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Ultrasonic encapsulation of cinnamon flavor to impart heat stability for baking applications

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ABSTRACT

The objective of this study was to enhance the heat stability of cinnamon flavor by ultrasonication-assisted microencapsulation and reduce the interaction of encapsulated cinnamaldehyde with yeast for baking applications. Microcapsules were formed by ultrasonication-induced cross-linking of chitosan and pectin. Cinnamaldehyde, the principal component of cinnamon essential oil, was incorporated with carrier oil into the cross-linked capsules. Capsule formation was verified using infrared spectroscopy and scanning electron microscopy. The formulation was spray dried and heated to determine the stability of the flavor at baking temperatures (150–250 °C). Gas chromatography was utilized to quantify the remaining cinnamaldehyde in the heated samples. Compared to pure cinnamaldehyde and the unsonicated formulation, the ultrasonicated microcapsules exhibited significantly higher cinnamaldehyde retention at high temperatures (> 150°C). Yeast growth studies were also performed in which *Saccharomyces cerevisiae* displayed less growth inhibition when subjected to encapsulated cinnamaldehyde versus pure cinnamaldehyde of the same concentration.

1. Introduction

Cinnamon, a spice utilized in baking, is usually derived from the bark of *Cinnamomum* trees. Cinnamaldehyde, the main component in cinnamon essential oil, plays the most important role in the definition of cinnamon flavor (Tian, Lei, Zhang, & Li, 2016; Unlu, Ergene, Unlu, Zeytinoglu, & Vural, 2010; Wong, Ahmad-Mudzaqqir, & Wan-Nurdiyana, 2014). When cinnamon is used for baking applications, two significant challenges exist. First, cinnamaldehyde is volatile and may undergo degradation at high temperatures. This can cause flavor evaporation and introduce unwanted degradation products into foods (Hermanto, Khasanah, KawijiAtmaka, Manuhara, & Utami, 2016). If stored over time, baked goods can consequently lose the cinnamon flavor or develop unwanted off-flavors (Hermanto et al., 2016). Second, cinnamaldehyde has exhibited antibacterial and antifungal properties. This has been exploited in applications such as pharmaceuticals, food processing and food packaging (Ali et al., 2005; Nielsen & Rios, 2000; Sanla-Ead, Jangchud, Chonhenchob, & Suppakul, 2012). However, while beneficial in medicinal and some food processing settings, these properties can be inhibitory when cinnamaldehyde is incorporated in the bread proofing process.

Yeast is used as a leavening agent in various baked products for its ability to produce carbon dioxide, which assists in dough rising and texture development. In yeast-raised bakery products, the cinnamon inhibit the yeast's ability to produce gas, leading to unrisen, denser breads (Pattison & von Holy, 2001). This phenomenon resulted in current cinnamon-bread making practice to add cinnamon flavor after proofing processing. To solve these issues, encapsulation has been used to increase the heat stability of cinnamaldehyde and prevent the loss of cinnamon flavor at high baking temperatures (Hermanto et al., 2016; Petrović, Stojanović, & Radulović, 2010; Ponce Cevallos, Buera, & Elizalde, 2010). The encapsulation also weakens the antagonistic reactions that cinnamaldehyde has with yeast, and enables the incorporation of cinnamon flavor in dough before bread proofing (Liakos et al., 2014).

Typically, emulsion can be used as a template which mediates flavor encapsulation (Lee, Tan, & Abbaspourrad, 2019; Lee, Tan, Ravanfar, & Abbaspourrad, 2019)Rajabi, Ghorbani, Jafari, Sadeghi Mahoonak, & Rajabzadeh, 2015). Most of the emulsion-templated systems require the use of synthetic surfactants (Gupta, Eral, Hatton, & Doyle, 2016) and cannot withstand high heat treatments. Therefore, a challenge exists to efficiently encapsulate flavors under high heat environments. Ultrasonication is the application of high intensity sonic waves of frequencies at 20 kHz or more in order to produce agitation and is particularly useful for the formation of microcapsules (Klaypradit & Huang, 2008; Tian et al., 2013). The agitation produces cavities of gas or liquid

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within the system that are capable of implosion. The release of energy from cavitation induced water to generate free radicals, which can assist in the chemical bonding of capsule materials. This can then lend ability for microcapsule formation (Borodina et al., 2014; Hashtjin & Abbasi, 2015).

