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ORIGINAL ARTICLE

Influence of Selected Gums and Pregelatinized Corn Starch on Reduced Fat Mayonnaise: Modeling of Properties by Central Composite Design

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Abstract In the present study 20 reduced fat and egg mayonnaise samples were produced with different levels of three fat replacers (xanthan, guar and pregelatinized corn starch) and egg/soy milk mixture as egg alternative. Different characteristics including rheological parameters, particle size distribution, stability, thermal stability and color parameters were characterized and optimized by response surface method through central composite design in order to investigate the performance of employed hydrocolloids along with soy milk. Rheology revealed non-Newtonian and shear thinning behavior for all samples and in contrast to pre gel corn starch, xanthan and guar increased shear thinning behavior. In addition, synergistic interaction between xanthan and pre gel corn starch and also between xanthan and guar was found by data analysis. Xanthan produced larger droplet size probably due to its negatively-charged structure through adsorption at the interface coated by positively-charged soy proteins or by bridging mechanism. Food hydrocolloids, used in this study, were found to be significantly effective in most of the responses. From the data achieved in this study, it can be concluded that because of capability of xanthan and pre gel corn starch in changing physico-chemical parameters, individually or synergistically, they can be used in production of mayonnaise and other food formulations as fat replacer, thickener and stabilizer.

Keywords Mayonnaise · Reduced fat · Xanthan · Guar · Pregelatinized corn starch

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Introduction

Mayonnaise, as an oil in water emulsion, is a highly desirable salad dressing and widely consumed because of its flavor and texture. But nowadays, as a consequence of health problems existing throughout the world, consumers can choose different versions of mayonnaise with lower levels of oil.

About one fourth of the American population has some forms of cardiovascular disease that can result in heart disease and stroke. These two are the first and third causes of death in the United States, accounting for more than 40 % of all deaths with high blood cholesterol being one of the risk factors for heart disease. The American Heart Association in 2006 reported that more than 2600 Americans die of cardiovascular disease each day [1]. The obesity epidemic has been attributed to energy imbalance, mainly because of increased food consumption and/or sedentary lifestyle, or both. Evidence suggests that lowering total energy intake along with a reduction in total fat intake can have a substantial impact on body weight and risk of chronic diseases [2]. In recent years many new and redesigned ingredients have been introduced as fat substitutes or fat replacers to help manufacturers reformulate traditional high fat food products into good-tasting, acceptable reduced fat alternatives [3].

Low fat products can be formulated by a variety of fat replacers including carbohydrate-based, protein-based and fat-based types. Generally, fat replacers are categorized into two groups: fat substitutes (fat-based) and fat mimetics (carbohydrate-based and protein-based). Starches and gums, carbohydrate-based fat mimetics, have structures different from fats and may be modified chemically, physically or enzymatically to mimic fat characteristics such as mouth feel, appearance and thickness. They are mainly used because of their unique ability to absorb water and develop viscosity [3–6].

Different formulations of mayonnaise containing low levels of oil have been developed by previous researchers.

Worrasinchai et al. (2006), Liu et al. (2007), Su et al. (2010), Mun et al. (2002) and Dolz et al. (2007) investigated functionality of different hydrocolloids including β-glucan, pectin, whey protein, xanthan, citrus fiber, modified rice starch and locust bean gum as fat replacer in mayonnaise formulations with various oil contents [7–11].

There are different ways by which starches are modified in order to improve their functionality. They are categorized into four main methods: chemical, physical, enzymatic and genetic methods or a combination of these ways may be used. Pregelatinization of starch is a physical method with high desirability because no chemical material is used in its production process. In pregelatinization, rapid drying prevents amylose and amylopectin crystallization, resulting a glassy structure with high and rapid hydration capacity. As this kind of starch absorbs both warm and cold water rapidly, with no additional heating to develop viscosity, it is called instant starch [12, 13].

Unmodified starch is not suitable in many processed food applications. For example, preparation of instant pudding using cold water or milk would require an instant thickener instead of an unmodified starch. Additionally, some heated preparations require a pregelatinized starch because either the temperature or time period is insufficient to properly gelatinize a conventional cook-up starch [14]. This kind of starch is used in several applications such as sauces, desserts, instant soups and bakery mixtures [15].

