Chitosan-based Delivery Systems for Volatile Molecules
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Abstract
This work has focused on the formulation of microcapsules based on chitosan hydrogels for flavor encapsulation thus profiting from the advantages offered by this natural biopolymer in terms of non-toxicity, and biocompatibility. The microcapsules were prepared with a multiple emulsion technique of oil-in-water-in-oil (O/W/O) type. Different formulations of the chitosan hydrogels were tested to investigate the effect of parameters such as the chitosan concentration and the addition of fillers or thickeners. The chitosan gels, emulsions and the crosslinked microcapsules were characterized in terms of their particle size, surface morphology, rheological and mechanical properties. This project showed that although the mechanical and rheological properties of the gel matrix can be tailored by the formulation, the barrier does not prevent the diffusion of the flavor out of the beads. Indeed, the high amount of water in the hydrogel beads favors the diffusion of the small surfactant molecules from the environment medium to the gel matrix which then extracts the flavor from the beads.

Chitosan properties
Chitosan is a biopolymer currently receiving a great deal of attention in different areas, from medical, pharmaceutical to industrial and food applications. It is the most commonly used polycationic polymer, obtained by alkaline deacetylation of chitin, which is the principal component of the protective skeleton of crustaceans and shellfish. The polymer chains possess reactive amino functional groups, making chitosan interesting for many purposes. It may show a range of covalent and non-covalent interactions, e.g., ionotropic (with polyphosphates), electrostatic, hydrophobic or hydrogen bonding. Its properties depend mainly on its average molar mass and on the degree of deacetylation. Chitosan is biocompatible and biodegradable, and versatile with regard to processing. Films, micro- and nanoparticles, porous scaffolds, fibers and hydrogels may be prepared depending on the application.

Methods
A Limonene-in-chitosan emulsion was dispersed in a continuous oil phase, thus forming a limonene/water/oil emulsion, the water phase being the chitosan solution. The chitosan phase was ionically cross-linked while stirring. Different gel formulations with added polymeric or particulate fillers and thickeners were evaluated.

Results
Steady shear flow experiments with different chitosan solution formulations
The addition of a thickener (top curve) increases the zero shear viscosity $\eta_0$ as compared to the pure chitosan solution whereas the addition of the other fillers has no significant effect on the viscosity. All the samples have similar shear thinning behavior.

Encapsulation
Encapsulation is a method used in the food and perfume industry in everyday products. The principle is to cover an active compound with a protective wall material against evaporation, reaction, migration or releasing. Many techniques have been developed, such as spray drying, spray chilling or spray cooling, extrusion, freeze drying, coaxervation and molecule inclusion. The choice of the appropriate technique depends on the application and also on the feasibility of production at an industrial scale. The materials used for encapsulation have to be food grade if they are to be used for the manufacture of foods. Otherwise, they should at least be environmental-friendly and be granted GRAS (generally regarded as safe) status. Common compounds are food biopolymers (proteins, carbohydrates), fats, low molecular weight surfactants and copolymers.

Due to the presence of cationic amine groups in its back-bone, chitosan may also be cross-linked by the addition of di- or tri-valent counteranions. This is the principle of the ionic gelation method.

Conclusion
The multiple emulsion has the advantage to be upscalable because based on a one-pot process. The addition of fillers and thickeners modifies the structure and rheological behavior of the chitosan gel. The formulations did not show good retention properties in flavor encapsulation.