirlings, Devlieghere, & Debevere, 2003). Consumers recognized off-flavors as an unpleasant aspect when selecting a food product. Therefore, eliminating or reducing these potential off-flavors is a major concern for developing new oxygen scavenger. Other advantages of cyclodextrin inclusion complex are its thermal and chemical stability. The cyclodextrin complexes are thermodynamically stable up to 200 °C (Gouin, 2004) and encapsulated flavors can provide better protection from volatilization during extrusion. Thus the cyclodextrin inclusion complex as an oxygen scavenger can then be extruded for further film applications.

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In this research, ascorbyl palmitate was selected as the active material in inclusion complex. Ascorbyl palmitate is a synthetic amphiphilc ascorbic acid and has similar physiological functions when compared with ascorbic acid. It has been studied in the food, pharmaceutical, and cosmetic industry due to its stability and antioxidant activity (Beddows, Jagait, & Kelly, 2001; Spiclin, Gasperlin, & Kmetec, 2001). Ascorbyl palmitate has also been proposed as an oxygen scavenger to remove headspace oxygen (Cort, 1974).

The objective of this study was to produce ascorbyl palmitate-β-cyclodextrin inclusion complex (IC) as a possible oxygen scavenger system. The influences of transition metal catalyst, storage temperature, and thermal processing on oxygen scavenging capability were investigated.

2. Materials and methods

2.1. Materials

β-Cyclodextrin (β-CD) and ascorbyl palmitate (AP) were purchased from Sigma–Aldrich (MO, USA). β-CDs were stored in drying oven at 35 °C to remove moisture prior to use. Iron chloride(II), tetrahydrate was purchased from J. T. Baker (NJ, USA). Ethanol (200 proof) was purchased from EMD biosciences (CA, USA). Iron powder (hydrogen reduced, IRON100) was purchased from Chemical Store (NJ, USA).

2.2. Preparation of inclusion complex

Three grams of β-CD were dissolved in 30 mL of an ethanol and water (1:2) mixture maintained at 80 °C on a hot plate. Nine grams of AP was dissolved in 90 mL of ethanol and was slowly added to the β-CD solution. The mixed solutions were continuously stirred on a hot plate at 60 °C for 4 h and then cooled to room temperature. Stirring was stopped when the solutions turned into slurry. The slurries were refrigerated overnight at 4 °C. The resulting white powder was collected by centrifugation at 4880 × *g* for 10 min. The final product was dried at room temperature in drying chamber for a week. The encapsulation efficiency (%) and ascorbyl palmitate loading (%) of inclusion complex were measured by UV spectrometer and they were 24% and 34%, respectively.

2.3. Scanning electron microscopy (SEM)

The surface morphology of the AP-β-CD-inclusion complex (IC) was examined by scanning electron microscopy (S-4800 UHR FE-SEM, Hitachi high technologies America, Inc.). Surfaces were prepared using platinum coating. SEM images were taken at 5 kV with 2.5K and 5K magnifications.

2.4. Wide angle X-ray diffraction (WAXD)

The XRD studies were carried out using a Scintag XDS 2000 (Scintag Inc., Santa Clara, USA) with a germanium detector equipped with Scintag DMSNT Version 1.37 software. The samples were scanned from the start angle of 5° to the stop angle of 60° at step size 0.02° and preset time 0.5 s.

2.5. Thermogravimetric Analyzer (TGA)

Thermal stability tests were performed using a Thermogravimetric Analyzer (Hires TGA 2950, TA instrument) with nitrogen. An equilibrium temperature of 25 °C was ramped to 120 °C (isothermal for 10 min) at a rate of 20 °C/min and then ramped to 600 °C at a rate of 30 °C/min. The samples weighing between 2 and 6 mg were used for the measurement.

2.6. Sample preparation for headspace analysis

One hundred milligrams of the AP or the IC with 10 mg of iron chloride(II) and 0.1 mL of water were added into a clear 20 mL headspace vial with a screw top cap and PTFE/Silicone septa for headspace analysis. The final samples were thermally processed for 10 min at 121 °C. Two vials were prepared for each composition.

