# Flavor Retention of Peppermint (*Mentha piperita* L.) Essential Oil Spray-Dried in Modified Starches during Encapsulation and Storage

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The effect of different commercial modified food starch carrier materials on the flavor retention of the essential oil (EO) of peppermint (*Mentha piperita* L.) during spray drying and storage was evaluated. The obtained results revealed that the emulsification and encapsulation efficiencies of peppermint EO were higher for all *n*-octenyl succinic anhydride (OSAN)-modified starches as compared to those of hydrolyzed starches (dextrins). The compositions of pure, emulsified, and encapsulated peppermint EOs in different matrices were quite similar; however, some changes in the percentages of some individual compounds were observed. Larger differences in the compositions of surface oils from various encapsulation products were obtained. Flavor components were released at different rates by each of the encapsulated products. The aroma binding capacity of different modified starch matrices to lock EO droplets depends on the water activity, and the leakage of aromas from encapsulated powder products during storage increased with increasing water activity.

**KEYWORDS: Peppermint; *Mentha piperita* L.; essential oil; microencapsulation; spray drying; aroma retention; flavor release; water activity; DHS; SHS; GC; GC-MS**

## INTRODUCTION

The encapsulation of active components in powder has become a very attractive process in the last decades, and the encapsulation of flavor ingredients is among the most important applications in the food industry. The main purpose of microencapsulation is to entrap sensitive ingredients, such as volatile and labile flavors, into solid carriers to increase their protection, reduce evaporation, promote easier handling, and control their release during storage and application. Spray-drying emulsions are a particularly simple and economically effective means of microencapsulating chemically reactive volatile oils and flavor compounds (*1–9*).

The encapsulation wall system is generally made of compounds that usually harbor hydrophilic and/or hydrophobic groups, which create a network like structure, such as starches, gums, gelatines, and polymers, and whose selection depends on the core material and desired characteristics of the microcapsules. Typical shell materials for flavor encapsulation include gum acacia, maltodextrins, hydrophobically modified starches, and their mixtures (*1*). An increasing research area is the development of alternative and inexpensive polymers that may

be considered natural like gum arabic and could encapsulate flavors with the same efficiency as gum arabic (*10*). Nevertheless, the ability of maltodextrins and chemically modified starches to retain volatiles during drying processes makes them the most commonly used coating materials as replacements for gum arabic in spray-dried emulsions (*6, 8, 11–17*). It is noteworthy that hydrophobically modified polysaccharides, such as octyl-substituted starches, alone have been used as shell materials in spray drying to encapsulate up to 50% flavor oils, while still maintaining free-flowing properties (*1, 13*).

In addition to protecting the flavors, the encapsulation provides controlled release. The controlled release of ingredients at the right place and the right time can improve the effectiveness of food additives, broaden the application range, and ensure optimal dosage (*1*). Several mechanisms have been reviewed on the release characteristics of encapsulated flavors. Rosenberg et al. (*2*) observed that the release of encapsulated volatile esters during storage increases by increasing the relative humidity (RH); he suggested that water uptake at a high RH destroys the capsule structure. Whorton (*18*) overviewed the basic release mechanisms in various capsules and linked the release of flavor from the spray-dried powder to the diffusion mechanisms of flavor and water, because the solubilization of the coating matrix with water would be followed by subsequent release of the encapsulated flavor. Whorton and Reineccius (*19*) evaluated the mechanism associated with the controlled release of flavors

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encapsulated in various maltodextrins and reported that aroma retention during storage improved with an increase in the dextrose equivalent (DE) value of maltodextrin. They suggested that the flavor release increased with the increase in water activity ($a_w$) to point where collapse occurred and correlated the release rate with the glass transition temperature and collapse temperature of wall materials. Several studies concerning the effect of RH on flavor release from microencapsulated flavor products have been published (2, 6−8, 20, 21). These studies revealed the complexity of the process depending on several variables; therefore, there is a need for further research, particularly focused on the effects of water activity on the ability of different wall materials to release volatile compounds. Such information could expand the existing knowledge and fill some gaps still present in the quality control and applications of various spray-dried encapsulated natural flavor products.

The main goal of this study was to investigate the effect of different carbohydrate carrier materials on flavor retention of peppermint essential oil (EO) during spray-drying encapsulation and storage. The following objectives were considered important tasks in achieving this goal: (i) to determine the emulsification efficiency and retention of volatile flavor compounds and to evaluate the efficiency of microencapsulation; (ii) to determine particle size distribution, moisture content, and water activities of spray-dried products; (iii) to assess the changes in the composition of peppermint flavors taking place during processing; (iv) to assess the release of volatiles from different modified starches matrices by dynamic headspace (DHS) gas chromatography (GC) analysis; and (v) to determine the aroma release from microencapsulated peppermint EO powder products during storage at different water activities by static headspace (SHS) GC.

## MATERIALS AND METHODS

**Materials.** Peppermint (*Mentha piperita* L.) EO (Mėta, Vilnius, Lithuania) was selected as the core material. The following modified food starch matrices were used as encapsulating agents: chemically *n*-octenyl succinic anhydride (OSAN)-modified starches HI-CAP 100 (refined from waxy maize), N-LOK (starch with corn syrup added), and CAPSUL (derived from waxy maize) and the acid- and/or enzyme-hydrolyzed starches (dextrins) ENCAPSUL 855 (refined from tapioca and maize starch) and CRYSTAL TEX 627 (refined from tapioca starch), which were obtained as a gift from National Starch Group; OSAN starches CIEmCap 12633 (stabilized and acid-thinned instant waxy maize starch), CIEmCap 12634 (spray-dried waxy maize starch ester), and CIEmCap 12635 (stabilized and acid-thinned instant waxy maize starch) were kindly supplied by Cerestar.

The identification of peppermint EO volatiles was performed using as reference compounds the following chemicals, which were purchased from various companies (Fluka and Sigma-Aldrich): 99% β-pinene (18172-67-3), 97% 3-octanol (589-98-0), 98% D-limonene (5989-27-5), 97% linalool (78-70-6), 99% menthone (14073-97-3), 99% L-(−)-menthol (89-78-1), 99% isomenthol (23283-97-8), 98% α-terpineol (562-74-3), 98.5% pulegone (89-82-7), 97% menthyl acetate (89-48-5), 98.5% β-caryophyllene (87-44-5), 98% α-humulene (6753-98-6), and 99% caryophyllene oxide (1139-30-6). Analytical grade solvents 99% *n*-pentane, 99.9% acetone, 99.5% diethyl ether, and 99% toluene were from Lachema (Czech Republic).

**Preparation of Microencapsulated Flavors.** The solutions of coating matrices (30% w/w) were prepared by dispersing dried powders in 40 °C deionized water, and after they were cooled, they were mixed overnight to enhance hydration. EO (15.25% w/w of matrix solids) was emulsified into the hydrated coating material. Homogenization was accomplished by an Ultra Turrax Ika 25 basic homogenizer (Janke & Kunkel GmbH&Co, Germany) operating at 13500 rpm for 7 min. Emulsions were spray-dried in a Büchi 190 Mini Spray Dryer (Büchi Labortechnik AG, Flawil, Switzerland) under the following param-

eters: spray nozzle (inlet) temperature, 200 ± 10 °C; outlet air temperature, 120 ± 10 °C; and pressure, 400 mm/H$_2$O.

