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Drying and Preservation of Phytochemicals from Elateriospermum Tapos Seed Oil using Combination of Freeze Drying and Microwave Technique

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Elateriospermum Tapos seed oil (ETSO) or known as perah seed oil contain high concentration of omega 3 fatty acid and exposed to lipid oxidation in the form of free oil. In this work, microencapsulation process of ETSO was formulated by using combination of freeze drying and microwave technique assisted freeze drying using maltodextrin (MD) and sodium caseinate (SC) as wall materials in order to protect the oil from oxidation. This kind of drying technique is a new technology of oil microencapsulation with faster drying time than conventional freeze drying. The main goal of this study was to evaluate the microencapsulation process on the physical and chemical characteristic of oil microcapsule. The microencapsulation effectiveness was determined in base of process yield and the microencapsulation efficiency. The white dry microcapsules were subjected to Field Emission Scanning Electron Microscope (FESEM) to study the powder morphology, Fourier Transform Infrared Spectroscopy (FTIR) to study chemical bonding and thermogravimetric (TGA) for thermal profile. Highest encapsulation yields of 82 % and microencapsulation efficiency of 42 % were achieved when the compositions of wall material used as encapsulation agents were 75 % maltodextrin and 25 % sodium caseinate, freeze drying time was 7 h and the ratio of oil-wall material was 1 : 4.

1. Introduction

Nowadays, consumers are becoming more concern on nutritious and healthier food. The benefits of omega-3 fatty acids such as their potential role in reducing the risk of coronary heart disease, inflammatory and immune disorders, colon cancer and in improving early development lead to the fortifications of oils with high in long chain omega-3 fatty acids in many food products. Pertaining to the abundance of unsaturated fatty acids and tocopherols in vegetables oil, they contribute the greater demand of the latter. ETSO is new local source of seed oil containing high linolenic acid (18 %) along with oleic acid (32.5 %) and linoleic acid. Perah seed demonstrates considerate amounts of other bioactive components, such as tocopherols (vitamin E), squalene and L.beta-sitosterols (Tan et al., 2013). Oil extracted from the seed can be applied in various food products. The fortification of oil in food products are impaired by chemical instability and exposed to oxidative damage when bared to oxygen, moisture, temperature and light due to the existence of polyunsaturated fatty acids. The oxidative deterioration leads to nutritional loss, unpleasant flavours, reduce shelf life and sensory properties of the oil (Calvo et al., 2010).
Oil microencapsulation has been applied in food industry to overcome those issues especially to protect food ingredients such as essential oils, colourant, lipid and flavours against oxidation (Goula and Adamopoulos, 2012). Wall system around the encapsulated material provide a barrier to protect the food ingredients from oxidation during food production and storage.The wall system also produces powders products with new properties and also controllable release during consumption (Adamiec and Kalemba, 2006). Many techniques of microencapsulation can be accomplished such as spray drying, freeze drying, extrusion, coacervation liposome entrapment, inclusion complexion, co-crystallisation, interfacial polymerisation and microwave.

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Drying is an important step in microencapsulation for storage purpose, normally in powder form. Freeze drying is known best to encapsulate heat sensitive material. However, the highest cost of freeze drying amongst of all drying operations become a constraint to its application (Velasco et al., 2003). Reducing drying time is one of the key research topics to improve the process economics. Combination of freeze drying and microwave is one of the promising microencapsulation technique to reduce cost by minimising the freeze drying time.

2. Materials and method

ETSO was obtained from local farm in Kuala Lipis, Pahang. Reagents such as sodium caseinate brand Sigma, Germany, maltodextrin brand Aldrich, USA and hexane were obtained from Syarikat Pustaka Elit, Johor.

2.1 Microencapsulation process

ETSO microencapsulation was performed by the formation of an emulsion of the core material (oil) in the wall solution using modified method of Calvo et al. (2012). Three different microcapsule models were evaluated in the present study. Different ratios oil and wall material (1 : 1, 1 : 4, 1 : 7) were evaluated for each studied wall materials. The emulsion was prepared by mixing ETSO with different percentage of wall solution (75 % MD: 25 % SC, 50 % MD : 50 % SC, 25 % MD : 75 % SC) at room temperature using a hot plate magnetic stirrer for 2 h. The prepared emulsion was frozen at −80 °C, freeze-dried by a lyophiliser (Alpha 1-2 LD Plus, Martin Christ, Germany) from 1 to 7 h instead of 1 to 2 d of normal operation. After the lyophilisation process, microcapsules were dried in microwave power 110 kW for 10 min. Then the microcapsules were grinded and transferred to double layer plastic bags.