Here, we present the construction of emulsified microcapsules using ultrasonication-assisted polymeric crosslinking of two natural polysaccharides: chitosan and pectin. In the presence of cavitation and free radicals, aqueous chitosan and pectin are well-suited to form linkages and encapsulate the hydrophobic cinnamaldehyde. The accessibility of amine groups in chitosan and carboxyl groups in pectin can provide the basis for amide bond formation. The strength of these linkages supplies stability to the polysaccharides and to the microcapsule as a whole (Borodina et al., 2014). Amide bonds are particularly stable because of resonance structure capabilities imparted by the linked carbonyl and amine groups (Kemnitz & Loewen, 2007; Mujika, Matxain, Eriksson, & Lopez, 2006). Robust amide bond strength as created by ultrasonication-assisted cross-linking can therefore provide better microcapsule stability under high temperatures.

This study presents a novel formulation to encapsulate cinnamaldehyde via ultrasonication. The formulation was investigated for its ability to impart heat stability to cinnamon flavor in addition to restricting the flavor's undesirable interactions with yeast for baking applications. By encapsulating cinnamaldehyde, baked goods can subsequently retain flavor longer and better maintain a desired structure and texture.

2. Materials and methods

2.1. Materials

Trans-cinnamaldehyde (99%) was purchased from Acros Organics (Geel, Belgium). Medium molecular weight chitosan (190–310 kDa) and pectin from citrus peel (Galacturonic Acid > 74.0%, methoxy group > 6.7%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Maltodextrin (DE = 15–20) was obtained from Bulk Supplements (Henderson, NV, USA) and vegetable oil was purchased from a local supermarket (Ithaca, NY, USA). Acetic acid, hydrochloric acid, and sodium hydroxide were purchased from VWR (Radnor, PA, USA). All other solvents and reagents utilized were of analytical grade and were obtained from VWR (Radnor, PA, USA).

2.2. Preparation of cinnamaldehyde filled ultrasonically crosslinked microcapsules

The preparation of cinnamaldehyde filled ultrasonically crosslinked microcapsules (CA-UCM) is described as follows. Individual aqueous solutions of chitosan (0.5%, w/v) and pectin (0.5%, w/v) were dissolved in deionized water with magnetic stirring for 30 min. The solutions were then adjusted to pH 2 with 0.1 M HCl or 0.1M NaOH and stirred for an additional 15 min. Cinnamaldehyde and vegetable oil (the carrier oil) were mixed at a 7:3 (w/w) ratio to comprise the total oil phase. Equal volumes of chitosan and pectin solution were added to the oil mixture at a ratio of 5:1 (v/v), respectively. The mixture was maintained at 4 °C and ultrasonicated by an ultrasonic probe (VibraCell 750 Ultrasonic Processor, Sonics and Materials Inc.) at 20 kHz, with 750 Watts of energy input for 15 min. Unfilled ultrasonically crosslinked microcapsules (UCM) were similarly prepared, without the inclusion of cinnamaldehyde and vegetable oil. Non-crosslinked microcapsules (NCM) of the cinnamaldehyde microcapsule formulation were also prepared by mixing the samples using vortex for 30 s instead of using ultrasonication.

2.3. Spray-drying of cinnamaldehyde filled ultrasonically crosslinked microcapsules

CA-UCM emulsions prepared as described in section 2.2 were mixed with 2 wt% maltodextrin and spray-dried to form spray-dried cinnamaldehyde filled ultrasonically crosslinked microcapsules (SD-CA-UCM) powder. The addition of maltodextrin was used to coat the CA-UCM with an additional layer and to assist in the spray-drying powder formation. The emulsions were spray-dried using an FT30MkIII-G Spray Dryer (Armfield Ltd., Hampshire, England). The product feed temperature was kept at 25 °C and an inlet air temperature of 150 °C was utilized in conjunction with an exhaust temperature of 55 °C. We operate with the drying air flow rate of 70 m^3/h, feed liquid flow rate of 375 mL/h, and an atomizer nozzle size of 0.5 mm. Powders were collected and stored at ambient conditions until characterization.

2.4. Microcapsule characterization

2.4.1. Microcapsule particle size and zeta-potential

Emulsion samples were diluted with deionized water upon formation and the average particle sizes and zeta potentials were measured via a Zeta-Sizer (Zetasizer Nano-ZS90, Malvern Instruments, Worcestershire, UK). For particle size measurements, a scattering angle of 90° was utilized with a Helium/Neon laser (λ = 633 nm). For electrical surface charge (zeta-potential) measurements, the emulsion droplets were measured using particle electrophoresis. Measurements were conducted on samples of CA-UCM, UCM and NCM in triplicate.

2.4.2. Fourier-transform infrared (FTIR) spectroscopy

Emulsion samples were frozen (−20 °C) and freeze-dried overnight (FreeZone Bench-top Freeze Dryer, Labconco). FTIR spectra of the freeze-dried samples were obtained using an FTIR spectrometer IR-Affinity-1S (Shimadzu, Kyoto, Japan) equipped with a single-reflection attenuated total reflectance (ATR) apparatus. Samples were scanned from 4000 to 400 cm^{-1}, using a resolution of 4 cm^{-1} and 64 scans Lee, Tan, Ravanfar, & Abbaspourrad, 2019).

