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Microencapsulation of black pepper oleoresin

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Abstract

Despite of solvent extracted spice oleoresin having many advantages over ground spices, its sensitivity to light, heat and oxygen is a disadvantage. One approach to overcome this is microencapsulation. The present work reports on microencapsulation of black pepper oleoresin by spray-drying, using gum arabic and modified starch as wall materials. The microcapsules were evaluated for the content and stability of volatiles, non-volatiles, total piperine and entrapped piperine for six weeks. Gum arabic offered greater protection to the pepper oleoresin than modified starch, as seen from the $t_{1/2}$, time required for a constituent to be reduced to 50% of its initial value.

Keywords: Black pepper oleoresin; Gum arabic; Modified starch; Encapsulation

1. Introduction

Solvent-extracted oleoresins exhibit a flavour profile close to the freshly ground spice, which make them an acceptable form of natural flavouring ingredient in a wide spectrum of food applications. In comparison to the ground spices, they are hygienic and can be standardized for acceptable flavour levels by blending. Unlike the essential oils, oleoresins contain natural antioxidants of the corresponding spices, which make them more stable. Oleoresins are quite concentrated and have good replacement value. They provide a better distribution in the finished products and require less storage space than the corresponding spices. However, spice oleoresins exhibit sensitivity to light, heat and oxygen, and have short storage lives if not stored properly. In black pepper oleoresin, poor storage life is a result of oxidative and polymeric changes involving the fatty oil component and monoterpinic hydrocarbons (e.g., α-pinene, β-pinene, limonene, sabinene and Δ^3-carene). Some chemical and organoleptic changes can also occur in the oleoresin during prolonged storage. Destruction of several pigments occurs under exposure to oxygen wherein the hydroxylic groups are converted into unstable ketones. These in turn decompose into colourless compounds with a shorter carbon skeleton (Gilbertson, 1971).

Microencapsulation protects the oleoresin against such destructive changes, and also converts it into a free-flowing powder. Besides, it also protects the flavours from undesirable interaction with food and minimizes flavour/flavour interaction (Reineccius, 1989; Versic, 1988). The microcapsules may range from several millimeters in size (0.2–5000 μm) and have multitudes of shapes, depending on the materials and methods used to prepare them (Balassa & Fanger, 1971). The simplest of the microcapsules may consist of a core surrounded by a wall or barrier of uniform or non-uniform thickness. The core may be composed of just one or several different types of ingredients and the wall may be single or double-layered. The retention of these cores is governed by factors such as its chemical

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nature, including the chemical functionality, relative volatility and polarity (Goubet, Leouere, & Voilley, 1998). Controlled diffusion, breakage of the capsules, dissolution and solvent effects can cause losses of the encapsulate. The degree of protection is generally calculated as the rate of its loss from the microcapsules. Of many methods available, spray-drying largely dominates the market for encapsulation of flavours. Carbohydrates, such as hydrolyzed starches (SHPs), emulsifying starches and gums (especially gum acacia) are the most common carrier materials (Reineccius, 1988, 1989). Being hydrophilic in nature, hydrolysed starch products have little affinity for hydrophobic flavour oils. Their hydrophilic nature can be changed by modifying them with *n*-octenyl succinic anhydride (*n*-OSA). *n*-OSA-treated starch contains hydrophobic octenyl side chains, which impart emulsifying capability to the starches. Most *n*-OSA starches used for encapsulation are depolymerized to lower the viscosity (Qi & Xu, 1999). Gums are also used for secondary effects such as stabilization of emulsion, encapsulation, and film formation. The flavour industry uses gum arabic as a fixative in spray-drying applications where the gum encapsulates the flavour compound, protecting it from oxidation and volatilization. Recovery and oxidation stability of orange oil encapsulated in gum arabic and emulsifying starches by spray-drying has been reported (Qi & Xu, 1999).

