Encapsulation of Sea Buckthorn Kernel Oil in Modified Starches

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ABSTRACT: Encapsulation of CO_2-extracted sea buckthorn kernel oil and the stability of the products were investigated. Maltodextrin and an emulsifying starch derivative were used for encapsulation by spray drying. Both shell materials significantly increased the storage stability of sea buckthorn kernel oil, even though in maltodextrin capsules 10% of the total oil was extractable from the surface of the capsule. The cornstarch sodium octenyl succinate derivative capsules contained essentially no surface oil. After 9 wk storage at controlled conditions (20°C, RH 50%), PV of the unencapsulated oil was above 90 meq/kg, whereas in the encapsulated oils, the PV was still around 20 meq/kg. The PV of the encapsulated oil was dependent on the storage conditions. A small increase in temperature (from 20 to 25–30°C) and a significant increase in humidity (from RH 50 to RH 50–70%) decreased the stability of capsules. This was associated with the physical state of the microcapsule matrix and may be linked with glass transition of the wall polymers.

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Incorporation of physiologically active oils in powder carriers is of great importance to the food industry, since microencapsulation improves the chemical stability of both liquid and solid ingredients. The procedure is also used to protect the functional compounds from escaping and to convert a liquid substance into a powder for easier processing. Various encapsulation methods have been proposed (1), of which spray drying is the most commonly used method for flavor encapsulation since it is economical and efficient (1,2).

The rate of oil oxidation in the powder depends on the composition of the wall material and the choice of emulsifier (2). Gum arabic (GA), a traditionally used carrier in spray drying, is a natural emulsifier that provides stability for volatile compounds during drying. However, it has some limitations. GA is collected from *Acacia* plants and its supply and quality are variable. Other common carriers for spray drying are chemically modified and hydrolyzed starches. Native starches have virtually no emulsification properties and thus cannot be applied, because emulsion formation and stability are critical factors in spray drying. Oxidized starches have been found to have properties similar or superior to those of GA in the spray drying of food flavors (3). However, some opposing results have also been presented (4,5). Hydrolyzed starches are usually used in blends with emulsifying materials (2). Encapsulation of orange oil by spray drying has been studied as a model system (3,4,6–9). Storage stability has been followed by measurement of the oxidation products of limonene (6–8).

Sea buckthorn (*Hippophaë rhamnoides* L.) is a hardy shrub that grows wild in Eurasia and has been domesticated in several parts of the world (10–14). In addition to producing juice extremely rich in vitamin C (up to 20 g/L) and flavonoids, sea buckthorn berries are used for edible and cosmetic oil production, especially in China, Russia, and, more recently, in Europe (15,16). It has been claimed and also shown that the oils have special health effects (15,17–19), that should be investigated in more detail. Relatively high contents of oil are found in both the kernels and the soft part of the residue of pressed berries (20–22). Sea buckthorn kernel oil is a significant source of tocopherols, tocotrienols, plant sterols, and carotenoids. The oil also contains the essential fatty acids linoleic acid (35–45%) and α-linolenic acid (20–36%) (21–25). It is thus important to protect the oil from oxidation by atmospheric oxygen. Pulp oil is more saturated, as more than half of the FA are palmitic and palmitoleic acids (20–22).

The aim of this study was to stabilize the potentially health-beneficial compounds of CO_2-extracted sea buckthorn kernel oil TG and other oil-soluble compounds and to avoid off-flavor development during storage. Oils were encapsulated in maltodextrin or emulsifying starch by spray drying. The oxidation stabilities of unprotected kernel oils and encapsulated oil powders during storage were investigated.

MATERIALS AND METHODS

Materials. Sea buckthorn kernel oils (with and without added antioxidant, sage extract) were obtained from Flavex Naturextrakte GmbH (Rehlingen, Germany). Hydrolyzed starch, maltodextrin (MD) with a dextrose equivalent of 18.5, was a

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product of Cerestar (Neuilly-sur-Seine, France). The emulsifying starch was the cornstarch sodium octenyl succinate derivative HiCap 100, obtained from National Starch & Chemical (Manchester, United Kingdom). The dextrose equivalent of the emulsifying starch derivative was between 32 and 37. GA was purchased from Sigma-Aldrich Finland (Helsinki, Finland). Petroleum ether (b.p. 40–60°C) and other chemicals from various sources were analytical grade.