2.4.3. Scanning electron microscopy

CA-UCM emulsion sample were air-dried and, in addition to SD-CA-UCM, were individually mounted on a scanning electron microscopy (SEM) sample holder and sputter coated (Denton Desk V Sputter) with gold. The samples were examined through a field emission scanning electron microscope (LEO 1550 FESEM, Carl Zeiss, New York, USA). SEM images were taken with accelerating voltage at 2 kV, at a 5 mm working distance, and an aperture size of 30 μm.

2.5. Gas chromatography analysis

2.5.1. Heat treatment

Pure cinnamaldehyde, NCM and SD-CA-UCM, at an equal cinnamaldehyde concentration, were heated in a furnace (Thermolyne Benchtop Furnace, Thermo Scientific) at 150, 200, and 250 °C for 10 min. The samples were left uncovered during heating in order for the cinnamaldehyde to evaporate. Subsequently, the heat-treated samples were allowed to cool to room temperature. Samples were analyzed according to a previously reported method, with slight modifications (Yeh et al., 2013). One mL each of ethyl acetate and deionized water were added to all samples for extraction. Samples were vortexed for 1 min, sonicated in a sonication bath for 10 min, and vortexed for an additional 1 min. Using vortex and low-intensity sonication were necessary to rupture the microcapsules and release the flavor into the organic ethyl acetate layer. Next, the mixtures were centrifuged at 959 × *g* for 10 min, and 100 μL of the organic layer of each sample was used for gas chromatography (GC) analysis. Non-heated samples at 25 °C were extracted using the same method and analyzed using GC for calculations of encapsulation efficiency.

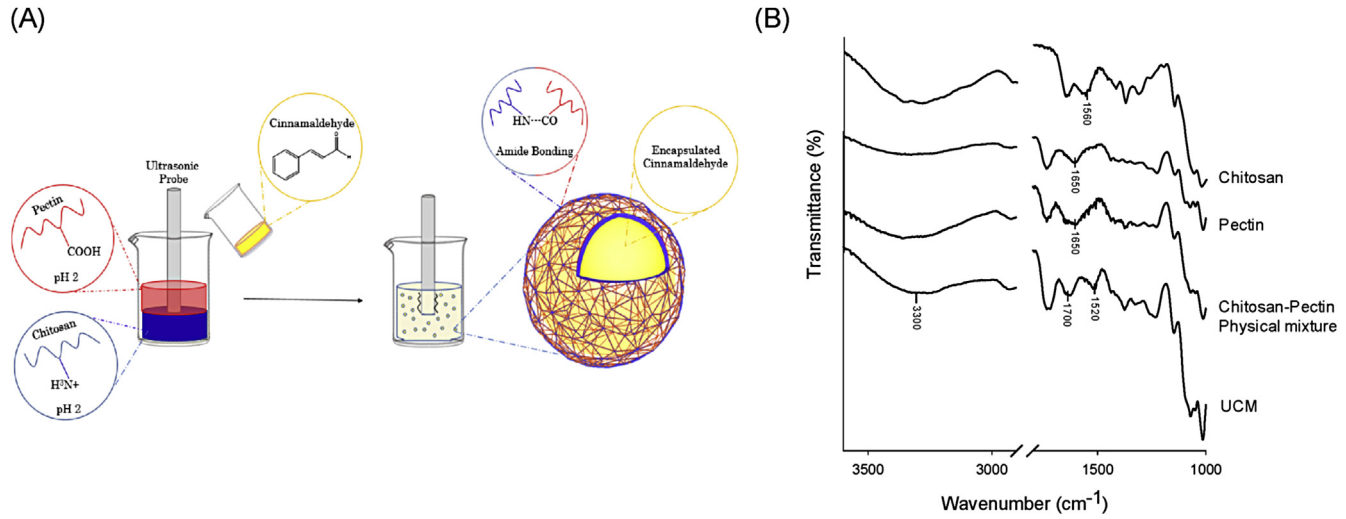

Fig. 1. (A) Cinnamaldehyde encapsulation schematic detailing capsule formation via ultrasonication-induced polymeric cross-linking of pectin and chitosan polysaccharides. (B) FTIR measurements of chitosan, pectin, chitosan-pectin physical mixture and UCM, detailing spectral changes corroborating the formation of amide bonds during ultrasonication.