2.7. Headspace analysis

GC–MS (GC2010/GCMS-QP2010S, Shimadzu) was used for analysis of volatile compounds. A RTX1 F&F fused silica capillary column (30 m length, 0.25 mm internal diameter with 0.25 μm film thickness) from Restek Chromatography Products (PA, USA) was used. The carrier gas was helium (99.99%) and was maintained at a constant flow rate of 1.22 mL/min. The thermally processed headspace vials were incubated at 45 °C for 30 min in chamber prior to injection. After incubation, 200 μL of sample headspace was injected into GC by autosampler (AOC5000 Auto injector, Shimadzu). An initial oven temperature of 45 °C was held for 1 min and ramped at 3 °C/min to 100 °C (holding for 2 min) and then ramped at 20 °C/min to 250 °C (holding for 10 min). Injector and interface temperature were 250 °C.

2.8. Sample preparation for oxygen content (%) analysis

For the oxygen content (%) analysis, glass Mason jars (250 mL) were used as the container. The metal lids were punctured to make a hole with the area of 28 mm^2 and then adhesive septa (Illinois Instrument, IL, USA) with the area of 254 mm^2 were attached both above and below the hole.

2.8.1. Sample preparation for the effect of transition metal catalyst on oxygen scavenging capability

One gram of the IC with 0.1 mL of water with or without 10 mg of transition metal catalyst (iron chloride(II)) was placed inside the jar with ambient air (20.90% O_2). The jars were covered by the lids and then the rings were tightened to provide an air tight closure. The final sample jars were stored at 23 °C.

2.8.2. Sample preparation for the effect of storage temperature on oxygen scavenging capability

One gram of the IC, ascorbyl palmitate (AP), or iron powder (IP) with 0.1 mL of water was placed inside the jar with ambient air (20.90% O_2). The jars were covered by the lids and then the rings were tightened to provide an air tight closure. The final sample jars were stored at two different storage temperature, 4 °C and 23 °C.

2.8.3. Sample preparation for the effect of thermal processing on oxygen scavenging capability

One gram of the IC, the AP, or the IP with 0.1 mL of water was placed inside the jar with ambient air (20.90% O_2). The jars were covered by the lids and then the rings were tightened to provide an air tight closure. The final samples were thermal processed and then stored at 23 °C.

2.9. Thermal processing

A pilot-scale rotary, single cage, water spray retort operating in static mode was employed in this research. Samples were thermally processed for 10 min at 121 °C and 30 psi using a Surdry Rotary Pilot Retort (Model APR-95, Stock America, NC, USA).

