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Effect of layer-by-layer polyelectrolyte method on encapsulation of vanillin

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ABSTRACT

The objective of this work was to microencapsulate vanillin by multilayer emulsion followed by spray drying, aiming to protect it and control its release. An electrostatic layer-by-layer deposition method was used to create the multilayered interfacial membranes around microcapsules with different compositions: (i) one-layer (soy protein isolate); (ii) two-layer (soy protein isolate – OSA starch); (iii) three-layer (soy protein isolate – OSA starch – Chitosan). The morphology of the microcapsules was analyzed by scanning electronic microscopy. The hygroscopicity, solubility, particle size, encapsulation efficiency, Fourier transform infrared spectroscopy and release into water (37 °C and 80 °C) were also examined. FTIR confirmed the interaction between the wall materials. All microcapsules were not very water-soluble or hygroscopic while three-layer microcapsules compared to one and two layer microcapsules have lower moisture content and predominantly shriveled surfaces. The results indicated it was possible to encapsulate vanillin with the techniques employed and that these protected the vanillin even at 80 °C. The reduced solubility and low release rates indicated the enormous potential of the vehicle developed in controlling the release of the vanillin into the food and pharmaceuticals.

1. Introduction

Vanillin is mainly used as an additive in food, beverages and pharmaceuticals. Vanillin is extracted from the seed pods of *Vanilla planifolia*; the addition of flavoring has multifunctional effects such as antimutagenic, antiangiogenetic, anticolitis, antisickling and antianalgesic effects [1,2]. In addition, vanillin is able to increase the concentration of neurotransmitter serotonin in the brain, which increases brain serotonin concentration, which leads to a reduced craving to consume food [2–4]. Vanillin's functionality and stability can be improved by its encapsulation into a suitable matrix. In recent years, the multi-layer technique as a method for the stability of the microcapsules was investigated. This technique involves the formation of multiple layers of biopolymers at the interface using a layer-by-layer (LBL) electrostatic deposition technique [5]. In this study, we examined the preparation and properties of microcapsules containing vanillin surrounded by interfacial membranes consisting of soy protein isolate (SPI), OSA starch and chitosan. These biopolymers were chosen because they are abundant natural biopolymers with opposite charges. SPI is positively charged at pHs below its isoelectric point (pI ≈ 4.6) and negatively charged at pH values above this value [6–8]. The OSA starch contains a negatively charged carboxylic acid part and could be absorbed to positively charged interface. In addition, OSA-starch can act as a viscosity enhancer, but its thickening capacity is quite limited compared with the capacity of other macromolecules used as thickeners. However, the combination of emulsifying and thickening properties of OSA starch can give a cost reduction of the final product because a lower concentration of stabilizing agents is needed [9–11]. Chitosan, a linear copolymer of glucosamine and N-acetyl glucosamine connected through β-(1-4) glucosidic linkage is a unique cationic polysaccharide and generally represented as a homopolymer. In addition, Chitosan is a very popular natural positively charged polysaccharide with functional properties and nutritional and physiological activities [12–16]. Spray drying is the most common procedure for microencapsulation in the food industry. This process is cost effective, flexible and produces particles of good quality [17,18]. Many researchers have used the spray drying process to encapsulate oils and flavors such as sunflower oil [19], avocado oil [20], coffee oil [21] and lycopene [22]. To our knowledge, no studies have been carried out on the using an SPI, OSA starch and chitosan to form three-layered interfacial membranes in microcapsules. This interesting issue deserves to be studied since it can represent a promising alternative for the food, ingredient and drug industries. Hence, the objective of the present work was to study the microencapsulation of vanillin by multi-layer technique,

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structurally evaluate the microcapsules obtained and examine their physicochemical properties and rate of release of the water.

2. Materials and methods

Soybean protein isolate (SPI) of food grade was purchased from Golhar Co (Mashhad, Iran). Chitosan (with a molecule weight of about 300 kDa and a 90% degree of deacetylation) was purchased from Bio basic Inc (Canada). National Starch and Chemicals GmbH, Germany supplied powdered OSA-starch (E1450). Sunflower oil was purchased from a local supermarket and used without further purification. Analytical grade vanillin, hydrochloric acid and sodium hydroxide were purchased from Sigma Chemical Company. Distilled and de-ionized water was used for the preparation of all solutions.