2.5.2. Quantification of cinnamaldehyde by gas chromatography

Gas chromatography with flame ionization detection (GC-FID, Hewlett Packard 5890 Series II, GenTech Scientific) was utilized to analyze the samples. Standards of cinnamaldehyde (99%) at known concentrations were used to construct a calibration curve. 0.8 μL of each sample was injected into a HP-5ms column (30m × 0.25 mm, I.D. 0.25 μm film, Agilent Technologies, CA, USA) with an initial column temperature of 60 °C, and ramped to 250 °C at a rate of 10 °C/min. The injector temperature was 250 °C, with an inlet pressure of 17 kPa. Hydrogen (99.49%) was utilized as the carrier gas (Yeh et al., 2013). Two injections were performed for each sample and each sample was analyzed in triplicate. Data was collected and analyzed via PeakSimple Chromatography Data Systems (SRI Instruments). Cinnamaldehyde retention before (at 25 °C) and after heating was calculated according to equation (1):

$$\text{Cinnamaldehyde Retention (\%)} = \frac{GC\ Detected\ Cinnamaldehyde}{Initial\ Cinnamaldehyde} * 100 \quad (1)$$

2.6. Thermogravimetric analysis

The thermogravimetric analysis (TGA) curves were obtained using a thermogravimetric analyzer (TGA Q500, TA Instruments, New Castle, DE, USA). The measurements were conducted under nitrogen gas at a flow rate of 60 mL/min. Approximately 8 mg of pure cinnamaldehyde, Freeze-dried UCM, and SD-CA-UCM were loaded individually onto the platinum pan and heated from 20 to 600 °C, at a rate of 10 °C/min. The thermogravimetric curve was plotted as the derivative of mass loss percent (%) over temperature (°C) *vs.* heating temperature (°C) (Lee, Jiang, Brenna, & Abbaspourrad, 2018). The first derivative curve was plotted using the Universal Analysis 2000 software (Version 4.5A, TA instruments, New Castle, DE, USA).

2.7. Yeast growth studies

A culture of *Saccharomyces cerevisiae* (6210/wild-type) was inoculated from a single colony of a streak plate in 5 mL of yeast peptone dextrose (YPD). The culture was incubated aerobically at 25 °C for 36 h until reaching an approximate optical density value of 2 at 600 nm. Stocks of NCM (non-crosslinked), SD-CA-UCM (crosslinked), and pure cinnamaldehyde samples were individually prepared with sterile deionized water to a concentration of 6.3 mg/mL 1% NCM, SD-CA-UCM or pure cinnamaldehyde was added to YPD solution to obtain 100x dilution treatments of 1 mL total volume. An inoculum of yeast culture (50 μL) was aseptically inoculated into 1 mL of each treatment in 15.6 mm assay wells, with untreated yeast in YPD as a control. Three replicates were conducted for each treatment. The samples were analyzed by a plate reader (SpectraMax iD3 Microplate Reader, Molecular Devices, CA, USA) at 30 °C at an absorbance of 600 nm for 15 h.

2.8. Statistical analysis

All experiments were carried out in triplicate and the results were expressed as mean ± standard deviation. IBM SPSS® version 24.0 (Chicago, IL, USA) was used to determine statistical significance results. One-way ANOVA was employed for all tests, with Tukey's post-hoc test, and all results were considered significant at $P < 0.05$.

3. Results and discussion

3.1. Formation of ultrasonically crosslinked cinnamaldehyde microcapsules

Chitosan and pectin were chosen as polymers for the fabrication of microcapsules because of the availability of their amine and carboxyl functional groups, respectively, which can participate in ultrasonication-induced polymer cross-linking. The amine groups of chitosan have a pK_a of ~6.2–7.0, resulting in full protonation below pH 6.2 (de Alvarenga, 2011). Meanwhile, the carboxyl groups of pectin have a pK_a of ~3.5 and will deprotonate and approach negative charge above this pH level (Opanasopit, Apirakaramwong, Ngawhirunpat, Rojanarata, & Ruktanonchai, 2008). At aqueous pH values of ~5–6, chitosan and pectin can form complexes through electrostatic interactions due to the opposite charges of their respective functional groups. To prevent this from occurring before ultrasonication and the inclusion of the oil phase, the pH of the aqueous chitosan and pectin solutions were adjusted to a value of 2 (Borodina et al., 2014; Tan, Pajoumshariati, Arshadi, & Abbaspourrad, 2019), to maintain all polymers in the protonated state.

