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Encapsulation of aroma compounds in biopolymeric emulsion based edible films to control flavour release

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ABSTRACT

Flavour loss strongly affects food quality. In order to decrease flavour changes during food conservation, different strategies could be used. Aroma compound encapsulation allows the protection of food flavour from loss and degradative reactions, like oxidation. Edible films could be an encapsulation matrix: in the case of emulsified film, lipid globules incorporated can act as carriers of active molecules, such as aroma compounds. Edible films prepared from ι-carrageenans are interesting for good mechanical and gas barrier properties.

The aim of this study was to encapsulate different aroma compounds in an ι-carrageenan emulsion based edible film. Release of ten aroma compounds was compared to that obtained from a lipid matrix, Grindsted Barrier System 2000 (GBS), was also used as an edible film formulation. Flavour release was followed by HS-SPME measurements. This study allowed the influence of both matrix and aroma compounds characteristics on flavour release to be investigated. This study presents new understanding of the role of emulsion based edible films as a matrix able to encapsulate aroma compounds. Carrageenans films were possible encapsulating matrixes because they showed better performances for retention of more polar aroma compounds than the usual lipid supports. Carrageenans films were able to retain volatile compounds during film-process formation, and to release gradually with time.

1. Introduction

The loss of quality in food can be related to the transfer of small molecules: in particular, loss of aroma compounds causes a reduction of flavour intensity and change in the typical food flavour. Aroma compounds transfer in dense system, depends on both sorption and diffusion. The sorption mechanism consists of adsorption, absorption and/or desorption of penetrant molecules and depends on the polymer-volatile compound affinity, whereas diffusion is related to their mobility within the polymeric network of the matrix. Thus, the volatile compounds and matrix characteristics must be taken into account to explain the transfer process. In particular, physicochemical characteristics of volatile compounds influence their release: aroma compound shape and size affect its diffusivity, whereas solubility is influenced by the compound nature, polarity, and ability to condense (Reineccius, 2009). In order to decrease flavour changes during food conservation, different strategies could be used. The encapsulation of aroma compounds represents a method to increase the effectiveness of flavouring without adding high levels of aroma compounds. Encapsulation can be defined as a process where a continuous thin coating is formed around solid particles, liquid droplets, or gas cells that are fully contained within the capsule wall (King, 1995). Encapsulation with edible films allows control of flavour loss, which strongly affects food quality during the processing or storage of food (Miller & Krochta, 1997; Reineccius, 2009; Reineccius & Risch, 1988). This technique allows controlled release, defined as a strategy by which one or more active agents or ingredients are made available at a desired site and time at a specific rate (Pothakamury & Barbosa-Canovas, 1995). In this way, edible packaging does not represent only an inert barrier but it has an active role and interacts with the food or with the surrounding media. Edible films could be applied to food as active packaging, with the aim of gradually releasing aroma compounds with time and thus of maintaining the characteristic flavour of food product. Edible films or coatings have been defined as "a packaging, a film, a coating or a thin protective layer which is an integral part of the food and/or can be eaten with" (Guilbert, 1986). Two categories of ingredients have been used as film forming substances. Protein (wheat gluten, whey protein isolate, caseinate, soy protein) and polysaccharide (starch, carrageenan, alginate) are used for their mechanical,

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structural and oxygen barrier properties, hydrophobic substances (lipids, lacs, varnishes, resins, essential oils and emulsifiers) for their good moisture barrier properties (Kester & Fennema, 1986). Composite films make possible to combine the advantages connected to the different components. ι-Carrageenan, a water soluble polymer with a linear chain mainly composed of alternated (1,3)-D-galactose-4-sulfate and (1,4)-3,6-anhydro-D-galactose-2-sulfate units, is promising as a film-forming material. In aqueous solutions, ι-carrageenans produces thermo-reversible gels when cooling below the critical temperature. The conformation then changes from random coiled single chain to the formation of double-helices of carrageenan chain (Karbowiak et al., 2006a). This three dimensional network formed by the polysaccharide double-helices in a gel state is then dried to obtain a compact solid film. Lipids can be either dispersed in hydrocolloid aqueous solution and dried to obtain an emulsified film or cast as a layer on the hydrocolloid film used as a mechanical support, in order to obtain a bilayer film. The food industry has been focusing its research on emulsified films, which require only one step in manufacture, as opposed to the three steps required for bilayer films. With the addition of lipids to form emulsified films, they can also be used to encapsulate active molecules such as aroma compounds (Karbowiak, Debeaufort, Champion, & Voilley, 2006b).

