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Influence of internal composition on physicochemical properties of alginate aqueous-core capsules

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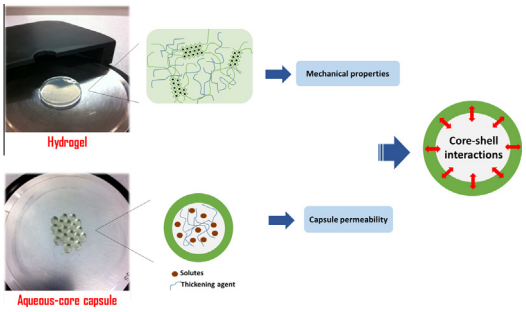
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: To enhance physicochemical properties of alginate aqueous-core capsules, conventional strategies were focused in literature on designing composite and coated capsules. In the present study, own effect of liquid-core composition on mechanical and release properties was investigated.

Experiments: Capsules were prepared by dripping a $CaCl_2$ solution into an alginate gelling solution. Viscosity of $CaCl_2$ solution was adjusted by adding cationic, anionic and non-ionic naturally derived polymers, respectively chitosan, xanthan gum and guar gum. In parallel, uniform alginate hydrogels were prepared by different methods (pouring, in situ forming and mixing). Mechanical stability of capsules and plane hydrogels were respectively evaluated by compression experiments and small amplitude oscillatory shear rheology and then correlated. Capsules permeability was evaluated by monitoring diffusion of encapsulated cochineal dye, riboflavin and BSA. The core–shell interactions were investigated by ATR-FTIR.

Findings: Results showed that inner polymer had an impact on membrane stability and could act as an internal coating or provide mechanical reinforcement. Mechanical properties of alginate capsules were in a good agreement with rheological behavior of plane hydrogels. Release behavior of the entrapped molecules changed considerably.

Findings: This study demonstrated the importance of aqueous-core composition, and gave new insights for possible adjusting of microcapsules physicochemical properties by modulating core–shell interactions.

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1. Introduction

Polysaccharide-based capsules are of widespread importance in the encapsulation field [1,2]. Their main functions are the successful encapsulation, transportation and controlled release of the capsule content to the external environment [3].

Among natural polysaccharides, sodium alginate is widely used. It is a water soluble anionic polysaccharide, mainly found in the cell walls of brown algae and can be isolated from the bacteria *Pseudomonas* and *Azotobacter* [4]. This natural polymer possesses several attractive properties such as good biocompatibility, wide availability, low cost, and simple gelling procedure under mild conditions [5]. Alginate is a co-polymer which consists of alternating β-D mannuronic acid (M) and α-L guluronic acid (G) linked in (1–4). These uronic acids units are distributed along the alginate chain in a pattern of blocks: homopolymeric sequences containing only mannuronic acid units (M Blocks) and guluronic (G blocks) and heteropolymeric blocks containing both mannuronic and guluronic units (MG blocks) [5]. Physical properties of sodium alginate are dependent of M/G ratio, sequence and molecular weight [6]. The gelation mechanism is driven by the interactions between G-blocks which associate to form firmly held junctions due to divalent cations. In addition to G-blocks, MG blocks also participate, forming weaker junctions [6]. The alginate hydrogel's cross-links involve electrostatic, hydrogen interactions van der Waals forces [7].

The millimeter-scale alginate aqueous-core capsules are widely used for a large range of applications from biotechnology to molecular gastronomy [8–10].

Concerning the manufacturing process, there are three main approaches for preparation of alginate liquid-core capsules of millimeter-scale size. The first one is based on milli-fluidic devices, by co-extrusion and electro co-extrusion of the inner core and Na-alginate drops into a $CaCl_2$ bath to form the alginate capsules, of which the membrane thicknesses is regulated by changing the ratio between the flow rates of the inner and outer solutions [11–13]. The second method is based on the formation of alginate beads hydrogel followed by coating with oppositely charged polymers and finally by alginate core removal using a chelating agent [14–16]. For the last approach, the $CaCl_2$ droplets containing the active molecule is dropped into a sodium alginate bath to form the inner side of the membrane, and then the partially gelled capsules are transferred into a $CaCl_2$ solution to complete the reticulation process [17].

In this method, generally a thickening agent must be added to the $CaCl_2$ solution in order to ensure the spherical shape and to prevent capsule shear deformation [17]. In previous studies, capsules with various core saccharides like sucrose [18,19], xanthan gum [20], dextran [21], carboxymethyl cellulose [17,18,22], guar gum [18], polyethylene glycol [23] and glycerol [24,25] were developed.