Upon ultrasonication of the aqueous and oil layers, high energy promotes the cross-linking reactions between the polymers (Borodina et al., 2014; Hashtjin & Abbasi, 2015). Amide bond and hydrogen bond formation between amines of free chitosan and carboxyl functional groups of pectin can construct a stable microcapsule structure while simultaneously incorporating the hydrophobic oil phase inside (Fig. 1A). In addition, cavitation produced from the high frequency sonic waves can generate free radicals that accelerate these chemical

reactions and facilitate the encapsulation process. In comparison to conventional encapsulation methods, ultrasonication induced amide cross-linking yields more stable polymer bonding. The inherent strength of amide bonds due to resonance coupled with the reactive environment produced by ultrasonically generated free radicals allows for the facile formation of stable microcapsules. Conditions of high intensity and energy cavitation are more favorable for plentiful, robust bond formation than typical electrostatic conditions (Leong, Martin, & Ashokkumar, 2017). Ultrasonication, however, generates concentrated amounts of heat, therefore emulsions were ultrasonicated while submerged in ice and covered to reduce any evaporation of the flavor compound. This constructed microcapsule structure has the potential to impart a high degree of stability to the encapsulated cinnamaldehyde. Chitosan and pectin also have good emulsifying properties, which further helps to retain flavor in a stable cinnamaldehyde emulsion (Nakauma et al., 2008; Wei, Wang, Zou, Liu, & Tong, 2012).

FTIR measurements were taken of the UCM sample, physical mixture of its polysaccharide constituents, and individual polysaccharides in order to confirm the cross-linking formation of amide bonds (Fig. 1B). The presence of amide bond formation is evidenced by several peaks. A new peak at 1700 cm^{-1} of the UCM spectrum is attributed to the carbonyl stretch (Amide I) of the newly formed amide bonds (Fig. 1B) (Coimbra et al., 2011; Maciel, Yoshida, & Franco, 2015). The peak at 1650 cm^{-1} of the pectin and physical mixture's spectrum correlates to the pectin's characteristic carboxyl functional groups (Bigucci et al., 2008). This peak is diminished in the UCM spectrum, suggesting the participation and subsequent depletion of the carboxyl groups in amide binding. Additionally, a shift is seen in the wavenumber of the N–H bend of the amine from the chitosan spectrum to the UCM spectrum. This decrease from 1560 cm^{-1} to 1520 cm^{-1} signifies the conversion of a primary amine, in this case the amine functional groups of chitosan, to a secondary amine, characteristic of amide bonds (Coates, 2006). Higher wavenumbers elucidate another difference between the chitosan and UCM spectra. Typically, peaks around 3300 cm^{-1} can be correlated to the N–H stretch of amines. In primary amines, this is evidenced by the appearance of two bands, as opposed to only one band in secondary amines (Coates, 2006). This primary amine phenomenon was observed between chitosan, physical mixture and UCM spectra, at higher wavenumbers of 3000–3500 cm^{-1}, again indicating the participation of primary amine functional groups in amide bonding to form secondary amines.

3.2. Characterization of cinnamaldehyde microcapsules

Two important metrics for evaluating microcapsules are their particle sizes and zeta potentials. These results for UCM and CA-UCM emulsions are shown in Table S1. As expected, the inclusion of cinnamaldehyde and vegetable carrier oil in the complex increased the particle size significantly. This serves as evidence that the encapsulation of cinnamaldehyde has occurred. The amount of oil included will affect the particle size, which in turn, can impact emulsion stability (Walker & Grant, 1998). The carrier oil amount was determined by screening various polysaccharide to oil ratios and observing which amount yielded the best cinnamaldehyde retention. A ratio of polymer to cinnamaldehyde oil at 1:20 (w/w) was selected for the cinnamaldehyde formulation. Despite the amount of cinnamaldehyde oil incorporated was large, the particle size of CA-UCM is in nano range. Positive zeta potential values were observed for both UCM and CA-UCM. This is likely due to the protonation of some free functional groups of both chitosan and pectin at an acidic pH of 2. Not every polymer functional group will participate in cross-linking, hence free groups will have the ability to protonate.

With the confirmation of the formation of amide bonds and particle size characterizations, SEM images were further taken to understand the morphologies of our systems (Fig. 2). The morphology of CA-UCM sample is shown in Fig. 2A. CA-UCM showed smooth, spherical droplets, suggesting successful microcapsule formation (Fig. 2A). Fig. 2B shows the morphologies of the SD-CA-UCM, where it exhibits clearly defined spherical morphologies. The average particle sizes varied between the UCM and CA-UCM, with the latter exhibiting larger sizes in correspondence with particle size measurements (Table S1). The SD-CA-UCM exhibit the largest particle size, due to the additional layer of maltodextrin used to assist powder formation. The spray-dried particles were also very smooth and close to an ideal spherical morphology, which suggests successful and practical encapsulation (Rajabi et al., 2015).

