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Enzymatically depolymerized mangosteen aril pectin as a stabilizer for low cholesterol mayonnaise

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Abstract

This research evaluated the influence of the mangosteen aril hydrolysate (MAH) on the rheological behavior, emulsion stability (ES) and textural properties of mayonnaise-like emulsions made from soybean oil and egg yolks. All emulsions showed a pseudoplastic behavior ($n < 1$) at 25°C, except for the 100% soybean oil formulation, which displayed Newtonian behavior. Formulations with MAH with varying degrees of pectin hydrolysis (DP18, DP31 and DP45) presented a higher ES and emulsion heat stability (EHS) than formulations with non-enzymatically treated mangosteen aril (DP12). Furthermore, the DP31 MAH preparation acted synergistically with egg yolk increasing the ES and EHS. From simplex-centroid mixture design, it was found that formulations with soybean oil/MAH/egg yolk (w/w) ratio compositions of 0.666/0.334/0, 0.333/0.333/0.333 and 0.167/0.666/0.167 with the DP45 MAH also showed high values of η_{app}, firmness, adhesive force and adhesiveness, which are similar in comparison to the commercial mayonnaise.

Introduction

Garcinia mangostana Linn., the purple mangosteen, is one of the most praised tropical fruits and belongs to the family *Clusiaceae* (syn. *Guttiferae*). It is originally a native fruit of the Sunda Island in Indonesia. There are several countries in Southeast Asia are the main producers including Malaysia, Philippines, Indonesia and Thailand. About 85 percents of the total production are belonged to Thailand. Mangosteen cultivation in Thailand is limited to the South and the East of the country due to climatic conditions. Surat Thani, Chanthaburi and Rayong are the three main provinces in Thailand that are commercially grow mangosteen (Morton, 1987; Osman and Milan, 2006). The edible aril (edible endocarp) is white, soft, juicy and sweet with a slightly sour taste (Yu *et al.*, 2007; Zadernowski *et al.*, 2009; Palapol *et al.*, 2009). Due to mangosteen is a tropical fruit, therefore it can be stored for a short time before over-ripens, so it is recommended to consume fresh. However, nowadays mangosteen is get processed in different forms such as canned fruit, frozen, processed into juice, jam, syrup and candy (Morton, 1987; Osman and Milan, 2006). Moreover, when the mangosteen aril is combined with the rind (inedible exocarp) it contains many bioactive compounds, such as phenolics, flavonoids and other antioxidants, which form the first line of defense against free radical damage, and are critical for maintaining optimum health and well-being (Percival, 1996). It has prebiotic and a total dietary fiber which can be divided into soluble dietary fiber (pectin) and insoluble fibers (Sangthawan and Anprung, 2012). Furthermore, it also contains vitamins and minerals, including vitamin A, vitamin C, thiamine, riboflavin, niacin, calcium, phosphorous and iron (Osman and Milan, 2006).

Plant cell walls consist of cellulose, hemicelluloses and pectin, which form a barrier for the release of the intracellular substances, such as antioxidants, phenolics, flavonoids, volatile compounds and colorants. Like any other fruits, these plant cell wall components can be degraded (hydrolyzed) by pectinase and hemicellulase enzymes therefore the intracellular contents, and especially the bioactive compounds, are then easily released (Chareonsiddhi and Anprung, 2010; Karunasawat and Anprung, 2010; Thaiphanit and Anprung, 2010; Thanatcha and Pranee, 2011; Kunnika and Pranee, 2011; Nattaporn and Pranee, 2011; Sangthawan and Anprung, 2012). In the case of mango, it was reported that mango pulp hydrolysate had a stabilizing property on oil-in-water emulsions containing sodium caseinate (Karunasawat and Anprung, 2010).

Mayonnaise is an oil-in-water emulsion containing 70-80% fat. It is prepared by mixing egg, vinegar, oil, and spices (especially mustard). Among these ingredients, the egg yolk is the most critical for the stability of mayonnaise product (Hasenhuettl, 2008). Egg yolk helps to reduce the interfacial tension between the oil and water phases by covering

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the oil droplets and creating a physical barrier to prevent flocculation (Walstra, 1986; McClements and Demetriades, 1998; Kiosseoglou, 2003). However, the main problem of using egg yolks is the associated health concern over its relatively high cholesterol content. There have been several different attempts tried to develop a low cholesterol mayonnaise with remain similar characteristics to the traditional egg yolk based mayonnaise (Laca *et al*., 2010).

To avoid or reduce the presence of cholesterol from yolk, alternative emulsifiers have been used, such as animal proteins (whey, crayfish, casein and meat proteins), vegetable proteins (soy, tomato seed, wheat, sunflower, pea and white lupin proteins) and some polysaccharides (Raymundoa *et al.*, 2002; Riscardo *et al.*, 2003; Bengoechea *et al*., 2006; Romero *et al*., 2008). The polysaccharide emulsifiers that are used in food applications such as gum arabic, modified starch, modified cellulose, depolymerized pectin and some galactomannans are used as a substituent instead of egg yolk (Garti and Reichman, 1993; Dickinson, 2003; Karunasawat and Anprung, 2010). Hydrophobic proteins that are covalently bound to a highly branched polysaccharide structure also have emulsifying properties. In addition, depolymerized citrus fruit and apple pectins can be used as stabilizers in oil-in-water emulsion (Mazoyer *et al*., 1999; Akhtar *et al*., 2002).

The rheological behavior of any given emulsion is an important factor to consider with respect to the required formulation, process condition and quality control of mayonnaise (Pons *et al.*, 1994; Peressini *et al*., 1998). Mayonnaise shows a pseudoplastic behavior ($n < 1$) depending on the processing time (Perressini *et al*., 1998; Batista *et al*., 2006). Accordingly, the Power law, Herchel Bulkley and Casson models have all been extensively used to explain the rheological behavior of mayonnaise and salad cream (Bistany and Kokini, 1983; Paredes *et al*., 1988, 1989; Ma and Barbosa-Canovas, 1995; Peressini *et al*., 1998).

The collected data indicated that pectins and/or depolymerized pectins with protein have an effect on the oil-in-water emulsion stability. In this study, a simplex-centroid mixture design was used to develop alternative low cholesterol mayonnaise formulations (Izidoro *et al*., 2008; Nikzade *et al*., 2012) using three different factors (soybean oil, mangosteen aril hydrolysate (MAH) and egg yolk compositions). The association of these three ingredients, represented by three linear in the simplex-centroid mixture design (Fig. 1) and the influence of MAH on the rheological behavior indicators of the consistency coefficient (K), flow behavior index (n), apparent viscosity (η_{app}), emulsion stability (ES), emulsion heat stability (EHS) and the textural properties of the mayonnaise were investigated.