In the present work three thickening agents (anionic, cationic, and neutral biopolymers, respectively) were chosen: xanthan gum (XG), chitosan (CS) and guar gum (GG). XG is an extracellular anionic polysaccharide secreted by the microorganism *Xanthomonas campestris*. It is a complex polysaccharide consisting of a primary chain of β-D-(1,4)-glucose backbone, which has a branching trisaccharide side chain comprised of β-D-(1,2)-mannose, attached to β-D-(1,4)-glucuronic acid, and terminates in a β-D-mannose [26].

CS is a cationic polysaccharide composed essentially by β-(1–4) linked glucosamine units together with some proportion of N-acetyl glucosamine units. It is obtained by extensive deacetylation of chitin; a polysaccharide widely spread in nature [27].

GG is derived from the ground endosperm of guar seeds (*Cyamopsis tetragonoloba*). This non-ionic polysaccharide has a backbone built up by D-mannopyranosyl residues linked β-(1–4) and usually bearing, in different extent, side chains of single galactopyranosyl units linked α-(1–6) [28].

For core–shell structures, the core composition could play an important role on the final physicochemical properties of capsules, for example mechanical stability could be affected by core swelling [12]. Guest molecules could be also incorporated in capsules core to interact with the encapsulated active molecule and to control its loading or release [29].

At the nanoscale, core composition could impact significantly the mechanical properties of core–shell spheres [30].

In the best of our knowledge, there is no information about the influence of aqueous-core composition on final physicochemical properties of the alginate liquid-core capsules. Studies, in which the thickening agent choice was justified, focused on the thickener diffusion after capsules preparation [31] or on control of capsule content viscosity to obtain a low viscous core [19] or to facilitate microorganisms' proliferation [23].

The aim of this work was to study the influence of the thickening agent on the physicochemical properties of alginate liquid-core capsules and to correlate them to plane hydrogels prepared by three gelation approaches. The density of alginate capsules were modulated by anionic XG, non-ionic GG and cationic CS. The mechanical properties of capsules membrane as well as permeability to three model molecules were studied.

2. Materials and methods

2.1. Materials

Sodium alginate (SA) from brown algae with a typical M/G ratio around 1.6 was purchased from Sigma Aldrich (Chemie, Steinheim, Germany). The average viscosity molecular weight of alginate was calculated using the Mark–Houwink–Sakurada correlation: $[\eta] = KM_v^a$. By measuring the zero-shear viscosity using a rotational rheometer (kinexus pro, Malvern Instruments, Orsay, France) equipped with a cone-and-plate (50 mm, 2°) geometry. The specific viscosity and subsequently the intrinsic viscosity $[\eta]$ can be achieved. The calculated intrinsic viscosity founds a value of 4.73 dL/g and thus an average molecular weight M_v of $1.69 \cdot 10^5$ was obtained [32].

Chitosan (CS) from shrimp shells (viscosity 0.02–0.3 Pa s, 1 wt% in acetic acid at 20 °C, Deacetylation ⩾ 75%), xanthan gum (XG) from *X. campestris*, guar gum (GG), Albumin from Bovine Serum BSA ($M_w \approx 66$ KDa), cochineal red dye ($M_w = 604.46$ g/mol), riboflavin ($M_w = 376.36$ g/mol) and D-(+)-Gluconic acid δ-lactone (GDL) were purchased from Sigma Aldrich (Chemie, Steinheim, Germany). Calcium chloride dihydrate and calcium carbonate were obtained from VWR (International, Leuven, Belgium), acetic acid 99–100% from Chem-lab NV (Zedelgem, Belgium) and tri-sodium citrate from Fisher scientific (Leicestershire, United Kingdom).

For alginate-FITC derivative synthesis, fluorescein isothiocyanate (FITC, isomer I), N-(3 dimethylaminopropyl)-N′-ethylcarbo diimidehydrochloride(EDC),N hydroxysulfosuccinimide sodium salt (NHSS) and 1,6-diaminohexane were purchased from Sigma–Aldrich (Chemie, Steinheim, Germany).

2.2. Solutions preparation and characterization

The cationic solution was prepared by dissolving 1 g of calcium chloride in 80 mL of 0.1 wt% acetic acid solution. Then XG, CS and GG powders were dispersed in stirred $CaCl_2$ for modulating viscosity to ensure the spherical shape of capsules and prevent their deformation by shear stress resulting from the stirring of alginate solution. The final pH was adjusted to 5 by adding some NaOH