J Incl Phenom Macrocycl Chem (2007) 57:591–596
DOI 10.1007/s10847-006-9279-7

ORIGINAL ARTICLE

Release kinetics of (–)-menthol from chewing gum

Hidefumi Yoshii · Aya Sakane · Daisuke Kawamura · Tze Loon Neoh · Hayato Kajiwara · Takeshi Furuta

Received: 15 May 2006 / Accepted: 20 October 2006 / Published online: 16 January 2007
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Abstract The release kinetics of (–)-menthol from chewing gum was investigated using various encapsulated powder of (–)-menthol. The apparatus of flavor release of chewing gum was made with a glass container of mashing homogenizer. Flavor release behavior could be correlated with Avrami's equation. Chewing gum containing (–)-menthol/γ-CD complex powder had longer retention of (–)-menthol compared with the β-CD complex powder and the (–)-menthol encapsulated in modified starches. The activation energies of (–)-menthol release from chewing gum were 106 kJ/mol for γ-CD complex and 74 kJ/mol for (–)-menthol/β-CD complex powder and emulsified (–)-menthol encapsulated in HI-CAP, respectively.

Keywords Cyclodextrin · Chewing gum · Release · Menthol

Introduction

Chewing gum is a good model to study the release of flavor because it offers the possibility of chewing a semi-solid food for a prolonged period of time, releasing flavor compounds progressively in a semi-controlled fashion. Flavor release is an important issue in food science and controlled flavor release is a key functionality that can be provided by microencapsulation. Chewing gum is a sensibility food to enjoy the flavor release and flavor retention.

Ovejero-Lopez et al. [1] studied flavor release from a mint-flavored chewing gum model system by atmospheric pressure chemical ionization mass spectroscopy (APCI-MS) and sensory time-intensity (TI). APCI-MS instrumental time profiles and TI are methods with high time resolutions. Haahr et al. [2] investigated flavor release measurement by atmospheric pressure chemical ionization ion trap mass spectrometry, construction of interface and mathematical modeling of release profiles. McGowan and Lee [3] investigated TI curves in corn zein chewing gum by the evaluation of the taste, texture and aroma of corn zein and by the enhanced method developed by MacFie and Liu [4]. Haahr et al. [5] studied the release of menthol and menthone from peppermint-flavored chewing gum as a function of chewing frequency, masseter muscle activity, chewing force, and saliva flow rate. Guinard et al. [6] investigated the relation between saliva flow and flavor release from chewing gum and concluded that parotid saliva flow may affect the flavor release rate, but not how much nor for how long flavor is released. Harvey and Barra [7] overviewed the real time breath and headspace analysis of flavor volatiles by APCI-MS.

Doyen et al. [8] studied volatile flavor release from an emulsion by the headspace analysis. Schober and Peterson [9] investigated flavor release kinetics of (–)-menthol dissolved in propylene glycol by APCI-MS.

H. Yoshii (✉) · A. Sakane · D. Kawamura · T. L. Neoh · T. Furuta
Department of Biotechnology, Tottori University, 4-101 Koyama Minami, Tottori 680-8552, Japan
e-mail: yoshii@bio.tottori-u.ac.jp

H. Kajiwara
Central Laboratory, LOTTE Co. Ltd, 3-1-1 Numakage, Minami, Saitama 336-8601, Japan

Porzio [10] reviewed flavor encapsulation on recent works. Taylor [11] reviewed all aspects of flavor release from food matrices and the subsequent delivery of flavor to the olfactory and gustatory receptors. de Roos [12] also reviewed the effect of texture and microstructure on flavor retention and release and indicated the effect of liquid flavor and spray-dried flavor in gum on flavor release from sugar based stick gum.

Among various flavor release control methods, molecular inclusion of cyclodextrins (CDs) is a useful and effective technique. CD molecule can be envisioned as a hollow truncated cone-shaped molecule with a hydrophobic interior cavity, with inner diameter of 5–8 Å [13]. Many flavor components could be encapsulated within CDs. CD can control flavor release and suppress flavor volatilization through formation of inclusion complex with flavor compounds. CD enhances the stability of flavors to oxygen, heat or light by including the flavor in the molecular cavity. Reineccius et al. [14] investigated the incorporation and retention on storage of a variety of spray-dried flavor/natural CD complex. Shiga et al. [15] investigated the encapsulation and release of spray-dried flavor encapsulated within a blended encapsulant of CD and gum arabic (GA). Shiga et al. [16] studied the flavor release behavior of flavor/CD complex in slurry solution under boiling conditions. Soottitantawat et al. [17] studied the microencapsulation of (–)-menthol by spray drying and its release characteristics from the spray dried flavor powder.