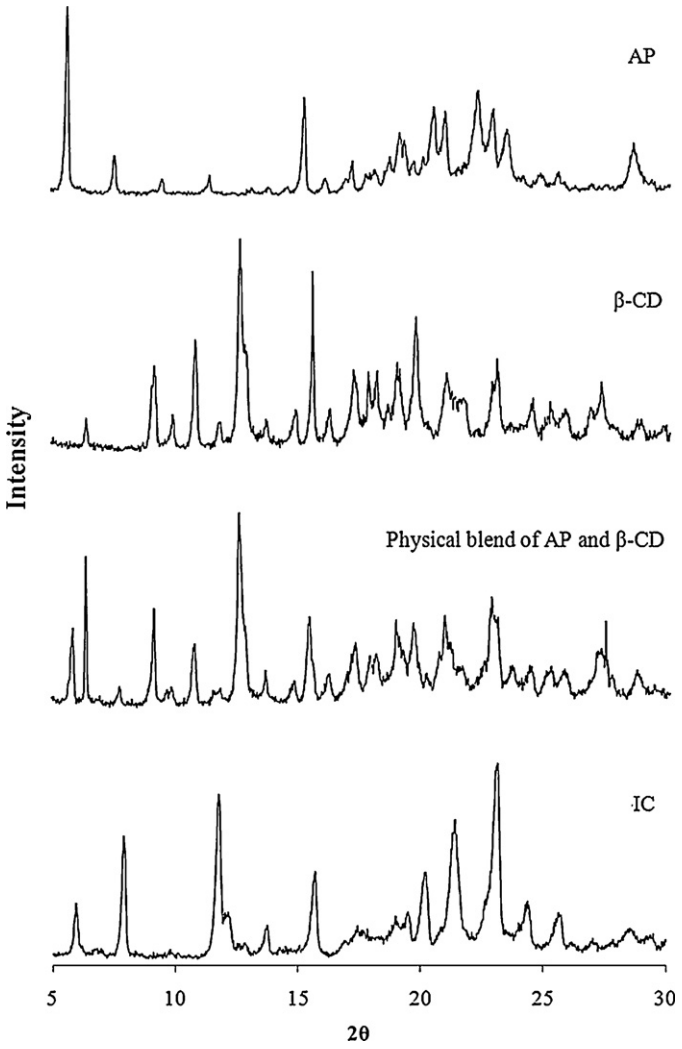

Fig. 1. Wide angle X-ray diffraction patterns.

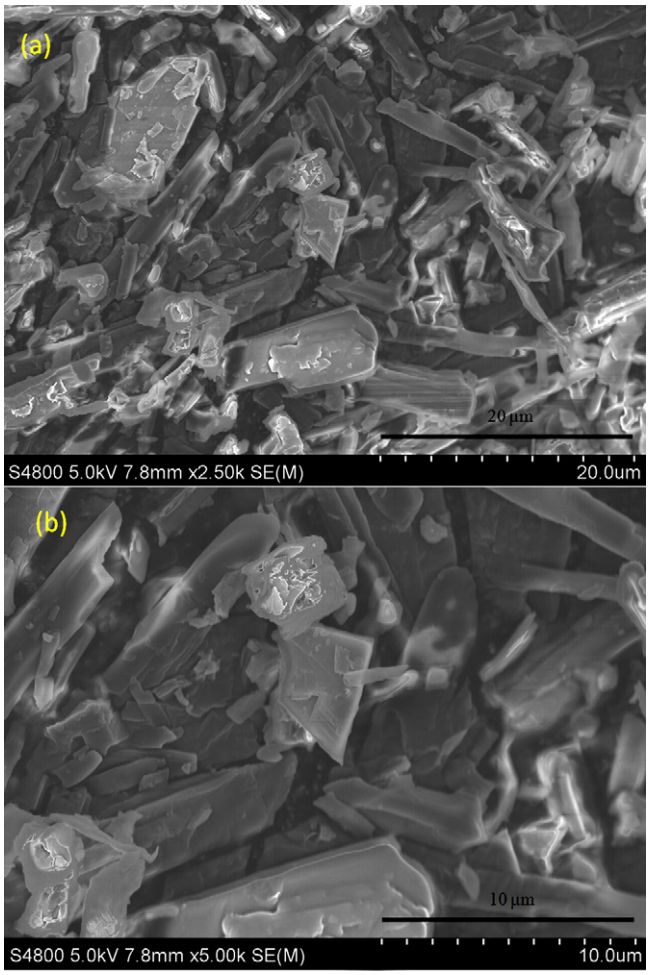

Fig. 2. SEM images of the IC (a) ×2.5K magnification and (b) ×5K magnification.

2.10. Oxygen content (%) analysis

The oxygen content in the jar headspace was analyzed by a headspace oxygen/carbon dioxide analyzer (model 6600, Illinois Instrument, IL, USA). A sampling needle with a 0.45 μm PTFE filter was inserted and 15 cc headspace gases were sampled through a septum. Calibration of headspace analyzer was done using ambient air after each sample measurement. All of the samples were measured in triplicate.

2.11. Statistical analysis

Statistical significance was determined by the analysis of variance (ANOVA) using SAS (version 9.1, SAS Institute Inc., North Carolina, USA). Differences among mean values were processed by Duncan's multiple range tests. Significance was defined at a level of $p < 0.05$.