2.2 Moisture

This analysis was conducted using Infrared Moisture Determination Balance (Kett, FD-620, Japan). 2.0 g of sample was used and heated at temperature 105 °C. Triplicates reading of moisture content and average were taken for each sample.

2.3 Microencapsulation Yield

The yield of extraction was calculated in terms of mass percentage as shown in Eq(1) followed the method used by Mohd Fauzi et al. (2011).

$$Yield\ (\%) = \frac{mass\ of\ oil\ extracted\ (g)}{mass\ of\ sample\ (g)} \times 100\ \% \quad (1)$$

2.4 Microencapsulation Efficiency

Microencapsulation efficiency modified procedure Calvo et al. (2012) was analysed after microencapsulation process. This analysis serves to caluculate the amount of unencapsulated oil present. 2.5 g of microcapsules was will be weighted in a beaker and 25 mL of hexane will be added and shaken by hand for 20 s at room temperature to extract superficial oil. A filter paper was used to filter the solvent mixture. Then, unencapsulated oil will be collected after removal of hexane. The same microcapsules powder was extracted by soxhlet extractor for 6 h using hexane as extracting solvent to determine the encapsulated oil. After that, hexane was removed and the extracted oil was measured. Microencapsulation efficiency (ME) was measured according to Eq(2). Total oil is calculated by the percentage of free oil content as described by Calvo et al. (2012).

$$ME = \frac{Total\ Oil - Surface\ Oil}{Total\ Oil} \times 100\ \% \quad (2)$$

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR unit was equipped with a deuterated triglycine sulphate (DTGS) as a detector and a KBr Germanium as a beam splitter, interfaced to a computer operated under windows based and connected to OMNIC operating software system was used for FTIR spectra acquisition. Automatic dehumidifier was used to diminish water vapor interface from the machine. A few drop of each sample were put onto the Attenuated Total reflectance (ATR) multibounce plate of crystal at controlled ambient temperature (25 °C). All spectra were recorded from 4,000 to 400 cm^{-1} co-adding 32 interferograms with measurement accuracy in vc the frequency data at each measured point of 0.01 cm^{-1}, due to the laser internal reference of the instrument. Each time this spectrum was subtracted from the background air spectrum. A new air spectrum was taken after every scan with sample. The ATR plate was carefully cleaned with ethanol and was dried with a soft tissue before taking the spectra of a new sample.

2.6 ThermoGravimetric Analysis (TGA)

TGA was carried out on a TA 2050 Instrument under nitrogen or air atmosphere at a purge rate of 50 mL/min. For each experiment, a sample of approximately 10 mg was used. A heating rate of 10 °C/min was applied, and the temperature was raised from 20 to 800 °C. In addition to the weight loss percentage (TG) curves, the derivative weight loss percentage (DTG) was calculated for each sample.

2.7 Field Emission Scanning Electron Microscope (FESEM)

Morphological study on the oil microcapsule powder will be observed by FESEM. It is be operated with X1,000, X25,000 and X100,000 magnification at 25 kV.

3. Result and discussion

Three oil microcapsules samples (sample A, B and C) were formulated with different percentage of wall compositions, different ratio oil to wall and different drying time to evaluate the microencapsulation process by freeze drying and microwave on the physical and chemical characteristic of the oil microcapsule. Microencapsulation formulation of sample A, B and C are summarised in Table 1.

Table 1: Microencapsulation of ETSO by using maltodextrin and sodium caseinate as wall materials

Sample	Encapsulant compositions (% MD - % SC)	Ratio oil-wall	Freeze Drying Time (h)	Moisture content (%)	M. Efficiency (%)	M. Yield (%)
A	75 % MD, 25 % SC	1 : 1	4	8.16	11.59	82.18
		1 : 4	1	9.15	37.23	82.15
		1 : 4	7	0.94	42.69	84.73
		1 : 7	1	7.40	6.18	82.49
		1 : 7	4	4.88	36.55	83.69
B	50 % MD, 50 % SC	1 : 1	1	11.70	3.92	80.94
		1 : 1	7	4.22	9.88	81.26
		1 : 4	4	2.23	28.77	84.77
		1 : 7	1	8.39	17.96	82.49
		1 : 7	7	2.12	26.58	81.38
C	25 % MD, 75 % SC	1 : 1	4	5.79	4.23	81.68
		1 : 1	7	2.85	15.22	80.44
		1 : 4	1	5.78	14.45	82.39
		1 : 4	7	0.25	18.85	80.69
		1 : 7	4	2.55	10.56	81.11