**Total and Surface Oil Determination.** The total oil content in the liquid emulsions and spray-dried microencapsulated products was determined in duplicate by distilling 10 g of liquid emulsion or encapsulated powder for 3 h in a Clevenger type apparatus (22). The volume of peppermint EO collected in the trap was multiplied by a density factor of 0.8969 g/mL to calculate the weight of oil recovered from the sample. The surface oil was washed from 10 g of spray-dried powder for 4 h in a Soxlet extraction apparatus by using pentane. One milliliter of pentane containing IS, 0.3% undecane (v/v), was added prior to extraction; each extract was concentrated at room temperature to ~10 mL by a Büchi rotary evaporator and then to a final volume of ~2 mL under a stream of nitrogen. The compositions of the pure initial, total (isolated from emulsions and processed products), and surface (nonentrapped into matrices) oils were analyzed by GC and gas chromatography−mass spectrometry (GC-MS).

**Release of Volatiles by DHS GC [DHS-ATD-GC-Flame Ionization Detection (FID)].** A 0.5 g amount of each encapsulated powder with the surface oil removed was placed into a 125 mL sample flask, which was placed in a water bath of 25 °C. The glass tops were connected to the nitrogen flow of 120 mL min$^{-1}$. One minute preflush was used to remove the volatiles accumulated in the headspace above the encapsulated product. Then, the sample was purged at timed intervals with nitrogen in order to trap released volatiles on Tenax traps (Perkin-Elmer, CN, Shelton, United States) packed with 225 mg Tenax GC (Tenax Chrompack, Bergen op Zoom, The Netherlands). Tenax tubes were changed every 2 min, and the total purge time was 30 min. Three replicates were carried out for each sample. One microliter of IS, 0.3% (v/v) undecane in pentane, was injected on Tenax prior to desorption. Trapped volatiles were desorbed from Tenax by a thermal desorption device (Perkin-Elmer ATD 400) for 3 min at 250 °C; the cold trap was held at 30 °C, the trap heating temperature was 250 °C and held for 1 min. After desorption, volatiles were directed through a heated transfer line and analyzed by GC.

**Release of Volatiles by SHS Analysis (SHS-GC-FID) at Different Water Activities.** A 0.05 g amount of spray-dried and pentane-washed encapsulated product was weighted into a 2 mL HPLC bottle, which was placed into headspace 22.3 mL vial over 2 mL of saturated salt solution to yield $a_w = 0.43$ (K$_2$CO$_3$) and 0.75 (NaCl) at 25 °C, tightly capped, and left for timed intervals of 0, 5, 30, 60, 240, 1440, 2880, 4320, and 6060 min at 25 °C to recover the volatiles that were released. After proper time periods, vials were transferred to an automated headspace autosampler (Perkin-Elmer HS 40 XL) and analyzed by GC. Four replicates were carried out for each sample.

**GC.** Diluted in pentane-pure EO, samples of retained after spray-drying total and surface oils (10 μL in 1 mL) were analyzed on a Fisons 8000 series gas chromatograph (Fisons Instruments Inc., Rodano MI, Italy) equipped with a FID and a DB-5 fused silica capillary column (polydimethylsiloxane, 5% phenyl, 50 m length, 0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA). The carrier gas was helium at a linear flow velocity of 32.7 cm s$^{-1}$ at 50 °C, which was equivalent to a 2.35 mL min$^{-1}$ volumetric flow; the detector's temperature was 320 °C, and the oven temperature was programmed from 50 (2 min) to 280 °C (hold 10 min) at the ratio of 5 °C min$^{-1}$. A split/splitless injector was used at 260 °C in split mode at a ratio of 1:5; the injection volume was 1 μL. The content of eluted compounds was expressed as a GC peak area percent; mean values were calculated from quadruplicate injections.

Volatiles trapped on Tenax (DHS analysis) and desorbed by a thermal desorption device were directed through a heated transfer line to the injection port of a Hewlett-Packard 5890 gas chromatograph (Hewlett-Packard, Wilmington, DE), equipped with a FID and a DB-5 fused silica capillary column (30 m length, 0.25 mm i.d., and 1 μm film thickness). The carrier gas was helium at a flow rate of 1.1 mL min$^{-1}$, which was equivalent to 27.6 cm s$^{-1}$ volumetric flow at 60 °C; the detector was heated at 300 °C, and the oven was programmed from 60 to 295 °C (10 min) at the ratio of 5 °C min$^{-1}$.

One milliliter of the headspace gas phase above the sample (SHS analysis) was automatically withdrawn using a Perkin-Elmer HS 40 XL autosampler and injected into a Perkin-Elmer XL gas chromatograph

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**Table 1.** Properties of Liquid Emulsion and Spray-Dried Microencapsulated Peppermint EO Products

| | HI-CAP 100 | N-LOK | CAPSUL | ENCAPSUL 855 | CRYSTAL TEX 627 | CIEmCAP 12633 | CIEmCAP 12634 | CIEmCAP 12635 |
|---|---|---|---|---|---|---|---|---|
| | liquid microencapsulated product | | | | | | | |
| total oil content (g 100 g$^{-1}$) | 15.03 cd | 14.44 bcd | 14.73 bcd | 13.54 a | 14.14 ab | 15.21 d | 14.44 bcd | 14.81 bcd |
| emulsification efficiency[a] (%) | 98.56 cd | 94.69 bcd | 96.59 bcd | 88.78 a | 92.72 ab | 99.74 d | 94.69 bcd | 97.11 bcd |
| | spray-dried microencapsulated product | | | | | | | |
| total oil content (g 100 g$^{-1}$) | 13.49 b | 12.15 e | 13.96 c | 6.10 a | 9.41 d | 14.94 g | 13.67 bc | 14.48 f |
| surface oil content (g 100 g$^{-1}$) | 0.20 cd | 0.18 bc | 0.25 def | 0.13 ab | 0.23 cdef | 0.08 a | 0.17 bc | 0.29 f |
| encapsulation efficiency[a] (%) | 87.15 b | 78.49 e | 89.90 c | 39.15 a | 60.19 d | 97.44 g | 88.52 bc | 93.05 f |
| moisture (mL 100 g$^{-1}$) | 1.83 a | 2.08 ab | 3.34 cd | 1.49 a | 3.39 cd | 2.35 ab | 2.85 bcd | 3.75 d |
| water activity ($a_w$) | 0.39 ab | 0.43 abc | 0.35 a | 0.45 bc | 0.44 bc | 0.44 bc | 0.49 cde | 0.55 e |
| particle size weighted mean diameter $d_{43}$ ($\mu$m) | 27.19 d | 34.99 f | 30.50 e | 11.9 a | 23.52 b | 137.63 h | 56.88 g | 24.82 c |
| specific surface area (m$^2$ g$^{-1}$) | 17.7 e | 16.6 d | 16.8 d | 0.7 a | 10.5 a | 4.3 b | 19.4 f | 17.4 e |

[a] Computed on the basis of a theoretical oil content of 15.25% of the solids. For letters a–h, values within rows followed by the same letter do not differ statistically at *P* = 0.05.

using injection times of 0.06 s. The autosampler was set up with the following parameters: oven temperature, 60 °C; time in oven, 0 min; needle temperature, 65 °C; transfer line temperature, 75 °C; pressurization time, 3 min; withdrawal time, 0.50 ; and GC cycle, 23 min. The gas chromatograph was equipped with a DB-5 (60 m length × 0.25 mm i.d.; 1.0 $\mu$m film thickness) and FID heated at 300 °C. The oven temperature was programmed from 50 (1 min hold) to 270 °C (1 min hold) increasing at 20 °C min$^{-1}$. The concentration of aromas in the gas phase was determined from the calibration curves. Calibration curves were constructed by injecting 1, 4, 8, and 10 $\mu$L of peppermint EO diluted in pentane (1% v/v) into the headspace vials and analyzing after approximately 24 h under the analogous GC conditions.