Despite low price and high ability to develop viscosity, there has been reported few documented research on employing pregelatinized starch in food formulations [16–18]. Therefore the objective of this study was to investigate the effect of this kind of physically-modified starch, as a fat replacer in combination with two commonly used gums namely xanthan and guar, on reduced fat and egg mayonnaise. Furthermore, possible synergistic interactions between noticed starch and xanthan or guar and also between the two gums were followed via applying different examinations, because possible synergistic interactions could reduce cost of the mayonnaise production.

Materials and Methods

Materials

Sunflower oil, egg, vinegar, salt, sugar and mustard were provided from market. Xanthan and guar gum were purchased from Sigma Aldrich Co. (USA). Preglatinized corn starch (ST, 1700 B) and citric acid were purchased from Pars Sta (Iran, Tehran) and Merck (Germany) companies, respectively. Full soy flour with protein content of 40 % was a gift from Toos Soya Co. (Iran).

Soy Milk Preparation

Hot water (90–95ºC) was added into full fat soy flour with the weight ratio of 3:1 w/w (water: full fat soy flour). Then this mixture was stirred with stirrer (SINBO SMX 2725 STAND MIXER, China) for 20 minutes at speed of 1. Finally, soy milk was established with protein content of 10 %.

Mayonnaise Preparation

Three fat replacers (xanthan, guar and preglatinized corn starch) and egg/soy milk mixture (egg alternative) were used to prepare 22 mayonnaise samples. According to the previous work (Rahmati et al., 2012) substitution of egg with soy milk up to 50 % would not affect mayonnaise physico-chemical properties; therefore, this level of egg substitution was selected [19]. Reduced fat and egg mayonnaise samples (20 samples) were prepared according to the following procedure and by using ingredients written in Table 1. To prepare different mayonnaises, first powder ingredients (salt, sugar, xanthan, guar, pre gel corn starch and mustard), water, 1/3 of vinegar and emulsifier (egg + soy milk) were mixed with stirrer for 4 minutes at speed 1. Then oil was added slowly in 5 minutes at speed 2 into the aqueous phase. The rest of the vinegar (2/3 of vinegar) was poured and mixed for 1 other minute. Then this pre emulsion was homogenized with the stirrer operating at speed 4 for 7 minutes.

Xanthan, guar and starch were not hydrated before use because this procedure is similar to the process that is done in the industries. To compare different properties, 2 control samples were also prepared with the formulations shown in Table 1. Each formulation was prepared one time and each experiment was performed in 2–4 replicates.

Rheological Experiments

Rheological measurements were performed by using Bohlin viscometer (Visco 88, Bohlin Ltd., UK) at 23ºC (ambient temperature). To determine flow parameters, flow behavior of all samples were fitted to Power law (eq. 1), Herschel-Bulkley (eq. 2), Bingham (eq. 3) and Casson (eq. 4) models at shear rates ranging from 14.2–200 1/s.

$$\sigma = k\gamma^{n} \quad (1)$$

Where σ(Pa) is shear stress, k (Pa.s^n) is consistency coefficient, γ (1/s) is shear rate and n (−) is flow behavior index.

$$\sigma = \sigma_{0} + k\gamma^{n} \quad (2)$$

Where σ(Pa) is shear stress, σ_0(Pa) is yield stress, k (Pa.s^n) is consistency coefficient, γ (1/s) is shear rate and n (−) is flow behavior index.

$$\sigma = \sigma_{0} + k\gamma \quad (3)$$

Table 1 Formulation of samples and table of face centered central composite experimental design and values of power law, pH and color parameters for mayonnaise samples

