

Microencapsulation of vitamin e from palm fatty acid distillate with galactomannan and gum acacia using spray drying method

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Abstract. Vitamin E from palm fatty acid distillate (PFAD) has been encapsulated using spray drying method with gum acacia (GA) and mixed of galactomannan from *Arenga pinnata* (GAP) with GA as encapsulating agent. Composite films with thickness vary from 0.542 – 0.779 mm were prepared by incorporating vitamin E onto matrix of GA (7 g) with various concentration of GAP (0.1; 0.2; 0.3 and 0.4 g). The film obtained from 0.2 g GAP and 1.3 g vitamin E showed better compatibility and have viscosity similar with standard (ISO 9001:2008 and ISO 22000:2005). That composition was used for spray drying method rendering micro-particle size 11 μm and the particle had spherical shape. Although the increment of GAP decreasing moisture content and the particle size from 16 μm to 11 μm , the yield of microcapsule, encapsulation efficiency, the amount of vitamin E absorbed and oxidation stability of vitamin E were increased.

1. Introduction

Vitamin E with low solubility is important for human health and usually occurred from food or supplement vitamin. Tocopherol and tocotrienol are the main compound of vitamin E which have high antioxidant properties that can block free radical, protecting cell membrane from lipid oxidation [1, 2]. Vitamin E also have been used as antioxidant in emulsion or milk product to prolonged storage time [3]. The concentration of tocopherol and tocotrienol in crude palm oil is around 600 – 1000 ppm. Palm fatty acid distillate (PFAD) is a by-product of purification process of crude palm oil which contained vitamin E. Most of vitamin E compound contained in PFAD is tocotrienol (70%) and tocopherol (30%) [4].

Vitamin E is very sensitive that its activity and stability are affected by light, humidity, oxygen and high temperature particularly when in storage [6]. In addition, vitamin E also has low solubility in water which therefore decreases the availability in body. Incorporation into polymer matrix is one of the possible ways to protect their availability and to improve the solubility (Goud et al., 2005). The best and cheapest method to encapsulating vitamin E is using spray drying method [7]. Spray drying is common process for microencapsulation lipid and flavour [5]. This method will produce powder with good quality, low water activity, easy to handle and could protect the active material from unnecessary reaction. The choice of protecting material and emulsion properties affect the efficiency process and stability of microencapsulation product [8].



There are some requirements to use as protecting material such as must have good characteristic (high solubility, good emulsion and low viscosity), easy to obtained and mixed with other protecting material [9]. The choice of protecting material affects the emulsion and characteristic of the particle after spray drying and in storage time [10]. Gum Arabic or gum acacia which contained galactomannan was the common protecting material using spray drying method. However the price of gum acacia is very expensive. Another galactomannan source is *Arenga pinnata* seed (or 'kolangkaling') which found abundantly in Indonesia and the utilization remain low [11]. Commonly *Arenga pinnata* seed only used for cocktail and soup food in Indonesia [12]. The main polysaccharide component contained in *Arenga pinnata* is galactomannan which is water soluble polysaccharide [13, 14] with ratio of galactose : mannose is 1 : 1.33 and the value of IC₅₀ is 22.109 mg/ml [14].

Other researchers have studied the microencapsulation of vitamin E using surfactant chitosan oligosaccharide [15], liposome [16], whey protein isolate [17]. Utilization microencapsulation technology to protect active compound could increase physical stability, protecting from chemical degradation and other food ingredient. Microencapsulation of vitamin E from palm oil produces a powder which has high antioxidant and good stability. As a powder, this product has advantages such as easy to use as food additive for food product. Gum acacia also already used as protecting material in one of oleo-chemicals companies in Medan. To the best of our knowledge no studied was found related to microencapsulation of vitamin E using galactomannan from *Arenga pinnata* or combination with other polysaccharide.

Based on that, the aim of this study is to explore the potency of galactomannan from *Arenga pinnata* (GAP) in combination with gum acacia as encapsulation material. The properties of encapsulated material such as emulsion stability, compatibility in form of film and viscosity were studied while the microcapsule product was characterized based on their surface morphology, lipid content, oxidation stability, yield, encapsulation efficiency, water content and the mixed compound interaction using Fourier Transform Infrared.