2.1. Solution preparation

The stock solution of SPI was prepared by dispersing SPI powder in deionized water and stirred for 5 min then the solution exposed to ultrasonic 500 W (Schaper model Unique USC 25 kHz) for 5 min at 50 °C and then centrifuged at 5000 *g* for 10 min [7]. As for the OSA starch stock solution, OSA starch powder was suspended in Na-acetate buffer (10 mM, pH 6). The solution placed in a boiling water bath under stirring for 10 min [10]. Medium molecular weight chitosan solution was prepared by dispersing weighted amount of the powdered material in to 10 mM Na-acetate (pH 4) [13]. These solutions were stored at room temperature for 24 h to ensure complete dissolution of these materials.

2.2. Emulsions preparation

A primary experiment was carried out to decide the optimum SPI, OSA starch and chitosan concentration needed to create the primary, secondary and tertiary emulsions. Primary emulsions were prepared by homogenizing 5 wt% sunflower oil with 95 wt% aqueous emulsifier solution (1% w/v SPI and 0.1%wt sodium azide) in high-speed blender (UltraTurrax T-25, IKA Instruments, Germany) followed by sonication for 2 min at a frequency of 20 kHz, amplitude of 60% (VCX 750, Sonics & Materials, Inc., USA). This emulsion was adjusted back to pH 3.5 using 1 M HCl. A secondary emulsion was prepared by mixing the primary emulsion with OSA-starch so the OSA starch concentration in the secondary emulsion was 0.8% w/v. The emulsion was sonicated for 1 min at frequency of 20 kHz, amplitude 60% to disrupt any floccules formed during the mixing. The secondary emulsions were adjusted back to pH 3.5 using 1 M HCl. Tertiary emulsion was formed by diluting the secondary emulsion with chitosan solution so the chitosan concentration in the tertiary emulsion was 0.5% w/v and then adjusted back to pH 3.5 using 1 M HCl. It should be noted that the oil phase fraction kept at 5% w/w in the secondary and tertiary emulsions by changing the ratios of emulsion, biopolymer and deionized water [23].

2.3. Viscosity

The apparent viscosities of samples were measured by a programmable rotational viscometer (LV ULTRA, Brookfield Engineering Laboratories, USA) at 25 °C using SC4-18 spindle and UL adaptor. The temperature of sample was maintained constant throughout the experiment by circulating water around the UL adaptor. In order to measure the apparent viscosity, continuous shear test was performed over the shear rate of 1–300 s^{-1}. Measurements were performed in triplicate and the data were averaged.

2.4. Spray dryer

Spray drying is a commercial process, which is widely used in large-scale production of encapsulated flavors and volatiles. The merits of the process have ensured its dominance, these include availability of equipment, low process cost, wide choice of carrier solids, good retention of volatiles, good stability of the finished product, and large-scale production in continuous mode [17]. The empirical models were generated from response surface methodology (RSM) to predict spray-drying condition considered in this research. Soy protein isolate and maltodextrin were used as wall material. Maltodextrin solutions at different concentration (5–15%wt), vanillin concentration (0.1–0.4%wt) and inlet temperature (180–200 °C) were the factors investigated with respect to moisture content, particle size and encapsulation efficiency. Response surface methodology was used to determine the optimum processing conditions that yield maximum encapsulation efficiency and minimum moisture content and particle size during drying of vanillin microencapsulate. The results revealed that microencapsulated powder obtaining at 184 °C with 8.5% maltodextrin concentration and 0.36% vanillin concentration was optimum among investigated samples in terms of its encapsulation efficiency, particle size and moisture content [24].

2.5. Moisture content

Moisture content of powder was determined gravimetrically by oven drying at 105 °C to constant weight.

2.6. Solubility

The solubility of the microcapsules were determined by a gravimetric method, which consisted of adding 0.5 g of the sample to an Erlenmeyer flask containing 50 mL of distilled water and homogenizing at 75 rpm for 30 min at room temperature. Then, the solution was centrifuged at 3000 *g* for 5 min and a 25 mL aliquot of the supernatant was transferred to a previously weighed Petri dish and maintained in an oven at 105 °C until complete evaporation of the water. The dishes were weighed and the solubility was calculated from the difference in weight [25].