3.3. Thermogravimetric analysis

TGA was conducted on the SD-CA-UCM powder and its constituents to further characterize the stability of the cinnamaldehyde microcapsules (Fig. 3). When heating, pure cinnamaldehyde showed bulk degradation around 146 °C (Fig. 3A). The UCM degraded at around 228 °C and higher (Fig. 3B). If there are no differences in heat stability between the pure cinnamaldehyde and SD-CA-UCM, one might expect to see a large peak around that temperature of 146 °C (Fig. 3C). Conversely, cinnamaldehyde peak did not appear at 146 °C in SD-CA-UCM sample, explaining that cinnamaldehyde is not entirely lost at a single temperature, rather it is gradually lost at higher temperatures, possibly with other microcapsule polymers. GC-analysis results, as discussed in the following section (section 3.4), show that considerable amount of cinnamaldehyde was presented in SD-CA-UCM. With these indications, TGA data shown in Fig. 3C serves to further substantiate the increased heat stability of the SD-CA-UCM. The first peak corresponding to sample weight loss of the encapsulated cinnamaldehyde is not detected until 210 °C (Fig. 3C). Additional peaks are seen in this spectrum at 311 °C and 364 °C. The cinnamaldehyde may be degrading at 210 °C or even in conjunction with other microcapsule components at higher temperatures. However, GC results indicate lasting encapsulated cinnamaldehyde retention up to around 250 °C (Fig. 4). In addition, the peaks of the SD-CA-UCM past 146 °C demonstrate that the encapsulation of cinnamaldehyde does indeed impart heat stability to the flavor. Heat must first penetrate or degrade the capsule wall materials before reaching the internal core to initiate cinnamaldehyde loss. This requires higher temperatures or longer times to evaporate the encapsulated cinnamaldehyde versus the free, pure cinnamaldehyde.

3.4. Gas chromatography analysis

After confirmation of microcapsule formation, GC analysis was used to determine cinnamaldehyde retention in the form of powder before and after heating. This experiment also served to confirm successful encapsulation of the cinnamaldehyde and determine the encapsulation efficiency. Spray-drying was conducted in order to produce a dry powder suitable for baking applications. For comparison, pure cinnamaldehyde and an NCM, were also analyzed.

Samples (SD-CA-UCM, NCM, pure cinnamaldehyde) were left at room temperature (25 °C) or heated at either 150, 200, or 250 °C. The subsequent objective was to determine the cinnamaldehyde remaining in the microcapsules that was not lost during heating (Fig. 4). Chromatograms showed that cinnamaldehyde was the only significant peak to elute besides the solvent (Fig. S1).

Cinnamaldehyde encapsulation efficiency of the samples was measured before heat treatment (25 °C) (Table 1). The cinnamaldehyde microcapsule emulsion exhibited high cinnamaldehyde retention, which suggests low loss occurred during sample preparation and processing, as cinnamaldehyde's vapor pressure and volatility are low. Concerning the spray-dried powder samples, the process of spray-drying induces unavoidable heating of the encapsulated cinnamaldehyde (Jafari, Assadpoor, He, & Bhandari, 2008). GC analysis of samples after spray-drying showed a loss of 50.2% of the original formulated cinnamaldehyde. This represents a loss of about half of the flavor

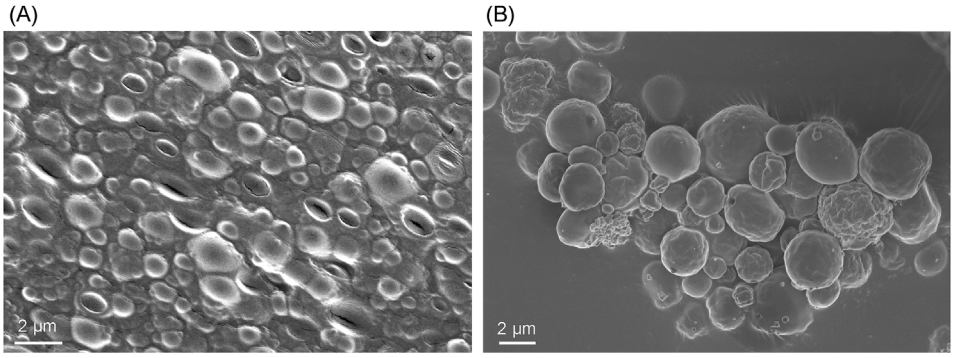

Fig. 2. SEM images of microcapsules corroborating capsule formation and morphology: (A) CA-UCM and (B) SD-CA-UCM.