Materials and Methods

Materials

Purple mangosteen fruits (*G. mangostana* Linn.) were purchased from a mangosteen orchard in Rayong province, Thailand. The ripe mangosteen fruits were then peeled, deseeded and blended at high speed for 3 min. Fresh hen eggs, soybean oil and all condiments were purchased from department stores in Bangkok, Thailand. Pectinex®Ultra SP-L, a commercial enzyme, was purchased from Novozymes Co., Ltd. (Copenhegen, Denmark). All other chemicals used in this study were analytical grade and were purchased from Sigma Chemical Co., Ltd. (St. Louis, MO, USA) or Sigma Aldrich Co., Ltd. (Steinheim, Germany).

Mangosteen aril hydrolysate (MAH) preparation

The enzymatic browning reaction of mangosteen aril was inhibited by blanching at 85°C for 3 min and then treating with 0-3% (v/w) Pectinex®Ultra SP-L (10292 PGU/ml) for 0-6 h. The hydrolysis reaction was stopped by heating at 100 ± 5°C for 5 min and then rapidly cooling. After that, the degree of hydrolysis (DH) of pectin in the resultant MAH was measured in terms of the reducing sugar content (mg glucose released / g fresh weight fruit) using the method of Nelson-Somogyi (Nelson, 1944).

Physicochemical properties of MAH measurement

The antioxidant activity was evaluated using the di(phenyl)-(2,4,6-trinitrophenyl)iminoazanium (DPPH) assay (Maisuthisakul *et al*., 2007) and the ferric reducing ability of plasma (FRAP) assay (Benzie and Strain, 1996). Total phenolic content was determined according to the method of Waterhouse (2005). Total flavonoid was determined as reported previously (Zhishen *et al*., 1999). Average droplet size ($d_{32} = \sum_i n_i d_i^3 / \sum_i n_i d_i^2$ where ni is the number of droplets with diameter di) was measured by a Malvern Mastersizer MS2000 static laser light-scattering analyzer (Malvern Instrument Ltd., UK) with a refractive index value of 1.52. Viscosity was measured by a C-VOR Rheometer (Bohlin Instruments, UK) using a cone and plate geometry sensor (40 mm diameter, 4° cone angle). The measurements were carried out at 25°C with a shear rate range of 0.1-150 s^{-1}. The apparent viscosity was measured at a shear rate of 100 s^{-1}.

Emulsion preparation (Mayonnaise)

For each of the 13 different emulsion preparations, 200 g of emulsion was prepared with the (w/w) ratio proportions of soybean oil/ MAH/ egg yolk shown in Table 1. The emulsions were prepared using a blender (Moulinex, AA W948, China) at high speed. In the first step, egg yolk and/or MAH and all condiments (sugar, salt, mustard and vinegar at 36, 3, 0.7 and 13.6 g/ 100 g for all formulations, respectively) were mixed together for 1 min. In the second step, soybean oil was slowly added and mixed for 2 min. Samples were kept in plastic boxes in a refrigerator at 6 ± 2°C until analysis.

Formulations and experimental design

R software (version 2.14) was used to demonstrate the optimum proportion of mayonnaise formulations. The simplex-centroid mixture design was used with the three variable proportion components of soybean oil (X1), MAH (X2) and egg yolk (X3), as shown in Table 1. Note that sugar, salt, mustard and vinegar at 36, 3, 0.7 and 13.6 g/ 100 g, respectively, were present in all formulations.

A full cubic model (Eq.1) was used to represent the fitted response values, and the statistical significance of each equation was determined by variance analysis (ANOVA), with significance being accepted at the $p < 0.05$ level.

$$Y = \sum_{i=1}^{q} \beta_i X_i + \sum \sum_{i<j}^{q} \beta_{ij} X_i X_j \sum \sum_{i<j<k}^{q} \sum \beta_{iijk} X_i^2 X_j X_k + \sum \sum_{i<j<k}^{q} \sum \beta_{iijk} X_i X_j^2 X_k + \sum \sum_{i<j<k}^{q} \sum \beta_{ijkk} X_i X_j X_k^2 \quad (1)$$

Where Y is the predictive dependent variable (ES, EHS, K, n, η_{app}, firmness, adhesive force or adhesiveness); β is the equation coefficient, determined according to Cornell (2002), and X is the proportion of the pseudo-component.

Emulsion stability (ES and EHS) measurement

Emulsion stability (ES)

The determination of the ES was modified from the method of Mun *et al.* (2009). The sample (~15 g) was preweighed (W_0) and then centrifuged at 8000 rpm for 30 min (Hettich Universal 32R, Germany). The precipitated fraction weight (W_1) was then measured. and the ES (%) was calculated from (W_1/W_0) x 100.

Emulsion heat stability (EHS)

The accurately weighed sample (W_0; ~15 g) was heated at 80°C for 30 min before being centrifuged and the centrifuged pellet weighed (W_1) and the EHS (%) was then calculated from (W_1/W_0) x 100

Table 1. Composition of the mayonnaise-like emulsion formulations with soybean oil, mangosteen aril hydrolysate (MAH) and egg yolk in a constrained, simplex centroid mixture design for these three components

Formulation	Ingredient proportions by weight		
	X1	X2	X3
F1	0.000	1.000	0.000
F2	1.000	0.000	0.000
F3	0.000	0.000	1.000
F4	0.666	0.000	0.334
F5	0.666	0.334	0.000
F6	0.000	0.666	0.334
F7	0.333	0.333	0.333
F8	0.000	0.334	0.666
F9	0.334	0.666	0.000
F10	0.334	0.000	0.666
F11	0.666	0.167	0.167
F12	0.167	0.666	0.167
F13	0.167	0.167	0.666

Where X1+X2+X3 = 1; X1 = oil, X2 = MAH and X3 = egg.

All formulations also contained sugar, salt, mustard and vinegar at 36, 3, 0.7 and 13.6 g/ 100 g, respectively.

Textural properties

The texture measurements of each mayonnaise sample were performed on a Texture Analyzer (TA. XT2i, Germany) with a 30 kg load cell and a back extrusion cell with a 45 mm diameter compression circle plate. Samples were scooped into an acrylic cylindrical container (60 mm internal diameter and 75 mm depth). One cycle was applied, at a constant crosshead velocity of 1 mm/s to a sample depth of 40 mm and then returned. From the resulting force-time curve, the values of texture attributes, i.e. firmness, adhesive force and adhesiveness were obtained using the Texture Exponent software for Windows. Firmness is the maximum force as the test cell penetrated into the sample. Adhesiveness is the negative force area representing the work necessary to pull the compression plunger away from the sample (Worrasinchai *et al.*, 2006). The maximum negative force is taken as an indication of the adhesive force (Liu *et al.*, 2007).