The objective of this work was to encapsulate different aroma compounds in emulsified ι-carrageenans films. Release of ten aroma compounds from emulsified films was compared to that obtained from a lipid matrix. In the food industry, flavours are often added to lipids, because of their affinity to hydrophobic phases. Emulsified carrageenans films could represent a lipidic phase surrounded with a second layer consisted of hydrocolloids network, that is supposed to have good gases barrier properties. Headspace solid phase microextraction–gas chromatography (HS-SPME–GC) analyses were carried out. Compared to other extraction techniques, SPME technique is advantageous since it is economic, faster and concentrates the headspace, thus allowing the detection of compounds with low concentrations.

2. Materials and methods

2.1. Materials

ι-Carrageenan was a gift from Degussa Texturant Systems (DTS, Baupte, France) and constituted the continuous matrix of the film. Anhydrous glycerol (98% purity, Fluka Chemical, Germany) was used as plasticizer in order to improve mechanical properties of carrageenan films. Fat used in this study, Grindsted Barrier System 2000 (GBS), supplied by Danisco (Bradbrand, Denmark), is an acetic acid ester of mono- and diglycerides made from edible, fully hydrogenated vegetable oil blended with beeswax, having a melting point of 57 °C. Glycerol monostearate (GMS) employed as emulsifier was purchased from Prolabo (99% purity, Merck eurolab, Fontenay-sous-Bois, France). The aroma compounds selected for encapsulation are typical flavours present in some food products (Fenaroli, 1975): ethyl acetate (EA), ethyl butyrate (EB), ethyl isobutyrate (EIB), ethyl hexanoate (EH), ethyl octanoate (EO), 2-pentanone (2P), 2-heptanone (2H), 2-octanone (2O), 2-nonanone (2 N), 1-hexanol (HOL). They were all supplied by Sigma–Aldrich (USA) with purities ⩾98%. Their physicochemical characteristics are given in Table 1.

2.1. Methods

2.1.1. Sample preparation

Two different systems were compared: a fat sample and a carrageenan emulsion-based film. The carrageenan film-forming solution was prepared by dispersing 6 g of ι-carrageenan powder in 200 mL of distilled water at 90 °C for 15 min under a 700 rpm magnetic stirring. Glycerol was added at a concentration of 30% of the carrageenan dry matter. The chosen carrageenan concentration is above the critical concentration required for gelation, as reported by Rees, Williamson, Frangou, and Morris (1982). Then, during the film formation, carrageenan molecules, in a random coil state in hot solution, undergo a coil to helix transition followed by helices association when cooled (Hossain, Miyanaga, Maeda, & Nemoto, 2001). The casting is done with the solution of carrageenan which turn to a gel state immediately because of the contact of a thin layer of the hot solution (90 °C) onto the room temperature casting support (about 25 °C). The drying is carried out at 30 °C, which is at temperature below the helix melting point reported for this polymer (Bryce, Clark, Rees, & Reid, 1982). To prepare emulsified films, another step is necessary before spreading of the film-forming solution in order to incorporate blends of GBS and GMS (90:10 w/w). The fat was added at the concentration of 30% to the plasticised film-forming solution composed of carrageenan and glycerol, according to Karbowiak et al. (2006b). A mix of ten aroma compounds was prepared. 1 mL of aroma compounds mix was

Table 1
Physicochemical characteristics of aroma compounds.