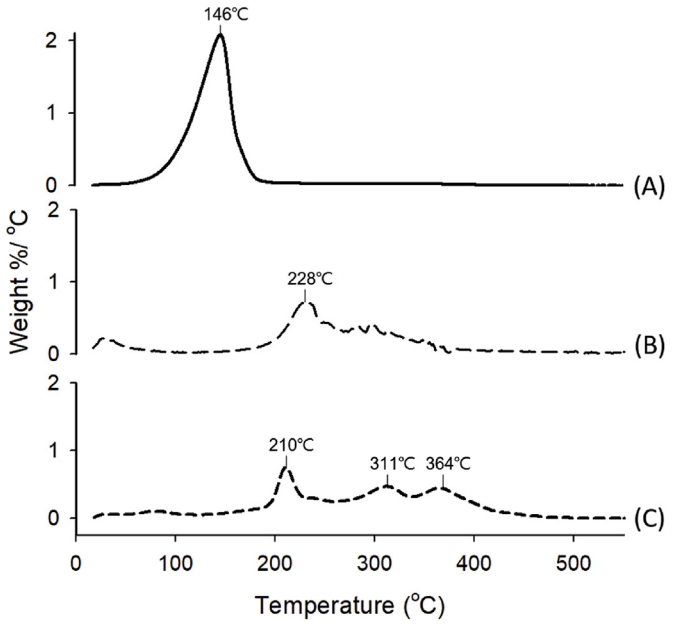

Fig. 3. First derivative TGA curves of (A) pure Cinnamaldehyde, (B) UCM, and (C) SD-CA-UCM.

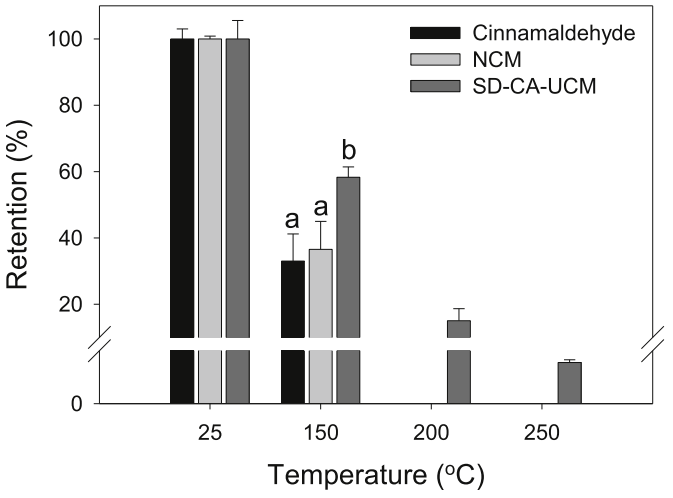

Fig. 4. GC derived cinnamaldehyde retention of SD-CA-UCM powder. Cinnamaldehyde and the NCM retentions are shown for comparison. Data points represented by different letters are significantly different ($P < 0.05$).

Table 1
Cinnamaldehyde retention (encapsulation efficiency) at 25 °C for cinnamaldehyde, NCM, CA-UCM, and SD-CA-UCM samples.

Formulation	Encapsulation efficiency (%)
Cinnamaldehyde	94.1 ± 3.0[a]
NCM	91.6 ± 0.8[a]
CA-UCM	92.7 ± 4.8[a]
SD-CA-UCM	49.8 ± 5.5[b]

Results were expressed as mean ± standard deviations. Data represented by different letters are significantly different ($P < 0.05$) by *t*-test.

during the spray-drying process. As cinnamaldehyde has a relatively low vapor pressure, the vast majority of the flavor loss is attributed to the spray-drying process and not spontaneous evaporation at room temperature. This spray-drying retention information was factored into the final cinnamaldehyde heating analysis. Sample cinnamaldehyde retentions for the furnace heating process were accordingly adjusted to represent the amount of cinnamaldehyde retained after spray-drying. A retention of 100% is thus equivalent to the total amount of cinnamaldehyde observed after spray-drying. This allowed for a direct comparison to be made between all samples.

Cinnamaldehyde evaporation, as observed by GC analysis and TGA, seems to occur between 100 and 150 °C (Figs. 3 and 4). Therefore, the retention differences between samples are not particularly of any concern at the lower heated temperatures below 100 °C where cinnamaldehyde is being lost at low rates. In addition, for baking applications, the range of 150–250 °C is of more interest. At 150 °C and 200 °C, the SD-CA-UCM had higher cinnamaldehyde retention than both the pure cinnamaldehyde and NCM (Fig. 4). This indicates that SD-CA-UCM powder exhibit increased heat stability to a greater extent. Concerning these samples at 200 °C, SD-CA-UCM powder exhibited 15% more retention than NCM and cinnamaldehyde alone, which exhibited complete flavor loss (0% retention). At 250 °C, the SD-CA-UCM powder retained a small but significantly different proportion of the cinnamaldehyde (1.5%) whereas the pure cinnamaldehyde and NCM retained no cinnamaldehyde (0%). The capsule wall materials evidently provide a source of heat resistance to the encapsulated cinnamon flavor, allowing for greater retention rates than the pure, unencapsulated cinnamaldehyde. Chitosan and pectin specifically have been shown to improve thermal properties of nanoparticles and films (Antoniou, Liu, Majeed, & Zhong, 2015; Lorevice, Otoni, de Moura, & Mattoso, 2016). This may be attributed to reduced polymer hydration due to crosslinking between the carbohydrates. The crosslinking can subsequently improve capsule permeability and heat transfer properties.