Rheological properties

Rheological measurements were performed on a rheometer (C-VOR Bohlin Instruments, UK) fitted with a cone and plate geometry sensor (40 mm diameter, 4° cone angle) (Chareonsiddhi and Anprung, 2010). All samples were measured at 25°C in the shear rate range of 0-300 s^{-1}. The apparent viscosity was measured at shear rate of 250 s^{-1}. The experimental data were fitted to the Power law model given by Eq. (2).

$$\tau = K\gamma^{n} \quad (2)$$

Where Ţ is the shear stress (Pa), K is the consistency coefficient (Pa.s), γ is the shear rate (s^{-1}) and n is the flow behavior index (dimensionless).

Results and Discussion

Physicochemical properties of mangosteen aril hydrolysate

The DH of pectin in the MAH, in terms of the reducing sugar content, is shown in Figure 2. Increasing the enzyme concentration or the hydrolysis time both significantly increased the DH of pectin in the MAH ($p \leq 0.05$), giving a range of 12-45 mg glucose/g fresh weight aril fruit, because the enzyme (Pectinex®Ultra SP-L) was able to degrade the glycosidic bond in the cell wall pectin, cellulose and hemicellulose (Sangthawan and Anprung, 2012).

In this study, four MAH with different DH of pectin were used to study their effect on the stability of the soybean oil-in-water emulsion. DP12 (12 mg glucose/g fresh weight of reducing sugar) was the MAH sample after heat treatment to inhibit the enzymatic browning reaction but without any enzymatic treatment, whilst DP18, DP31 and DP45 were enzyme treated samples with a reducing sugar content (pectin DH level) of 18, 31 and 45 mg glucose/g fresh weight, respectively, and are shown in Figure 2.

It can be seen from Table 2 that the FRAP antioxidant activity, total phenolic and total flavonoid levels were significantly increased ($p \leq 0.05$) with an increasing DH of pectin in the MAH samples. Note, however, that the DPPH antioxidant level activity actually remained the same at DP18 and then decreased with further increases in the DH of pectin. In contrast, the particle size and viscosity of the MAH significantly decreased ($p \leq 0.05$) with an increasing DH of pectin in the MAH samples, which may be due to the degradation of the pectin, cellulose and hemicellulose polysaccharide components of the plant cell wall (Jayani *et al.*, 2005; Zhang *et al.*, 2006). Consequently, the release of free water into the system decreased the viscosity of the MAH (Lee *et al.*, 2006; Abdullah *et al.*, 2007; Charoensiddhi and Anprung, 2010).

Table 2. Physicochemical propertiesa of the four selected mangosteen aril hydrolysates (MAH) with different degrees of pectin hydrolysis

Physicochemical properties	Sample codes			
	DP12	DP18	DP31	DP45
Degree of hydrolysis (mg glu/g fw)	12.3 ± 0.12[d]	18.4 ± 0.19[c]	31.4 ± 0.32[b]	44.9 ± 0.42[a]
Antioxidant activities				
- DPPH (EC_{50}; µg dw/µg DPPH)	11.6 ± 0.22[a]	11.5 ± 0.13[a]	5.7 ± 0.11[b]	3.1 ± 0.04[c]
- FRAP (µg TE/ g dw)	34.1 ± 0.38[c]	34.4 ± 0.53[c]	37.5 ± 0.50[b]	45.5 ± 0.70[a]
Total phenolic (mg GAE/g dw)	8.9 ± 0.64[cd]	9.0 ± 0.50[c]	12.5 ± 0.35[b]	16.0 ± 0.82[a]
Total flavonoid (mg CE/ g dw)	1.0 ± 0.29[c]	1.2 ± 0.08[c]	2.4 ± 0.32[b]	3.1 ± 0.15[a]
Particle size (µm)	33.1 ± 1.54[a]	23.8 ± 2.27[b]	19.8 ± 1.19[c]	14.1 ± 0.68[d]
Viscosity at 100 s^{-1} (mPa.s)	194.3 ± 4.56[a]	158.7 ± 3.04[b]	86.9 ± 3.92[c]	52.7 ± 2.41[d]

[a]Data are shown as the mean ± 1 SD and are derived from independent repeats. Means within a row that are followed by a different lower case superscript letter are significantly different (P < 0.05). dw = dry weight basis; fw = fresh weight basis; TE = Trolox equivalent; GAE = Gallic acid equivalent; CE = Catechin equivalent.

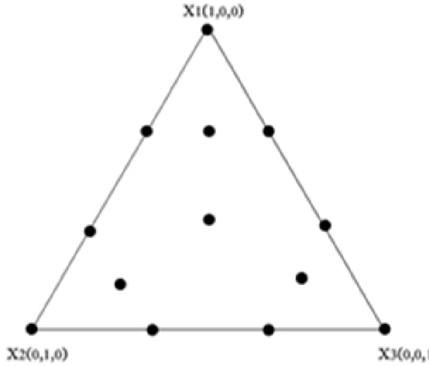


Figure 1. Simplex-centroid design for three component mixture

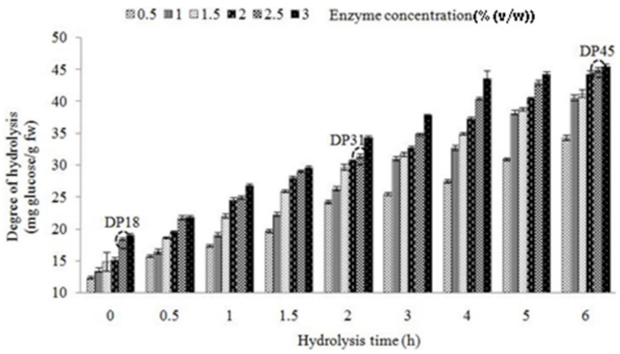


Figure 2. The degree of hydrolysis of pectin in mangosteen aril hydrolysates treated with Pectinex®Ultra SP-L enzyme at a concentration of 0.5-3.0% (v/w) for 0-6 h. Data are shown as the mean ± SD and are derived from independent repeats. Means with a different lower case letter are significantly different (P < 0.05; Duncan's MMT). MAH with a pectin degree of hydrolysis of 18, 31 and 45 mg of glucose / g fresh weight are shown as DP18, DP31 and DP45, respectively.

