FTIR spectroscopy as a tool for surface characterization of SA-CS-PMCG polyelectrolyte complex microcapsules

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INTRODUCTION AND OBJECTIVE

This work is focused on study of surface characteristics of sodium alginate–cellulose sulphate–poly(methylene-co-guanidine) (SA-CS-PMCG) microcapsules using Fourier transform infrared spectroscopy (FTIR). SA-CS-PMCG microcapsules represent a multicomponent polymeric system and are used for encapsulation of pancreatic islets (Lacík 1998, Wang 1997, Lacík 2006). Transplantation of encapsulated pancreatic islets is believed to be a promising strategy in the treatment of diabetes type I without the need for immunosuppression. Surface properties of polymeric microcapsules such as elemental and molecular composition and residual charge seem to have importance in regards to the biocompatibility of microcapsules in the host organism (Tam 2009).

Design and applications of functional materials such as microcapsules used especially in biomedicine in a contact with living tissue require well-characterized materials. This requirement is associated with the development of different experimental methods. Among them, FTIR has an important position. FTIR is presented as a rapid, precise and sensitive method that should be easy applicable for surface characterization of polymeric microcapsules (van Hoogmoed 2003, Tam 2005, Thanos 2006, Thanos 2007, Tam 2011, de Haan 2011). FTIR should reveal the information on chemical composition of the microcapsule surface as well as on the mutual interactions of polymers responsible for stabilization of microcapsules formed by polyelectrolyte complexation (Tam 2009).

In this study, FTIR was used in two modes (ATR-FTIR and micro-ATR-FTIR using microscope) to investigate the surface molecular composition of different types of SA-CS-PMCG microcapsules distinguished by: (a) chemical composition (microcapsules with different SA/CS ratio), (b) CS coating (non-coated vs. coated microcapsules), and (c) water content (analysis of hydrated vs. dry samples). In order to obtain a deeper insight into the complexation process during microcapsule formation, also the individual components and their binary mixtures were investigated using FTIR.

MATERIALS AND METHODS

Preparation of microcapsules and binary mixtures of microcapsule components

Microcapsules were prepared using air-stripping apparatus equipped with a coaxial nozzle. The polyanionic solution containing SA and CS in a certain ratio was air-stripped into the stream of polycation PMCG solution flowing in a loop reactor (Anilkumar 2001). The raction time in the loop reactor was 40 s. One aliquot from each microcapsule batch was coated with 0.1 wt.% CS for 10 min. Microcapsules were stored in 0.9 wt.% NaCl solution. Binary mixtures of microcapsule components (SA+CS, SA+PMCG, and CS+PMCG) were prepared by mixing of individual components solutions with final concentrations 4 wt.% SA, 5 wt.% CS, and 5 wt.% PMCG. In case of SA/CS mixture, a viscous solution was obtained. In case of SA/PMCG and CS/PMCG mixtures, a white coloured precipitate was obtained.

ATR-FTIR and micro-ATR-FTIR

FTIR spectra were measured using spectrometer Nicolet 8700 FT-IR (Thermo Scientific, USA) equipped with Smart iTR germanium crystal and Nicolet Continuum Microscope. Individual microcapsule components in the form of powders, dehydrated binary mixtures and SA-CS-PMCG microcapsules were measured using ATR-FTIR mode (resolution 4 cm^{-1}, number of scans 64 for powders or 128 for binary mixtures and microcapsules). Binary mixtures and microcapsules were dehydrated directly on the ATR crystal during cca. 2 hours. SA-CS-PMCG microcapsules were measured also in a hydrated form using micro-ATR-FTIR mode (resolution 8 cm^{-1}, number of scans 64). All experiments were done in duplicates. Spectrum of 0.9 wt% NaCl storage solution was subtracted from all spectra as background.

RESULTS AND DISCUSSION

Characteristic groups in FTIR spectrum of SA-CS-PMCG microcapsules are shown in Figure 1. The asymmetric stretching vibration of carboxylic group of sodium alginate is observed near 1620 cm^{-1} and is overlapped with the second peak of N-H group of PMCG [N-H (II)]. The first peak of the vibration of N-H group of PMCG [N-H (I)] is located near 1500 cm^{-1}. The symmetric stretching vibration of the carboxylic group of sodium alginate is located near 1400 cm^{-1}. Asymmetric stretching vibration of SO_2

group of cellulose sulphate was observed near 1200 cm^{-1}. The peak of C=O bonds (C-O-O) vibrations in SA and CS is found in the region near 1000 cm^{-1}.

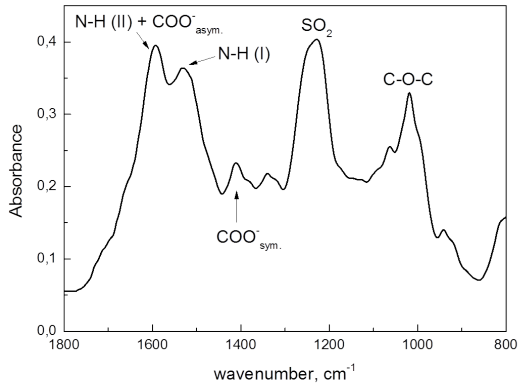

Figure 1 : Micro-ATR-FTIR spectrum of SA-CS-PMCG microcapsules measured in hydrated form (resolution 8 cm^{-1}, number of scans 64)

Table 1 shows that no clear trend was observed in shifting of characteristic peaks as a function of different composition (capsules with different SA/CS ratio (capsules type A-C) distinguished also by CS coating (type 1 vs. 2)). Neither the differences were seen for using different modes of FTIR (ATR-FTIR vs. micro-ATR-FTIR data) on dried and swollen microcapsules. In case of the complexation process, the main shifts were observed by the transition from individual components to binary mixtures. However, in case of microcapsules, the shifts were not significant neither systematic compared to pure components.

Table 1: Group frequencies of characteristic ATR-FTIR peaks for individual microcapsule components, binary mixtures and microcapsules

	N-H (II) (cm^{-1})	N-H (I) (cm^{-1})	COO^- asym. (cm^{-1})	COO^- sym. (cm^{-1})	SO_2 (cm^{-1})	C-O-C (cm^{-1})
SA component			1602	1412		1033
CS component					1228	1016
PMCG component	1604 -1558	1526				
(SA + CS) mixture			1622	1417	1236	1023
(SA + PMCG) mixture		1556		1417		1032
(CS + PMCG) mixture	1622	1532			1232	1021
A1 capsules		1529 ± 6		1405 ± 1	1244 ± 13	1024 ± 1
A2 capsules		1525 ± 1		1414 ± 4	1248 ± 7	1025 ± 1
B1 capsules		1531 ± 3		1412 ± 5	1241 ± 20	1024 ± 10
B2 capsules		1529 ± 3		1407 ± 3	1223 ± 5	1017 ± 1
C1 capsules		1528 ± 1		1408 ± 2	1225 ± 3	1018 ± 1
C2 capsules		1529 ± 1		1409 ± 3	1225 ± 3	1017 ± 2

CONCLUSIONS

FTIR has been recommended by other groups as a tool for characterization of microcapsule surface. However, in our hands, the systematic FTIR analysis of polymeric microcapsules has not provided sufficient resolution to obtain reliable information about the differences in surface chemistry of SA-CS-PMCG microcapsules as well as to contribute to our understanding about the complexation process. Further details on using FTIR on other microcapsules and alternative techniques will be discussed during the poster session.

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