2. Materials and Methods

2.1. Materials

The materials such as *Arenga pinnata* seed was obtained from local market in Medan, North Sumatera – Indonesia while PFAD was from local oleo-chemicals company in Medan. All the chemicals were obtained from local distributor and was used without any purification.

2.2. Procedures

2.2.1. Preparation of Emulsion

Gas chromatography (GC) was used to analyse the component contained in vitamin E PFAD using AOCS Ce5-86 method. The ratio of α , β , γ and δ of tocopherol and tocotrienol were analysed using high performance liquid chromatography (HPLC) using a mixture of n-heptane and ethyl acetic in the ratio of 97:3 (v/v) as stationary phase (AOCS Ce8-89). Extraction of galactomannan from *Arenga pinnata* seed was conducted following our previous method [14].

Preparation of emulsion for microencapsulation vitamin E was carried out based on the procedure from one of oleo-chemicals industry following regulation of ISO 9001:2008 and ISO 22000:2005 with slightly modification. GAP was dissolved in deionized water at temperature of 70°C under stirrer at 1500 rpm. After that, gum acacia (GA) was added to the GAP solution followed by addition of vitamin E and stirred for 30 min. The mixed solution was examined for viscosity and stability. Next, a 95 ml of mixed solution was poured to petri dish (diameter 9 cm) and dried in oven blower at 35°C for 10 hours and was stored in desiccator before used. The physicochemical properties of the film formed from this procedure were determined by thickness using micrometre and the surface morphology using scanning electron microscope (SEM).

2.2.2. Viscosity Analysis of Emulsion

Sample was added to viscometer Brookfield tube and raised until spindle was covered by the solution. The spindle was rotated at speed of 60 and 100 rpm at temperature of 70°C and the viscosity value shown was recorded in %CP and torque.

2.2.3. Stability Analysis of Emulsion

Stability of emulsion was determined by observing the mixed solution of GAP, GA and vitamin E. Observation was conducted after the mixed solution was heated at 70°C and stirred at 1500 rpm for 30 min. The time that vitamin E was separated from the solution was recorded..

2.2.4. Microencapsulation using Spray Drying Method

Vitamin E, water, GAP and GA was mixed based on the formulation that given uniform compatibility and viscosity which related to industry standard. Those formulation was used for spray drying method with initial temperature was 70°C for 15 min. Next, the mixed solution was filtered using filter bag 1000 micron and had spray dryer using hot air (180 – 200°C).

2.2.5. Yield Analysis of Microcapsule Powder

The yield analysis of the powder product was conducted following equation below.

$$Y = \frac{Wp - (Wp \times MCp)}{Wf - (Wf \times MCf)} \times 100\% \quad (1)$$

Where:

Wp = weight of microcapsule product

Wf = weight of mixed solution before spray drying

MCp = weight of water contained in microcapsule product

MCf = weight of water contained in mixed solution

2.2.6. Water and Lipid Content Analysis in Microcapsule Product

Water content contained in microcapsule was determined using moisture analyser AND MX-50. 5 gram of sample was putted in glass plate and the drying process was begun. The moisture value was automatically appeared in the screen. Lipid content analysis was conducted using soxhlet extraction method with petroleum benzene as the solvent.

2.2.7. Oxidation Stability Analysis of Microcapsule

The microcapsule was putted in closed glass bottle and was stored at 60°C to increase the oxidation process. The oxidation stability was measured using 2 different methods such as p-aniline value for peroxide and the vitamin E content using HPLC started at zero time (after drying) and after 2 day storage [8].