Emulsion stability (ES) and emulsion heat stability (EHS)

The EHS was lower than the ES for all formulations (Table 3). Among the 13 different formulations the formulation without MAH (F4) and formulation F11 with the DP18, DP31 and DP45 MAH preparations yielded the highest ES and EHS values, whilst the lowest ES and EHS values were obtained for the samples with only soybean oil (F2) or egg yolk (F3). Increasing the DH of pectin in the MAH generally resulted in high ES and EH values, but this was not the case for all formulations, although it was always higher with DP18, DP31 and DP45 compared to with the DP12 MAH. In other words, MAH (DP18, DP31 and DP45) could be used as an alternative stabilizer for oil-in-water food emulsion. This is likely to be due to the increasing DH of pectin

Table 3. Experimental results for emulsion stability (ES), heat stability (EHS), K, n, viscosity, firmness, adhesive force and adhesiveness of mayonnaise-like emulsion formulations

Sample	Code	ES (%)	EHS (%)	K	n	Viscosity (Pa.s)	Firmness (g)	Adhesive force (g)	Adhesiveness (g.s)
NT	F1	69.2^{cdef}	64.8^{def}	4.06^{no}	0.38^{pq}	0.12^{hi}	68.7^{c}	-77.6^{f}	-85.5^{ef}
(DP12)	F5	48.9^{lmn}	46.8^{klm}	4.61^{klm}	0.57^{g}	0.46^{c}	55.1^{f}	-117.3^{d}	-123.5^{d}
	F6	61.7^{fij}	59.1^{ghi}	2.93^{pq}	0.43^{lmno}	0.13^{h}	62.5^{d}	-84.0^{ef}	-85.0^{ef}
	F7	61.0^{ij}	56.6^{i}	4.08^{no}	0.50^{h}	0.24^{e}	43.1^{h}	-79.0^{f}	-76.0^{fg}
	F8	40.9^{opq}	38.7^{pqr}	1.25^{s}	0.41^{no}	0.05^{jkl}	32.1^{l}	-18.8^{mnopqr}	-13.0^{ijk}
	F9	45.5^{mnop}	42.2^{lmnop}	4.83^{jk}	0.45^{ijk}	0.24^{ef}	45.5^{g}	-37.7^{jkl}	-34.0^{hi}
	F11	88.9^{ab}	83.9^{b}	17.1^{a}	0.43^{mno}	0.70^{a}	130.8^{a}	-305.0^{b}	-282.5^{b}
	F12	44.1^{mnop}	41.7^{mnop}	4.65^{kl}	0.43^{lmno}	0.21^{efg}	31.0^{lm}	-26.2^{klmn}	-32.5^{hij}
	F13	37.2^{q}	33.4^{r}	0.48^{tuv}	0.63^{e}	0.07^{jkl}	21.25^{rs}	-18.0^{mnopqr}	-2.00^{k}
MAH	F1	70.4^{cde}	67.8^{de}	4.73^{mno}	0.36^{qrs}	0.11^{hi}	59.3^{e}	-74.4^{fg}	-61.5^{fg}
(DP18)	F5	57.6^{jk}	55.6^{i}	4.18^{no}	0.61^{ef}	0.45^{c}	60.6^{e}	-123.2^{d}	-102.5^{de}
	F6	66.7^{efghi}	62.0^{fgh}	8.33^{f}	0.30^{tu}	0.12^{h}	37.9^{j}	-46.0^{ij}	-61.0^{fg}
	F7	66.1^{efghi}	63.5^{efg}	3.14^{p}	0.50^{h}	0.22^{efg}	38.9^{j}	-62.5^{gh}	-71.0^{fg}
	F8	44.4^{mnop}	41.3^{nop}	1.21^{s}	0.41^{no}	0.05^{jkl}	32.4^{l}	-18.5^{mnopqr}	-12.0^{ijk}
	F9	48.9^{lmn}	44.7^{lmn}	4.70^{k}	0.46^{ijk}	0.24^{ef}	54.0^{f}	-27.3^{klm}	-33.0^{hij}
	F11	90.4^{a}	88.0^{a}	14.86^{b}	0.42^{mno}	0.63^{b}	103.3^{b}	-246.9^{c}	-220.5^{c}
	F12	46.1^{mno}	43.2^{lmno}	4.07^{no}	0.46^{ijk}	0.19^{efg}	30.3^{m}	-26.0^{klmn}	-32.0^{hij}
	F13	40.1^{opq}	37.3^{pqr}	0.36^{uv}	0.69^{d}	0.06^{jkl}	20.7^{rs}	-8.05^{opqr}	-2.00^{k}
MAH	F1	73.8^{bc}	69.0^{d}	5.19^{ij}	0.25^{v}	0.09^{hij}	27.9^{n}	-40.2^{jk}	-17.0^{ijk}
(DP31)	F5	59.4^{j}	54.7^{ij}	1.92^{r}	0.67^{d}	0.38^{d}	23.4^{pq}	-59.2^{hi}	-53.5^{gh}
	F6	68.6^{defg}	65.2^{def}	4.22^{lmno}	0.29^{tu}	0.09^{hij}	25.1^{op}	-18.1^{mnopqr}	-13.0^{ijk}
	F7	67.3^{defgh}	63.4^{efg}	4.68^{kl}	0.41^{no}	0.20^{g}	22.0^{qr}	-20.3^{mnopqr}	-16.0^{ijk}
	F8	46.2^{mno}	43.4^{lmno}	1.29^{s}	0.39^{op}	0.04^{jkl}	17.6^{t}	-12.4^{mnopqr}	-3.0^{k}
	F9	49.2^{lm}	47.1^{kl}	6.30^{h}	0.29^{tu}	0.13^{h}	36.1^{k}	-25.3^{klmn}	-22.5^{ijk}
	F11	93.4^{a}	90.5^{a}	13.0^{c}	0.44^{klmn}	0.59^{b}	45.3^{g}	-94.5^{e}	-77.5^{fg}
	F12	48.9^{lm}	43.8^{lmno}	4.81^{jk}	0.35^{rs}	0.13^{h}	24.8^{op}	-19.7^{mnopq}	-16.0^{ijk}
	F13	40.9^{opq}	38.4^{opqr}	0.69^{tu}	0.59^{fg}	0.05^{ijk}	6.10^{x}	-11.8^{mnopqr}	-2.50^{k}
MAH	F1	70.6^{cde}	67.7^{de}	4.49^{klmn}	0.29^{tu}	0.08^{hij}	26.4^{no}	-18.7^{mnopqr}	-14.5^{ijk}
(DP45)	F5	53.3^{kl}	50.5^{jk}	2.90^{pq}	0.67^{d}	0.35^{c}	24.1^{pq}	-23.8^{lmno}	-21.5^{ijk}
	F6	63.5^{fghij}	58.1^{hi}	2.10^{r}	0.36^{qrs}	0.06^{jkl}	19.6^{s}	-13.6^{mnopqr}	-5.00^{k}
	F7	62.1^{ghij}	58.4^{hi}	4.47^{klmn}	0.43^{lmno}	0.19^{fg}	22.1^{qr}	-21.5^{mnop}	-18.5^{ijk}
	F8	42.7^{nopq}	38.9^{opq}	0.86st	0.46^{ijk}	0.04^{jkl}	15.6^{u}	-11.4^{mnopqr}	-2.00^{k}
	F9	46.2^{mno}	40.3^{nopq}	5.38^{i}	0.32^{t}	0.13^{h}	32.5^{l}	-22.9^{lmnop}	-22.0^{ijk}
	F11	91.3^{a}	87.2^{ab}	10.2^{e}	0.48^{hi}	0.56^{b}	40.8^{i}	-59.3^{hi}	-53.5^{gh}
	F12	47.7^{lmn}	43.7^{lmno}	3.79^{o}	0.36^{qrs}	0.11^{hi}	20.6^{rs}	-16.0^{mnopqr}	-10.0^{ijk}
	F13	39.5^{pq}	35.6^{qr}	0.42^{tuv}	0.63^{e}	0.04^{jkl}	14.2^{uv}	-11.0^{nopqr}	-1.50^{k}
No MAH	F2	15.2^{r}	12.2st	2.60^{q}	0.76^{c}	0.69^{a}	13.3^{v}	-3.15^{s}	-0.00^{k}
	F3	14.6^{r}	10.9^{t}	0.04^{v}	0.89^{a}	0.02^{l}	9.65^{w}	-6.75^{pqr}	-0.00^{k}
	F4	92.8^{a}	87.3^{ab}	17.5^{a}	0.44^{klmn}	0.71^{a}	131.8^{a}	-348.3^{a}	-311.0^{a}
	F10	46.6^{mno}	41.89^{mnop}	0.21^{v}	0.86^{b}	0.09^{hij}	11.2^{w}	-8.5^{opqr}	-2.50^{k}
CMA	CMA1	73.0^{bcd}	68.4^{de}	7.51^{g}	0.36^{qrs}	0.22^{efg}	20.4^{rs}	-14.7^{mnopqr}	-9.00^{ijk}
(Full-fat)	CMA2	88.3^{a}	84.8^{b}	11.9^{d}	0.38^{pq}	0.35^{c}	21.7^{qr}	-21.0^{mnopq}	-13.5^{ijk}
	CMA3	92.0^{a}	90.0^{a}	17.2^{a}	0.42^{mno}	0.69^{a}	132.5^{a}	-297.0^{b}	-300.0^{ab}
	CMA4	76.7^{b}	74.5^{c}	2.84^{pq}	0.45^{jkl}	0.13^{h}	19.2^{rs}	-21.4^{mnop}	-17.0^{ijk}