Menthol is a highly volatile cyclic terpene alcohol, which has been used as a flavor. Liu et al. [18] studied the molecular encapsulation of (–)-menthol in CD to prevent flavor loss during drying by the single droplet method and proposed a simple mathematical model for estimating the flavor retention. Kant et al. [19] studied the binding and release of volatile compounds to and from β-CD in model aqueous systems by using the static equilibrium headspace and dynamic headspace dilution method to investigate the temporal aroma release from reduced fat yogurt.

Controlled release of flavors from capsule matrices seemed to be a useful application. In this study, the encapsulation of emulsified (–)-menthol by spray drying was carried out with GA and modified starch such as HI-CAP or CAPSUL as wall material. The flavor release characteristic of chewing gum containing (–)-menthol encapsulated either within a wall material or in a CD. The release kinetics of (–)-menthol from chewing gum was investigated using various encapsulated (–)-menthol powder.

Materials and methods

Materials

(–)-Menthol and GA were purchased from Soda Aromatic Co., Ltd. (Tokyo, Japan). Modified starches (CAPSUL and HI-CAP 100) were obtained from Nippon NSC Co., Ltd. (Tokyo, Japan). Both of CAPSUL and HI-CAP 100, which were derived from waxy maize base, were modified with *n*-octenyl succinic anhydride (OSA) for use in the flavor encapsulation process. HI-CAP 100 was blended with high-dextrose equivalent (DE) corn syrup solids to obtain a final DE of 32-37. (–)-Menthol encapsulated β-, and γ-CD were gifts from Cyclochem Co., Ltd. (Kobe, Japan). Other organic chemicals used were of analytical grade.

Preparation of the emulsified (–)-menthol liquid

Wall material of GA, HI-CAP 100, or CAPSUL was added into distilled water to obtain a 30% w/w mixture and allowed to hydrate overnight. (–)-Menthol was melted by heating up to 55°C and added to the solution at 55°C at a mass ratio of 0.25 to wall material. The mixture was homogenized by using a Polytron homogenizer (PT-6100, Kinematic GA, Littau, Switzerland) at rotational speed of 8,000 rpm for 3 min. The (–)-menthol emulsion fed immediately to the spray dryer while its temperature was being held at 55°C.

Preparation of encapsulated (–)-menthol powders

The (–)-menthol emulsion was fed through Ohkawara-L8 spray dryer (Ohkawara Kakouki Co., Ltd., Yokohama, Japan), equipped with a centrifugal atomizer as explained previously [16]. The operating conditions of the spray dryer were as follows: inlet air temperature, 180°C; outlet air temperature, 100 ± 5°C; feed rate, 45 mL/min; air flow rate, 100 kg/h; rotational speed of atomizer, 30,000 rpm. Finished powder was stored in a hermetically sealed bottle at –80°C until analysis. Retention of (–)-menthol during spray drying was defined as the ratio of the flavor in the powder to its initial amount in the feed liquid.

Quantification of encapsulated (–)-menthol

One tenth of a gram of the spray-dried powder was dispersed in 1 mL of water in a glass bottle, and 4 mL of acetone with cyclohexanone (1 μl mL^{-1}) as internal standard was added, followed by forceful mixing with a vortex mixer for 1 min. To extract encapsulated

(–)-menthol into the organic solvent, the mixture was heated in a heating block at 90°C for 30 min with intermittent shaking. Then, after cooling down, 2 μL of the supernatant was injected into a gas chromatograph (GC-14B, Shimadzu Corporation, Kyoto, Japan) equipped with a PEG-20M packed glass column (2 m length × 3.2 mm internal diameter) and a flame ionization detector. The temperature of detector and injector were set at 230 and 200°C, respectively. The column temperature was controlled at a constant value of 170°C with nitrogen as the carrier gas at 150 kPa of inlet pressure. The internal standard method was used to calculate the amount of (–)-menthol. All the samples were analyzed in duplicate and the data were presented as an average.