**GC-MS.** GC-MS analyses were performed using a Perkin-Elmer Clarus 500 gas chromatograph coupled to a Perkin-Elmer Clarus 500 series mass selective detector (Perkin-Elmer Instruments) in the electron impact ionization mode at 70 eV; the mass range was *m/z* 29−550. Volatile compounds were separated using an Elite 5 MS capillary column (dimethylpolysiloxane, 5% diphenyl, 30 m length, 0.25 mm i.d., and 0.25 $\mu$m film thickness; Perkin-Elmer Instruments). The oven temperature was programmed from 50 (for 2 min) to 280 °C (hold 10 min) at the ratio of 5 °C min$^{-1}$. The carrier gas, helium, was adjusted to a linear velocity of 36.2 cm s$^{-1}$ at 50 °C or 1.0 mL min$^{-1}$ volumetric flow. The split mode was used at a ratio of 1:20 and an injector temperature of 250 °C.

The components were identified by comparison of their Kovats retention indices (KI) relative to $C_5−C_{18}$ *n*-alkanes obtained on a nonpolar column with those provided in the literature (*23*) and by comparison of their mass spectra with the data provided by the NIST (version 1.7) mass spectral library. Additionally, the identity of many compounds was confirmed by coinjection of reference compounds.

**Determination of Water Activity, Moisture Content, and Particle Size Distribution.** The water activity of spray-dried powders was determined in triplicate using an AquaLab Water Activity Meter (Decagon, WA). Potassium chloride was used as a standard to calibrate the water activity analyzer.

The moisture was determined by a distillation with toluene method. A 10 g sample of encapsulated oil was refluxed with 100 mL of toluene for 2.5 h in a boiling 250 mL flask fitted with a Biddable−Sterling trap and a water-cooled condenser. The volume of the collected water was read directly from the trap.

The particle size distribution of encapsulated powder products was determined by a laser diffraction-based Malvern particle size analyzer Mastersizer 2000 (Malvern Instruments Inc.). Powders were characterized as the particle size weighted mean diameter $d_{43}$ ($\mu$m) and specific surface area (m$^2$ g$^{-1}$).

**Statistical Analysis.** Data were statistically handled by one-way analysis of variance (ANOVA, version 2.2, 1999). Duncan's multiple-range test was applied for the calculation of the significant differences among the peppermint EO products microencapsulated into different wall materials, at the probability level *P* = 0.05.

## RESULTS AND DISCUSSION

**Properties of Liquid Emulsion and Spray-Dried Microencapsulation Products.** The content of oil in the liquid-homogenized peppermint EO emulsions was from 13.5 (ENCAPSUL 855) to 15.2 g 100 g$^{-1}$ (CIEmCap 12633); consequently, the emulsification efficiency varied from 88.8 to 99.7% (**Table 1**). Most likely, some oil was lost by evaporation; however, the possibility of the incomplete oil recovery also should be considered. There were no statistical differences in emulsification efficiency for almost all OSAN-modified starches at *P* = 0.05, while some differences were observed for hydrolyzed starch liquid emulsions. The emulsification efficiency depends mainly on the emulsifying properties of matrix and its ability to form films at the interfaces between the emulsion phases; our findings are in agreement that hydrolyzed starches usually lack the emulsification efficiency (*11*). Some loss of oil could also be attributed to the effect of emulsion droplet size. The molecular dimensions seem to play a significant role in the loss of flavor because they are directly related to the diffusion of molecules. The large atomized droplets have a reduced surface area to volume ratio that results in better core retention, but it also takes a longer time for film formation around the large atomized droplets in the drying process, which could be associated with a greater loss of volatile substances (*24*, *25*). In general, aroma compounds are better retained in the smaller emulsion particles than in the larger ones, and consequently, the flavor should evaporate more easily from large emulsion particles during atomization (*7*). High volatility and solubility of flavor compounds might also lead to a higher loss of flavors during spray drying (*26*).

The retention of volatiles and the effectiveness of microencapsulation are the most important characteristic features of the process, and they mainly depend on the total oil retained in the matrices after spray drying and the content of oil that is directly entrapped inside the capsules. The total oil contents of different encapsulation products were statistically different at *P* = 0.05 and ranged from 6.1 (ENCAPSUL 855) to 14.9 g 100 g$^{-1}$ (CIEmCap 12633) (**Table 1**), which demonstrates that the retention of volatiles was strongly dependent on the type of solid matrix used. The lowest ability to retain peppermint EO was obtained for hydrolyzed starches matrices, and this is in agreement with previously published data that maltodextrins retain aroma compounds well that are water soluble or soluble at their use level, while the poor retention of insoluble flavors is associated with the inferior emulsification properties of maltodextrins (*20*). For example, when esters were encapsulated

in several maltodextrins, poorer results as compared to those achieved with gum arabic were obtained. Moreover, even the combinations of gum arabic with various maltodextrins yielded lower retentions as compared to the systems consisting of pure gum arabic at the same solids concentration. The superior properties of gum arabic can be explained by its emulsification properties and its tendency to form films at the interfaces between the emulsion phases. The retention capacity depends on the DE value, so far as the balanced polymer length might assist in trapping the volatiles during drying. These hydrolyzed starches offer the advantages of being relatively inexpensive, flavorless, and low in viscosity at high solids content; however, they lack lipophilic characteristics and emulsion-stabilizing effects on water insoluble flavors. The OSAN-modified starches due to their high emulsification properties are recognized for their excellent retention of insoluble aroma components during spray drying and can be used at a higher infeed solids level than gum acacia (*11*).

The content of oil remaining on the surface of the spray-dried powder is an important factor for storage stability; surface oil can easily oxidize resulting in unacceptable off-flavors. The content of surface oil on encapsulated powder particles varied from 0.1 (CIEmCap 12633) to 0.3 g 100 g$^{-1}$ (CIEmCap 12635). The mean particle size of material may greatly influence its reactivity or the quality of the end product. Determining the diameter or the projected area of a large number of individual particles, a continuous number-weighted distribution of particle diameters of projected area was determined. The mean particle size ($d_{43}$) ranged from 11.4 (ENCAPSUL 855) to 137.6 $\mu$m (CIEmCap 12633). It should be noted that some studies attempting to explain the effect of emulsion and spray-dried powder particle size on the retention and stability of entrapped flavorings were reported previously; however, until now, published results in some cases are rather controversial. For example, Risch and Reineccius (*27*) reported that feed emulsion particle size influenced the shelf life of encapsulated orange EO, which was longer in the case of larger particles. Chang et al. (*24*) reported similar results on the effect of powder particle size; a larger size resulted in a better protection against oxidation. Soottitantawat et al. (*7*) studied the influence of emulsion and powder size on the stability of spray-dried encapsulated D-limonene into gum arabic, maltodextrin, and modified starch HI-CAP 100 and found that flavor release as well as the rate of oxidation decreased with the increase in powder and emulsion particle size. However, some other studies obtained opposite results to the above-mentioned findings (*26, 28*).

The low surface oil content is important for providing storage stability to encapsulated flavor products. The surface oil content is strongly related to the emulsion droplet size; it was reported that the larger size of emulsion droplets yielded a higher surface oil content (*7, 26, 27*). This fact is associated with the easier breakdown of the large emulsion particles during atomization. However, the dependence of final encapsulated powder particle size on the surface oil content was not so evident (*7, 26*). In this study, we found that the CIEmCap 12633 encapsulation product had the largest particle size diameter and, thus, produced the lowest surface oil content due to their smallest surface area (**Table 1**). It should be noted that the specific surface area of encapsulated powders varied in a very wide range, from 0.7 to 19.4 m$^2$ g$^{-1}$. In general, there was no clear correlation between the size of spray-dried particles and the content of surface oil. Kim and Morr (*3*) suggested that factors other than powder particle size control the surface oil content in the microencapsulated orange oil.