Characteristics	Ethyl-acetate	Ethyl-butyrate	Ethyl-iso-butyrate	Ethyl-hexanoate	Ethyl-octanoate	2-Pentanone	2-Heptanone	2-Octanone	2-Nonanone	1-Hexanol
Odour[a]	Ether, pineapple	Fruit, pineapple	Apple-like odour	Fruity, banana, pineapple	Fruity, floral odour (wine–apricot note)	Acetone-like	Banana, slightly spicy odour	Floral and bitter, green fruity odour	Rose and tea-like flavour	Fruity and aromatic flavour
Chemical formula	$C_4H_8O_2$	$C_6H_{12}O_2$	$C_6H_{12}O_2$	$C_8H_{16}O_2$	$C_{10}H_{20}O_2$	$C_5H_{10}O$	$C_7H_{14}O$	$C_8H_{16}O$	$C_9H_{18}O$	$C_6H_{14}O$
Molecular weight ($g\ mol^{-1}$)	88.1	116.2	116.2	144.2	172.3	86.13	114.8	128.2	142.2	102.2
Density at 25 °C ($g\ mL^{-1}$)[b]	0.89	0.80	0.80	0.88	0.87	0.80	0.81	0.81	0.82	0.82
Solubility in water ($g\ L^{-1}$)[b]	121.53	10.91	11.89	1.76	0.37	23.48	5.03	2.32	1.07	1.94
Log K[d]	0.76[b]	1.44[b]	1.25[b]	2.83[b]	3.9[b]	0.91[b]	1.97[b]	2.5[b]	3.03[b]	2.03[c,d]
Saturated vapour pressure at 25 °C (Pa)	12510[e]	1885[e]	–	215[e]	–	–	–	187[e]	–	107[e]

[a] Fenaroli (1975).
[b] Calculated by ACD labs 9.0 software.
[c] Rekker (1977).
[d] Philippe (2003).
[e] Covarrubias-Cervantes et al. (2004).

pre-solubilised in 2.4 g of melted fat before being dispersed into the film-forming solution. Once all of these components are melted under magnetic stirring, the hot solution was emulsified with an homogeniser (Ultra-Turrax model T25 IKA, Labortechnik, ODIL, France) at 24,000 rpm for 1 min. In order to obtain a film, the water was removed by drying in a ventilated chamber KBF 240 Binder, ODIL, France) for 8 h with temperature and relative humidity fixed at 30 °C and 50% RH, respectively. Related to the second system considered, fat samples were prepared by adding the aroma compounds mix to melted GBS, with the same ratio used for the edible film.

2.1.2. HS-SPME procedure

In order to follow aroma compound release, flavoured melted GBS was transferred into a 10 mL vial. Related to release from edible films, slices of dried film were overlapped into a 10 mL vial. In both cases, samples occupied the same volumes and vials were sealed immediately with a Teflon lined septum and screw cap. Each measurement was carried out at the equilibrium and a minimum time of 180 min was determined for equilibration. After the dosage, the vial was opened for a fixed time to allow aroma compound release. The sampling times were 0, 25, 88, 122, 160 h for the film sample and 0, 25, 88, 122 h for the fat matrix. After the sampling time, the vials were closed for at least 180 min and the flavour dosage was carried out. The same vials were used for each analysis time.

The samples were incubated at 25 °C and 50%RH.

After equilibration, the headspace of the samples was sampled using an SPME fibre coated with CAR/PDMS (carboxen/polydimethylsiloxane, thickness 75 μm) which, in preliminary experiments, exhibited the highest overall extraction efficiency compared to other fibres. The fibre was manually exposed to the sample headspace for 60 min at 25 °C. Finally, the fibre was withdrawn into the needle holder and immediately introduced into the GC injection port for 15 min at 190 °C, in order to confirm the full desorption of the fibre. All samples were analyzed in triplicate.

2.1.3. GC conditions

The volatile flavour compounds present in the headspace of film and GBS samples were analyzed by an 3800 Varian GC system equipped with a flame ionization detector (FID) and a packed Carbowax column (length = 3 m, i.d. = 2.2 mm). Oven temperature was programmed at 50 °C for 5 min, then ramped to 160 °C at 3 °C/min and held for 5. Nitrogen was used as the carrier gas, while hydrogen and air were used as ignition gases. Detector temperature was set at 200 °C.

3. Results and discussion

To investigate the possibility of using edible films as flavour carriers, different aroma compounds were added to carrageenans films. Flavour release from two matrices, one consisted of only Grindsted Barrier System 2000, GBS, and the other one consisted in emulsified film (cg wf), was followed by dosing aroma compound in the headspace. Different aroma compounds were chosen in order to consider the influence of flavour physico-chemical properties on release from solid media: ethyl acetate, ethyl butyrate, ethyl iso-butyrate ethyl hexanoate, ethyl octanoate, 2-pentanone, 2-heptanone, 2-octanone, *n*-hexanol. Therefore, it was possible to study the influence of both chemical function and chain length on flavour release at 25 °C. The flavour mix was added to the lipidic phase of the two matrices, as it generally happens to carry out flavouring in food industry. Different trials were carried out in order to select the method for dosing flavour. The SPME dosage instead of the solvent extraction was chosen, because of the complexity of the matrices and the low aroma compound quantity in the samples. The aim of this experimental work was to understand if a carrageenan emulsion-based film could represent a good encapsulating matrix for aroma compound. Therefore we performed an headspace analysis with the aim of characterizing the solid matrix. For this reason, an exhaustive SPME was used, which occurs when the fiber is left in the sample headspace until equilibrium is reached (the maximum possible amount is adsorbed on the fiber) (Roberts, Pollien, & Milo, 2000).