Ingredients	Oil	Egg	Soy milk	Vinegar	Salt	Sugar	Citric acid	Mustard	Gums starch	Water
Reduced fat & egg samples	45	6	6	12	0.5	5	0.1	0.4	CCD [1]	Up to 100 %
Control 1	70	6	6	12	0.5	5	0.1	0.4	0	0
Control 2	70	12	0	12	0.5	5	0.1	0.4	0	0
Run	Xanthan	Guar	Pre gel corn starch	pH	Power law K	Power law n	R^2	L*	a*	b*
1	0	0.3	4	3.9	15.41	0.415	0.992	94.57	−7.80	11.53
2	0.3	0.3	4	4	87.60	0.195	0.971	94.68	−8.25	13.86
3	0.3	0.15	3	3.96	69.13	0.170	0.995	94.73	−7.68	12.06
4	0.15	0.15	3	3.97	46.45	0.248	0.966	94.54	−7.70	11.74
5	0.3	0	2	3.97	21.66	0.316	0.998	94.84	−7.53	9.55
6	0.15	0.15	3	3.95	36.56	0.260	0.979	94.55	−7.59	11.46
7	0	0	4	3.94	10.18	0.433	0.998	95.80	−8.44	12.85
8	0	0.15	3	3.92	15.15	0.394	0.990	95.85	−8.93	13.76
9	0.3	0.3	2	3.94	54.36	0.172	0.988	94.55	−8.01	10.31
10	0.15	0.15	3	3.96	36.97	0.271	0.999	94.12	−7.77	11.38
11	0	0.3	2	3.90	17.79	0.306	0.995	95.83	−8.65	13.28
12	0.15	0	3	3.96	31.31	0.286	0.969	95.71	−7.77	13.85
13	0.15	0.15	3	3.99	52.64	0.220	0.973	94.71	−7.72	11.13
14	0.15	0.3	3	3.90	56.76	0.203	0.976	94.42	−7.63	11.36
15	0.15	0.15	3	3.95	42.73	0.243	0.999	94.39	−7.76	11.26
16	0.15	0.15	4	3.93	47.26	0.266	0.990	94.91	−7.85	12.13
17	0.15	0.15	2	3.95	28.55	0.269	0.979	94.53	−8.87	11.89
18	0.3	0	4	3.98	47.49	0.271	0.994	95.05	−7.95	11.59
19	0.15	0.15	3	3.98	43.90	0.270	0.964	94.40	−7.76	11.77
20	0	0	2	3.99	1.16	0.641	0.999	94.90	−7.48	12.08
Control 1	0	0	0	3.77	14.3	0.328	0.998	94.42	−8.60	15.52
Control 2	0	0	0	3.84	20.43	0.226	0.997	94.27	−8.28	14.42

[1] According to central composite design (CCD)

Where σ(Pa) is shear stress, k (Pa.s^n) is consistency coefficient, γ (1/s) is shear rate and σ_0(Pa) is yield stress.

$$\sqrt{\sigma} = \sqrt{\sigma_0} + k_c\sqrt{\gamma} \quad (4)$$

Where σ(Pa) is shear stress, σ_0(Pa) is yield stress, k (Pa$^{0.5}$.S$^{0.5}$) is consistency coefficient and γ (1/s) is shear rate.

pH Measurement

A fixed amount of each sample was diluted with 95 cc distilled water and pH of samples was measured by the pH meter (Meterohm, Ion analysis, Switzerland).

Particle Size Measurement

Samples were diluted (1: 100) using 0.1 % SDS solution and particle size ($d_{3,2}$), specific surface area and span (span is a measure of the width of a distribution [20]) values of mayonnaise emulsions were determined employing particle sizer (Fritsch Particle sizer Analysette 22, Fritsch Co., Germany).

$$d_{(3,2)} = \sum n_i d_i^3 \Big/ \sum n_i d_i^2 \quad (5)$$

Where n_i is the number of the droplets showing diameter d_i.

$$\text{SSA(specific surface area)} = 6\varphi/d_{3,2} \quad (6)$$

Where φ is the oil fraction.

$$\text{Span} = [d(v,90) - d(v,10)]/[d(v,\ 50)] \quad (7)$$

Where d (v, 90), d (v, 10) and d (v, 50) are particle diameter at 90, 50 and 10 % cumulative volume.

Stability and Thermal Stability Experiments

To determine stability value at room temperature, a fixed amount of each sample (8±0.5 g) was transferred into cylindrical plastic containers (1.4 cm internal diameter and 12 cm height) and centrifuged at 5,000 rpm for 15 minutes. Then emulsion stability at room temperature was determined by the following equation:

$$\%\ S = H/H_0 \times 100 \quad (8)$$

Where % S is the percentage of stability, H is the height of emulsion phase after centrifugation and H_0 is the initial emulsion height transferred into the tube. Thermal stability was determined by the same procedure but tubes were incubated at 80˚C for 30 minutes prior to centrifugation.