2.7. Fourier transforms infrared spectroscopy (FT-IR)

The FTIR measurements were performed for structural analysis of micro particles. The dry samples were mixed with KBr and pressed into pellets. FT-IR spectra of samples were obtained from wave number 400–4000 cm^{-1} using a FT-IR spectrophotometer (Shimadzu 6650, Japan).

2.8. Hygroscopicity

A sample of about 1 g was placed in desiccators with a saturated solution of NaCl (relative humidity of 75.3%). After one week, the samples were weighted and the hygroscopicity was expressed as the quantity of adsorbed moisture per 100 g of sample (g/100 g) [26].

2.9. Encapsulation efficiency

The method described in Rodraguez et al. [27] to calculate encapsulation efficiency was adapted: about 0.1 g of the sample were dissolved in 10 mL of ethanol in a sealed vial. After mixing, the tubes remained at rest in the dark for about 2 h for decantation of the encapsulation material. Absorption was read in a spectrophotometer (Shimadzu UV-160 A) in the 231-wavelength nm and using a previously elaborated standard curve, it was possible to calculate

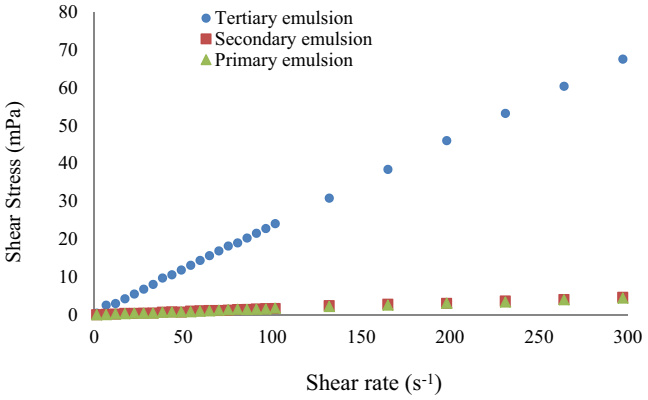

Fig. 1. Flow curves of emulsions.

the concentration of vanillin present in the microcapsules. Encapsulation efficiency was calculated as the quantity of vanillin present in the capsules compared to the vanillin initially used to produce them [27].

2.10. Particle size distribution

The particle size distribution was measured using a laser light diffraction instrument (SALD-2101, Shimadzu, Japan). A small powder sample was dispersed in 99.5% acetone and the particle distribution was monitored during five successive readings. The particle size was expressed as the mean volumetric size d_{43} (De Brouckere mean diameter), which is the mean diameter of a sphere with the same volume, and is generally used to characterize a particle.

2.11. Particle morphology

The particle was evaluated by scanning electron microscopy (SEM), and for such, the samples were mounted to the specimen holder with a double-sided adhesive tape and vacuum coated with gold. The observations were made using a scanning electron microscope (Leo 1450VP) and a voltage of 20 kV.

2.12. Release of vanillin from the microcapsules in hot water

The release was analyzed according to the methodology of Rocha-Selmi et al. [25]. Falcon tubes containing a suspension with 5% (mass basis) of capsules were placed in a water bath with shaking at temperatures of 37 (human body temperature) and 80 °C (to simulate heat treatment). Aliquots were removed after 0, 15, 30, 45, 60, 75 and 90 min, for quantification of the vanillin using the same methodology used to determine the encapsulation efficiency [25].

2.13. Statistical analysis

The data were analyzed statistically by the analysis of variance (ANOVA) and Turkeys' tests using the SPSS program (SPSS Statistical Software, Inc., Chicago, IL, USA). The results were considered statistically significant when $\alpha \leq 0.05$.

3. Results and discussion

3.1. Rheological behavior of emulsions

Fig. 1 shows the flow curves for the primary, secondary and tertiary emulsions. It was observed that all emulsions were showed Newtonian behavior. Similar behavior was observed in emulsions composed of avocado oil and maltodextrin–whey protein isolate [20] and in beverage emulsions composed of orange oil and seven types of gum Arabic [28]. It was also observed (Fig. 1), that tertiary emulsions showed Newtonian behavior, and chitosan increased the viscosity of a continuous phase; however, a significant ($p < 0.05$) difference in the viscosity was observed between tertiary and primary and secondary emulsions while the addition of OSA starch to primary emulsion had no effect on the viscosity of the secondary emulsion (Table 1).

Table 1
Viscosity of emulsions.