3. Results and discussion

3.1. Inclusion complex formation

The X-ray diffraction profiles of the ascorbyl palmitate (AP), β-cyclodextrin (β-CD), and AP-β-CD inclusion complex (IC) are shown in Fig. 1. It was observed that inclusion complex formation induced large shifts in the Wide Angle X-ray Diffraction (WAXD) signals of AP and β-CD. Furthermore, the IC had different WAXD signals compared with physical mixture of AP and β-CD. Those results clearly demonstrated the formation of inclusion complex between AP and β-CD. The surface morphologies of the ICs were taken using SEM (Fig. 2) and the ICs generally formed a rode-shape. Particle sizes of the IC were ranged from 1 to 20 μm and this could have implications on transparency when the ICs are incorporated into packages or packaging films. Fig. 3 displays that the % weight loss for the IC, AP, and β-CD ranging from 25 to 600 °C. The IC had better thermal stability than AP which also indicated the formation of inclusion complex between AP and β-CD.

3.2. Headspace analysis

Off-flavor byproducts are another issue in some oxygen scavengers (Miranda & Speer, 2005; Ozdemir & Floros, 2004). In this research, off-flavor profiles were analyzed using GC–MS (Fig. 4). When utilizing AP as an oxygen scavenger that is not in the form of a cyclodextrin inclusion complex, eight different volatile byproducts were detected, including 2-methyl-heptane, hexanal, 2,3-dimethyl-hexane, furfural, heptanal, octanal, nonanal, and decanal. When utilizing the IC as an oxygen scavenger, only five byproducts were detected, including hexanal, furfural, heptanal, octanal, and nonanal. Moreover, those five byproducts were

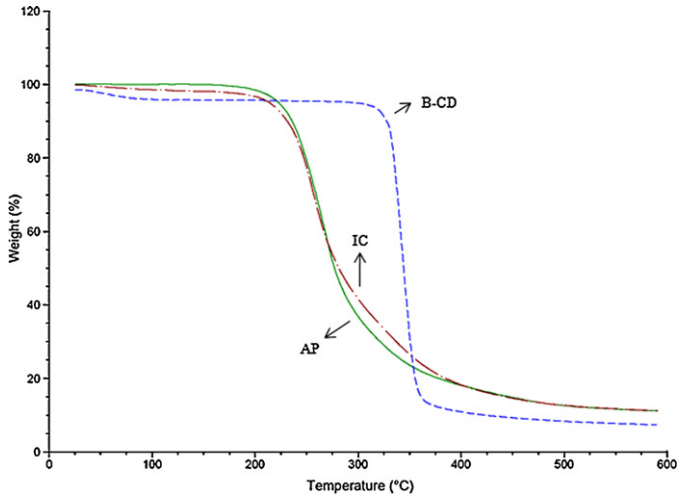

Fig. 3. TGA thermograms of β-CD, IC, and AP.

detected in lower concentrations. Fig. 5 clearly illustrates the reduction in off-flavor compounds by the IC as compared to the AP.

3.3. Oxygen content analysis

Generally, some oxygen scavengers such as oxidizable polymers, ethylenically unsaturated compounds, and ascorbic acid all require a transition metal catalyst to increase oxygen scavenging rate to satisfy the requirements of most commercial application (Matthews & Depree, 2001; Schmidt, Solis, & Ching, 2006; Teumac, Zenner, Ross, Deardurff, & Rassouli, 2004). Therefore, the effect of transition metal catalyst on the oxygen scavenging rate of the IC was investigated in this research. Results demonstrated that there was no significant difference in oxygen scavenging rate between the IC with or without the metal catalyst (Table 1). It implies that the IC does not require the transition metal catalyst to increase the oxygen scavenging rate. Therefore, inclusion complex technique can utilize 100% natural compounds as an oxygen scavenging system.

Table 1
Oxygen scavenging capability of the IC with or without transition metal catalyst.