Emulsification of oils. GA was used along with MD to form a stable emulsion of sea buckthorn oils for spray drying. GA (20 wt%) was dissolved in water and homogenized with MD solution (40 wt%) and oil (from 10% to 40% of dry weight) with a Heidolph DIAX 600 (Kelheim, Germany) homogenizer at 24,000 rpm three times for 1 min. Droplet size distributions were checked in fresh MD emulsion, in MD emulsions stored for 1 h and 2 h, and in HiCap emulsions to confirm stability during the drying process.

Particle size distributions. Oil droplet size distributions were analyzed by a Coulter LS 230 (Miami, FL) instrument using the small volume module. The sample was fed as an emulsion. The circulating liquid was water; thus, the refractive index of water (1.332) was used for the background. Both laser diffraction (laser 750 nm, particle sizes 0.4–2000 μm) and polarized intensity differential scattering (particle sizes 0.04–0.4 μm) of monochromatic light at three wavelengths (450, 600, and 900 nm) were used. The pumping speed was 50% maximum. The oil droplet size distribution was calculated by geometric volume statistics with an optical model that assumed the particles to be spherical in shape. Duplicate measurements were performed.

Spray-drying emulsions. Emulsions were spray dried by a Niro Mobile Minor (Soeborg, Denmark) laboratory spray dryer with a rotating atomizer. The inlet air temperature was adjusted to 200°C, and the outlet air temperature was kept at 80 ± 2°C by controlling the flow rate. Rotation speed of the atomizer was 25,000 rpm. Samples were collected in the chamber and the cyclone collection vessels.

Surface oil determination. A sample (10 g) was dried at 105°C for 30 min in an extraction thimble. The thimble was extracted for 3 h in a Soxhlet extractor with 180 mL of petroleum ether. The solvent phase was taken into a tared flask, and the petroleum ether was evaporated. The oil was determined gravimetrically and considered as the surface oil. Triplicate determinations were performed.

Oil content determination. Two grams of powder was weighed and mixed with 2 mL of 94 wt% ethanol. The sample was then mixed with 10 mL of 8 M HCl and placed on a boiling water bath for 30 min with occasional stirring. The sample was poured quantitatively into a Mojonnier flask by flushing once with 5 mL of ethanol and three times with 8 mL of diethyl ether; 25 mL of petroleum ether was added, and the sample was gently shaken for 5 min. Phase separation was allowed to occur, and the clear upper phase was poured into a tared beaker. The residue was re-extracted with 30 mL of an ether/petroleum ether mixture (1:1) for 5 min. The upper phase was added to the beaker and the solvent was evaporated. The cooled beaker was weighed and the oil content was calculated. Triplicate determinations were performed.

Extraction of encapsulated oil for PV determination. A sample containing about 2 g of oil was weighed into a beaker and mixed with 20 mL of ethanol and 100 mL of 8 M HCl. The hydrolysis was performed by placing the sample in a boiling water bath for 9 min with occasional mixing. After cooling, the sample was extracted in a separation funnel with 80 mL of ethanol and 100 mL of ether/petroleum ether (1:1) mixture. The solvent was poured into a tared flask and the water phase was re-extracted with an additional 50 mL of the solvent mixture. The organic phases were combined and the solvent was evaporated. The PV of the extracted oil was determined.

PV determination. PV (meq/kg) was determined by adding 30 mL of an acetic acid/chloroform solution (3:2, vol/vol) into the oil flask, after which 1 mL of saturated potassium iodide solution was added. The stoppered flask was kept in the dark for exactly 1 min. Thirty milliliters of distilled water was added; the mixture was titrated with 0.01 M sodium thiosulfate solution until the yellow color disappeared. An indicator, 0.5 mL of 1% starch solution, was added and the titration was continued until the blue color disappeared. Triplicate measurements were performed.

Glass transition determination. Glass transition temperatures were determined with a Mettler DSC820 (Dietikon, Switzerland) differential scanning calorimeter equipped with a liquid nitrogen cooling system. A sample of 10 mg was weighed in an aluminum pan, and the pan was sealed. Heating and cooling rates were 10°C/min. The temperature range of the scans was between −100 and 130°C, depending on the water content. All samples were first heated to destroy the thermal history of the sample, then cooled and reheated. Glass transition was taken as the midpoint of baseline shift in the second scan. Duplicate measurements were performed.