2.2.8. Efficiency Encapsulation

The efficiency encapsulation was determined based on Bae and Lee (2008) method with modification. A 15 ml of hexane was added to 1.5 gram of microcapsule in closed glass bottle and be shaken with hand for 2 min at room temperature. The mixed of solvent was separated using Whatman No. 1 filter paper and the residue was washed three times with 20 ml of hexane. Next, the solvent was evaporated at 60°C and the residue was weighed. The efficiency encapsulation was calculated based on the equation below.

$$Efficiency\ Encapsulation = \left[\frac{TO - SO}{TO} \right] \times 100\% \quad (2)$$

Where:

EE = efficiency encapsulation

TO = Weight of total lipid content

SO = Weight of lipid extracted

3. Results and Discussion

3.1. Composition of Vitamin E PFAD

Crude palm oil contained vitamin E in the range of 600 – 1000 ppm which tocopherol (21 – 31%) and tocotrienol (66 – 79%) are the main compound. However, most of vitamin E was lost during refinery process (Schwartz *et al.*, 2008). Vitamin E could be extracted from PFAD as refinery by product (Fizet, 1993). Based on the GC analysis, the main components of PFAD was vitamin E as showed in figure 1 while figure 2 presented the components of vitamin E.

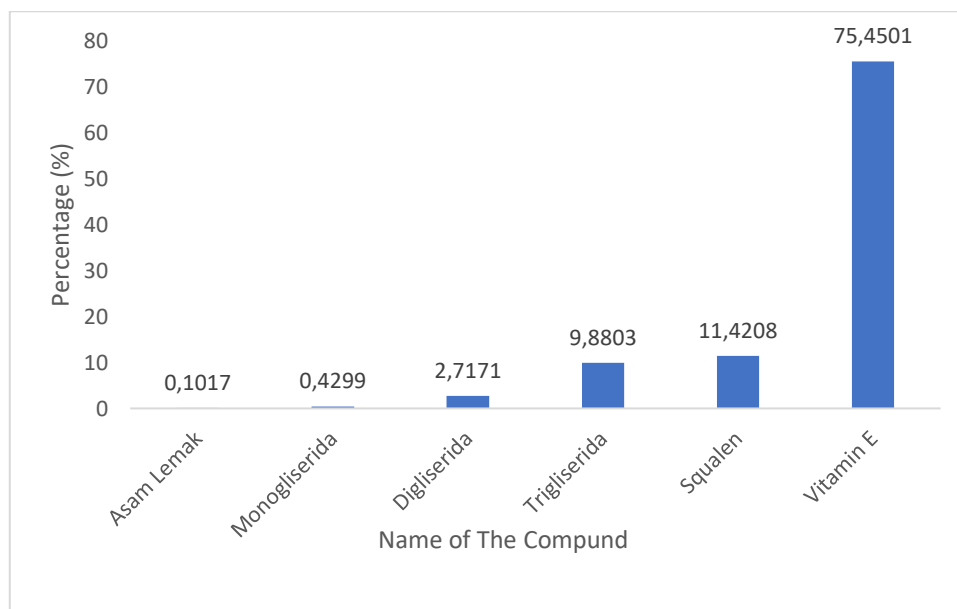


Figure 1 Components of vitamin E from PFAD

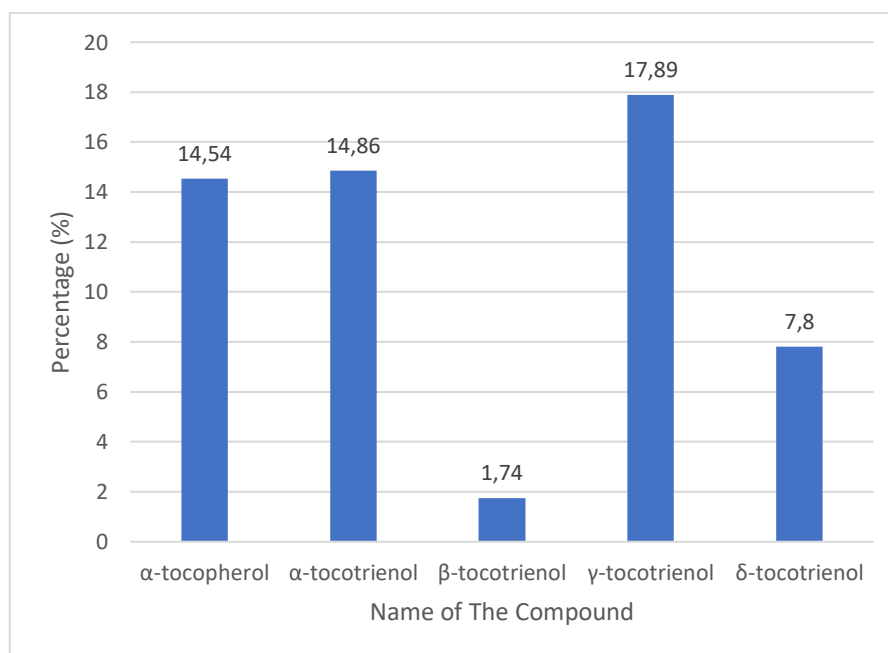


Figure 2 Components of vitamin E

3.2. Characterization of Emulsion

The emulsion was formed from mix of GAP varied from 0.1 gram to 0.4 gram, 7 gram of GA and 1.3 gram of vitamin E as shown in table 1. Those emulsion composition was also used for film preparation.

Table 1. Formulation Emulsion

Materials	Formulation (gram)						
	1	2	3	4	5	6	7
GAP	-	0.1	0.2	0.3	0.4	0.4	0.3
GA	7.0	7.0	7.0	7.0	7.0	-	7
Vitamin E	1.3	1.3	1.3	1.3	1.3	1.3	-
Deionized Water	91.7	91.6	91.5	91.4	91.3	98.3	92.7