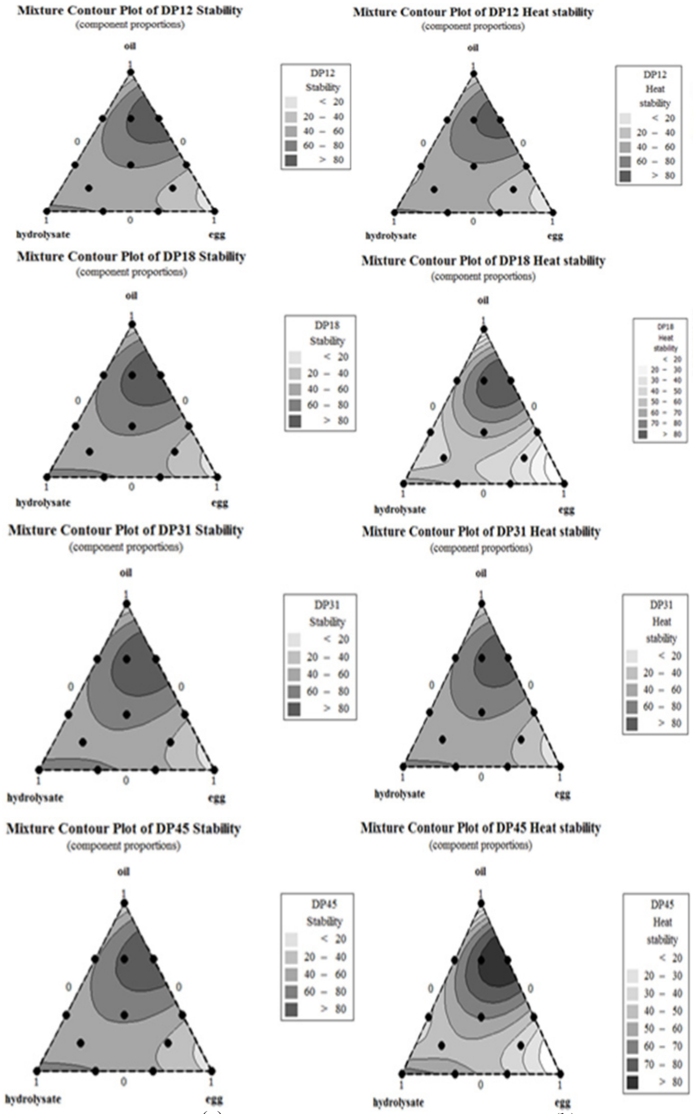
Mean values in a column with different letters are significantly different ($p \leq 0.05$). NT = Non-enzymatic treatment, MAH = Mangosteen aril hydrolysate, CMA = Commercial full-fat mayonnaise, DP = Degree of polymerization or number of monomeric units in a polymer of MAH

leading to a more polar pectin in the MAH and so a larger equilibrium between the hydrophilic and hydrophobic groups involved in the ES and EHS (Karunasawat and Anprung, 2010).

From Table 4 (Eqs. 3-4, 11-12, 19-20 and 27-28), the data for ES and EHS fitted well to the full cubic model with a high determination coefficient (R^2 of 0.9754 – 0.9835) for all formulations, where an R^2 value of over 80% means the model is adequate (Kargozari *et al.*, 2010). The increase in the ES and EH values were principally due to the level of MAH (X2) in the composition. Meanwhile soybean oil (X1) and egg yolk proportions (X3) had a lower contribution on the ES and EHS, there was a significant co-influence among these three factors, as shown in Fig. 3a and 3b. Moreover, as higher DH of pectin in the MAH increased the ES and EHS, where the dark color area in the ternary contour plots increased with an increasing DH of pectin in the MAH.

The instability of the mayonnaise-like emulsion may be caused by coalescence, which is the result of oil droplet convergence. The most effective means for preventing coalescence is avoiding the oil droplets from getting too close together, for example by generating a sufficiently strong repulsive force between droplets (Nikzade *et al.*, 2012). Thus, the instability of some formulations, such as the soybean only (F2), may be caused by oil droplet coalescence because this formulation had insufficient stabilizer to decrease the interfacial tension between the oil and water phases (Walstra, 1986; McClements and Demetriades, 1998; Kiosseoglou, 2003).

The stability of the F11 emulsions, which contained egg yolk and MAH, were not significantly different to that of emulsion F4, which did not contain MAH but just egg yolk. It can be noticed that the



(a) (b)

Figure 3. Ternary contour plots of the effect of the processing components on the (a) stability (ES) and (b) heat stability (EHS) of emulsions with different degrees of hydrolysis of pectin in the mangosteen aril hydrolysate (MAH).

ES and EHS values of formulation F11 with DP31 was higher than that for F4, which suggests that MAH (DP31) had a synergistic effect with eggs in maintaining the emulsion stability.