Storage stability tests. About 30 g of oil and the same amount of powder were spread on a petri dish for storage stability tests. The dishes were kept open to allow contact with air. Samples of oils and encapsulated oils were stored under controlled and ambient conditions: without light exposure (20°C and RH 50%), and with exposure to daylight, storage at ambient conditions (approximately 25–30°C and RH 50–70%). Storage time for oils depended on their stabilities, varying from 1 wk (oil without antioxidant) at ambient conditions to 9 wk (oil with added antioxidant) at controlled conditions. The encapsulated oils without antioxidant were stored for 4 wk and the encapsulated oils with added antioxidant were stored for 9 wk.

RESULTS AND DISCUSSION

Emulsion formation of oil. When encapsulating sea buckthorn oil in MD, GA was used as 50% of the amount of oil. Stability of the emulsion was determined by measuring the distribution of the oil droplet size in fresh emulsions and in emulsions stored for 1 and 2 h. The median droplet size was less

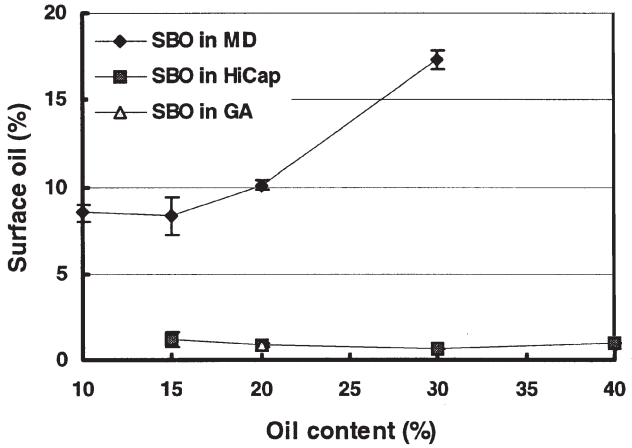

FIG. 1. Surface oil contents of sea buckthorn kernel oil (SBO) encapsulated in maltodextrin (MD), emulsifying starch (HiCap), and gum arabic (GA) calculated as surface oil percentage of total oil in the microcapsules. SD are presented in the error bars.

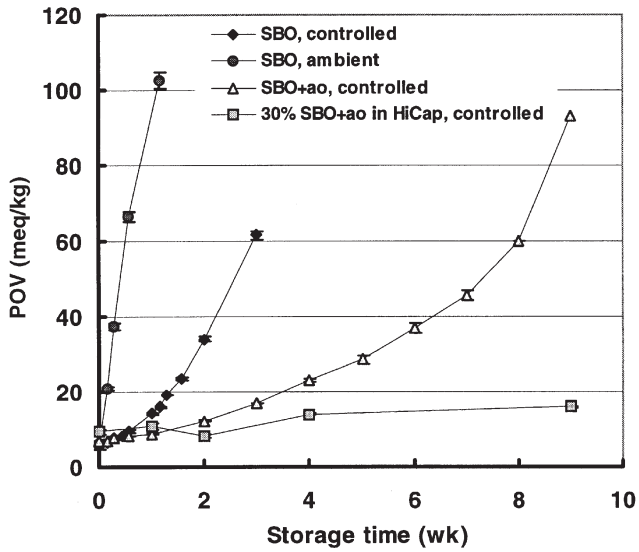

FIG. 2. Storage stabilities of SBO with (+ao) and without added antioxidant and encapsulated oil in HiCap under controlled (RH 50%, 20°C, dark) and ambient (RH 50–70%, 25–30°C, daylight) conditions. SD are presented in the error bars. For abbreviations see Figure 1.

than 2 μm in the MD/GA emulsion and from 0.3 to 0.5 μm in the HiCap emulsion. No changes in droplet size were detected during storage. Differences in emulsion droplet sizes could be attributed to differences in viscosity of the wall material solutions. Droplet size in emulsions has been reported to have an effect on the retention of volatile compounds during spray drying (2).