	0 h	1 h	24 h
IC	20.90%	17.23%	16.63%
IC w/catalyst	20.90%	17.70%	16.93%

It has been reported that differences in storage or working temperature affect the oxygen scavenging capability many oxygen scavenging systems, especially the oxygen scavenging rate. Higher storage temperature typically induces higher oxygen scavenging rate and capacity relative to lower storage temperature (Solis & Rodgers, 2001; Zerdin, Rooney, & Vermue, 2003). In this research, the effect of storage temperature on oxygen scavenging capability was investigated. The samples were stored at two different storage temperatures; refrigeration temperature (4 °C) and room temperature (23 °C). Results for the comparison of the oxygen scavenging capability of the IC with AP, and iron powder (IP) at 23 °C were shown in Fig. 6a. The IC exhibited a superior oxygen scavenging capability when compared to AP and IP. An initial, headspace oxygen content (%) of 20.9% was decreased to 5.8% after 5 days of storage by the IC. There was a 75% reduction of headspace oxygen by the IC while only 1 and 5% reduction of headspace oxygen by AP and IP, respectively. Furthermore, the IC also had better oxygen scavenging capability than AP and IP at 4 °C (Fig. 6b). An initial, headspace oxygen content (%) of 20.9% was decreased to 14.7% by the IC after 6 days of storage. In this research, IP did not show a good oxygen scavenging capacity when compared to previous research (Charles, Sanchez, & Gontard, 2006). It was assumed that the test condition in this research is not an optimum condition for iron oxidation.

A higher processing temperature typically results in an activation of oxygen scavenger prior to its intended usage (Solis & Rodgers, 2001). Therefore, the effect of thermal processing on oxygen scavenging capability of the IC, AP, and IP were investigated (Fig. 7). An initial, headspace oxygen content (%) of 20.9% was decreased to 12.2% after thermal processing and 2 days of storage at 23 °C by the IC. The IC had a higher oxygen scavenging capability