The moisture content of spray-dried encapsulated peppermint EO products ranged from 1.5 (ENCAPSUL 855) to 3.8 mL 100 g$^{-1}$ (CIEmCap 12635). It was reported that there is a proportional relationship between moisture content in the powder and viscosity of the liquid emulsion (*29*). The structure and porosity of powder particles are additional parameters determining their water-holding properties during drying (*30*); the differences in drying rate as well as inlet and outlet air temperatures also should be considered (*3*). The water activity was determined in the whole spray-dried peppermint EO powder products and in the powder from which the surface oil has been removed, because further analyses on flavor release were performed with the latter product. Thus, the $a_w$ of the whole powder was in ranges from 0.54 (HI-CAP 100) to 0.76 (ENCAPSUL 855), while after removing surface oil, the $a_w$ decreased and was from 0.35 (CAPSUL) to 0.55 (CIEmCap 12635) (**Table 1**).

The effectiveness of microencapsulation is calculated either by subtracting nonentrapped into capsules surface oil from the total oil retained after drying or by hydrodistillation EO from the matrix after washing out the surface oil by the solvent (*5*). The efficiency of microencapsulation of peppermint EO via spray drying into different modified starches varied from 39.2 (ENCAPSUL 855) to 97.4% (CIEmCap 12633); significant differences at $P = 0.05$ were determined between encapsulated peppermint EO products. As was already mentioned, hydrolyzed starches lack lipophilic characteristics and, consequently, do not retain water insoluble aromas well (*11, 20*). While the use of OSAN-modified starches, such as CAPSUL and HI-CAP 100 derived from waxy maize base, involves the addition of lipophilic groups in their structure, HI-CAP 100 was blended with the high DE corn syrup solids reaching the final DE of 32−37 and in this way was designed for the high load encapsulation agent (*8*). Fine emulsions are usually more stable during the atomization and spray drying, and for the properly selected matrix, the size of emulsion droplets is a significant factor for flavor retention (*26*).

Thijssen and Rulkens (*31*) showed that the concentration of solids and their ratio with aroma compounds are very important factors for volatile retention during spray drying. Evaporation of volatiles during spray drying is associated both with the interactions of droplets being dried with hot air and with the process of droplet formation (atomization). Menting and Hoogstad (*32*) suggested that volatiles are able to leave the drying droplets before the crust forms around such droplets or until the termination of the first stage of the drying process. Further losses are possible if volatiles can pass through the crust by means of diffusion in the solid or through pores and/or channels; solids concentration and drying temperature are very important because of their effect on crust formation. Rulkens and Thijssen (*33*) in their "selective diffusion theory" suggested that the diffusion coefficients of water and volatiles are reduced as the water concentration decreases due to drying. As a result of differences in the molecular weight of water and volatiles, the reduction in the diffusivity of the volatiles is more pronounced than that of water. Once the crust has formed, the diffusivity of volatiles is so low that for all practical purposes the volatiles are entrapped in the drying solid matrix, while water can still diffuse through the crust, which therefore becomes effectively a selective membrane. Polar volatiles are also held in the dry matrix by hydrogen bonding (*2*).

Numerous studies attempted to explain the mechanism of volatiles retention, and it was recognized that process parameters as well as the nature of flavoring and carrier material are

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**Table 2.** Changes in the Total Oil Composition after Processing in Both Liquid-Emulsified and Spray-Dried Encapsulated Products as Compared with Pure Initial EO[a]

| no. | compound | KI on DB5 | pure EO | HI-CAP 100 | | N-LOK | | CAPSUL | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | emulsion | powder | emulsion | powder | emulsion | powder |
| 1 | limonene[c,e] | 1032 | 0.6 bc | 0.5 a | 0.5 abc | 0.5 a | 0.4 a | 0.5 abc | 0.5 abc |
| 2 | menthone[c,e] | 1166 | 19.5 cde | 18.8 abc | 19.0 bcde | 19.0 bcde | 18.8 abc | 19.3 bcde | 19.3 bcde |
| 3 | *iso*-menthone[b,d] | 1176 | 16.0 bc | 15.8 abc | 16.0 bc | 15.8 abc | 15.3 a | 16.4 c | 15.8 abc |
| 4 | menthol[c,e] | 1194 | 47.5 a | 49.5 cde | 49.1 bcde | 49.3 bcde | 50.0 de | 48.5 bc | 48.5 bc |
| 5 | *iso*-menthol[c,e] | 1197 | 0.8 abc | 0.9 bcde | 0.9 abcde | 0.9 abcde | 0.7 a | 1.0 cde | 0.9 abcde |
| 6 | α-terpineol[c,e] | 1201 | 0.9 c | 0.8 b | 0.8 b | 0.8 b | 0.9 cd | 0.8 b | 0.9 cd |
| 7 | *cis*-carveol[d] | 1241 | 0.8 a | 0.8 a | 0.8 a | 0.8 a | 0.8 a | 0.8 a | 0.8 a |
| 8 | pulegone[c,e] | 1249 | 2.2 e | 1.9 a | 2.1 d | 2.1 bcd | 2.1 d | 2.1 cd | 2.1 d |
| 9 | piperitone[d] | 1264 | 1.5 g | 1.0 a | 1.3 de | 1.2 bc | 1.3 cd | 1.2 bc | 1.4 f |
| 10 | menthyl acetate[c,e] | 1300 | 4.3 ab | 4.3 ab | 4.3 ab | 4.3 ab | 4.3 ab | 4.3 ab | 4.2 a |
| 11 | β-caryophyllene[c,e] | 1433 | 1.3 ab | 1.0 a | 1.5 abcd | 1.3 ab | 1.0 a | 1.0 a | 1.5 abcd |
| | % RSD[f] | | 3.2 | 2.4 | 4.5 | 5.5 | 2.4 | 2.4 | 2.7 |

| | ENCAPSUL 855 | | CRYSTAL TEX627 | | CIEmCap 12633 | | CIEmCap 12634 | | CIEmCap 12635 | |
|---|---|---|---|---|---|---|---|---|---|---|
| no. | emulsion | powder | emulsion | powder | emulsion | powder | emulsion | powder | emulsion | powder |
| 1 | 0.5 abc | 0.4 a | 0.5 abc | 0.5 abc | 0.5 a | 0.6 bc | 0.5 abc | 0.6 bc | 0.5 abc | 0.6 c |
| 2 | 19.8 cde | 18.5 ab | 18.1 a | 18.8 abc | 18.5 ab | 20.0 e | 18.8 abc | 19.3 bcde | 19.0 bcde | 19.5 cde |
| 3 | 16.1 bc | 15.8 abc | 15.8 abc | 16.2 bc | 15.5 abc | 16.1 bc | 16.2 bc | 15.8 abc | 16.0 bc | 15.3 a |
| 4 | 48.3 ab | 50.0 e | 49.1 bcde | 49.0 bcde | 50.1 de | 48.3 ab | 49.0 bcde | 49.3 bcde | 49.0 bcde | 49.5 cde |
| 5 | 0.8 abc | 0.9 bcde | 1.1 e | 0.8 abc | 0.8 ab | 0.8 ab | 0.9 bcde | 0.80 abc | 0.8 abc | 0.8 abc |
| 6 | 0.8 b | 0.9 cd | 0.8 b | 0.9 cd | 0.8 b | 0.8 b | 0.8 b | 0.8 b | 0.8 b | 0.1 a |
| 7 | 0.9 bc | 0.8 abc | 0.8 a | 0.8 abc | 0.8 a | 0.9 bc | 0.8 a | 0.8 abc | 0.8 a | 0.9 c |
| 8 | 2.1 d | 2.0 bc | 2.0 ab | 2.1 d | 2.0 bc | 2.1 cd | 2.1 cd | 2.1 d | 2.1 d | 2.1 d |
| 9 | 1.2 b | 1.3 cd | 1.2 bc | 1.3 cd | 1.2 cd | 1.2 cd | 1.2 bc | 1.2 bc | 1.2 bc | 1.3 ef |
| 10 | 4.3 abc | 4.2 a | 4.4 bc | 4.2 a | 4.3 ab | 4.4 bc | 4.3 abc | 4.4 c | 4.3 ab | 4.3 ab |
| 11 | 1.3 ab | 1.0 a | 2.0 d | 1.0 a | 1.8 bcd | 1.3 ab | 1.5 abcd | 1.0 a | 1.5 abcd | 1.0 a |
| | 1.9 | 3.6 | 2.5 | 3.0 | 4.4 | 2.3 | 1.2 | 2.0 | 1.3 | 2.4 |

