P-050	**Effects of heat treatment on the properties of alginate-chitosan hybrid membranes of lipophilic liquid core microcapsules.**

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INTRODUCTION AND OBJECTIVES

Fats and lipids are an essential part of the food industry due to their contribution to the sensory, nutritional and functional properties of the food products. In addition, recent studies emphasize potential health benefits of some lipophilic materials such as reduction in the occurence of cardiovascular diseases via consumption of polyunsaturated fatty acids (PUFA) (Mozaffarian D. et al. 2010).

Therefore there is a growing interest in integrating lipophilic functional groups into novel food products. However, lipophilic materials are subject to many processing losses such as oxidation and evaporation (Kanner 1992).

To prevent such problems and prolong the beneficial effects of these lipophilic groups, encapsulation technology can be utilized. Dripping is a safe, efficient, economical encapsulation method for lipophilic materials which can be carried out in mild conditions. The aim of this work is to assess the effects of heat treatment on the mechanical properties of alginate-chitosan hybrid membranes of lipophilic liquid core microcapsules produced by dripping method combined with a chitosan coating step.

MATERIALS AND METHODS

Algogel 3001 (M/G = 0.64) was obtained from Cargill (France). $CaCl_2 \cdot 2H_2O$ salt was obtained from Panreac Quimic (Spain). Chitosan (Chitosan from shrimp shells) was obtained from Sigma Aldrich (France). Eucalyptus oil used in the study was obtained from Cooper Chemicals. Commercial grade sunflower oil was used and it was obtained from local markets. All other chemicals and surfactants used in the study were of analytical grade.

A custom made *8-nozzle-dripping-device* was used in the experiments to produce the microcapsules with dripping tips of 0.38 mm inner diameter. An Easy-Load II Peristaltic Pump (Cole-Parmer Instrument) was utilized for pumping the oil emulsion through the 8 nozzle dripping device into the alginate bath.

Encapsulation of Lipophilic Material in Calcium-Alginate Membrane
A W/O emulsion was prepared with 36 mL of 120 g/L $CaCl_2 \cdot 2H_2O$ as water phase and 120 mL oil mixture consisting of 80 mL sunflower oil and 40 mL of eucalyptus oil. A surfactant mixture of 1.2 mL was used (43 % Span 85 and 57 % Tween 85 by volume). 15 g/L Algogel 3001 solution and 10 g/L chitosan solution was prepared in 1 % w/v glacial acetic acid solution.

The oil emulsion was pumped into the alginate solution, stirred at a rate of 340 rpm, at a rate of 8-10 mL/min through the 8 nozzle dripping device at a dripping height of 10 cm for 1 minute. The capsules were kept in the alginate solution for 1 hour to allow for complete formation of calcium alginate layer.

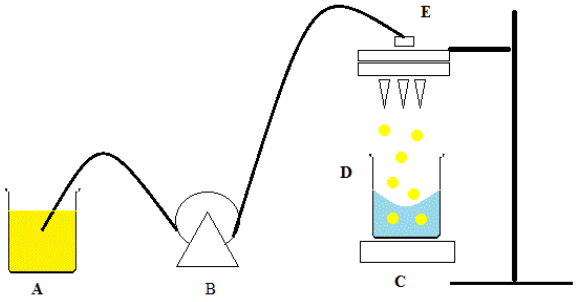

Figure 1 : Schematic representation of dripping method

Coating with Chitosan
Capsules produced at the dripping step are screened and washed with physiological NaCl solution and are then transferred into the continuosly stirred chitosan solution for 1 hour. After the coating step is complete, the capsules are weighed and divided into 3 groups in equal mass for heat treatment. First group of capsules (Method A) were put into water bath at 70 ^{o}C for 10 minutes with constant agitation. The capsules are then screened and washed with physiological NaCl and then kept at 4 ^{o}C. Method B and Method C are the same with Method A except the heat treatment temperatures are 50 ^{o}C and 30 ^{o}C respectively.

Capsule Shell Thickness Measurement
3 samples of each capsule production method were taken and their shell thickness were measured by Skyscan 1174 tomography device. Images were taken every 2 degrees and 2 repeat images were taken.

DMA Analysis
Capsules produced through Method A,B and C were dried in a fluidized bed dryer at 25 ^{o}C and 8% relative humidity for 1 hour. The membrane strenght of the capsules were analyzed with DMA Q800 (TA

Instruments S.A.R.L., Paris, France). 10 samples of each method were analyzed at 5% strain / min and 0.05 N preload.