Reports on microencapsulation of spice oleoresins in the scientific literature are scant. Microencapsulation of garlic oleoresin by spray-drying, using edible gums as wall material, has been described (Xiang, Yang, Li, Wang, & Cheng, 1997). Zilberboim, Kopelman, and Talman (1986) utilized a spray-drying process to encapsulate paprika oleoresin and several volatile esters in gum arabic. Microencapsulation of capsicum oleoresin, in a gum mixture composed of carrageenan and maltodextrin at a ratio of 0.5–3.5:9.5–7.0 was studied (Xiang et al., 1997). Microencapsulation of red pepper oleoresin using gum arabic and modified starch has also been tried (Jung & Sung, 2000).

Black pepper is valued mostly for its spicy aroma and piquant pungent taste. Oleoresin, produced by solvent extraction of dried powdered pepper, contains both aroma and pungency principles (Premi, 2000). Extraction yields of oleoresin have been reported to be in the range 5–15% while the volatile oil and piperine contents can be 15–27% and 35–55%, respectively (Purseglove, Brown, Green, & Robbins, 1980). The volatile oil, piperine and the other non-volatile constituents cumulatively account for the quality of black pepper oleoresin. The active constituent of pepper, piperine is sensitive to light and oxygen. It can undergo hydrolysis to piperidine and piperinic acid, and also photolysis to *iso*-chavicine, which lacks the typical pepper characteristics. There are no reports on encapsulation of black pepper oleoresin. In the light of this information, an attempt has been made to encapsulate pepper oleoresin by spray-drying, using gum arabic and a commercially available modified starch – HiCap100 as the wall materials. The stability of oleoresin in its free and encapsulated form has been evaluated in terms of its total volatiles, non-volatiles and piperine content, all of which characterize a black pepper oleoresin.

2. Materials and methods

2.1. Materials

Gum arabic was obtained as a gift sample from TIC Gums, USA. Modified starch (HiCap100) was obtained from National Starch, USA. Black pepper (*P. nigrum*, var. Malabar) was procured from the Spice Board of India, Kerala, India. Standard piperine was procured from M/s. Sigma chemical Co., St. Louis, USA. Tween-80 was procured from E. Merck (India). All chemicals used were of AR grade.

2.2. Methods

2.2.1. Extraction and analysis of the pepper oleoresin

Black pepper oleoresin was prepared by ethanolic extraction in 1:17 proportion of dried ground black pepper for 16–17 h (Borges & Pinto, 1993). Piperine content of black pepper oleoresin was determined using a UV spectrophotometer by measuring the absorbance at 343 nm in chloroform, as described by Fagen, Kolen, and Hussong (1955). Total volatiles and non-volatiles were analyzed by the reported method (Ranganna, 1977); 0.2 g of the oleoresin was accurately weighed in an evaporating dish and kept in a hot air oven at 100 °C for 45 min. The evaporating dish was cooled and weighed again. The loss in the weight corresponds to volatile oil and the mass left behind to that of the non-volatiles or fixed oils. All the results were expressed as % w/w of the oleoresin sample.

2.2.2. Preparation of microcapsules by spray-drying

40 g of gum arabic and the commercial modified starch (i.e., Hi-Cap) were dispersed individually in distilled water at 60–70 °C, and final volume made to 100 ml. One gramme (2.5% based on carrier) of oleoresin was then added to the mixture. This mixture was emulsified in a shear homogenizer for 5 min at 3000 rpm until the oleoresin dispersed completely. Two drops of Tween-80 were added to aid emulsification. The resultant slurry was spray-dried in a Büchi-190 model mini spray drier (Büchi, Switzerland) (inside chamber dimension: 100 cm height, 60 cm diameter.) equipped with 0.5 mm diameter nozzle. The pressure of compressed air for the flow of the spray was adjusted to 5 bars. The inlet and outlet air temperatures were maintained at 178 ± 2

and 110 ± 5 °C, respectively. Feed rate was adjusted to 300 ml/h. The microcapsules were collected from the collecting chamber. These powders were filled in air-tight, self-sealable polyethylene pouches and stored in a dessicator containing calcium chloride to prevent moisture absorption prior to further studies.