[a] For letters a–f, values within rows followed by the same letter do not differ statistically at $P = 0.05$. [b] *iso*-Menthone + *neo*-menthol (∼1,1:1). [c] Identified on the basis of the Kovats index and mass spectrum. [d] Identification based on a very good match of mass spectra. [e] Identification confirmed by coinjection of the reference compound. [f] % RSD, average coefficient of variance of individual compounds.

determinant factors (*2*, *12*, *34*−*37*). For instance, Goubet et al. (*12*) reviewed on retention of volatiles by carbohydrates and emphasized the importance of molecular weight, the presence of different chemical groups, the polarity, and their relative volatility.

**Changes in the Composition of Peppermint Volatiles Taking Place during Processing.** The changes in the composition of complex aroma mixtures during encapsulation, i.e., emulsification and especially spray drying, are unavoidable. The information on such changes is required to obtain high quality preparations with a specified flavoring and/or antimicrobial activity. For this purpose, volatiles from liquid-emulsified and spray-dried encapsulated products were isolated by hydrodistillation and analyzed by GC and GC-MS (*17*). Menthol (47.5%), menthone (19.5%), *iso*-menthone + *neo*-menthol (1.1:1) (16.0%), menthyl acetate (4.3%), and pulegone (2.2%) were the major compounds among 57 volatiles identified in pure peppermint EO used as the initial material for the encapsulation (**Table 2**).

The compositions of pure, emulsified, and encapsulated in different starches matrices peppermint EO were quite similar; however, some changes in the percentages of some individual compounds were observed (**Table 2**). For instance, the content of volatile monoterpene β-pinene (KI = 936) in the encapsulated powders was ∼2−3 times lower as compared to that in the initial EO. The content of other monoterpene limonene after processing was also slightly lower as compared to the pure EO; however, no significant differences ($P = 0.05$) were found between HI-CAP 100, CRYSTAL TEX 627, CIEmCap 12633, CIEmCap 12634, and CIEmCap 12635 products. On the contrary, the percentages of a major oxygenated terpene menthol were significantly higher in the processed products ($P = 0.05$) than

in the initial EO (**Table 2**). However, in most cases, there were no significant differences in the content of menthol between emulsified and spray-dried samples produced of the same wall material. For instance, in the case of CAPSUL, menthol constituted 48.5% in both the oil extracted from emulsion and the spray-dried powder (**Table 2**). The changes in the content of menthone and *iso*-menthone in total oils after processing were less remarkable; however, their percentages in the processed products in some cases were significantly different ($P = 0.05$) from that in the initial EO, while the content of menthyl acetate in the oils from the processed products was not significantly different ($P = 0.05$) to the pure EO (**Table 2**). In general, no statistical differences ($P = 0.05$) were found between the contents of 3-octanol (KI = 995), *trans*-piperitol (KI = 1214), octanol acetate (KI = 1224), *neo*-methyl acetate (KI = 1276), *iso*-pulegyl acetate (KI = 1280), *iso*-menthyl acetate (KI = 1314), δ-elemene (KI = 1346), β-bourbonene (KI = 1395), β-elemene (KI = 1399), aromadendrene (KI = 1452), α-humulene (KI = 1466), germacrene D (KI = 1492), β-bisabolene (KI = 1510), δ-cadinene (KI = 1532), and caryophyllene oxide (KI = 1596) present in the EOs extracted from the processed products and in the pure EO used as a core material. These above-mentioned minor compounds were found in negligible amounts (≤0.4%) and were not included in the **Table 2**.

Some differences in the composition of surface oils from various encapsulation products were also observed (**Table 3**). The content of more volatile and hydrophobic monoterpenes, such as β-pinene and limonene, considerably decreased; these constituents in the surface oils washed from encapsulated powders were not detected or present in trace amounts. Also, the percentages of menthone and *iso*-menthone in the surface oils were significantly lower than in the pure EO. For instance,

**Table 3.** Surface Oil Composition after Processing in Spray-Dried Encapsulated Products as Compared with Pure Initial EO[a]

| | | | | | | surface oil from | | | | |
| | | | HI-CAP | | | ENCAPSUL | CRYSTAL | CIEmCap | CIEmCap | CIEmCap |
| compound | KI on DB5 | pure EO | 100 | N-LOK | CAPSUL | 855 | TEX 627 | 12633 | 12634 | 12635 |
|---|---|---|---|---|---|---|---|---|---|---|
| menthone[c,e] | 1166 | 19.5 d | 12.2 b | 10.9 b | 14.2 c | 7.2 a | 10.9 b | 11.6 b | 12.2 b | 14.9 c |
| *iso*-menthone[b,d] | 1176 | 15.9 e | 13.4 bc | 13.4 bc | 14.4 d | 10.5 a | 13.1 b | 12.7 b | 14.1 cd | 14.4 d |
| menthol[c,e] | 1194 | 47.5 a | 57.5 c | 60.3 ef | 54.7 b | 62.9 f | 61.4 ef | 59.7 cde | 58.0 cd | 54.0 b |
| pulegone[c,e] | 1249 | 2.2c d | 2.0 bcd | 2.0 bcd | 2.3 d | 1.7 a | 1.9 ab | 2.1 bcd | 2.2 cd | 2.2 cd |
| piperitone[d] | 1264 | 1.4 a | 1.5 bc | 1.5 bc | 1.5 bc | 1.5 bc | 1.5 bc | 1.5 bc | 1.5 bc | 1.6 c |
| menthyl acetate[c,e] | 1300 | 4.0 bc | 4.0 bc | 4.0 bc | 4.0 bc | 4.0 bc | 3.0 a | 4.0 bc | 4.0 bc | 4.0 bc |
| *β*-caryophyllene[c,e] | 1433 | 1.3 d | 1.2 cd | 0.9 ab | 0.9 ab | 1.0 b | 0.8 a | 0.9 ab | 1.0 b | 1.0 b |
| % RSD[f] | | 3.2 | 1.0 | 0.2 | 2.3 | 3.7 | 3.2 | 3.5 | 1.5 | 2.3 |