Emulsion	Primary	Secondary	Tertiary
Viscosity (mPa s)	$0.015^{a} \pm 0.0025$	$0.016^{a} \pm 0.0038$	$0.23^{b} \pm 0.03$

3.2. Fourier transformed infrared spectroscopy (FTIR)

FTIR spectroscopy was used to study the interaction between the layers. Fig. 2(A) shows the FTIR spectra of OSA starch, one layer and two layers microcapsules. The FTIR spectrum of OSA starch showed a characteristic absorption band at 3387 cm^{-1} and 2929 cm^{-1}, which could be attributed to the hydroxyl groups (O—H) and C—H stretching vibration of the glucose unit, respectively. The absorption at about 1650 cm^{-1} is due to residual bound water [29]. The addition of OSA starch to one-layer microcapsules caused a decrease in the wave number COO— (COO symmetric stretching vibrations) from 1454 to 1446 cm^{-1}. At the same time, the peak of hydroxyl shifted from 3395 to 3359 cm^{-1}. These changes are consistent with an increase as the hydrogen. The infrared spectra of chitosan, two and three-layer's microcapsules were presented in Fig. 2(B). The FTIR spectrum of chitosan showed characteristic absorption bands at 3433 cm^{-1} (O—H stretching which overlaps the NH stretching in the same region), 2878 cm^{-1} (C—H stretching vibrations), 1648 cm^{-1} (C=O stretching, amide I) [30]. The addition of chitosan to two-layer microcapsules caused a change in wave number COO— from 1654 and 1446 cm^{-1} to 1647 and 1451 cm^{-1}, respectively.

3.3. Particle size and morphology

Particle size distributions of the microcapsules prepared with different formulation are shown in Fig. 3. All microcapsules showed a unimodal distribution, indicating good powder homogeneity, with one peak representing a predominant size. The powders exhibited a very large size range, which is typical of particles produced by spray drying [17]. The three-layer microcapsules showed greater size, probably due to their higher emulsion viscosity (Table 2). According to Hogan et al., the mean microcapsules size varies directly with the emulsion viscosity at constant atomizer speed. Increase the viscosity of the emulsion was causing the formation of larger microcapsules and thus, the larger the microcapsules obtained by spray drying [31]. The microcapsules produced from tertiary emulsion showed predominantly shriveled surfaces (Fig. 4A). It is shown that a more viscous feed will produce larger droplet sizes with irregular shapes due to the slow process of film formation around the droplets. The damage of the particles surfaced integrity (fissures, shrinkage) and increase of the surface area, maybe contributed to the increase of un-encapsulated vanillin. However, the analysis of the surface morphology of the microcapsules by SEM (Fig. 4B and C) revealed smoother surface and less roughness of the one-layer and two-layer microcapsules. These results indicated that OSA-starch has great film-forming capacity, which can positively influence the microencapsulation process. On