2.2.3. Scanning electron microscopy (SEM)

Particle size and structure of spray-dried microcapsules were evaluated with a scanning electron microscope, Model No. SU 30 (Cameca, France). The microcapsules were attached to SEM stubs of 1″ diameter using 2-sided adhesive tape. The specimen were coated with gold–palladium (Plasma deposition method) and examined on the SU 30 model at 15 kV.

2.2.4. Analysis of entrapped piperine (EP) and total piperine (TP) within the microcapsule

The spray-dried microcapsules were analysed for EP and TP by the method of Fagen et al. (1955) with slight modifications. 10 mg of microcapsules were washed with 0.5 ml of absolute ethanol, filtered through Whatman No. 1 filter paper and the residue left from the above washing was dissolved in chloroform, and the volume made to 10 ml in a standard volumetric flask, sonicated for 4–5 min, filtered and used to estimate EP by measuring absorbance at 343 nm. Total piperine was estimated after dissolving 10 mg of sample in 10 ml chloroform in a standard volumetric flask. Piperine was estimated for each sample as stated in Section 2.2.1.

2.2.5. Analysis for total volatiles (TV) and non-volatiles (NV) of ether extract of the microcapsule interior

Although most substances encapsulated by spray-drying or some other techniques are volatile, the entrapped phase containing wholly or partially nonvolatile can be estimated. The method entails extraction of the non-volatiles in an organic solvent from an aqueous solution (Maleeny, 1961). Some of the volatiles could also be extracted by this method. The non-volatile entrapped phase is separated from the microcapsules and the amount extracted by the organic solvent can be determined by weighing the residue after evaporation. Conversely, if it is assumed that only the encapsulating agent is water-soluble, the concentration of this component in the sample can be ascertained by evaporation of the water phase of the extraction.

250 mg of the sample was weighed accurately. To this, 15 ml of diethyl ether and 5 ml distilled water were added, blended in a Waring blender at 3000 rpm for at least 30 s until complete dispersion. Splattering of the container walls with undissolved particles was avoided. 5 ml of 95% ethyl alcohol were then added and mixed again at 3000 rpm for at least 30 s. The mixture was quantitatively washed with water into a separating funnel. This was allowed to stand until the layers separated. The bottom aqueous layer was drawn into another separating funnel. To this fraction, a mixture of 10 ml diethyl ether and 5 ml ethyl alcohol was added, shaken well, and the phases were allowed to separate. The bottom aqueous layer was drained into a weighed flask. The ether extracts were combined and washed with 10 ml of water to ensure complete removal of the water-soluble components. These materials were then transferred to the weighed flask to determine the water-soluble fractions. The combined ether extract was transferred to another preweighed flask. The solvents were evaporated and the flask dried in an oven for 2–4 h at 105 °C. The results were reported as % non-volatile ether extract (NV) and %total volatiles (TV) from % ether extract (EE) as follows:

(i) % NV = $R_e/S \times 100$, in which, S is the weight of sample and R_e is the weight of ether-soluble residue.
(ii) % EE = $100 + W - (R_w/S \times 100)$, where, S is the weight of sample, R_w is the weight of water-soluble residue, and W is the water content of sample.
(iii) % TV = % EE − % NV.

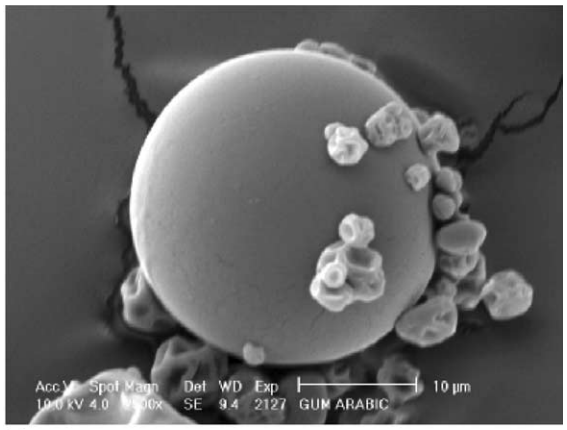
2.2.6. Stability of the EP, TP, TV and NV within the microcapsules

The samples were analyzed over a period of 6 weeks for total piperine (TP), entrapped piperine (EP), and also for total volatiles and non-volatiles. The percentage retention of all these analytes was calculated by the formula (analyte at 'X' storage time) × 100/(analyte at zero storage time). A semi-log plot of percentage retention of all these analytes vs. time, according to Cai and Corke (2000), was done to obtain the rate constant (k) as the slope of the graph. Half-life ($t_{1/2}$) for the retention of piperine was calculated from the rate constant as $0.693/k$.