Rheological properties

The flow behavior of the mayonnaise-like emulsions was described well by the Power law model at 25°C (Figure 4). The shear rate and shear stress showed a non-linear relationship with a high determination coefficient (R^2 = 0.9215-0.9985), supporting that the experimental data fitted the Power law model.

Formulations F4 and F11 with the non-enzymically treated MAH (DP12) had a higher shear stress than the other formulations, in accord with the determined K, n and η_{app} values (Table 4),

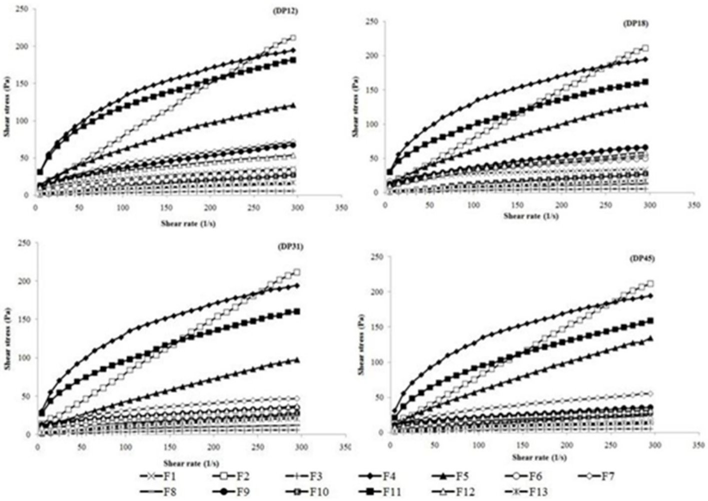


Figure 4. Flow curves of mayonnaise-like emulsions fitted by the Power law model at 25°C

where formulation F11 with DP12 had the highest K and η_{app} values but the lowest n value and were not significantly different from formulation F4. The n values showed that the rheological properties of all emulsions were pseudoplastic and the η_{app} of all samples decreased with increasing shear rates. Except for formulation F2 (soybean oil only), the tendency of the n to display Newtonian behavior whilst the K does not change significantly with increasing shear rates (James, 1992). Pseudoplastic behavior has been reported in previous studies on different mayonnaise compositions (Batista *et al*., 2006; Worrasinchai *et al*., 2006; Izidoro *et al*., 2008; Fonseca *et al*., 2009).

The ternary contour plots of K, n and η_{app} are shown in Fig. 5, whilst their respective regression equations all fitted well to full cubic model with a high determination coefficient for all samples (R^2 > 80%), as summarized in Table 3. The increase in the K value was principally due to the MAH (X2) and soybean oil (X1) contents, respectively (Table 4; Eqs. 5, 13, 21 and 29). Nevertheless, although the egg yolk composition (X3) had a lower contribution to K, it was a significant cofactor with soybean oil (X1X3) as observed in Figure 5a, where the magnitude of the K coefficient increased with increasing oil proportions. This is in accord with that reported before (Gladwell *et al*., 1986).

The increase in the n was principally due to the egg composition (X3), with only a small contribution from the soybean oil and MAH concentrations (X1 and X2), as seen in Figure 5b and Table 4 (Eqs. 6, 14, 22 and 30). The increase in the η_{app} was principally due to the soybean oil fraction (X1). Nevertheless, although the egg yolk (X3) content had a lower contribution it had a significant influence in the co-presence of oil (X1X3), as seen in Figure 5c and Table 4 (Eqs. 7, 15, 23 and 31). Indeed, the η_{app} of mayonnaise has been reported previously to increase with increasing

Table 4. Regression coefficients and correlations for the model to experimental data in mixture design

Eqs.		R^2
DP12		
$ES=14.9X1+69.7X2+14.6X3-82.9X1X2-89.5X1X3+55.7X2X3+152.7X1X2X3$	(3)	0.9754
$EH=12X1+65.2X2+11X3-78.1X1X2-83.1X1X3+51.9X2X3+175.4X1X2X3$	(4)	0.9782
$K=2.74X1+4.34X2+0.26X3-5.95X1X2-81.79X1X3+2.36X2X3+12.76X1X2X3$	(5)	0.9488
$n=0.76X1+0.38X2+0.89X3-0.27X1X2+2.72X1X3-2.27X2X3-0.63X1X2X3$	(6)	0.9905
$\eta_{app}=0.69X1+0.13X2+0.03X3-0.56X1X2-2.45X1X3-0.12X2X3-0.09X1X2X3$	(7)	0.9856
$firmness=13.6X1+70.5X2+9.8X3-260.3X1X2-522X1X3+77.7X2X3+499.9X1X2X3$	(8)	0.9557
$adhesive\ force=5.2X1+81.6X2+7.8X3-727.4X1X2-1407X1X3+23.3X2X3-973.6X1X2X3$	(9)	0.9648
$adhesiveness=1.7X1+88.7X2+1.9X3-779.1X1X2-1300.4X1X3-77.2X2X3-865.6X1X2X3$	(10)	0.9766
DP18		
$ES=14.9X1+70.7X2+14.4X3-91.7X1X2-76.9X1X3+71.7X2X3+182.4X1X2X3$	(11)	0.9788
$EH=11.9X1+68.1X2+10.8X3-106.6X1X2-65.9X1X3+75.9X2X3+124.7X1X2X3$	(12)	0.9795
$K=2.7X1+4.99X2+0.1X3-12.62X1X2-71.65X1X3-9.91X2X3+66.35X1X2X3$	(13)	0.9440
$n=0.76X1+0.36X2+0.89X3+0.05X1X2+2.85X1X3-1.86X2X3-1.71X1X2x3$	(14)	0.9913
$\eta_{app}=0.69X1+0.12X2+0.02X3-0.37X1X2-2.31X1X3-0.05X2X3+0.75X1X2X3$	(15)	0.9896
$firmness=13.9X1+60.2X2+9.5X3+81X1X2-481.1X1X3+164.2X2X3+477.9X1X2X3$	(16)	0.9776
$adhesive\ force=6X1+76X2+7X3-589X1X2-1306X1X3+86X2X3-1302X1X2X3$	(17)	0.9766
$adhesiveness=2X1+63X2+X3-435X1X2-1188X1X3+5X2X3-1062X1X2X3$	(18)	0.9659
DP31		
$ES=15X1+74.2X2+14.6X3-106.7X1X2-83.1X1X3+72.3X2X3+139.3X1X2X3$	(19)	0.9835
$EH=11.9X1+69.5X2+10.9X3-101X1X2-82.3X1X3+87X2X3+149.8X1X2X3$	(20)	0.9699
$K=2.67X1+5.37X2+0.1X3+14.43X1X2-74.51X1X3+3.28X2X3+21.81X1X2X3$	(21)	0.9704
$n=0.76X1+0.25X2+0.89X3-1.08X1X2+2.71X1X3-2.19X2X3+0.39X1X2X3$	(22)	0.9844
$\eta_{app}=0.69X1+0.09X2+0.02X3-0.85X1X2-2.29X1X3-0.02X2X3-0.01X1X2X3$	(23)	0.9914
$firmness=13.9X1+27.4X2+8.5X3+174.4X1X2-405.1X1X3+72.4X2X3+404.1X1X2X3$	(24)	0.9383
$adhesive\ force=7X1+40X2+4X3+112X1X2-1004X1X3+215X2X3-991X1X2X3$	(25)	0.8907
$adhesiveness=3X1+16X2-2X3+200X1X2-902X1X3+161X2X3+894X1X2X3$	(26)	0.8890
DP45		
$ES=15.1X1+71.1X2+14.7X3-93.4X1X2-85.6X1X3+59.6X2X3+144.3X1X2X3$	(27)	0.9779
$EH=12.1X1+68.1X2+11.1X3-93.7X1X2-83X1X3+59.4X2X3+102.5X1X2X3$	(28)	0.9839
$K=2.68X1+4.55X2+15.95X1X2-67.14X1X3+6.9X2X3+34.18X1X2X3$	(29)	0.9847
$n=0.76X1+0.29X2+0.89X3-1.21X1X2+2.65X1X3-1.75X2X3+0.69X1X2X3$	(30)	0.9911
$\eta_{app}=0.69X1+0.09X2+0.02X3-0.67X1X2-2.33X1X3+0.11X2X3-0.26X1X2X3$	(31)	0.9924
$firmness=14.2X1+25.9X2+8.3X3+156.8X1X2-366.9X1X3+105.3X2X3-365.8X1X2X3$	(32)	0.9037
$adhesive\ force=6X1+17X2+3X3+368X1X2-964X1X3+246X2X3-950X1X2X3$	(33)	0.8732
$adhesiveness=3X1+13X2-2X3+334X1X2-891X1X3+202X2X3-886X1X2X3$	(34)	0.8831