From Table 1, it can be seen that increasing ratio oil to wall materials and increasing the percentage of sodium caseinate reduce the moisture content at same drying time. Moisture content is the most influence factor in promoting lipid oxidation especially in oil microencapsulation. High value in moisture content will contribute the increment of omega-3 degradation and encouraging the growth and development of molds, bacteria and other microorganisms as stated by Dian et al. (1996). Moisture content gives high influence on physical changes of the solid matrix of microencapsulated oils and lead to the accessibility of oxygen to the oil. Relative protection of a high-viscosity solid matrix in the glassy amorphous state is achieved after drying process of microencapsulated oil (Velasco et al., 2003). It is suggested that combination of 75 % MD and 25 % SC with ratio oil to wall is 1 : 4 with 7 h drying time by freeze dryer could be a good coating material for microencapsulation of ETSO which highest encapsulation efficiency about 42.69 %. This result is an agreement with Calvo et al. (2012) with better encapsulation efficiency by increasing the percentage of maltodextrin. Velasco et al. (2003) concluded that freeze-dried samples showed lower microencapsulation efficiency compared to hot air drying but more resistant to oxidation. All formulation gives good encapsulation yield more than 80 %.

3.1 FTIR

Figure 1 showed FTIR spectra of control, microcapsule sample A, B and C. Microcapsule sample and control showed clear band shift at 2,926 cm^{-1} and 2,849 – 2,855 cm^{-1}, attributed to the symmetric and assymetric stretching vibration of the aliphatic CH_3 and CH_2 group which is typical functional group of fatty acids in ETSO. FTIR spectra of microcapsule samples showed the characteristic bands and intense peaks corresponding to

proteins which attribute to sodium caseinate as wall material at 1,638 – 1,655 cm $^{-1}$.The FTIR spectra for all microcapsule samples were found identical which showed similar characteristic phenomena. Microcapsule