[a] For letters a–f, values within rows followed by the same letter do not differ statistically at $P = 0.05$. [b] *iso*-Menthone + *neo*-menthol (~1,1:1). [c] Identified on the basis of the Kovats index and mass spectrum. [d] Identification based on a very good match of mass spectra. [e] Identification confirmed by coinjection of the reference compound. [f] % RSD, average coefficient of variance of individual compounds.
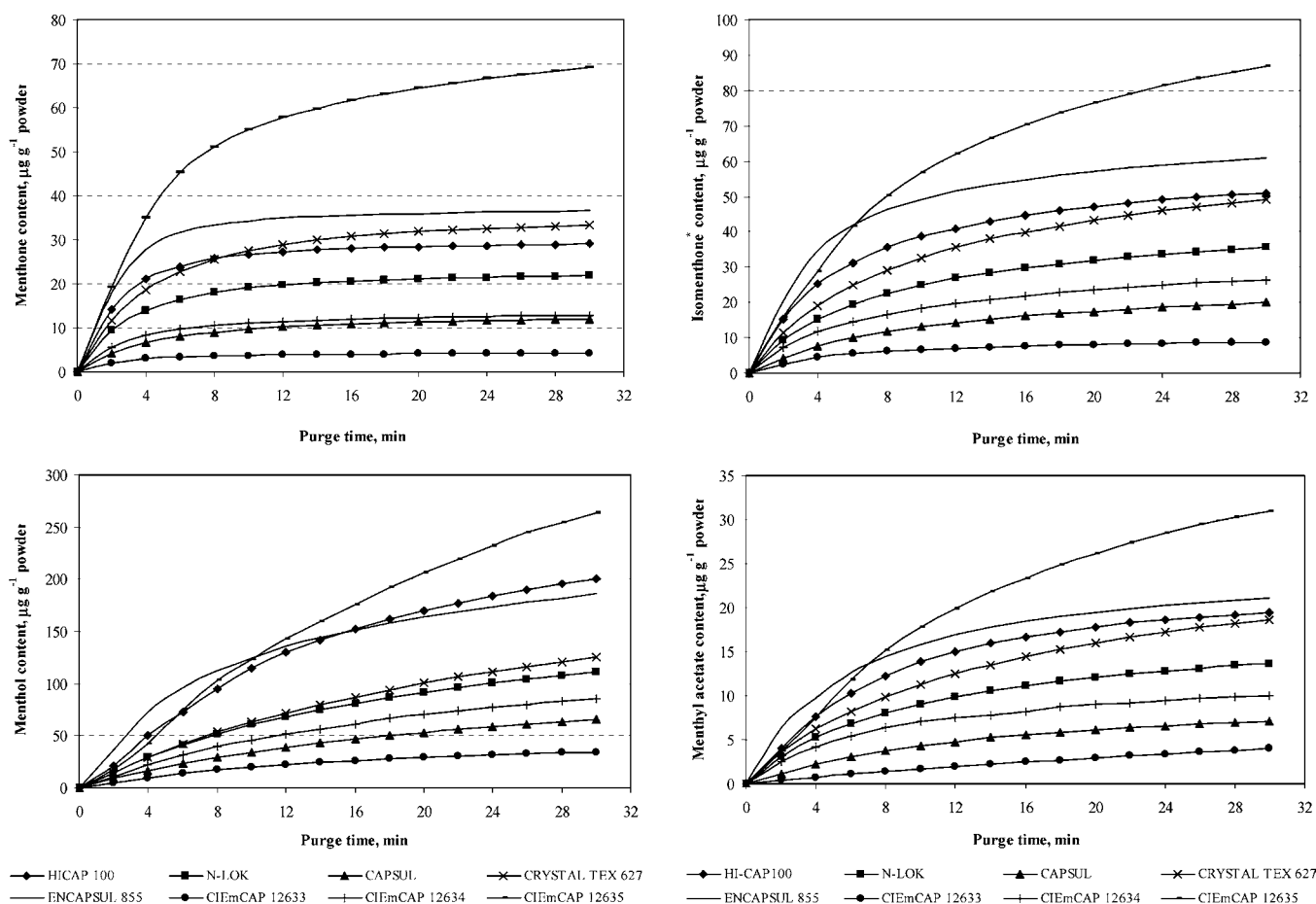


**Figure 1.** Amounts of major volatiles released from microencapsulated peppermint EO products by DHS analysis; *iso*-menthone + *neo*-menthol (~1.1:1).

the content of menthone in the initial EO was 19.5%, while in the surface oils it was significantly different ($P = 0.05$) and varied from 7.2 (ENCAPSUL 855) to 14.9% (CIEmCap 12635). In general, these results could be explained by the losses of more volatile hydrophobic compounds not entrapped in the capsules and consequently not protected from evaporation. Consequently, the content of less volatile compound menthol in the surface oils (54.0−62.9%) was remarkably higher than in the initial EO (47.5%). The changes in the percentages of piperitone and pulegone during processing were less remarkable; also, the content of menthyl acetate in the oils extracted from the processed products was not significantly different ($P = 0.05$) from that in the initial EO (**Table 3**).

**Flavor Release of Peppermint EO Volatiles by DHS-ATD-GC-FID.** The recovery of peppermint EO volatiles that were released into the headspace from spray-dried encapsulated products, with surface oil removed, was determined as a function of nitrogen purge time up to 30 min. It is evident that components were released at different rates by each of encapsulated products (**Figure 1**). The rate of release should depend on various factors, such as different chemical structures and properties of wall materials, the binding capacity of matrices to lock EO droplets, different physicochemical properties of individual aroma components, and storage conditions. The total amount of volatiles released during 2 min of purge treatment varied from 12.0 (CIEmCap 12633) to 97.9 $\mu g\ g^{-1}$ (ENCAP-

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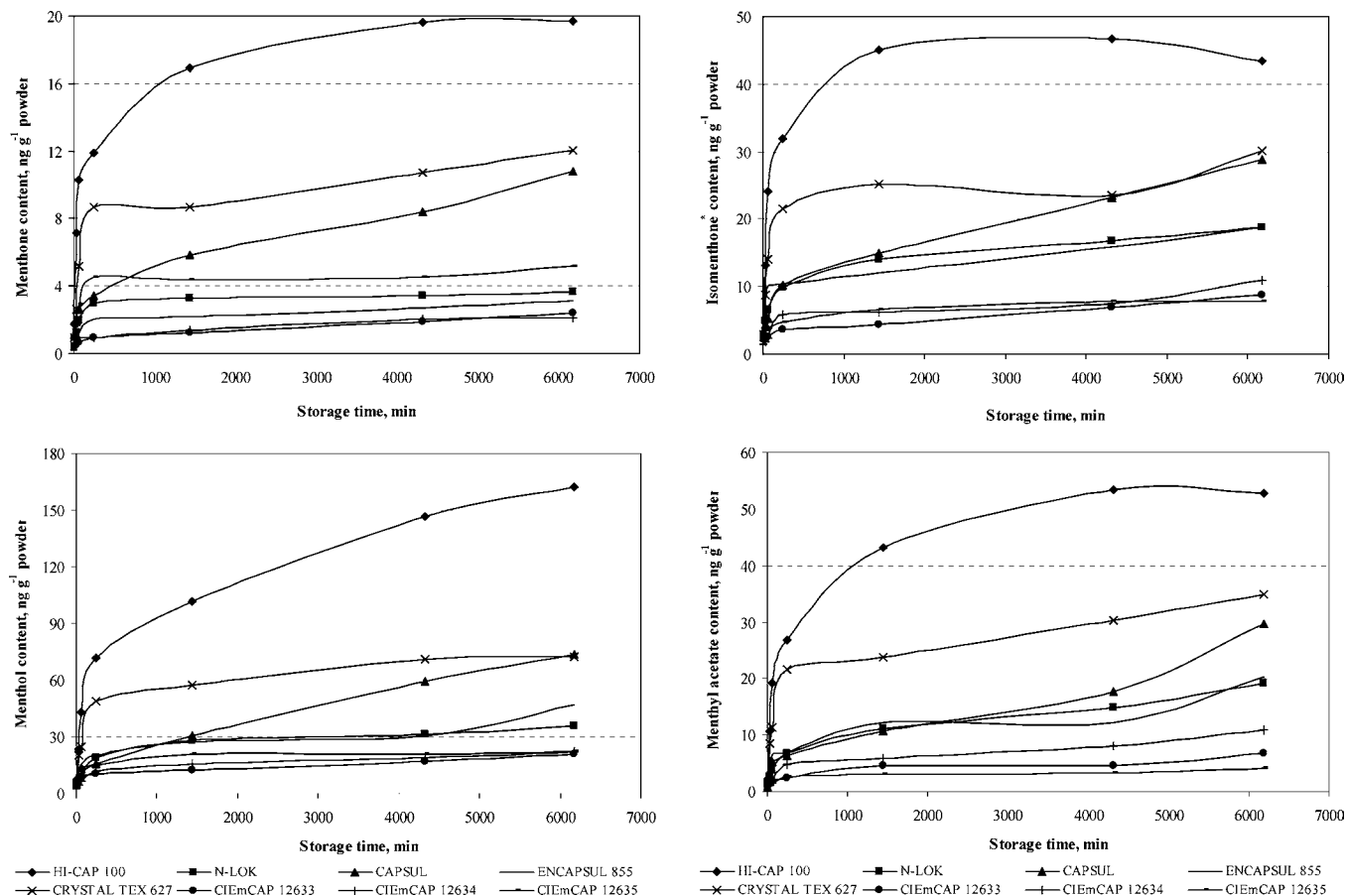*J. Agric. Food Chem.,* Vol. 55, No. 8, 2007 **3033**