Eqs.= equation, R2= determination coefficient, X1= oil, X2= MAH, X3= egg.

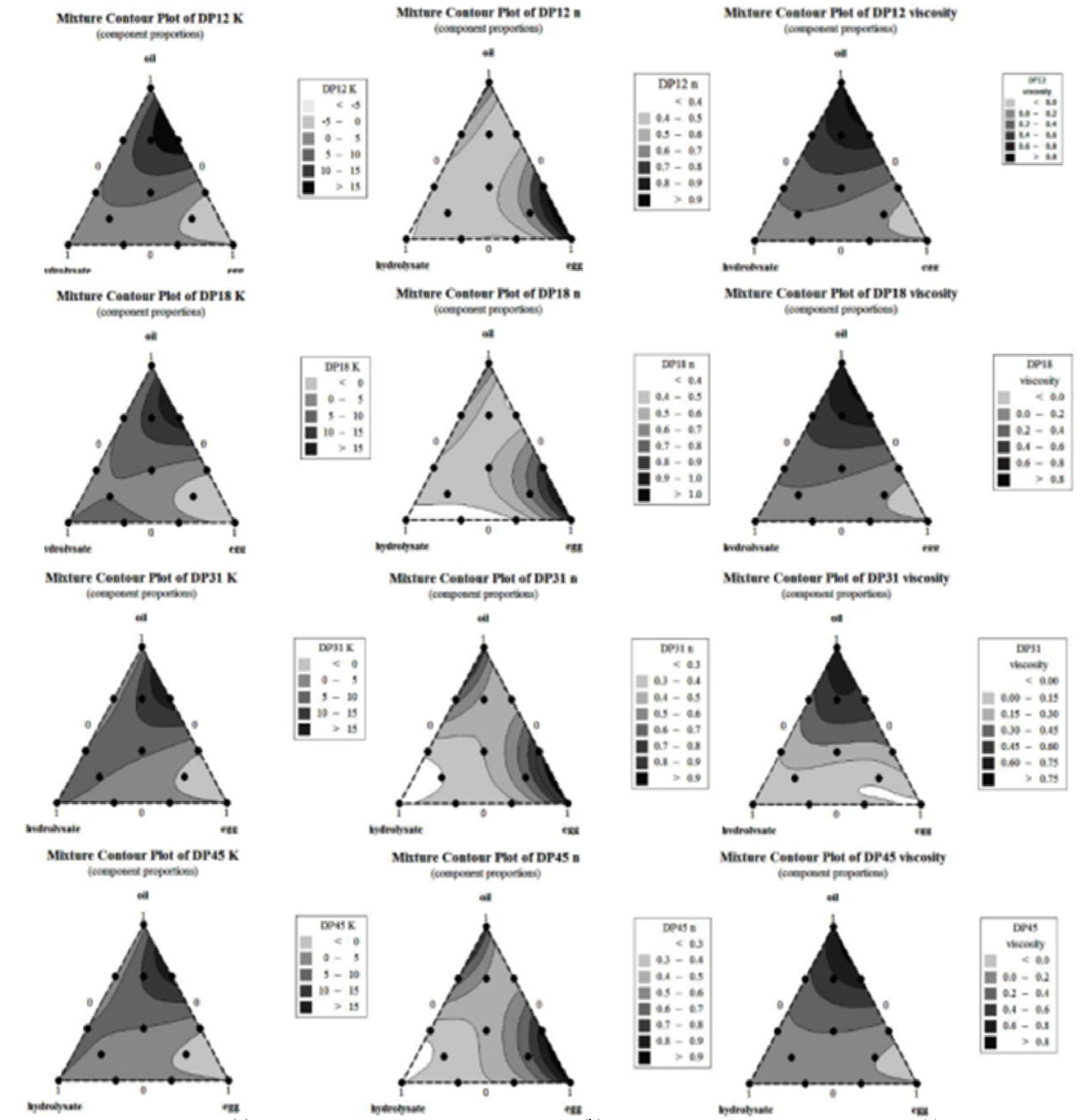
proportions of oil and green banana pulp (stabilizing agent) (Izidoro *et al.*, 2008). Moreover, increasing the DH of pectin in the MAH decreased the K and η_{app} values, while it increased n (Figure 5), which may all be caused by the decreasing particle size of MAH with an increasing DH of pectin.

From the comparison of the η_{app} of the 13 formulations and the four commercial mayonnaises (CMA1-4), it was found that formulation F11 with DP12 had a similar apparent viscosity to CMA3, whilst formulations F7 with DP31 and DP45, F5 with DP45, and F9 and F12 with DP45 were similar to CMA1, CMA2 and CMA4, respectively (Table 3). In addition, these mayonnaise-like formulations with the MAH had various η_{app} values (0.13-0.70 Pa.s) that depended on the composition of the mayonnaise.