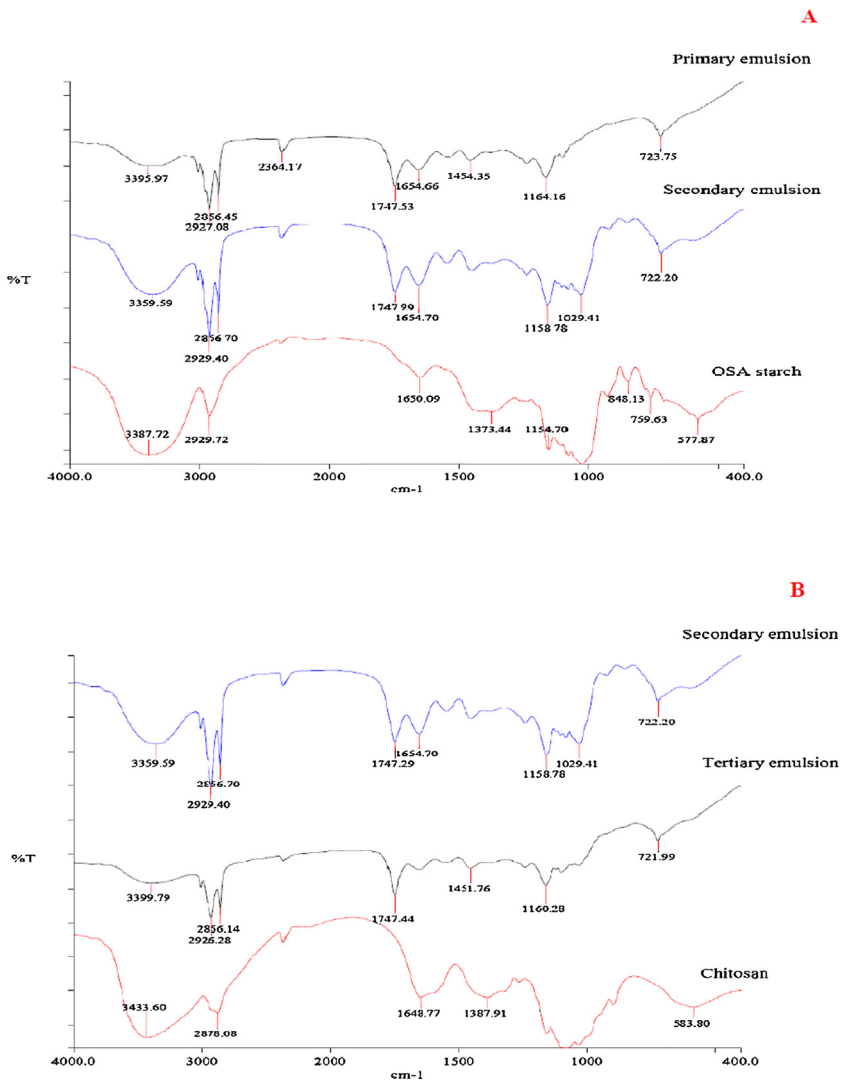

Fig. 2. FT-IR spectra of (A) OSA starch, one layer and two layers and (B) chitosan, two and three-layers microcapsules.

Table 2
D (4, 3) and D 90 values of microcapsules.

One-layer		Two-layer		Three-layer	
D (4, 3) (μm)	D 90% (μ)	D (4, 3) (μm)	D 90% (μm)	D (4, 3) (μm)	D 90% (μm)
7.19 ± 1.57	20.34 ± 1.38	7.48 ± 1.95	22.04 ± 1.64	13.63 ± 1.78	36.46 ± 2.28

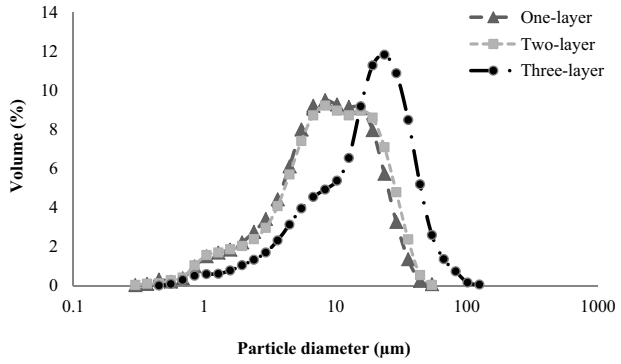

Fig. 3. Size distribution of microcapsules.

the other hand, the samples produced from secondary emulsion had particles with smooth surfaces, which imply better flow properties [17,31]. The smooth surface can be a result of the faster film formation, which also explains the better encapsulation efficiency in these samples.

3.4. Physicochemical characterization of the microcapsules

Table 3 shows the values obtained for moisture content, solubility, hygroscopicity and encapsulation efficiency of the powders. The moisture content of the microcapsules varied from 2.32 to 3.64 (%) being within the range expected for spray-dried products [25]. The addition of OSA starch to primary emulsion had no significant effect on the moisture content of microcapsules while incorporation of chitosan to secondary emulsion and formation of tertiary emulsion leads to reduction of moisture content in the microcapsules. This is probably related to the chitosan increases viscosity

Table 3
Measurement of moisture content, hygroscopicity, solubility and encapsulation efficiency of the various microcapsule formulations.

Treatments	Moisture content (%)	Solubility (%)	Hygroscopicity (g/100 g of powder)	Encapsulation efficiency (%)
One layer	3.61 ± 0.063[a]	11.415 ± 2.548[a]	11.3 ± 0.02[a]	51.91 ± 2.53[a]
Two layer	3.09 ± 0.056[a]	12.275 ± 0.305[a]	8.7 ± 0.031[a]	44.59 ± 3.329[a]
Three layer	2.32 ± 0.3[b]	10.163 ± 0.69[a]	10.2 ± 0.02[a]	27.49 ± 2.67[b]

There were no significant differences among the samples with the same letters in the same column ($p < 0.05$).

and increase viscosity reduced the amount of water available for evaporation, the result was a decrease in moisture content [17].