**Figure 2.** Release kinetics of volatiles from microencapsulated peppermint EO products by SHS analysis at $a_w = 0.43$; *iso*-menthone + *neo*-menthol ($\sim$1.1:1).

SUL 855); the amount of major compound menthol, constituting more than 47% of total EO, was from 4.4 to 36.6 $\mu$g g$^{-1}$, respectively. The range of concentrations oil volatiles during 30 min purge was from 58.9 (CIEmCap 12633) to 524.8 $\mu$g g$^{-1}$ (CIEmCap 12635), of which the amount of released menthol was constituted of 34.4–264.0 $\mu$g g$^{-1}$, respectively. Menthone, as the second major component of peppermint EO ($\sim$20%), during timed purge treatment, was released from 2.0/4.3 (CIEmCap 12633) to 19.2/69.2 $\mu$g g$^{-1}$ (CIEmCap 12635) (**Figure 1**).

On the basis of the results obtained, the most effective matrix to retain peppermint EO volatiles was OSAN starch CIEmCap 12633 (**Table 1**); the amounts of emitted volatiles into the headspace above this spray-dried product varied from 12.0 to 58.9 $\mu$g g$^{-1}$ (**Figure 1**). CAPSUL was the second least leaking matrix in our study; the amounts of the released volatiles were from 18.4 to 121.1 $\mu$g g$^{-1}$. On the contrary, OSAN starch CIEmCap 12635 was the most leaking wall system; the amounts of emitted volatiles varied from 67.0 to 524.8 $\mu$g g$^{-1}$. It is clear that the most intensive permeability of volatiles from microencapsulated products was observed during the first 6 min of purge treatment, and then, appropriate slopes of volatiles were indicated in all matrices tested (**Figure 1**).

It could be concluded that OSAN-modified starches CIEmCap 12633 and CAPSUL resulted in the highest retention of peppermint volatiles and that these matrices could be recommended when slow release of volatiles is required. On the contrary, both hydrolyzed starches ENCAPSUL 855 and CRYSTAL TEX 627 showed the poorest retention of peppermint EO; the leakage of volatiles into the headspace from these matrices was faster, and consequently, they could be

applied when a rapid release of aroma compounds into the environment is needed.

**Flavor Release of Peppermint EO Volatiles by SHS-GC-FID at Different Water Activities.** The release time course of peppermint EO volatiles in spray-dried encapsulated products was measured at 25 °C and $a_w = 0.43$ and 0.75. The permeability of OSAN-modified starch CIEmCap 12633 was the lowest at 0.43 $a_w$, and the total amount of volatiles released varied from 16.9 to 52.2 ng g$^{-1}$. The highest amount of volatiles was collected above HI-CAP 100 wall system (34.2/367.6 ng g$^{-1}$) (**Figure 2**). In general, the most intensive aroma release was observed during the first 60 min of storage. Menthol, as a major compound of peppermint EO, was the most strongly bound by CIEmCap 12633; the released amount above this starch product ranged from 4.3 to 20.9 ng g$^{-1}$, while a significantly higher amount of menthol was emitted from HI-CAP 100 encapsulated product (7.0/162.4 ng g$^{-1}$). The amount of released menthone varied from 0.6 to 2.1 ng g$^{-1}$ for CIEmCap 12634 and from 1.8 to 19.7 ng g$^{-1}$ for HI-CAP 100 encapsulation products. Quite similar results were obtained for other peppermint volatiles. For example, the highest amounts of released *iso*-menthone, pulegone, and menthyl acetate were determined from HI-CAP 100 encapsulated EO products and varied in ranges of 3.1 and 43.4, 0.3 and 3.3, and 2.1 and 52.8 ng g$^{-1}$, respectively.

The total amount of peppermint volatiles released at 0.75 $a_w$ was in the range of 32.2/151.3 (CIEmCap 12633) and 37.5/891.7 ng g$^{-1}$ (N-LOK); the highest loss of peppermint volatiles was observed in the headspace above OSAN starch N-LOK and dextrin ENCAPSUL 855 (**Figure 3**). The results obtained clearly indicate that RH ($a_w =$ RH/100) possesses a pronounced effect
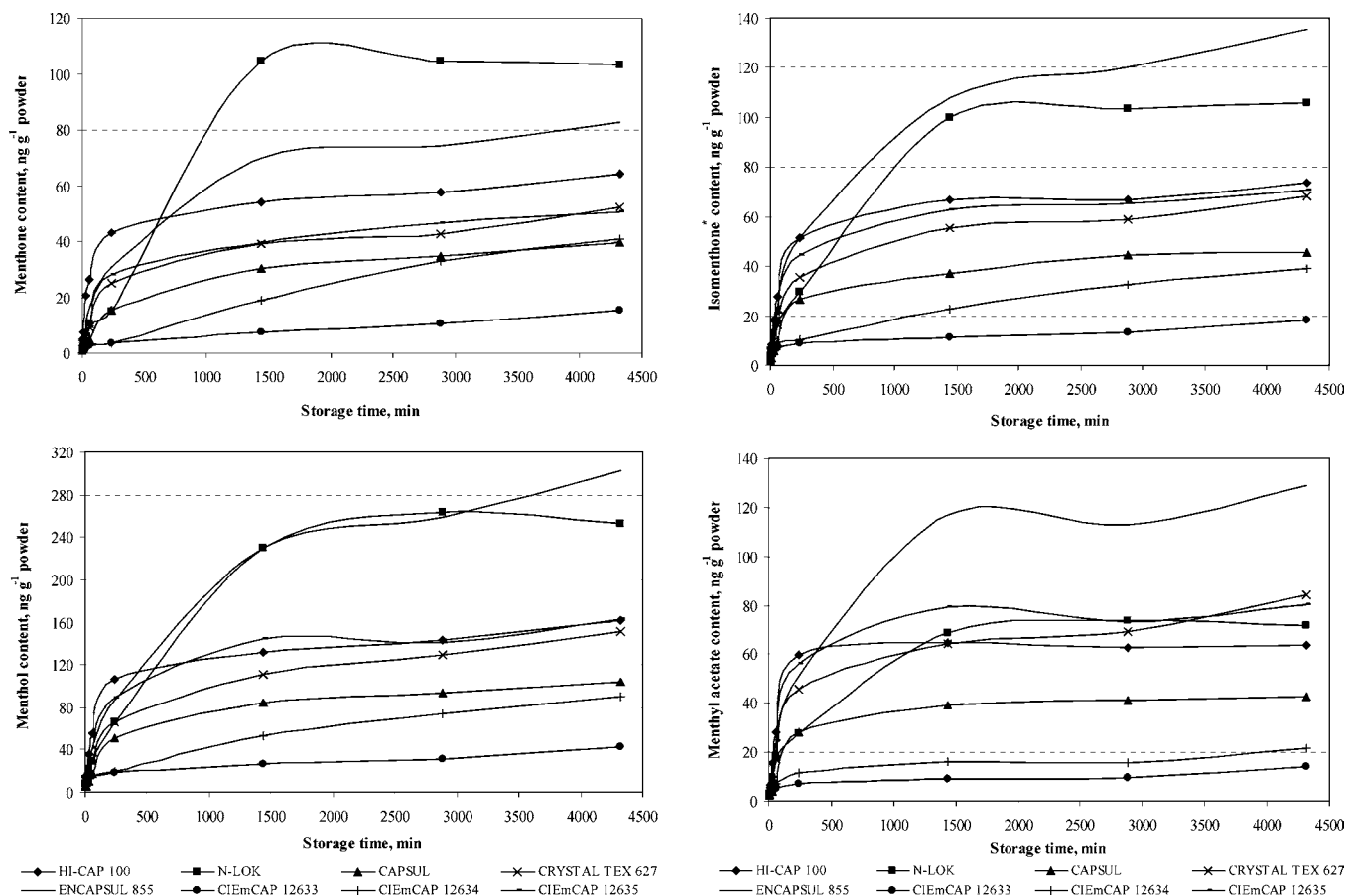
**Figure 3.** Release kinetics of volatiles from microencapsulated peppermint EO products by SHS analysis at $a_w = 0.75$; *iso*-menthone + *neo*-menthol (~1.1:1).