Preparation of chewing gum containing (–)-menthol powders

Thirty grams of gum base (LOTTE Co., Ltd. Tokyo) were put in the ceramic bowl and was heated in an electric microwave oven (980 W) for 40 s. Then, the gum base was then added with 250 μL of distilled water and heated again for 20 s. About 1.2 g of (–)-menthol encapsulated powder or 2 g of (–)-menthol/CD complex powder were mixed thoroughly into the softened gum base by kneading with a wooden rolling pin. The chewing gum containing (–)-menthol was heated more for another 20 s. The softened gum containing encapsulated (–)-menthol powder or (–)-menthol/CD complex powder was molded in a Teflon rectangular mold (30 × 70 × 2 mm). Every gram of the prepared chewing gum contained 2.9–3.7 mg (–)-menthol. The retention of (–)-menthol during the preparation of chewing gum was 83–94%. The water content of chewing gum was 3.5–4.2%. The results are the average of the triplicates in each sample.

Release of (–)-menthol from chewing gum

Chewing gums of a columnar shape, which measure ca. 5.5 mm in diameter and 2 mm in height were drawn with a cork borer. About 0.2 g of the columnar chewing gum was formed into a pellet ball. Figure 1 shows the apparatus to measure (–)-menthol release from chewing gum. This chewing instrument was placed in an oven at a constant temperature (30–50°C). The chewing vessel is a homogenizer (18 mm diameter × 117 mm height) with two gas-flow holes. The pellet chewing gum was put into the homogenizer. Eighty microliters of distilled water were added to the gum pellet. The chewing mechanism was simulated by the up-down movement of the Teflon piston

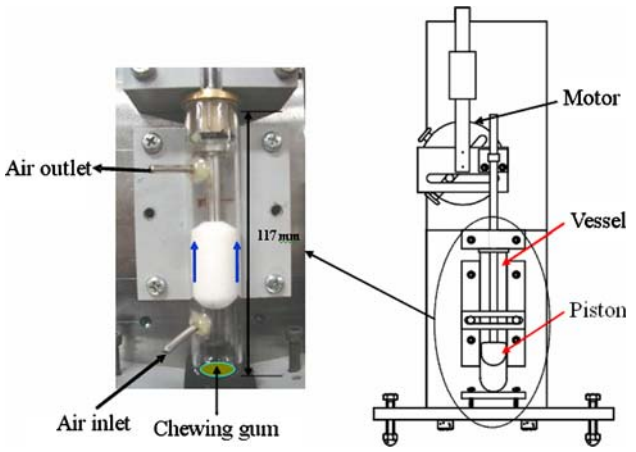

Fig. 1 Release experiment apparatus to measure (–)-menthol release from chewing gum

(8 × 30 mm height) at the rotational speed of 28 min^{-1}. Air-flow rate was set at 60 mL/min. At prescribed time intervals, chewing gum was removed from the vessel. The residual amount of (–)-menthol in the chewing gum was measured by the solvent extraction method described above for quantification of encapsulated (–)-menthol. The retention of (–)-menthol in the release experiment was expressed as the ratio of the remainder of the flavor to its initial content. Avrami's equation (Eq. (1)) or Weibull distribution function was employed in this work. Avrami's equation was successfully applied to describe the shelf life failure [20], and later applied to the release time-courses of the encapsulated flavors [21, 22].

$$R = \exp[-(kt)^n] \quad (1)$$

where R is the retention of (–)-menthol, t is the storage time, k is the release rate constant, and n is a parameter representing the release mechanism.

Results and discussion

Retention of (–)-menthol during molding of chewing gum

(–)-Menthol was evaporated during heating for the molding of chewing gum. Table 1 shows the retention of (–)-menthol in various wall materials. The retention of (–)-menthol/γ-CD complex was 90.8%, which was higher than that of β-CD complex. HICAP gave the highest retention of 92.9%. The average content of (–)-menthol in chewing gum was about 3.46 mg/g chewing gum.

Table 1 Retention of (–)-menthol during formation of chewing gum with electric microwave oven

Powder	GA	CAPSUL	HI-CAP	β-CD	γ-CD
(–)-Menthol content in powder (g/g)	0.174	0.173	0.176	0.109	0.095
(–)-Menthol in gum (mg/g)	3.46	3.76	3.39	2.97	3.74
Added (–)-menthol (mg)	4.10	4.05	4.26	3.56	4.12
Retention of (–)-menthol	0.843	0.929	0.884	0.834	0.908