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Based on table 2, the viscosity of GAP was higher than GA which 0.4 gram of GAP has viscosity of 3.95 cP while 7 gram of GA is only 2.92 cP. Therefore it can be concluded that in the increment of GAP the viscosity of emulsion increased rendering increasing of the thickness of the film. The viscosity value that similar with the standard (cP 13.2 and torque 27.0%) was obtained from formula 3 and 4 using GAP 0.2 gram and 0.3 gram. The stability analysis was conducted by observing the solubility of GAP, GA and vitamin E after heated at 70°C and stirred at 1500 rpm for 30 min. The time for vitamin E separated from the emulsion was used to determine the emulsion stability. As shown in table 2, the stability of GAP was lower than GA which probably due to the emulsifier properties of GA was 4 times higher than GAP.

Table 2 the viscosity and stability of emulsion and the thickness of the film

Formulasi	Viscosity at 70°C				Stability (second)	Thickness of Film (mm)
	60 rpm		100 rpm			
	cP	%Torque	cP	%Torque		
1	2.92	5.8	2.74	9.0	126	0.542
2	4.45	8.9	4.08	13.6	378	0.601
3	5.73	11.4	5.49	18.43	395	0.635
4	7.75	15.5	7.08	23.36	412	0.646
5	9.22	18.4	9.93	33.10	507	0.779
6	3.95	7.9	3.57	10.20	30	0.101
7	7.43	14.9	7.86	26.20	-	0.684

The formulation 3 showed better compatibility based on the film morphology as shown in figure 3. Therefore formulation 3 was used for spray drying. This result is similar with other researchers founded that efficiency encapsulation was affected retention property and ability to form film of the material protecting [8].

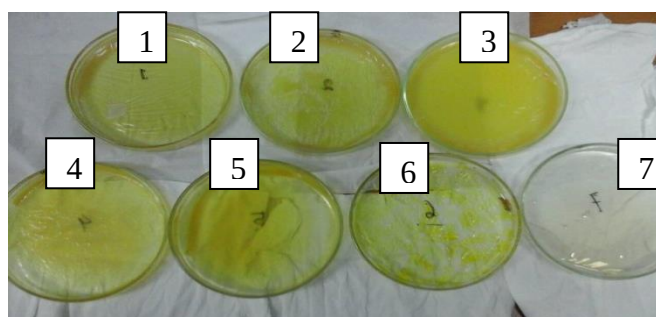


Figure 3 the films of mixed GAP, GA and vitamin E**3.3. Characterization of Microcapsule**

Based on the compatibility film formed from formulation 1 to 7, the formula 3 was chose for spray drying method with minimum capacity was 1000 gram as shown in table 3. The microencapsulation process was started with heated the water until 70°C followed by addition of GA under stirred at 3000 rpm for 30 min which was continued for 15 min after the addition of vitamin E. The sample was used for spry dry using heat air with temperature input ranging from 180 – 200°C and output temperature was 90°C. The sample was pumped with using peristaltic pump with flow rate was 20 rpm. The microcapsule was accommodated in closed bottle followed by determined the weight. Similar procedure also conducted with or without the addition of GAP which already dissolved in water.