Core Leakage Analysis

To facilitate higher amounts of core leakage, dripping was done through 4 mm inner diameter tips. The resulting, large capsules were treated in the same way as method A, B and C respectively. The capsules were then dried in a fluidized bed dryer at 25 °C and 8% relative humidity for 1 hour. The dried capsules were placed on petri dishes and put into an owen maintained at 40 °C. The capsules were taken out of owen, transferred to another beaker. The petri dishes were washed with ethanol and wiped with a tissue paper to remove the leaked oil. The capsules were then weighed at 1,2,4,8,24,48,72 and 96th hour and data was collected.

RESULTS AND DISCUSSION

Shell Thickness Measurement

The shell thickness measurements obtained through tomography are as follows:

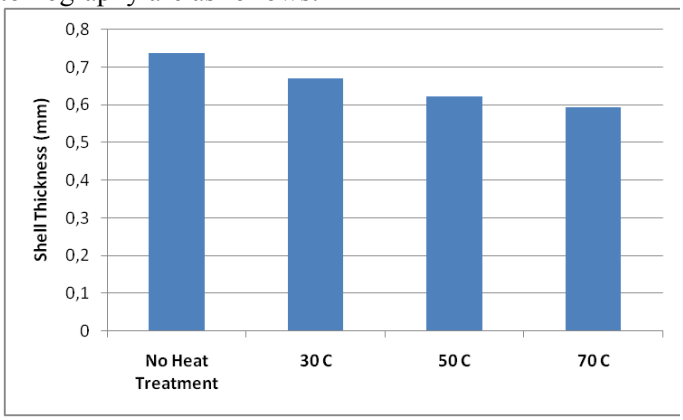

Figure 2 : Shell thickness of capsules with respect to heat treatment temperature

Alginate gels are relatively thermo stable, however chitosan has thermal shrinking property (Hsieh et al. 2006). As seen on the figure, as the temperature level of the heat treatment increases the chitosan coated on the alginate surface shrinks and forms a thinner layer.

DMA Analysis

As it can be observed from the figure below, the mechanical strength of the dried capsules increased as the heat treatment temperature level was increased due to higher shrinking of chitosan which leads to firmer membrane structure.

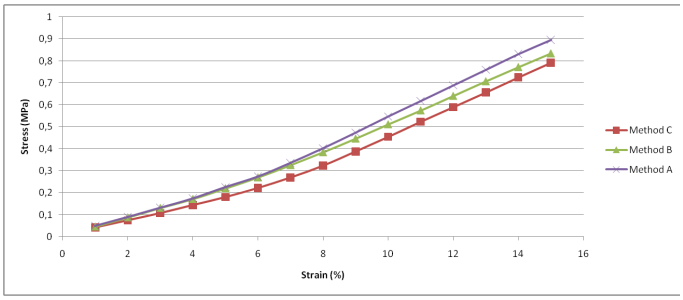

Figure 3 : Stress strain curve of dried capsules

Core Leakage Analysis

The core leakage analysis shows that the method A capsules result in the lowest leakage ratio compared to the total mass, implying a firmer surface due to shrinked chitosan layer. The results are also in agreement with the work of Hsieh et al. in which the release rate of citronella oil encapsulated in chitosan capsules was reduced dramatically as the heat treatment temperature increased.

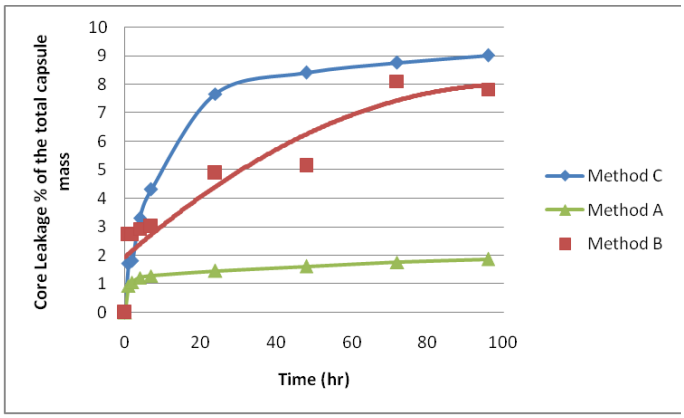

Figure 4 : Core leakage ratios of dried capsules

CONCLUSIONS

The physical and mechanical properties of chitosan alginate hybrid membrane was enhanced as the heat treatment temperature increased due to the heat shrinking property of chitosan. Chitosan, coated on the alginate gel via electrical interaction of negatively charged alginate molecules and positively charged chitosan molecules can be forced to form a firmer layer if heat is applied, resulting in a firmer, stronger and less permeable layer.

However, research is needed on the extent of the effect of heat treatment on the content of the heat sensitive material on the liquid core. There is also the need for optimizing the production conditions to make smaller capsules since the capsules produced through the 0.38 mm inner diameter tips resulted in 3.5-4.0 mm diameter capsules when wet and 2.0-2.4 mm diameter capsules when dried.

REFERENCES

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