Textural properties

The textural properties (firmness, adhesive force and adhesiveness) all fitted well to the full cubic model with a high determination coefficients (Table 4; $R^2 > 80\%$). The increase in the firmness, adhesive force and adhesiveness were due to the level of MAH (X2) (Table 4; Eqs. 8-10, 16-18, 24-26 and 32-34). Nevertheless, the egg yolk (X3) and soybean oil (X1) contents had a much lower contribution on these parameters, even in the simultaneous presence of soy bean oil (X1X3). The oil-egg edge yielded the highest textural properties, which can also be observed in Fig. 6. Increasing the DH of pectin in the MAH decreased the firmness, adhesive force and adhesiveness (Figure 6), which is similar to that previously reported in the literature for the composition of low-fat oil-in-water emulsions stabilized by white lupin protein, where the firmness and adhesiveness increased with the protein, xanthan gum and oil concentrations (Raymundoa *et al.*, 2002).

Comparison of the textural properties (firmness, adhesive force and adhesiveness) between the 13 different formulations and the four commercial mayonnaises revealed that formulation F11 with DP12 had similar textural properties to CMA3, whilst F7 with DP31 and DP45, and F5 and F12 with DP45 had similar textural properties to CMA1, CMA2 and CMA4, respectively (Table 3). Thus, the effect of MAH on the emulsification resulted in textural properties that were similar to full fat commercial mayonnaises.

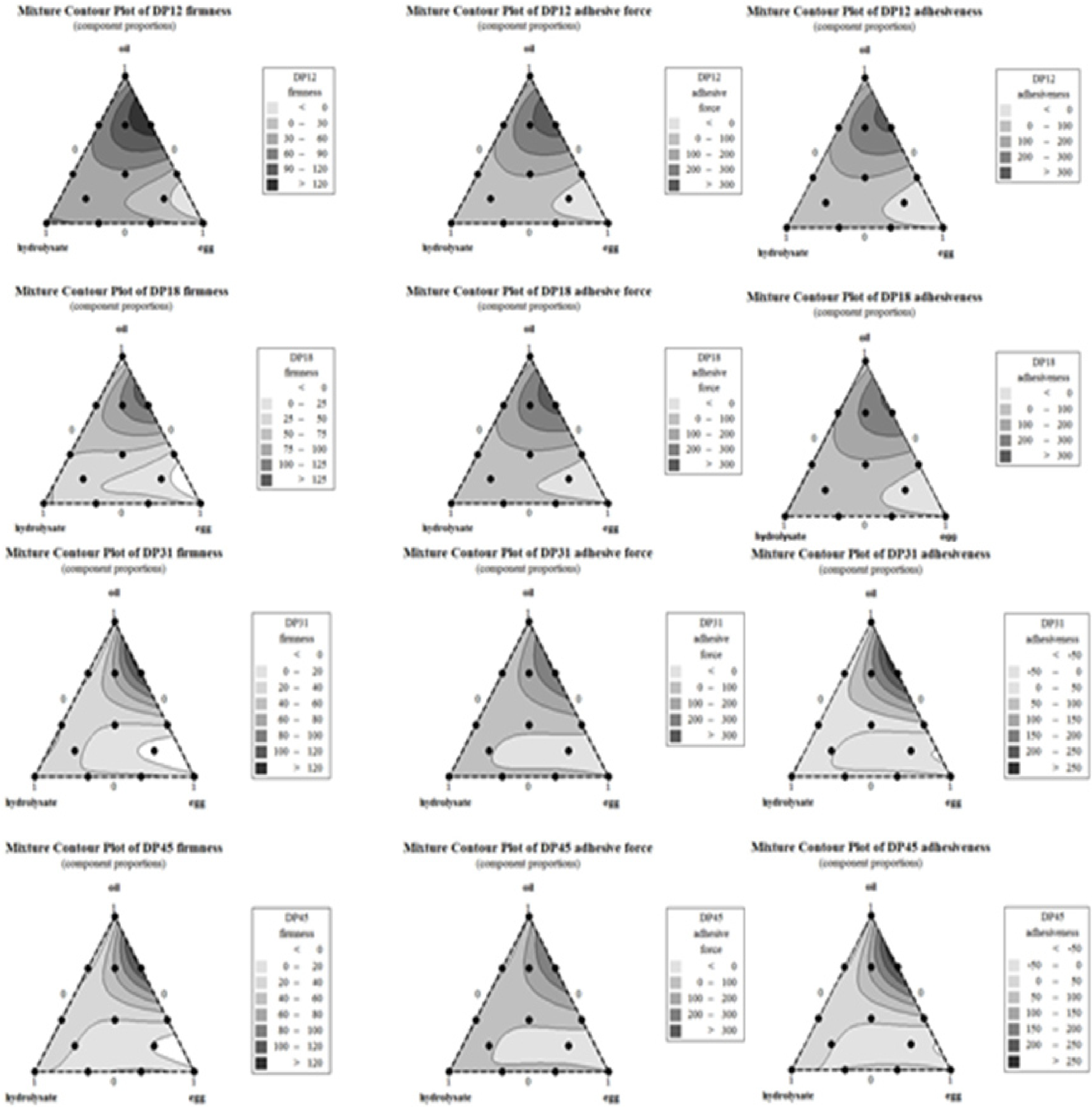


(a) (b) (c)

Figure 5. Ternary contour plots of the effect of processing components on the (a) K, (b) n and (c) viscosity of emulsions with different degrees of hydrolysis of pectin in the mangosteen aril hydrolysate (MAH).

Conclusions

All mayonnaise-like emulsions at 25°C, showed pseudoplastic behavior ($n < 1$) except for the all soybean oil formulation (F2) that tended to display Newtonian behavior. Rheological data were well described by the Power law model. Formulation using MAH with a low DH of pectin (DP18) and (w/w) soybean oil/MAH/egg yolk proportion of 0.666/0.167/0.167 had significantly higher values for all parameters except n than formulations with MAH with a higher DH of pectin (DP31 and DP45) ($p \leq 0.05$). MAH (DP31) had a synergistic effect with the egg yolk content for maintaining the ES and EHS. MAH (DP18, DP31 and DP45) could be used as an alternative stabilizer for oil-in-water food emulsion. Formulations with a (w/w) ratio of soybean oil/ MAH/ egg yolk of 0.666/0.334/0, 0.333/0.333/0.333 and 0.167/0.666/0.167 had similar η_{app}, firmness, adhesive force and adhesiveness values to the commercial mayonnaises. In addition, MAH (DP45) had the highest bioactive compound contents and was an excellent source of dietary fiber with fairly well-balanced soluble and insoluble dietary fiber content. These results can be used as database for the improvement of low cholesterol and / or low



(a) (b) (c)

Figure 6. Ternary contour plots of the effect of processing components on the (a) firmness, (b) adhesive force and (c) adhesiveness of emulsions with different degrees of hydrolysis of pectin in mangosteen aril hydrolysate (MAH).

fat mayonnaise with a higher nutrition value and similar textural properties to full-fat commercial mayonnaises.

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