Table 3 Formulation of Microencapsulation

Materials	Formulation		Weight Feed (gram)	
	Microencapsulation (%)			
	A (GA)	B (GA:GAP)	A (GA)	B (GA:GAP)
Air	60	60	600.00	600.00
GAP	-	0.4	-	4.04
GA	14	13.6	140.10	136.15
Vit. E	26	26	260.16	260.21
Total	100	100	1000.26	1000,40

Table 4 Some parameters of microcapsule

Parameters	Microcapsule	
	A	B
Yield (%)	53.1524	64.0918
Water Content (%)	3.40	3.08
Particle Size (µm)	16	11
Lipid Content (%)	61.8253	62.4414
Unencapsulated Lipid (%)	24.3097	18.7224
Efficiency Encapsulation (EE) (%)	60.6800	70.0160

The yield occurred from microencapsulation process was below 100% as showed in table 4 which because some of microcapsule stick to the wall of spray drying column. In addition, some of the particles have small size which brought by hot air flow and could not separate from the cyclone. Furthermore, small size particle was stuck in the filter and hence could not collect. However with addition of GAP 4 gram in 1000 gram solution could increase the yield of microcapsule around 17.07%. The water content was decreased to 9.41%. Water content is one of important parameters which affect the quality of dry microcapsule powder. Low water content could inhibit fungi or bacteria growth which could degrade the product (Master, 1979). Buckle et al. showed that high water content could degrade the product therefore the maximum of water content is less than 8%. Therefore based on our study the addition of GAP could increase the storage time of microencapsulation due to low water content.

The efficiency encapsulation was increase at 13.33 with increasing of GAP which due to increasing of emulsion stability. This was similar with other researcher findings that application of more than 2 protecting material could increase efficiency encapsulation. Furthermore, Carneiro et al. concluded that efficiency encapsulation was affected by the type of protecting material used. Poor stability could produce low efficiency encapsulation [8]. The quantity of encapsulated lipid raised in the high efficiency encapsulation (Barbosa et al., 2005). Figure 4 G and I showed that there are some black dot which probably is unencapsulated vitamin E. In comparison no black dot appeared in figure 4 H and J which mean all the vitamin E has been encapsulated. Therefore it can be concluded that addition of GAP could increase the encapsulation process. Based on the figure 4 I and J the size of

microcapsule was decrease in addition of GAP. Bigger size of microcapsule shown the mixing is not homogenized which have low emulsion stability. In addition using different protecting material also affects the morphology of microcapsule (Carneiro at al., 2013). This was shown in figure 4 that in addition of GAP produce oval shape which have smooth surface.