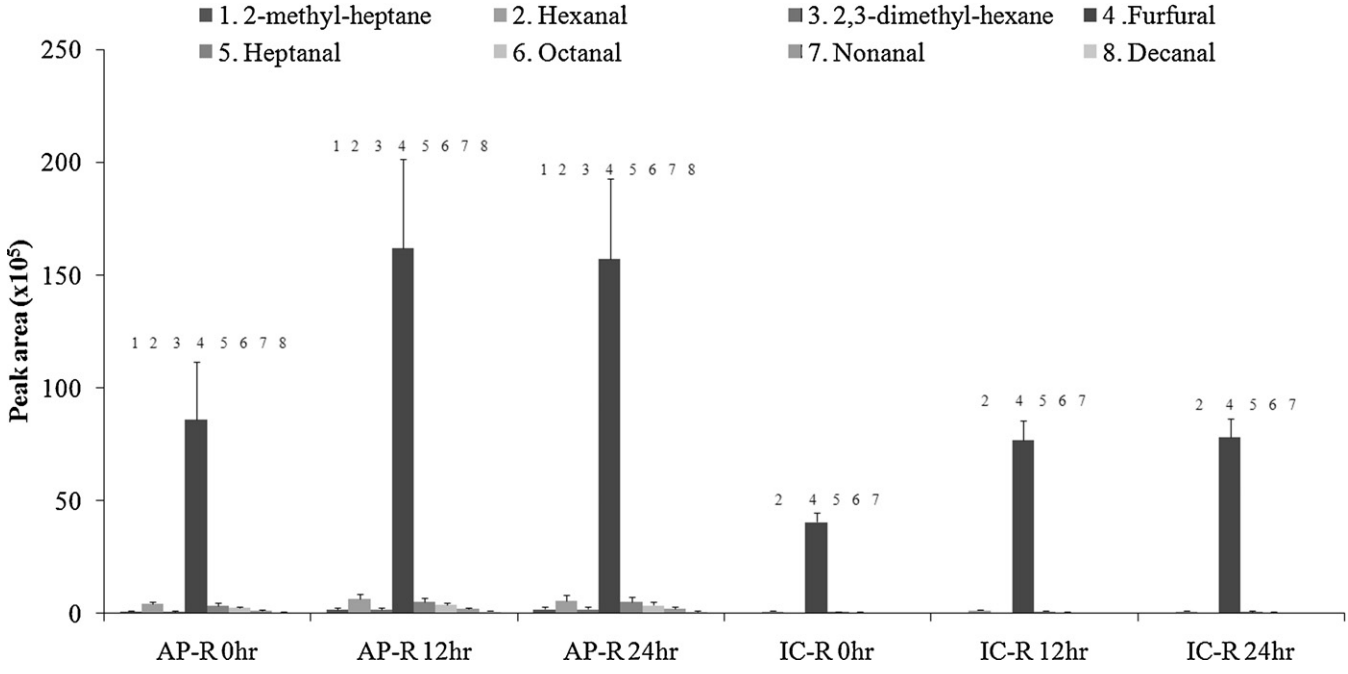

Fig. 4. Off-flavor profiles of the AP and the IC after thermal processing.

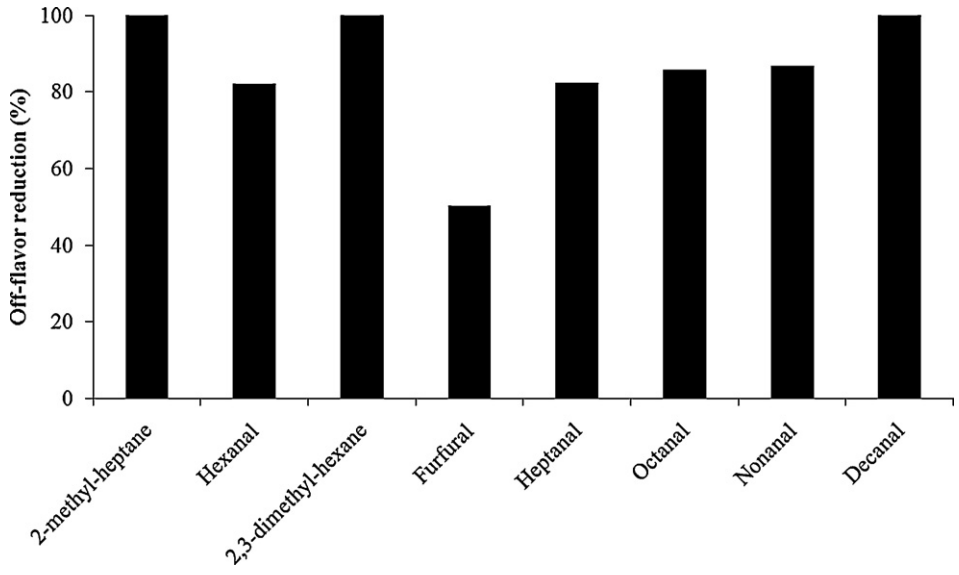

Fig. 5. Off-flavor reduction (%) by the IC.

than AP and IP after thermal processing due to its higher thermal stability as shown in Fig. 3.

3.4. Oxygen scavenging capacity and rate

Generally, the scavenging capacity of various scavengers has been observed to be as low as 1 cc O_2/g and with a scavenging rate of 0.1 cc O_2/g day (Jerdee et al., 2003). Previous research reported that iron powder sachet has oxygen scavenging capacity of 39–79 cc O_2/g (Charles et al., 2006). In addition, the oxygen scavenging film which containing 5% Amosorb has oxygen scavenging capacity of 0.86 cc O_2/g and oxygen scavenging rate of 0.79 cc O_2/g day (Galdi, Nicolais, Di Maio, & Incarnato, 2008). In this research, the oxygen scavenging capacity and rate for the IC at 23 °C was calculated utilizing the initial oxygen content at 0 h and oxygen content at 126 h. The IC had a oxygen scavenging capacity of 37.85 cc O_2/g and an oxygen scavenging rate of 7.21 cc O_2/g day. These results demonstrate that the IC can be used as effective oxygen scavenger.