For the solubility parameters, there was no significant difference between values obtained for microcapsules (Table 3). Lower values for solubility of microcapsules were desirable in the encapsulation of flavors because conferred the possibility of controlled release to the medium and alterations in ionic strength [26]. The values from this study were similar to those obtained by Talita-Comunian et al. which obtained solubility values between 8.14 and 16.5% for ascorbic acid that was microencapsulated by complex coacervation using gelatin and gum Arabic [26].

The hygroscopicity of the microcapsules varied over the range of 8.7–11.3 g water absorbed/100 g sample for three formulations of study microcapsules, with no significant differences between (Table 3). The values obtained in the present work were lower than those obtained by Nori et al. for propolis microcapsules obtained by complex coacervation, using soy protein isolate and low methoxyl pectin as the wall materials [32] and Rocha-Selmi et al. for aspartame microcapsules obtained by gelatin and gum arabic as the encapsulating agents [25]. Therefore, the results obtained for this work were better than the results found in the literatures because reduction the value of hygroscopicity makes packaging and handling of the material easier.

For the encapsulation efficiency, there were significant differences between three layer microcapsules with two and one layer microcapsules (Table 3). These results indicated that the microencapsulation efficiency was higher in the spray-dried primary and secondary emulsion compared to the spray-dried tertiary emulsion. This was probably due to increase in viscosity, as the result of chitosan incorporation. Increase in viscosity reduces retention of vanillin due to slow formation of discrete droplets during atomization, difficulties in droplet formation and the larger exposure during atomization [17,18]. It shows that increase the viscosity of the tertiary emulsion produced larger size with irregular shapes due to in difficulties in droplet formation at higher viscosities. Finney et al. explained that while large particles have a reduced surface area in a volume ratio, which would result in better core retention, there would be also a long time for film formation around the large droplets during the process resulting in the greatest loss of volatile substances [18]. Another reason for the lower encapsulates efficiency observed for three-layer particles could be related to the surface morphology. Fig. 4 shows three-layer microcapsules have the dented surface. Formation of dented surface of three-layer microcapsules attributed to the shrinkage of particles during drying process that result in an increase of their surface area, may contribute to the increase of the un-encapsulated vanillin. Rocha et al. observed encapsulation efficiency values between 21 and 29% for microcapsules of lycopene obtained by modified starch (Capsul) as the encapsulating agents [22]. Mendanha et al. observed encapsulation efficiency values between 78 and 91% for microcapsules