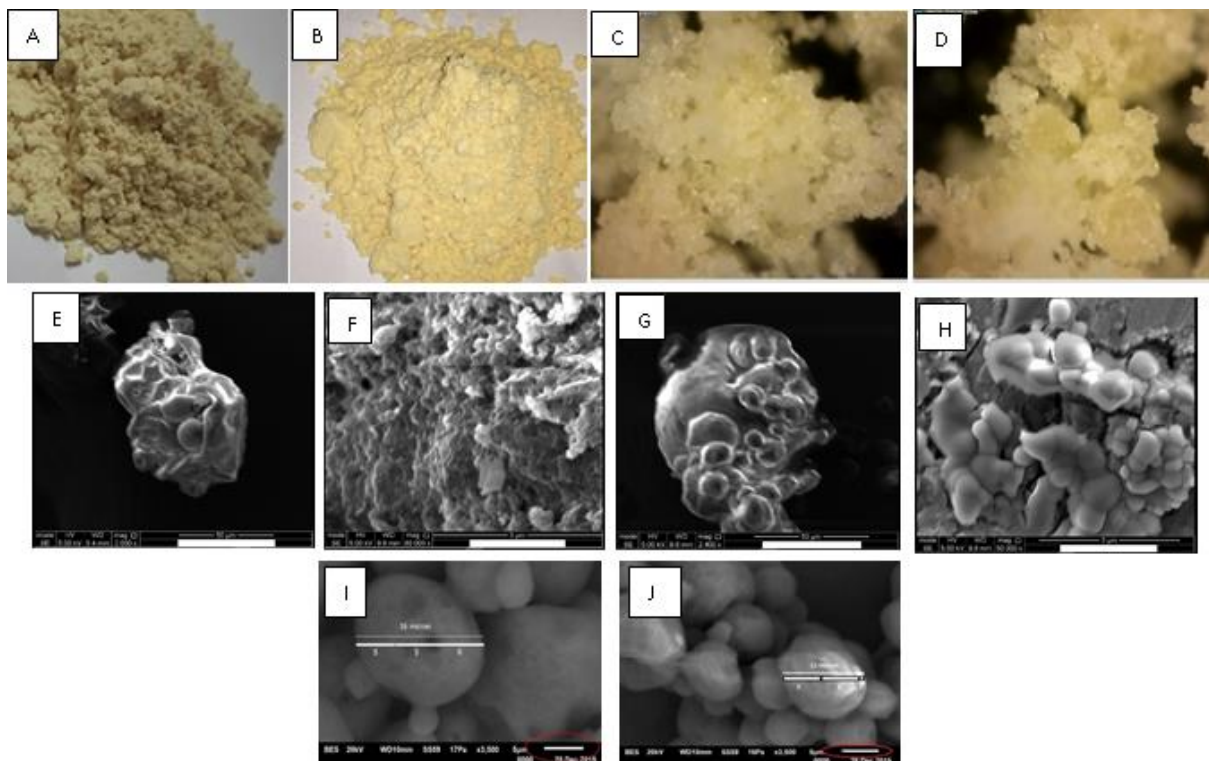


Figure 4 the photo of (A) microcapsule A; (B) microcapsule B and the SEM images of (C) microcapsule A; (D) microcapsule B; (E) gum acacia powder; (F) GAP powder; (G) microcapsule A; (H) microcapsule B; (I) the size of microcapsule A (16 μm); (J) the size of microcapsule B (11 μm).

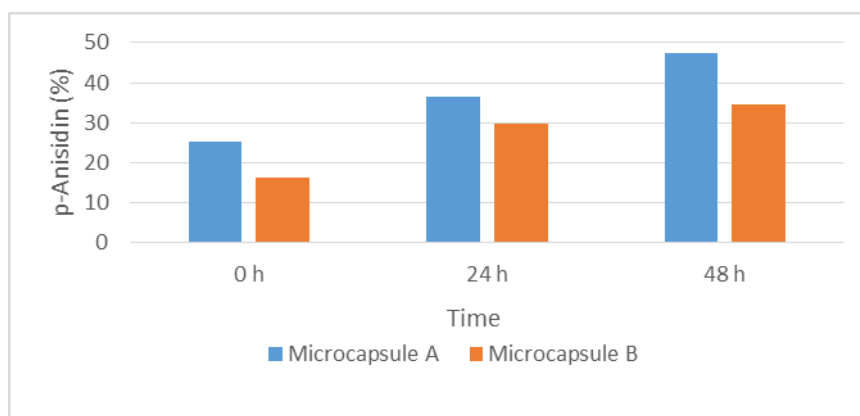


Figure 5 Oxidative Stability of Encapsulated Vitamin E PFAD by p-Anisidin Value Method (Microcapsule A and B).

Oxidation stability of microcapsule A and B showed by p-anisidine value as presented in figure 5. No oxidation was detected at 0 hour. As shown in figure 5 the total vitamin E was only slightly

decreased in the increasing storage time. The addition of GAP as protecting material have lowering p-anisidine value which mean encapsulated vitamin E have good stability.