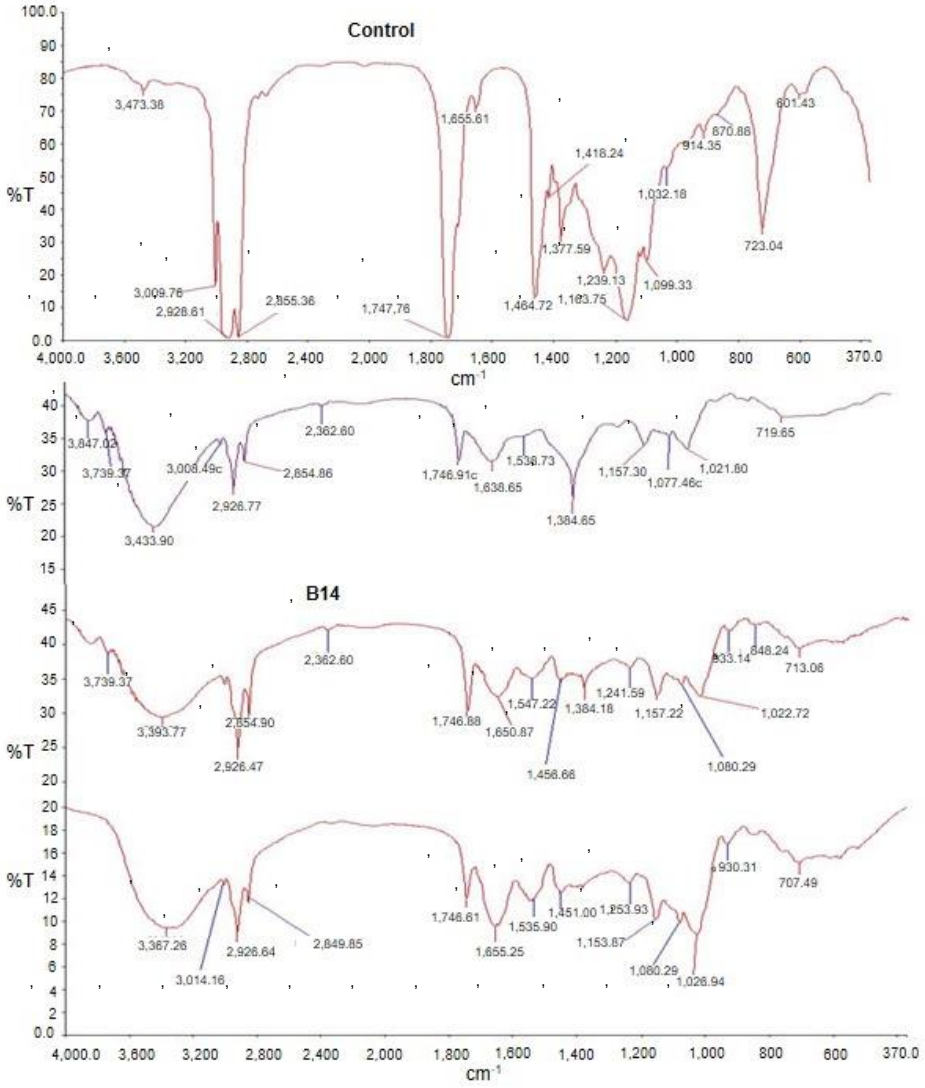

Figure 1: FTIR spectrum of ETSO, microcapsules sample A (encapsulant compositions: 75 % MD, 25 % SC), sample B (encapsulant compositions: 50 % MD, 50 % SC) and sample C (encapsulant compositions: 25 % MD, 75 % SC).

sample spectrum demonstrated a broad band at 3,367 – 3,393 cm^{-1} which can be attributed to O-H stretching vibrations. The peak at 1,746 cm^{-1} represented the ester carbonyl bond (C-O) functional group of the triglycerides. Maximum absorbance at 3,009 cm^{-1} for control is due to the composition as vegetable oils contain higher proportion of linolenic or linoleic acyl groups. The clear shift of the 3009 cm^{-1} band is noticed in microcapsule samples, attributed to the C-H stretching vibration of *cis*-double bond, to the 3,008 - 3,014 cm^{-1} bands. The structure of control and microcapsule samples is different due to the oil had undergone polymerisation by microencapsulation process. The spectral region between 2,700 cm^{-1} to 3,700 cm^{-1} exhibited different intensity between microcapsule samples and control at same band shift. The control exhibited similar characteristic of ETSO which in agreement of the study done by Azlan Hadi Tan et al. (2013).

3.2 TGA

TGA analysis was aimed to investigate the thermal behaviour of samples from microcapsule powders of ETSO for sample A, B and C. The TGA curves of three formulations of ETSO microencapsulation are shown in Figure 2. All samples showed similar degradation patterns with three main thermal events referring to the

three materials used in the formulation; maltodextrin, sodium caseinate and ETSO. Sample C showed high thermal stability followed by sample A and sample B. By increasing the percentage of maltodextrin in wall compositions, mass loss has slightly increased which indicate slight changes to the microcapsules thermal stability. The first degradation occurred above 200 °C corresponding to degradation of polysaccharides (maltodextrin) which is an endothermic transition. In this stage, 21.4 %, 18.6 % and 16 % of mass loss for sample A, B and C is occurred, respectively. Bothara and Singh (2012) concluded in their study, polysaccharides start to decompose slowly at 250 - 280 °C and produce high char (86.8 % and 88.2 %) at the final temperature. The formation of H_2O, CO and CH_4 resulted from dehydration, depolymerisation and pyrolitic decomposition which are involved in these high temperature stages. The second degradation was observed around 300 °C corresponding to degradation of sodium caseinate (Marinho et al., 2015). In this stage, 33.1 %, 39.4 % and 25.2 % of mass loss for sample A, B and C is occurred, respectively. It seems that sample C has highest protein thermal stability. By decreasing the ratio of oil to core, the mass loss increased 7.9 to 14.2 %, indicating a slight change in the microencapsulation thermal properties. Barreto et al. (2003) explained, the protein thermal degradation occured at temperatures above 300 °C since inter and intra-molecular hydrogen bonding are broken up at raising temperatures during heating which lead to the gradual loss of the initial ordered structure of the polymer matrix. The third degradation was observed around 400 °C corresponding to autoxidation mechanism in the ETSO which are chain reactions initiated by the formation of free radicals. At initial stage of oxidation, the generation of primary oxidation products such are hydroperoxides are subsequently react with oxygen to form intermediate oxidation products such as aldehydes and acids which accelerating the degradation process These intermediate products evaporate at higher heating rates before they can react with oil solution that shifting to higher value. A relatively higher energy is needed initially to initiate the chain reactions but a lower energy used during the oxidation process occur as the accumulation of free radicals which is related to the concentration of free radicals and reactants is reached (Micic et al., 2015).