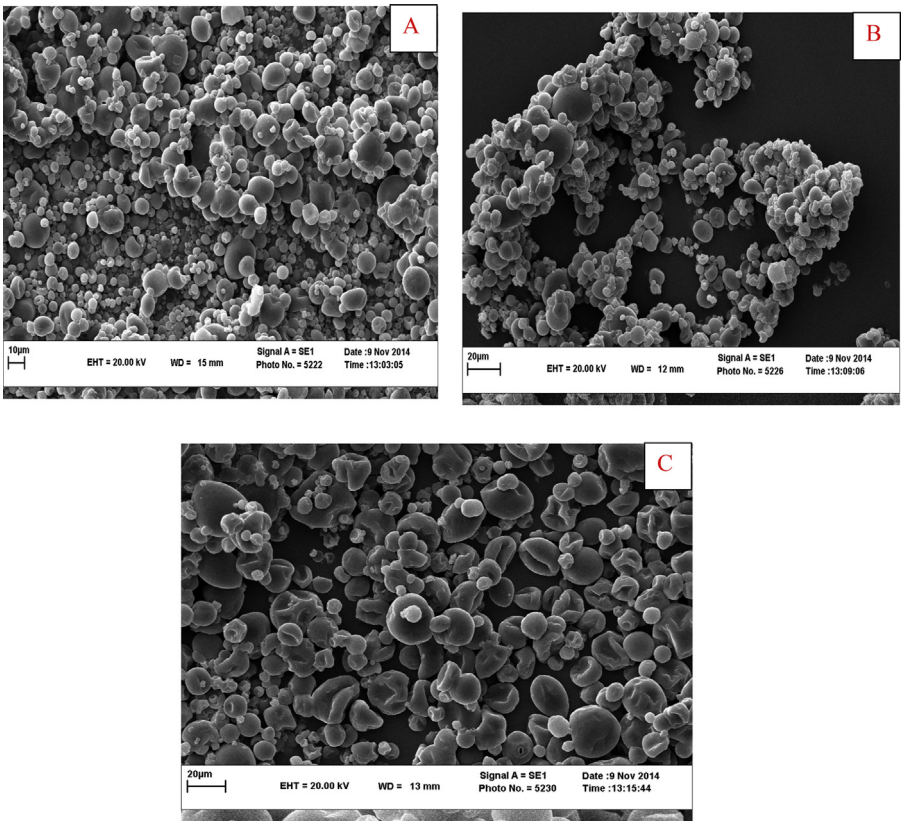

Fig. 4. Morphology of (A) One-layer, (B) two-layer and (C) three-layer microcapsules.

Table 4
Kinetic parameters of microcapsules according to Korsemey-Peppas model.

Temperature (°C)	One-layer			Two-layer			Three-layer		
	n	MDT (h)	R^2	n	MDT (h)	R^2	n	MDT (h)	R^2
37	0.235	1.078	0.88	0.373	1.24	0.86	0.251	1.775	0.93
80	0.316	0.862	0.96	0.441	0.982	0.97	0.258	1.722	0.96

of casein hydrolysate obtained by double emulsion followed by complex coacervation using soy protein isolate and pectin as the encapsulating agents [8].

3.5. Release of vanillin from the microcapsules into water at 37 and 80 °C

To find out the mechanism of vanillin release, first 60% vanillin release data was fitted in Korsmeyer-Peppas model (Eq. (1)) [33].

$$\frac{Q_t}{Q_e} = Kt^n \quad (1)$$

where Q_t/Q_e is the fraction of the drug released at time t, K is a constant corresponding to the structural and geometric characteristics of the device and n is the release exponent that is indicative of the mechanism of the vanillin release. Although release rate constant K is the measure of vanillin release, but it should not be used to characterize vanillin release due to the differences in vanillin release kinetics. So the mean dissolution time (MDT) used for comparison of release profiles of different formulations because it shows the vanillin release-retarding efficacy of the polymers used in a formulation [12,34]. A higher value of MDT indicates a higher flavor retarding ability of the polymer and vice versa. Mean Dissolution Time (MDT) was calculated from the following equation (Eq. (2)), value of K and n were calculated according Korsmeyer-Peppas equation [12,33].

$$\text{MDT} = \left[\frac{n}{(n+1)}\right].K^{-1/n} \quad (2)$$

The Korsmeyer-Peppas model best explained the vanillin release as its value of R^2 was greater than 0.86 for all formulations. The value of "n" from 0.235 to 0.441 indicates that vanillin release mechanism from all microcapsules were diffusion controlled [12,34]. MDT values of one-layer, two-layer and three-layer microcapsules were found to be 1.078, 1.24 and 1.775 h at 37 °C, which showed that three-layer microcapsules had more release retarding efficacy (Table 4). It is likely that the chitosan layer hampered the release of vanillin, further; Particle size distribution (D 90%) of three-layer microcapsules became higher than one-layer and two-layer microcapsules (Table 2), which the decrease in surface area with increasing Particle size distribution (D 90%) would be predicted to delay volatiles release. The decreasing flavor volatiles release with increasing particle size distribution (D 90%) could be related to increased matrix retention through structural, rheological and textural differences [35]. It could be seen that an increase in temperature lead to reduce in the MDT of one-layer and two-layer microcapsules, resulting in a facilitating volatiles release. In addition, analyzing the two tested temperatures showed the three-layer microcapsules were relatively resistant to high temperature (80 °C) and increasing the temperature did not lead to decrease in the MDT of the three-layer microcapsule (Table 4).

4. Conclusion

According to the proposed objectives and the obtained results, this study showed that the use of multilayer technique prior to spray drying of vanillin microcapsules made it possible to protect it and control its release. All microcapsules were not very water-soluble or hygroscopic while three-layer microcapsules compared to one and two layer microcapsules had lower moisture content and predominantly shriveled surfaces. In addition, although three-layer microcapsules compared to one and two-layer microcapsules had a less encapsulation efficiency, but three-layer microcapsules had more release-retarding efficacy.

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