Surface oil in spray-dried samples. To evaluate the main parameter affecting the stabilization against oxidation by spray drying, the amount of oil extractable from the surface of the particle was determined in different encapsulated samples (Fig. 1). The surface oil was thought to be critical to powder stability, since oil droplets on the surface of the particle may be less protected against atmospheric oxygen.

Surface oil content of the HiCap capsules was very low and was independent of the oil content of the powder up to 40% oil content (Fig. 1). MD powder had more surface oil, approximately 10% of the total oil, and it increased drastically when the oil content of the powder exceeded 20%. By replacing all MD with GA, the surface oil content was reduced to the same level as in the emulsifying starch. The low surface oil content in HiCap powder could be attributed to the small droplet size in the emulsion. With a smaller droplet diameter, smaller droplets would be in close contact with the surface, and thus oil would be less easily extractable.

Stability of nonencapsulated and encapsulated oils. Autoxidation of the sea buckthorn kernel oils is shown in Figure 2. The storage conditions had an enormous effect on oil stability, even though the ambient temperature did not exceed 30°C. This could be explained by exposure to light, which decomposed the natural antioxidants of the oil and thus left the unsaturated oil less protected against atmospheric oxygen. Color loss, indicating decomposition of β-carotene (26), was observed over a longer time range than peroxide formation. The role of carotenoids in sea buckthorn oil stability has been reported by Gao *et al.* (27), who showed that, in the lipophilic fraction of sea buckthorn berries, antioxidant capacity was increased significantly as total carotenoid content increased. In our study, the added antioxidant (sage extract) prolonged the shelf life of the oil considerably; however, after 6 wk storage, the PV was above 30 meg/kg. The protective effect of encapsulation in HiCap was obvious when the PV of the encapsulated and nonencapsulated sea buckthorn oil (with added antioxidant) during the storage were compared. After 9 wk of storage under controlled conditions, the PV was well under 20 mg/kg in the encapsulated oil, whereas the corresponding value in the nonencapsulated oil was over 90 mg/kg (Fig. 2). The initial PV in the encapsulated oil were higher than they should have been because the oil extraction procedure decreased the oil quality. Therefore, the change in PV of unprotected oil was determined for comparison and showed an increase from 5.7 to 11.0 meg/kg during the extraction procedure. However, even though the values determined for encapsulated oils were somewhat higher than the actual ones, possible changes in stability should still have been recognized.

Sea buckthorn kernel oil with added antioxidant (sage diterpene phenols) was used for encapsulation to study the stabilizing effect of the wall polymers. Microcapsules with 20% oil in MD and with 20 and 30% oil in HiCap were prepared. The storage was carried out in the dark (20°C, RH 50%). All the encapsulated samples were stable during the 9 wk of storage (Fig. 3). No difference was observed between the stabilizing effects of the two wall materials. Thus, neither surface oil content nor oil droplet size in powder particles had a major effect on stability over the duration of storage.

Preliminary studies on the effect of storage conditions were carried out with sea buckthorn kernel oil without added antioxidant. Oil content in the powder was 20%. Storage stability was followed for 4 wk (Fig. 3). The stability of the

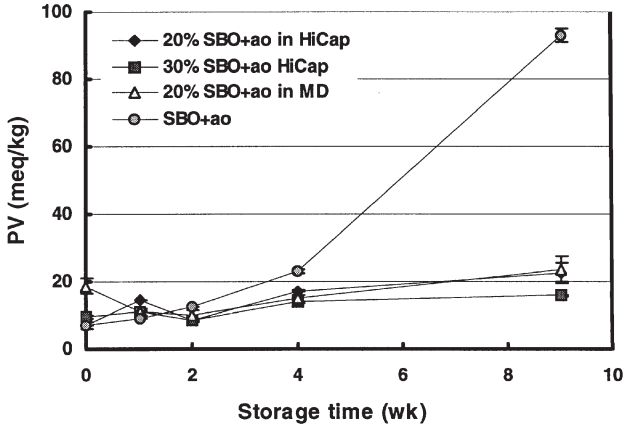

FIG. 3. Stabilities of SBO with antioxidant (+ao) encapsulated in HiCap and MD under controlled (RH 50%, 20°C, dark) conditions. SD are presented in the error bars. For abbreviations see Figure 1.

encapsulated oils was highly dependent on humidity, temperature, and light exposure (Fig. 4). A MD wall, in particular, seemed to protect oil less efficiently at ambient conditions. This could have been caused by the relatively high amount of surface oil compared to HiCap or, perhaps more likely, by the changes occurring in the polymer as relative humidity increased.