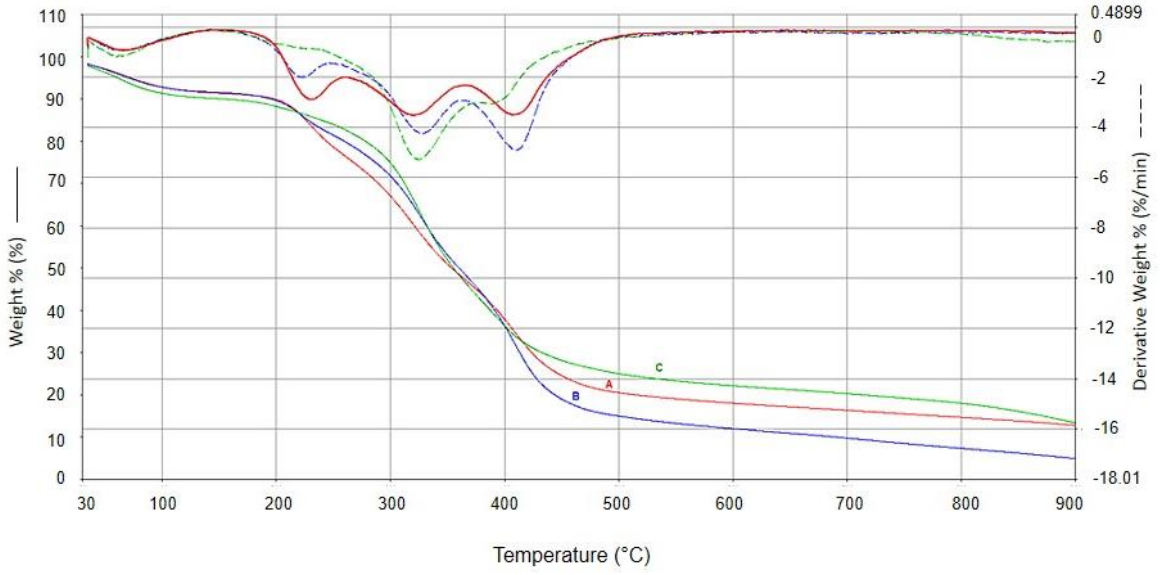

Figure 2: TGA curves of different formulation of ETSO microencapsulation

3.3 FESEM Analysis (Powder Morphology)

Figure 3 demonstrate the morphology of ETSO microcapsules of sample A which gives highest microencapsulation efficiency of 42.69 %. The surface of microcapsule is irregular in structure and matrix type of encapsulation. The FESEM images of microcapsules obtained at lower magnification shows the porous structure and rough surface. The formations of spherical microcapsules were clearly showed with magnification of X100,000. The liquid product is first frozen and then the water is sublimated and dismissed in the freeze drying process. During freezing, from ice crystals or air bubbles retained and formed cavities which result the porous structure and the solid network should be able to support this porous structure. If the temperature of the dehydrating porous product is above *T*g, the viscosity of the solid material may not be enough to hold the structure and lead to “collapse” or shrinkage (Fariasa et al., 2007). High oxidative stability

microcapsules powder during storage provides better oil protection against oxidation. The capsules have lower permeability to gases that protect the core material efficiently.

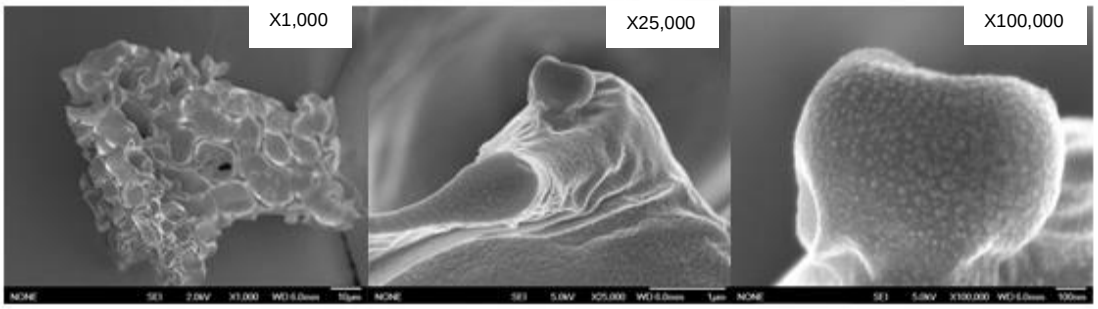

Figure 3: FESEM image of the sample A (Ratio oil-wall = 1 : 4, wall compositions = 75 % MD + 25 % SC, drying time = 7 h by freeze dryer + 10 min by microwave); Magnification of X1,000, X25,000 and X100,000.

4. Conclusions

Microencapsulation of ETSO by freeze drying and microwave technique has successfully shortened the drying time to achieve low moisture content compared to normal process of freeze dryer. The processing cost will be reduced. This study contribute to the progress of microencapsulation technology in processing and storage as well as exploring the benefits of underutilised seed in Malaysia.

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