Measurements were done in triplicate

Effect of wall material on release of (–)-menthol in chewing gum

The effect of wall materials of encapsulated (–)-menthol powder on the retention of (–)-menthol in gum during chewing at 40°C is shown in Fig. 2. The solid line is the regression of data for three encapsulants data with Avrami's equation. The release rate constant, k and the mechanism number, n were 2.67×10^{-4} s^{-1} and 0.71 respectively. GA, HI-CAP 100, or CAPSUL was used as the wall material with a ratio of (–)-menthol to wall material of 0.20. The retentions of (–)-menthol during spray drying were 72% for GA, 85% for CAPSUL, and 87% for HI-CAP 100. HI-CAP 100 showed the highest (–)-menthol retention. However, the release rates of (–)-menthol from chewing gum were almost the same as shown in Fig. 2. As for 30 min of chewing, the retentions of (–)-menthol in gum were about 50%. This result suggests that the rate-limiting factor of (–)-menthol release might be the diffusion in the gum-base as a semi-permeable membrane. Therefore, the wall materials didn't affect the release rate.

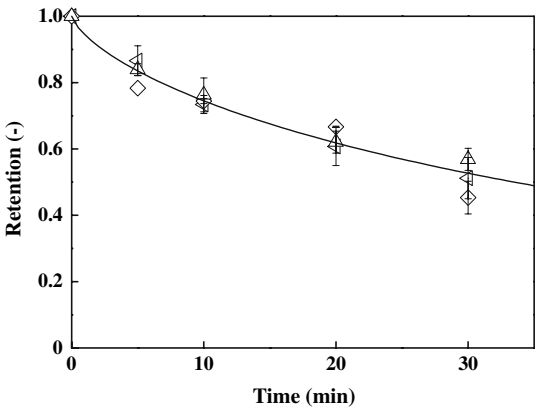

Fig. 2 Effect of wall materials of encapsulated (–)-menthol powder on the retention of (–)-menthol in gum during chewing at 40°C. Chewing rate, 28 min^{-1}; air flow rate, 60 mL/min; water addition, 40% w/w. The error bars indicate 95% confidence levels. Wall material: CAPSUL, ◇; HI-CAP, △; GA, ◁

Effect of CD on the release of (–)-menthol in chewing gum

Cyclodextrin can be utilized in foods mainly as carriers for molecular encapsulation of flavors and other sensitive ingredients. Liu et al. [18] indicated that β-CD appeared to be a better encapsulant for (–)-menthol than α- and γ-CD during spray drying. In their headspace experiment using 400 ppm menthol solution, the stability constants were 370 dm^3/mol for β-CD and 120 dm^3/mol for α-CD and γ-CD. Szente and Szejtli [23] studied the change of flavor load in twelve different natural and synthetic flavor/β-CD complexes during long-term storage of 14 years under normal condition at 25°C and 60% relative humidity. In their study, (–)-menthol/β-CD complex was stable for 14 years with almost 100% of the flavor remained encapsulated. Reineccius et al. [14] measured CD effects on menthol concentration in headspace above 2:1 water/ethanol by headspace gas chromatography. Their data indicated that β-CD had higher affinity for (–)-menthol than γ-CD.

The effect of complexation of (–)-menthol and CD on the release rate of (–)-menthol during chewing was studied. Figure 3 shows the release of (–)-menthol from chewing gum containing (–)-menthol/CD complex powders at 40°C. Figure 3 also shows the regression line for the release of (–)-menthol encapsulated in HI-CAP. In Fig. 3, the solid lines were the regression lines with Avrami's equation. Table 2 shows the kinetic parameters of Avrami's equation. (–)-Menthol/γ-CD complex showed higher flavor retention than complex

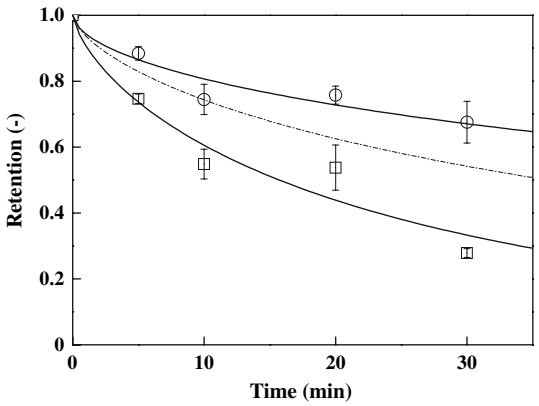

Fig. 3 Release of (–)-menthol from chewing gum containing (–)-menthol/CD complex powders. Chewing temperature, 40°C; chewing rate, 28 min^{-1}; air flow rate, 60 mL/min; water addition, 40% w/w. Wall material: γ-CD, ○; β-CD, □. The error bars indicate 95% confidence levels. The solid lines are the regression lines for (–)-menthol/CD complex powders with Avrami's equation. The dotted line is the regression line for the release of (–)-menthol encapsulated in HI-CAP in Fig. 2

