Investigation of multilayer microcapsules based on electrostatic adsorption of soy protein isolated fibrils and high methoxyl pectin containing diacetyl

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Introduction: Microencapsulation has become an important technique in the food industry. One of the methods of producing microcapsules is to use layer-by-layer adsorption, in which oppositely charged polyelectrolytes are adsorbed consecutively onto a colloidal template. Creating multilayer films based on electrostatic interactions between oppositely charged components was introduced in 1991 by Decher et al. Layer-by-layer (LbL) polyelectrolyte deposition has become a popular technique for preparing polyelectrolyte capsules because of its ability to create highly tailored capsule shells through a simple, inexpensive and easily controllable adsorption process. It has been applied to produce capsules of various sizes, ranging from the nanometer to micrometer scale, with well-defined barrier properties. In this technique, assembly is driven by the electrostatic attraction of oppositely charged materials to form polyelectrolyte shells. The structure of the polyanion layer is determined mainly by the electrostatic interactions between the polyanions used. The mechanical strength and permeability of the capsules can be controlled by varying the number of layers or by changing the characteristics of the encapsulating materials. The purpose of this study was to produce microcapsules using supramolecular assemblies consisting of common food ingredients such as soy protein isolate (SPI) and high methoxyl (HM) pectin. Moreover, some features of the developed microcapsulation were studied.

Materials and methods: SPI fibrils were prepared based on the method developed by Akkerman et al. (2008) and its morphology was studied using transmission electron microscopy (TEM) and atomic force microscopy (AFM). 0.5% (w/w) SPI fibril and pectin solutions were prepared by mixing at pH 3.5 were left stirring overnight. The LbL process for the production of microcapsules with protein fibril-reinforced nanocomposite shells has been described in Humblet-Hua et al., 2012. It starts with the production of A 2% w/w emulsion of (0.05 gr diacetyl in 1.95 gr sunflower oil) in fibril SPI solution is produced using a homogenizer with a rotor-stator dispersion tool using a setting of 13500 rpm for 90 S. Because the proteins are below their isoelectric point, the emulsion droplets have a positive charge. To avoid interactions between the nonadsorbed SPI and the biopolymer of the next layer, the droplets are separated from the serum by means of centrifugation. After the isolation, the droplets are dispersed into a solution of HMP. The HMP is negatively charged at the chosen pH of 3.5. The bilayered droplets can be isolated and dispersed in a fibril solution to deposit a third layer of a positively charged mixture of SPI fibrils. Subsequently, additional layers of HMP and SPI fibrils can be deposited by repeating the same procedures. Some features of the microcapsulation, including size, zeta potential, and morphology and release kinetics were studied.

Results & discussion: TEM and AFM micrographs showed that SPI fibrils obtained had a contour length of a few hundred nanometers, thickness of between 1 and 10 nm and its structure is highly branched. One of the most common problems reported in previous studies using the LbL technique to produce multilayer particles, is the tendency for flocculation. In the present system, this problem was not observed. The size distribution of isolated emulsion droplets (templates) did not change significantly from 1-layer droplets to 5-layer droplets. In other words, the emulsion droplets were stable against flocculation after applying more layers of polyelectrolytes. The Sauter mean diameters D (3, 2) of these droplets fluctuated between 5 and 7 µm and slightly increased as the number of layers increased; noting that the emulsion droplets were poly-dispersed. Another possible problem that may occur using the LbL technique is the complex formation between non-adsorbed protein and the pectin molecules. These complexes with a typical diameter smaller than 1 nm were not detected here. Result showed that the zeta potential distribution of emulsion droplets reverses from about plus (+) 30 mV (odd number of layers with SPI fibrils as outer layers) to about negative (-) 20 mV (even number of

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layers with HMP as outer layers) confirming the layer-by-layer adsorption based on electrostatic attraction. Comparing SEM of microcapsules with various numbers of layers, an improvement in shell strength can be seen. Indentation is observed on 1-layer microcapsules showing that there are defects on the shell. They could be formed during the drying process or they are shell defects due to incomplete coverage of materials, meaning more layers are needed to fully cover the microcapsule shell. These defects are seen less on 5-layer microcapsules. These observations indicate that the more layers the more consistent the shells and the more resistant. It is against the physical drying process. Results showed that the time of the maximum in release shifts to higher values as the number of layers of the capsules increased. We clearly see that increasing the number of layers in the shell of the capsules leads to a delay of the release of diacetyl and maximum release time as a function of the number of layers is increasing steadily which show the release can be delayed even more by adding additional layers. These results prove that the release properties of the multilayer capsules can be tuned by controlling the number of layers in the shell of the capsules. The modeling results of four different kinetic models are indicated that the Rigter–Peppas was an appropriate model for diacetyl release prediction from multilayer microcapsulation. It could be attributed that the release mechanism is mostly governed by the Swelling–Fickian mechanism.

**Conclusion:** In this study, the microcapsules were produced using the LbL technique and food-grade SPI fibrils and HMP. The microcapsules had a poly-disperse size distribution. No flocculation of microcapsules during applying of additional layers was observed. It was found that increasing the number of layers, decreases the release rate of diacetyl. The diacetyl release data were kinetically evaluated by zero-order, first-order, Higuchi, and Rigter–Peppas models and the results showed that the release phenomena is mostly governed by the Fickian mechanism. Since the materials are food-grade, the applications of these microcapsules can include food products or pharmaceutical purposes.

**Keywords:** Multilayer microcapsules, Controlled release, Soy protein isolated fibril, Pectin, Diacetyl