Amorphous and partially crystalline polymers go through a glass transition as the temperature is increased. Water acts as a plasticizer in the system, lowering the glass transition temperature of the polymer. A system that is relatively stable below its glass transition temperature could become considerably more permeable to oxygen in the rubbery state (28,29). Glass transition temperatures (Fig. 5) and water vapor sorption isotherms (30) were determined for pure MD and HiCap. During equilibration of the samples at high humidity (RH 75 and 81%), sorption gel formation was observed, as reported in the literature

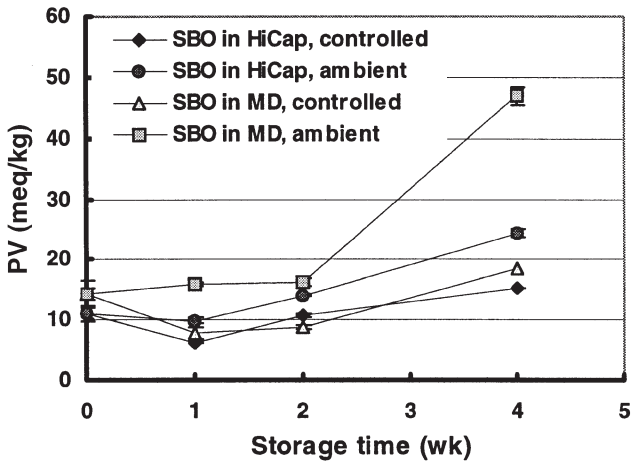

FIG. 4. Stabilities of SBO without added antioxidant encapsulated in HiCap and MD under controlled (RH 50%, 20°C, dark) and ambient (RH 50–70%, 25–30°C, light exposure) conditions. SD are presented in the error bars. For abbreviations see Figure 1.

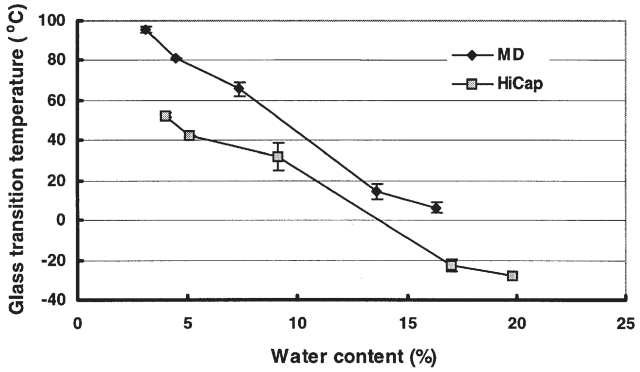

FIG. 5. Glass transition temperatures of encapsulation matrixes, MD and HiCap. SD are presented in the error bars. For abbreviations see Figure 1.

(31).At water contents of 7 and 8%, glass transitions occurred at about 70°C for MD and 30°C for HiCap (Fig. 5). Thus, both polymers were in a glassy state when stored in the controlled conditions (RH 50%, 20°C). As environmental humidity increased to 70% at ambient conditions, polymers sorbed more water. Glass transition temperatures decreased as the absorbed water plasticized the polymers. The glass transition temperature was then below the storage temperature; thus, the samples were in a rubbery state during storage at ambient conditions. This observation could explain the loss of oil quality in MD microcapsules. The oxygen barrier property of HiCap seemed to be less sensitive to glass transition than did MD.

Since the oil itself was substantially less stable at ambient conditions (Fig. 2), more research is needed to determine the effects of storage conditions on long-term stability of MD and HiCap microcapsules.

Both hydrolyzed and chemically modified starches are potential encapsulation materials for sea buckthorn kernel oil to increase the storage stability of the oil. Even though considerably more oil was extractable from the surface of the MD than from HiCap microcapsules, the surface oil did not seem to play a major role in the oxidation process. The stability of the encapsulated oil was dependent on storage conditions, indicating that the physical state of the wall material was important. When the microcapsules were stored at conditions in which the wall polymers were in the glassy state, oil stability increased compared to the situation in which the polymer matrix was in the rubbery state.

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