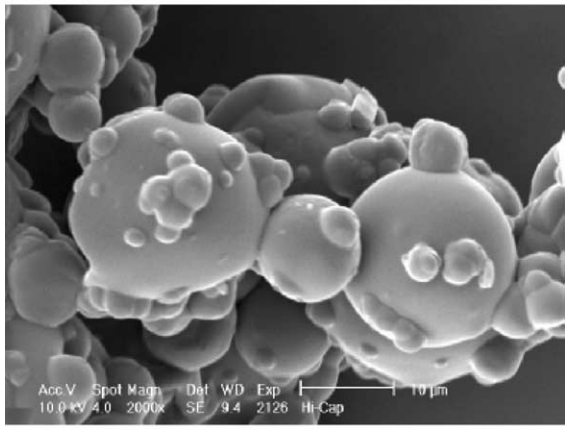
3. Results and discussion

3.1. SEM of microencapsulated black pepper oleoresin

Microcapsules prepared by spray-drying of black pepper oleoresin using gum arabic and the modified starch as wall materials were observed for size and shape from the SEM. Microcapsules prepared from modified starch had granule sizes ranging from 5 to 15 μm, while that using gum arabic had slightly bigger size of 7–20 μm (Fig. 1). In both the cases, microcapsules were found to be nearly spherical with smooth surface (Buffo, Probst, Zehentbauer, Luo, & Reinneccius, 2002; Rosenberg, Koeplman, & Talmon, 1985; Varavinit, Chaokasem, & Shobsngob, 2001).



(a)



(b)

Fig. 1. Spray dried microcapsules of black pepper oleoresin in (a) gum arabic, (b) modified starch (HiCap-100).

3.2. Analysis of EP, TP, NV and TV in free and encapsulated oleoresin

The black pepper oleoresin extracted by ethanol had an initial value of 39.1% piperine, 26.8% TV, and 73.3% NV. This oleoresin was encapsulated in gum arabic and modified starch (HiCap-100) and evaluated as detailed earlier.

The stabilities of TP in black pepper oleoresin and that of EP and TP in microcapsules prepared from the two wall materials are shown in Figs. 2 and 3. Similarly, Figs. 4 and 5 show stability of TV and NV in free and encapsulated oleoresin.

The piperine content of oleoresin stored at 30 °C (room temp.) decreased from an initial value of 39.1–36.2% over a period of six weeks. There was an increase in the concentration of NV as a result of the decrease in the concentration of TV for free oleoresin. These changes are mainly loss of volatiles, chiefly due to improper storage conditions. To reduce the losses of piperine and volatiles from the oleoresin, storage under cold conditions in a moisture-free air-tight container and encapsulation or adsorption on inert carrier material has been recommended (Gilbertson, 1971).

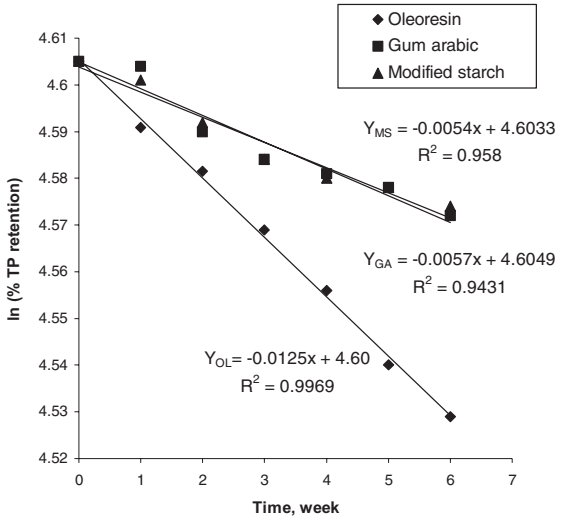


Fig. 2. Stability of total piperine (TP) in free and microencapsulated black pepper oleoresin.