The headspace of the samples was sampled using an SPME fibre coated with CAR/PDMS (carboxen/polydimethylsiloxane). Vials were partially filled with the two samples, covered only for the time needed to reach chemical equilibrium before dosing. Between two measurements, vials were opened and kept in a ventilated cell at 50% RH. cg wf samples consisted of film slices placed in the vials, where fat samples formed a homogeneous matrix: both reaching the same volume in the vials. The quantification of aroma compounds from two solid matrices show different experimental difficulties. The two samples were very different and the drying step in the preparation of the carrageenan film strongly affects the remaining flavour quantity at time 0. It is very difficult to obtain two kinds of these very different samples with the same flavour quantity. The Area Counts ratio instead of the aroma compounds concentration was considered in order to avoid the influence of the flavour quantity on the release kinetics. That is, in this way it is possible to compare the release behaviours without considering the flavour quantity. Moreover, the concentration of the aroma compound at the beginning of the kinetic is strongly affected by the sorption phenomenon measured with the partition coefficient. The release behaviour is affected also by the diffusion, which is not related to the initial quantity of diffusing compound. It is possible to assume that the kinetics release from gbs could be similar to the kinetics from the film, if the aroma compounds release would have been performed with more elevated sampling time. However, we considered only the first time of the kinetics and in the sampling times considered, the behaviour of the flavours from the two matrices was very different.

Results obtained for methyl-ketones are reported in Figs. 1 and 2. Results obtained for esters are reported in Figs. 3 and 4. Results obtained for hexanol are reported in Fig. 5. They are all expressed as At_i/At_0, which corresponds to area counts at time i and area counts at time 0 ratio. As observed, aroma compounds release behaviours differ comparing the two matrices. Concerning cg wf films, all the aroma compounds considered were rapidly released from the samples: in the case of ethyl butyrate and ethyl octanoate they completely disappeared after 122 h. Some of aroma compounds encapsulated in the matrices were not detectable in the headspace since the beginning, like ethyl acetate and ethyl isobutyrate: they probably had been lost during sample preparation because of their high volatility. In the case of GBS sample, aroma compounds concentration decreased slightly with time increasing, for all compounds considered except for ethyl octanoate. Different kinetics seemed to characterise flavour release from the two samples. Release from fat matrix follows a first order reaction, because aroma concentration decreased in a linear way with time increasing, though the release from cg wf films seemed to follow a second order reaction. This could be indicating that diffusion represented a step limiting reaction in the case of cg wf films, related to the complex structure. The concentration of a volatile compound in one or between several phases, depends on the characteristics of the pure volatile compound. Vapour pressure, solubility, partition coefficients and activity coefficients, are some equilibrium parameters which depend on both, temperature and physico-chemical properties of the pure volatile compound. Among these, vapour pressure and consequently aroma compound volatility strongly influences kinetic release. Covarrubias-Cervantes, Mokbel, Champion, Jacques, and Voilley (2004) measured saturated vapour pressure at temperature

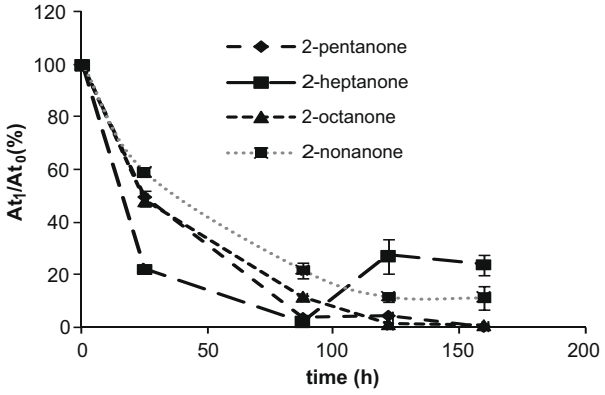

Fig. 1. Methyl-ketones release from ι-carrageenan–GBS emulsified films at 25 °C.