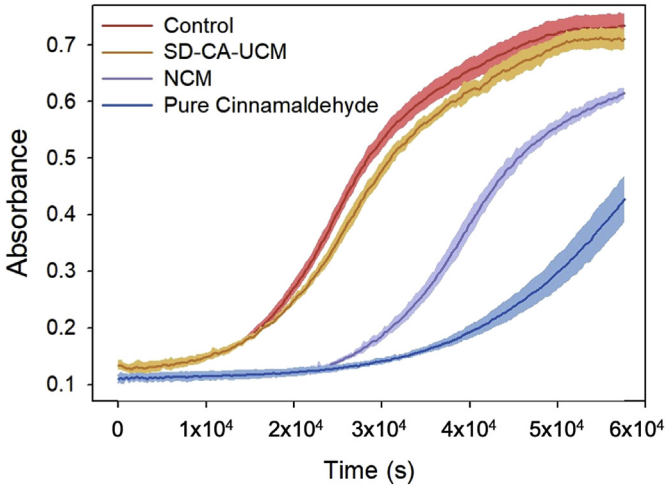

Fig. 5. Yeast growth curves of untreated control yeast, SD-CA-UCM treated yeast, NCM treated yeast, and pure cinnamaldehyde treated.

3.4. Yeast growth studies

In addition to demonstrating increased cinnamaldehyde heat stability from encapsulation, yeast growth studies were conducted to examine the effect encapsulation had on cinnamaldehyde's antifungal properties. *S. cerevisiae* was allowed to grow in wells after treatment with either pure cinnamaldehyde, NCM, or SD-CA-UCM (Fig. 5). A yeast control group with no treatment exhibited the greatest amount of growth. Cinnamaldehyde did inhibit *S. cerevisiae* growth, which has been seen in the literature (Sanla-Ead et al., 2012). Between the cinnamaldehyde treatments, the yeast growth was greater when subjected to SD-CA-UCM than NCM and pure cinnamaldehyde ($P < 0.05$). This indicates that cross-linking of the microcapsule does protect the cinnamaldehyde better than the non-crosslinked microcapsules. Together, encapsulation does in fact inhibit the antifungal capacity of the molecule. We believe the physical barriers provided by the microcapsule walls prevent the cinnamaldehyde flavor from reaching the yeast, which limits interactions and allows the yeast to grow at a more optimal rate than when subjected to pure cinnamaldehyde. This has implications for baking, as proper growth of yeast in dough allows for increased rates of fermentation and subsequent gas production, yielding better volume and texture (Pattison & von Holy, 2001). Therefore, utilizing ultrasonically-encapsulated cinnamon flavor should produce better products at various sensory levels.

4. Conclusions

This study proposes a formulation for encapsulating cinnamaldehyde utilizing ultrasonication. Chitosan and pectin are polymers that were found to be suitable for forming microcapsules capable of incorporating the hydrophobic cinnamon flavor in an aqueous continuous phase. Microcapsule synthesis was verified via FTIR analysis, which indicated the formation of amide bonds. Capsule morphology was also observed under SEM, in which spherical particles were visually discerned. GC was utilized to determine the encapsulation efficiency and cinnamaldehyde retention in samples heated at temperatures of 15015 16 –250 °C. Compared to pure cinnamaldehyde and the unsonicated mixture of the formulation, the cinnamaldehyde microcapsules displayed significantly higher flavor retention at baking temperatures (150–250 °C). This indicated that encapsulation imparted greater heat stability to the encapsulated flavor. Thermogravimetric analysis also corroborated this fact. When comparing heating curves, the cinnamaldehyde microcapsule formulation depicted lower cinnamaldehyde loss at a higher temperature than that of pure cinnamaldehyde, representing improved heat stability. Additionally, yeast growth tests were conducted, and *S. cerevisiae* showed superior growth when subjected to cinnamaldehyde microcapsule powder versus pure cinnamaldehyde of the same concentration. This signifies the reduction of the antifungal properties of cinnamaldehyde due to encapsulation. In conjunction, the improved heat stability and reduced yeast interaction demonstrates that this particular formulation and method of encapsulating cinnamon flavor can potentially yield baked products of higher flavor and texture quality than unencapsulated cinnamon flavor. In addition, less amount of encapsulated flavor would be required to achieve the same organoleptic qualities of normal cinnamon, potentially reducing costs for food manufacturers.

Declaration of interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2019.105316.

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