To measure mayonnaise stability at low temperature, 90 g of each sample was placed in 2˚C for 3 months.

Color Measurement

Image processing technique was used to perform color measurement. Photographs (Jpeg format) in RGB color space system were taken, employing a fixed light source, by camera (Canon, power shot A520) connected with computer using Zoom Browser EX 5.0 software. Then photographs were converted into L , a , b color space system using Image J (1.40 g) software (NIH Co., United States).

Statistical Design

20 formulas were determined by response surface method with central composite design and analysis of variance ($p<0.05$) was used to establish significance of differences using Design-Expert software (version 6.0.2, Stat-Ease Inc.).

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} {x_1}^2 + \beta_{22} {x_2}^2 + \beta_{33} {x_3}^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (9)$$

Equation 9 is a second order polynominal equation used by the software to fit on the data established for different parameters. In this equation Y is the response (dependent variable), x_1, x_2 and x_3 were considered as the concentrations of xanthan, guar and pregelatinized corn starch (independent variables) respectively and β_0, β_1, β_2, β_3, β_{11}, β_{22}, β_{33}, β_{12}, β_{13} and β_{23} are the regression coefficients. The terms that were statistically non-significant ($p>0.05$) were omitted from the initial models and the experimental data were refitted to produce the final reduced model. In addition, some non-significant variables were added again to the model due to the quadratic or interaction effects.

The response surfaces of models were plotted for different characteristics as a function of 2 variables and the third one was kept fixed at the central level. The correlation between the response and independent variables can be readily seen in the response surface plots. These plots show the simultaneous interaction of two parameters on the responses [21].

Results and Discussion

Statistical Analysis

The regression coefficients, sum of squares, R^2 and adjusted R^2 are given in Tables 2 and 3. Each response was evaluated

Table 2 Model coefficients and sum of squares for experimental variables of each response including power law consistency coefficient, flow behavior index and particle size

Source	Consistency coefficient		Flow behavior index		Particle size	
	Model coefficients	Sum of squares[1]	Model coefficients	Sum of squares	Model coefficients	Sum of squares
Model	−61.62	8237.31	+1.01	0.22***	+5.51	7.57***
Xanthan	+15.41	4864.23***	−1.67	0.11***	+0.14	1.67**
Guar	+64.24	1442.88***	−1.67	0.043***	−6.97	0.27
Starch	+46.65	712.67***	−0.28	0.0015	+0.43	3.91***
Xanthan^2	−139.71	27.18	+2.20	0.0067*	+9.65	0.13
Guar^2	−55.49	4.29	+0.53	0.0003	+15.65	0.34
Starch^2	−7.37	149.72	+0.03	0.0033	−0.13	0.04
Xanthan × guar	+283.05	324.49**	+0.73	0.0022	+2.05	0.01
xanthan × starch	+43.69	343.61**	+0.06	0.0007	−2.02	0.74*
guar × starch	−3.32	1.99	+0.32	0.019**	+0.29	0.01
residual		305.97		0.013		0.89
Lack of fit		122.68		0.011*		0.55
Pure error		183.29		0.0018		0.33
R^2		0.96		0.94		0.89
Adj R^2		0.93		0.89		0.80

[1] *: $P<0.05$, **: $P<0.01$, ***: $P<0.001$

as a function of linear, quadratic and interaction terms of the independent variables including xanthan, guar and pre gel corn starch. The adequacy of the models was determined using sum of squares, p-value, R^2, adjusted R^2 and lack-of fit analysis. Analysis of variance was performed to investigate the adequacy of the RSM models and determine the significance of different parameters. The independent and dependent variables were fitted by the second order polynomial equation to the experimental data.