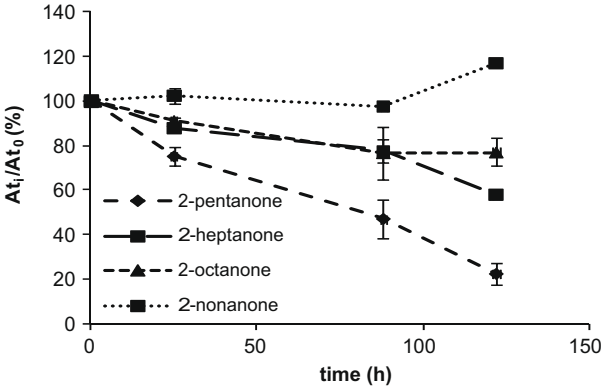

Fig. 2. Methyl-ketones release from GBS matrix at 25 °C.

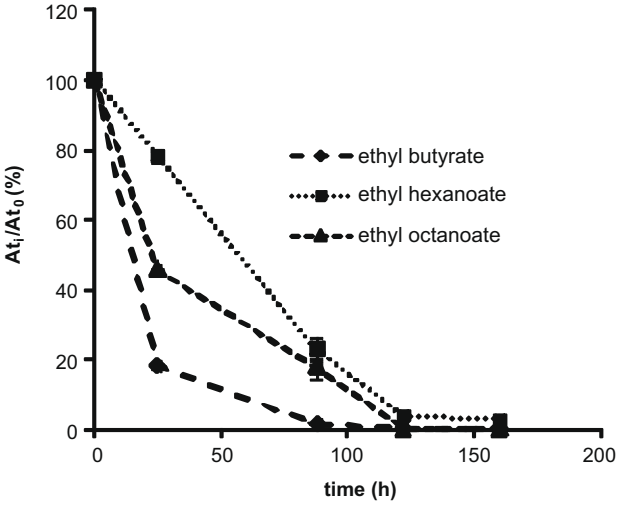

Fig. 3. Ethyl-esters release ι-carrageenan–GBS emulsified films at 25 °C.

from 25 °C to −40 °C for several pure aroma compounds. Results of saturated vapour pressure at 25 °C for some of the aroma compounds used in our study are reported in Table 1. The volatility of a pure aroma compound decreased with the increasing of the number of the carbon atoms in the aliphatic chain. Moreover, saturated vapour pressure for ethyl-esters was higher than that of methyl-ketones, at any given temperature.

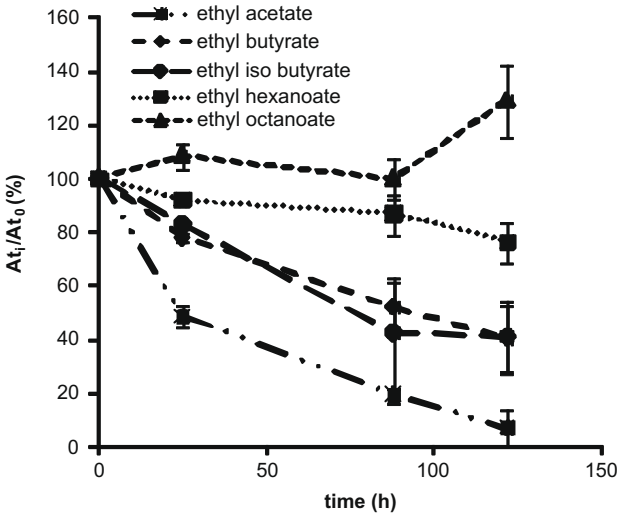

Fig. 4. Ethyl-esters release from GBS matrix at 25 °C.

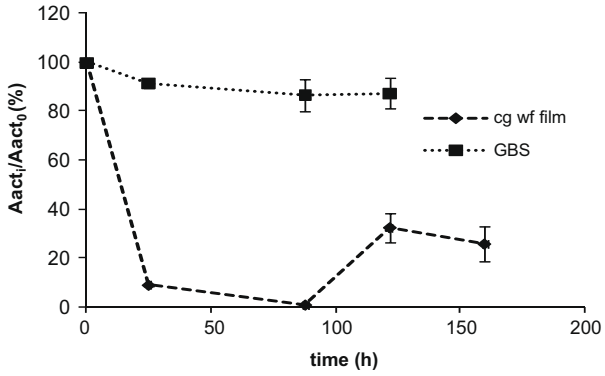

Fig. 5. *n*-Hexanol release from ι-carrageenan–GBS emulsified films and GBS matrices at 25 °C.