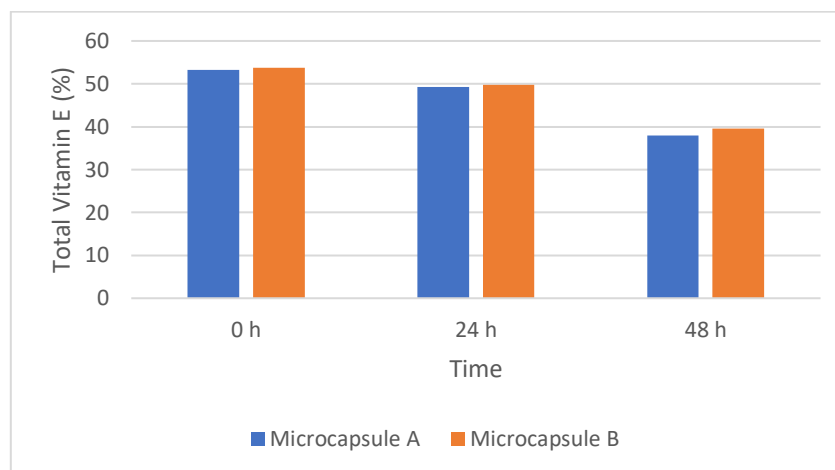


Figure 6 the total vitamin E contained in microcapsule A and B in several time

FT-IR spectroscopy was used to identify interaction between vitamin E and protecting material in microcapsule. The absorbance spectra of GAP, GA, vitamin E, microcapsule A and B were recorded in the region of $4000 - 400 \text{ cm}^{-1}$ as shown in figure 7. A peak at 3500 cm^{-1} appeared in all spectra which were a stretching vibration of OH group. Two strong peaks at region of $2800 - 3000 \text{ cm}^{-1}$ represent stretching of C-H group while peak at 1732 cm^{-1} which only appeared in spectra of vitamin E represent stretching of C=O group. This was because vitamin E also contained triglyceride, diglyceride, monoglyceride, fatty acid and squalene. Figure 7 D and E showed the mixed of vitamin E, GAP and GA which have similar peaks with each pure compound. Therefore it can be concluded that there was interaction between all the components without any changes in their structure. This result was similar with other researcher findings [18, 19].

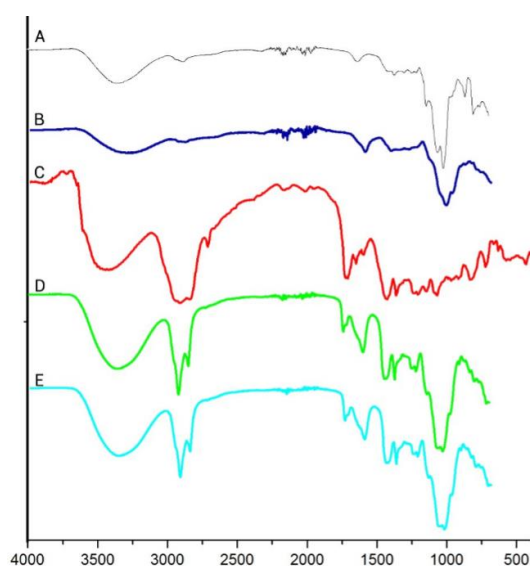


Figure 7 the FT-IR spectrum of (A) GAP; (B) gum acacia; (C) vitamin E PFAD, D) microcapsule A and (E) microcapsule B

4. Conclusion

The encapsulation vitamin E PFAD has been successfully conducted using spray drying method with GAP and GA as protecting material. Composite films with thickness vary from 0.542 – 0.779 mm were prepared by incorporating vitamin E onto matrix of GA (7 g) with various concentration of GAP (0.1; 0.2; 0.3 and 0.4 g). The formulation 3 and 4 which used GAP 0.2 gram and 0.3 gram, respectively, showed the viscosity value which similar with the standard. That composition was used for spray drying method rendering micro-particle size 11 μm and the particle had spherical shape. Although the increment of GAP decreasing moisture content and the particle size from 16 μm to 11 μm , the yield of microcapsule, encapsulation efficiency, the amount of vitamin E absorbed and oxidation stability of vitamin E were increased.

5. References

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