on the leakage rates of peppermint EO volatiles from different encapsulation products, which was greatly accelerated by an increase in $a_w$. However, the effect of the increased $a_w$ was less considerable for HI-CAP 100 (from 1.5 to 2.0), CRYSTAL TEX 627 (from 1.4 to 3.2), CAPSUL (from 1.1 to 2.9 times), and CIEmCap 12633 (from 1.9 to 3.3) wall systems, as compared with that of N-LOK (from 1.4 to 8.6), ENCAPSUL 855 (from 2.3 to 11.4), CIEmCap 12634 (from 1.7 to 6.8), and CIEmCap 12635 (from 2.0 to 8.1), respectively. For instance, after increasing the $a_w$ from 0.43 to 0.75, the amounts of the released menthol increased by 1.1/2.1, 2.0/8.2, 1.2/3.2, 1.2/9.8, 1.3/2.1, 1.6/2.5, 1.4/4.8, and 1.3/7.9 times from HI-CAP 100, N-LOK, CAPSUL, ENCAPSUL 855, CRYSTAL TEX 627, CIEmCap 12633, CIEmCap 12634, and CIEmCap 12635 encapsulation products, respectively. The amount of the released menthone at 0.75 $a_w$ was higher to that at 0.43 $a_w$ by 2.7−3.6 times for HI-CAP 100 and 3.5−31.9 times for N-LOK encapsulation products (**Figures 2** and **3**).

Our results obtained are in agreement with other studies. Rosenberg et al. (2) determined comparatively high retention of volatile esters at 64% RH, which sharply dropped at 75% RH, and total loss of volatiles was obtained at 97% RH. The effect was attributed to the changes of matrix structure, and no drastic changes were obtained at 64% RH, and water uptake caused some swelling and bridging of the capsules; a further increase of RH to 75−92% caused progressive dissolution of the wall polymer, until at 97% RH a pastelike mass was formed (2). In another study, Yoshii et al. (6) showed that the release of ethyl butyrate from gum arabic, maltodextrin, and soybean soluble polysaccharide at 50 °C was greatly accelerated by an increase in RH from 45 to 75%, which was explained by the

change of matrix structure as it was mentioned earlier by Rosenberg et al. (2) that water uptake at higher RH destroyed the capsule structure. However, ethyl butyrate emulsified with soybean soluble polysaccharide was completely lost at 75% RH in 12 h; therefore, it was suggested that the release of ethyl butyrate was closely related to the presence and concentration of water molecules surrounding the powder (6). Whorton and Reineccius (19) studied the behavior of other esters and reported quite similar findings. They suggested that as long as the individual structure of the capsule remains intact, a high retention of volatile is maintained; once the capsule structure is damaged by water uptake, the release rates increase, and this can possibly be the result of the higher mobility of flavor (8). Soottitantawat et al. (21) investigated the effect of 23, 51, 75, and 96% RH on the release of water insoluble D-limonene from encapsulated powder at 50 °C and observed that considering only 23 and 96% RH, the release rate increased with increasing RH, while comparing the 51 and 75% RH, the release of D-limonene at 51% RH was higher than that observed at 75% RH. They suggested that the release of D-limonene is closely related at least to the water activity of powder and that it mainly resulted from diffusion of this volatile from the matrices (21). For partially water soluble compounds, dissolved flavors can increasingly diffuse through the coating matrices with an increase in the water activity; consequently, the release of flavors intensifies (8).

It can be summarized that OSAN starch CIEmCap 12633 was the least emitting coating material in our study; other OSAN-modified starches CAPSUL and CIEmCap 12634 were also very effective in retaining peppermint EO; in addition, these materials were sufficiently stable during storage at different $a_w$

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values. Modified starch HI-CAP 100, although, retained comparatively high amounts of peppermint EO volatiles after spray drying (**Table 1**) was remarkably less stable during storage comparing to other matrices, particularly at 0.43 $a_w$. This finding is in agreement with previously published study on model L-menthol encapsulation (*8*), where at 8% RH the amount of L-menthol released was the highest from HI-CAP 100, as compared to that from CAPSUL and gum arabic; at 33 and 51% RH, the differences between OSAN starches were less remarkable, but still, the amount of volatiles released was slightly higher than from gum arabic, and at 75 and 83% RH, L-menthol was better protected with HI-CAP 100 matrix than by gum arabic but not enough as compared with that of CAPSUL (*8*). It was concluded that water uptake resulted in a change of matrix structure increasing the dissolution of L-menthol; the release of encapsulated L-menthol is controlled by the diffusion mechanism through the wall of particles. Therefore, it can be suggested that with core materials that are partially water soluble the ultimate retention is determined by the combined effects of molecular diffusion and core droplet mobility.

It could be concluded that loss of peppermint EO volatiles during storage was more intense at a higher $a_w$ level. Most likely, the effect of water activity on the release of encapsulated flavors is associated with the structural changes of coating matrices. The slower release of volatiles at low $a_w$ is most likely due to the lower mobility of flavor molecules in the glassy state of the capsule matrices; at high $a_w$ levels, the matrix starts to plasticize, resulting in the increase of release rates of the possibly higher mobility of flavors. To obtain more comprehensive explanations on the differences of modified starches wall systems applied in our study, it can be suggested that more detailed studies with model systems (e.g., pure volatile compounds) should be performed and the glass transition temperature as a critical determinant in the encapsulated powder matrix going from a glassy amorphous state to a rubbery amorphous state as a powder storage at the specific water activities must be determined.

**ABBREVIATIONS USED**

EO, essential oil; OSAN, *n*-octenyl succinic anhydride; DE, dextrose equivalent; RH, relative humidity; $a_w$, water activity; DHS, dynamic headspace; SHS, static headspace; KI, Kovats retention indices; RSD, relative standard deviation.

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