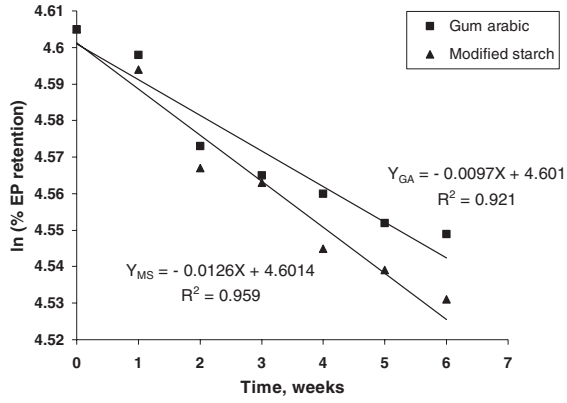


Fig. 3. Stability of entrapped piperine (EP) in microencapsulated black pepper oleoresin.

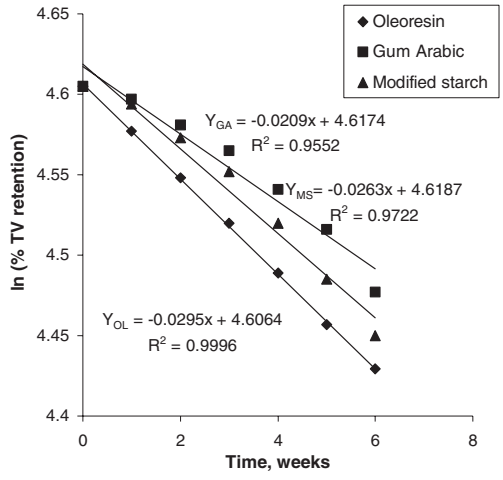


Fig. 4. Stability of total volatiles (TV) in free and microencapsulated black pepper oleoresin.

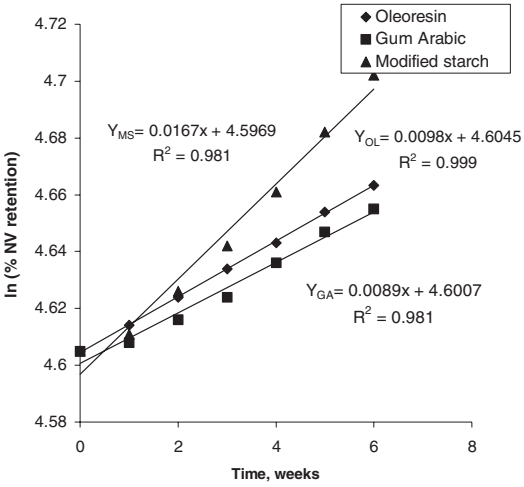


Fig. 5. Stability of total non- volatiles (NV) in free and microencapsulated black pepper oleoresin.

The value of EP in microcapsules was higher in gum arabic than in modified starch. The pattern of TP was also similar to EP. The % retention of volatiles (TV) and non-volatiles (NV) within the microcapsules was also higher for gum arabic than for modified starch, as was evident from their retention over a six week period.

The extents of entrapment of piperine and volatiles and non-volatiles depend on the nature of carrier material used. The efficient entrapment of piperine and volatiles in gum arabic is due to good film-forming capability and their plastic rather than glassy property (Plasticity is known to prevent cracking of the protection matrix). (Bertolini, Siani, & Grosso, 2001; McNamee, O'Riordan, & O'Sullivan, 1998; Rosenberg, Kopelman, & Talmon, 1990; Sankarikutty, Sreekumar, Narayanan, & Mathew, 1988; Sheu & Rosenberg, 1995).