Table 2 Kinetic parameters of Avrami's equation

Powder	γ-CD	β-CD	HI-CAP
n	0.57	0.72	0.71
k (s^{-1}) × 10^4	1.10	6.35	2.67

with β-CD and also encapsulated (–)-menthol powder with modified starches. This result is very interesting because the stability constant of (–)-menthol/γ-CD complex is higher than that of the complex with β-CD. This result was in disagreement with that reported by Liu et al. [18] presumptively due to the different systems in which the release characteristics of the (–)-menthol/CD complexes were investigated. de Roos [12] reported that liquid flavor in chewing gum had higher release rate than encapsulated flavor in chewing. He considered the flavor resorption of chewing gum for liquid flavor. Higher retention of (–)-menthol for γ-CD might be due to the resorption of (–)-menthol to γ-CD. Figure 4 shows the release rates of (–)-menthol from γ-CD and β-CD by differentiation of the retention curves in Fig. 3. The release peak of (–)-menthol from γ-CD and β-CD were almost the same at about 0.5 min. The peak intensity of the release of (–)-menthol from β-CD was 1.78 times as high as that from γ-CD. These results indicate that (–)-menthol/γ-CD complex powder is useful to remain higher content of (–)-menthol in chewing gum. Harvey and Barra [7] showed nosespace release profiles of menthol from chewing gum containing an equivalent flavor dosage in liquid form or encapsulated in a Flexrome® product.

Effect of temperature on release rate

In order to study the effect of temperature on the release mechanisms and also to calculate the activation energy for the release of (–)-menthol from chewing gum, the release of (–)-menthol was investigated at 37, 40, and 50°C. The release rate constants were calculated and plotted against the reciprocal of absolute temperature according to Arrhenius equation (Fig. 5). The release rate constants increased with the increase of temperature. The activation energies of menthol release from chewing gum were 106 kJ/mol for (–)-menthol/γ-CD complex and 74 kJ/mol for (–)-menthol/β-CD complex. In this study, the water addition was 40% of chewing gum weight. The release rate of flavor from chewing gum depends on saliva behavior. Therefore, the release mechanism and release rate of (–)-menthol from chewing gum are under investigation for various conditions at high water content containing (-)-menthol encapsulated in CD and modified starch.

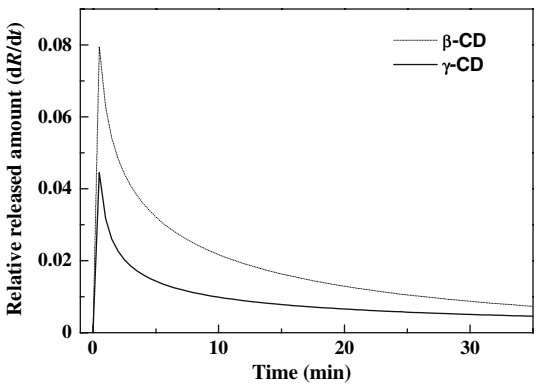

Fig. 4 Release rates of (–)-menthol from γ-CD and β-CD by the differentiation of the retention curves of (–)-menthol in Fig. 3. The solid line is for γ-CD and the dotted line is for β-CD

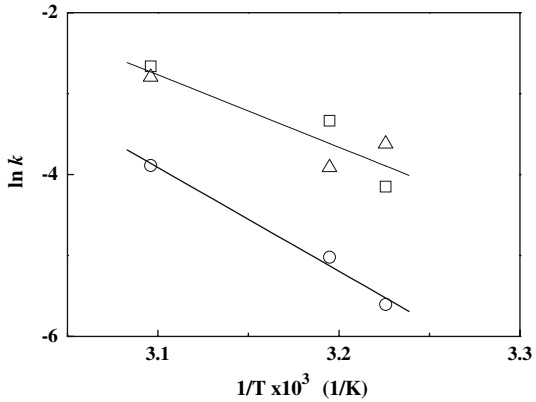

Fig. 5 Arrhenius plot of (–)-menthol release rate constant. γ-CD, ○; β-CD, □; HI-CAP, △

Acknowledgements This study was partly supported by a Grant-in-Aid for Scientific Research (No. 15580108) from the Ministry of Education, Science, and Culture of Japan.

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