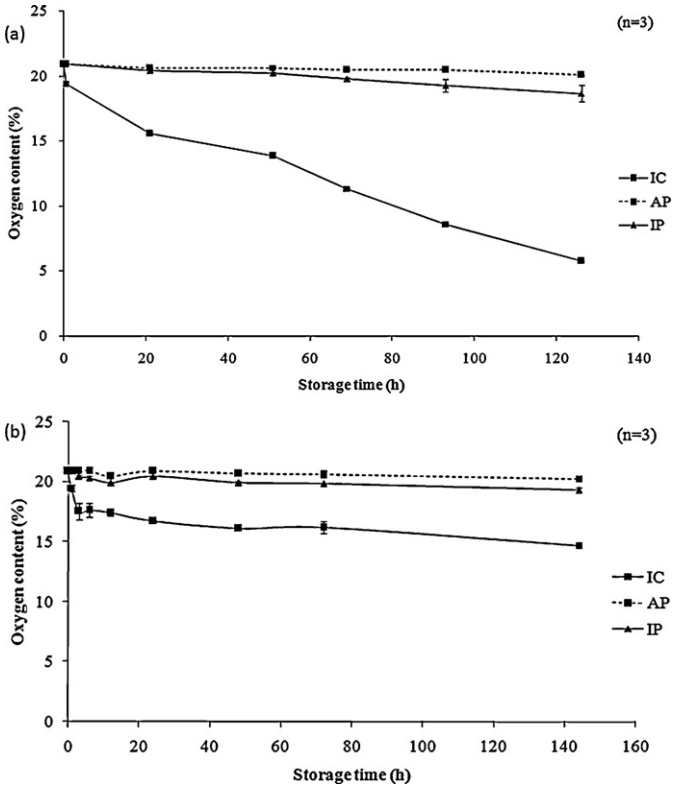

Fig. 6. Oxygen scavenging capability of the IC, the AP, and the IP at (a) 23 °C and (b) 4 °C.

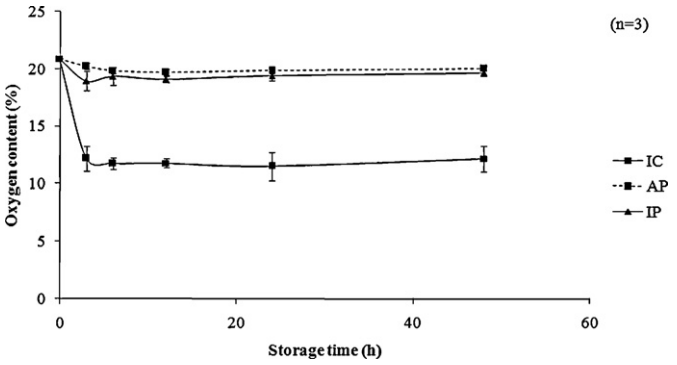

Fig. 7. Oxygen scavenging capability of the IC, the AP, and the IP after thermal processing.

In an aqueous cyclodextrin solution, the interior of the molecule contains water molecules. Upon formation of an inclusion complex, the water molecules are replaced by hydrophobic materials (Szejtli, 1998). Thus, the interior of the inclusion complex is more hydrophobic than a simple cyclodextrin molecule. In this research, the increase in hydrophobicity of the IC interior may cause attraction of oxygen molecules to the IC interior and the IC can physically entrap oxygen inside the complex structure. In addition, this physical entrapment may increase the reaction between oxygen and the AP of the inclusion complex. Therefore, the IC had higher oxygen scavenging rate and capacity than AP.

4. Conclusion

In this research, an ascorbyl palmitate-β-cyclodextrin inclusion complex (IC) was developed and evaluated as a possible oxygen scavenger. The IC had less off-flavor byproducts than AP during oxygen scavenging reaction. Although off flavors are reduced

by the IC, off flavors are still exist. Therefore, further sensory analysis or migration test need to be conducted for future application in respect to off flavor production. The IC may be combined with other bio-based oxygen scavengers, which produce off-flavor byproducts, to remove or reduce the oxygen scavenging reaction byproducts. Overall, the IC had higher oxygen scavenging capacity and rate than AP and IP. In addition, the IC had better oxygen scavenging capability than AP and IP after thermal processing due to its higher thermal stability. Therefore, the IC may be extruded to produce an oxygen scavenging film and may be used in various thermal processing applications such as retort pouches. This research demonstrated that the inclusion complex technique is valuable to developing an effective oxygen scavenger.

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