Results obtained for esters and ketones series were compared in order to investigate the influence of chain length on flavour release. Comparing ketones release from cg wf sample with that obtained with esters, the latter resulted faster: esters compounds were released before than the ketones, confirming the strong influence of vapour pressure on aroma compound release. This behaviour could also indicate that the ketone group was involved in weak interactions with the ι-carrageenan –OH group, as previously observed for permeability of methylcellulose films to methyl-ketones (Quezada Gallo, Debeaufort, & Voilley, 1999).

In Figs. 1 and 2, it is possible to observe methyl-ketones release from cg wf and from GBS, respectively. In both cases the release is inversely related to length chain; in fact, 2-pentanone, 2-octanone and 2-nonanone have the same chemical function with increasing chemical length: release rate decreased as chain length increased from both matrixes. In opposite to the behaviour of others compound, 2-heptanone showed a different behaviour in cg wf sample: indeed it was expected to have a release rate higher than 2-octanone and 2-nonanone, because of chain length. If compared with the compounds with a higher chain length, its release was lower in the second part of the kinetic. Moreover, 2-pentanone release was not significantly different from that obtained for 2-octanone, after 100 h. This behaviour was observed only for the cg wf matrix and not for GBS matrix. Related to permeability of methylcellulose films and LDPE films to methyl-ketones, a different behaviour was observed for 2-heptanone compared to 2-octanone and 2-nonanone

(Quezada-Gallo et al., 1999). At low concentration, 2-heptanone transfer was lower than 2-octanone and 2-nonanone, in spite of its shorter carbon chain. This behaviour was observed only for methylcellulose films and not for plastic films. The particular 2-pentanone and 2-heptanone release could be explained considering their greater polarity, respect of that of the other ketones considered. Probably, in GBS matrix the factor that mostly influenced ketones release was chain length and molecule size: compounds with higher chain length were also more hydrophobic and showed more affinity to lipid phase. In cg wf sample, 2-pentanone and 2-heptanone were released slowly from the matrix because of their affinity to hydrophilic phase, in spite of their shorter chain length: carrageenans matrix represented a hydrophilic network which retained more polar compounds (Karbowiak et al., 2006b). Solute polarity is an important factor in transfer process and it particularly affects sorption process. Some authors showed that aroma compounds are adsorbed more easily in matrices with similar polarities (Arora, Hansen, & Armagost, 1991; Reineccius & Risch, 1988). Comparing esters release from the two matrixes, different behaviours related to the matrices were observed. Ester release from GBS matrix was affected by chain length: aroma compounds with shorter chain were released faster from the fat sample, following size order. As previously discussed about ketones release, in GBS matrix the main factor affecting flavour release seemed to be molecule size and hydrophobicity. Concerning to cg wf films, ethyl octanoate was supposed to be retained more than other esters because of its size that strongly affects diffusivity. Ethyl octanoate was almost completely lost after 100 h, showing a release rate higher than the two others esters compounds considered. As in the case of 2-heptanone, we have to consider that ethyl octanoate is characterised by a high log *P* that make this compound more inclined to hydrophobic phases. Thus, its release increased when encapsulated in polar network like carrageenans films. As it is possible to observe in Fig. 5 1-hexanol release appeared very different comparing the two matrices. The very fast *n*-hexanol release from films compared to the high retention in fat sample could probably be due to its higher hydrophobic character (Covarrubias-Cervantes et al., 2004).

4. Conclusions

This work focused on the encapsulation of different aroma compounds with emulsion ι-carageenans based edible films. Release of methyl-ketones, ethyl-esters and alcohol from cg wf films was compared with that obtained from GBS sample. Release from the two matrixes resulted very different. We could hypothesize that in fat sample aroma compounds release is more affected by factors related to diffusivity, whereas in carrageenans emulsified films affinities between volatile compounds and polymer strongly influences sorption phenomena and thus release.

Carrageenans films resulted as possible encapsulating matrixes: they showed better performances for retention of more polar aroma compounds. Carrageenans films were able to retain volatile compounds during process film formation, and to release gradually with time. These properties could be exploited with the aim of flavour food product by using food surface coating technologies.

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