3.3. Stability of EP, TP, NV and TV in free and encapsulated oleoresin over a six-week period

The stability of TP, EP and TV in the microcapsules and free oleoresin was evaluated from semi-log plots of their values with storage time in weeks (Figs. 2–4). A sharp decrease in the % piperine and % volatile contents of the free oleoresin was observed. The linear nature of the graph indicates that the decreases in the % volatiles and piperine follow first order kinetics. This study reveals that oleoresins are sensitive to heat and lose volatiles and characteristic pungent components under improper storage conditions. There were also possibilities that the top note components such as monoterpenes, which are mainly responsible for 'peppery'-like aroma, volatilize easily under high temperature conditions (Boelens, 2000; Sharma & Arya, 1995). The half-life, $t_{1/2}$, that is the time required for the reduction of a value to 50% of its original was calculated from the slope 'k' as $t_{1/2} = 0.693/k$. The half-life for oleoresin stored at 30 °C, based on piperine and volatiles, was found to be 55.44 and 23.49 weeks. From the half-life, it is evident that piperine has better stability in the oleoresin than have volatiles.

The loss of these constituents from the microcapsules, with both the wall materials, also follows first order kinetics during the six-week storage study. The stabilities and half-lives of these constituents in free and microencapsulated oleoresin, as obtained from first order kinetics, are shown in Table 1. As opposed to EP, TP and TV of NV increased with storage time for all wall materials (Fig. 5). All the experimental results obtained indicate gum arabic to have better encapsulation ability for piperine in the oleoresin than has modified starch. The $t_{1/2}$ for TP loss in free oleoresin, oleoresin encapsulated in gum arabic and encapsulated modified starch were 55.54, 121.57 and 128.33 weeks, respectively. Both modified starch and gum arabic gave TV comparable to that in free oleoresin, indicating no stabilizing effect. The values of $t_{1/2}$ with respect to TV were 23.49, 25.76 and 26.34 weeks for free oleoresin, gum arabic and modified starch, indicating no major advantage of microencapsulation. For EP, gum arabic gives better protection than does modified starch. Stability of NV is higher in microcapsules from gum arabic than microcapsules of modified starch and free oleoresin.

Table 1
Regression analysis of EP, TP, TV and NV in the microcapsules[a,b] and oleoresin[b]

Type	Oleoresin	$t_{1/2}$ (weeks)	Gum arabic	$t_{1/2}$ (weeks)	Modified starch	$t_{1/2}$ (weeks)
EP	–	–	$Y = -0.0097X + 4.601$ $R^2 = 0.921$	71.44	$Y = -0.0126X + 4.601$ $R^2 = 0.959$	55
TP	$Y = -0.125X + 4.604$ $R^2 = 0.994$	55.44	$Y = -0.0057X + 4.604$ $R^2 = 0.943$	121.57	$Y = -0.0054X + 4.603$ $R^2 = 0.958$	128.33
TV	$Y = -0.0295X + 4.606$ $R^2 = 0.999$	23.49	$Y = -0.0269X + 4.605$ $R^2 = 0.997$	25.76	$Y = -0.0263X + 4.6187$ $R^2 = 0.972$	26.34
NV	$Y = 0.0098X + 4.4.6045$ $R^2 = 0.999$	70.71	$Y = 0.0089X + 4.6007$ $R^2 = 0.981$	77.86	$Y = 0.0167X + 4.5969$ $R^2 = 0.981$	41.49

[a,b] Oleoresin at 2.5% based on carrier material used.
[b] R^2 indicates the correlation coefficient.

4. Conclusions

Gum arabic was found to be a better wall material for encapsulation of pepper oleoresin than is modified starch. The protection offered to piperine was very clear from the experiment carried out in this work, although the same cannot be said for TV. The free-flowing nature of all these microcapsules is of advantage to the food processing industry. There seem to be differences of opinion as to which carrier is the best encapsulating aid. Work with different carrier materials, their blends and their physicochemical nature, deffecting the entrapment of this complex flavour system needs to be elaborated.

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