Table 3 Model coefficients and sum of squares for experimental variables of each response including specific surface area, span, stability and thermal stability

Source	Specific surface area		Span		Stability		Thermal stability	
	Model coefficients	Sum of squares [1]	Model coefficients	Sum of squares	Model coefficients	Sum of squares	Model coefficients	Sum of squares
Model	+1.52	0.75***	+1.11	0.54	−38.44	5723.50***	−49.21	6166.18***
Xanthan	−0.35	0.16**	−0.97	0.28**	+321.41	2547.22***	+266.80	3031.08***
Guar	+1.87	0.01	−2.91	0.01	+186.18	504.10***	+130.34	524.18***
Starch	−0.42	0.37***	+0.60	0.00	+46.47	1014.05***	+46.08	1471.37***
Xanthan^2	−3.57	0.01	+4.02	0.02	−440.60	270.27***	−367.47	188.00***
Guar^2	−5.13	0.03	+8.24	0.09	−205.05	58.54**	−165.25	38.02*
Starch^2	+0.08	0.02	−0.08	0.02	−5.06	70.51**	−5.06	70.64**
Xanthan × guar	−0.11	0.00005	−0.05	0.00001	−132.22	70.81**	−6.66	0.18
Xanthan × starch	+0.76	0.11**	−0.44	0.03	−21.00	79.38***	−13.16	31.20*
Guar × starch	−0.01	0.00005	+0.05	0.00061	−19.16	66.13**	−10.50	19.85
Residual		0.08		0.23		34.81		55.88
Lack of fit		0.06		0.14		27.94		44.56
Pure error		0.01		0.08		6.88		11.32
R^2		0.90		0.70		0.99		0.99
Adj R^2		0.81		0.43		0.98		0.98

[1] *: $P<0.05$, **: $P<0.01$, ***: $P<0.001$

Table 4 Final equation refitted on experimental data in terms of actual factors

Variable	RSM models after removing non-significant variables	R^2	adj R^2
Power law K	Power law K=−80.32-26.50×xanthan+37.62×guar+61.97×starch −10.01×starch^2+283.05×xanthan×guar+43.69×xanthan×starch	0.958	0.939
Particle size	Particle size=+6.38+3.34×xanthan-6.46×guar-0.32×starch +17.91×guar^{2-} +2.02×xanthan×starch	0.875	0.830
Specific surface area	Specific surface area=+0.86-1.44×xanthan+1.78×guar+0.07×starch-5.02× guar^2 +0.76×xanthan×starch	0.867	0.819
Span	Span=+2.04–1.1×xanthan-2.75×guar+8.26×guar^2	0.611	0.538
Stability	Stability=−38.44+321.41×xanthan+186.18×guar+46.47×starch-440.60× xanthan^2 -205.05×guar^2-5.63×starch^2-132.22×xanthan×guar-21.00× xanthan×starch-19.16 × guar×starch	0.994	0.988
Thermal stability	Thermal stability=−44.33+265.80×xanthan +97.84×guar +44.51× starch-367.47 ×xanthan^2-165.25×guar^2-5.06×starch^2 -13.16×xanthan×starch	0.987	0.980

Models with high coefficients of determination for almost all responses, ranging from 0.89 to 0.99 (except for span), exhibited that models were significantly fitted for all responses. Therefore, at least 89 % of variability of different properties could be explained by the models obtained by response surface method.

In addition fitness of the models was evaluated through the lack-of-fit analysis, which indicated the suitability of almost all RSM models to accurately predict the variation in different responses. Insignificant lack of fit ($p>0.05$) for all variables studied showed that the polynomial models were satisfactorily suitable in predicting the corresponding responses. However, significant lack of fit for Power law flow behavior index indicates that this RSM model has not enough accuracy and actual and predicted data are not in good agreement. Lack of fit test, used in regression and design of experiments, assesses the fit of the model. If the p-value of lack of fit is less than selected α-level (in this case 0.05), evidence exists that the model does not accurately fit the data.

Therefore, high agreement between predicted and actual values indicated that the second order polynominal regression models (except for the power law flow behavior index) were adequate enough to determine optimum formulation. Final equations after removing non-significant terms are shown in Table 4.

Rheological and Flow Properties

The flow parameters obtained by fitting the data to Power law, Herschel-Bulkley, Bingham and Casson models. High coefficients of determination for Power law model (0.96–0.99) revealed the adequacy of this rheological model to describe flow behavior of mayonnaise samples.

In some cases, negative values were obtained for Herschel-Bulkley apparent yield stress. As a result, in spite of high R^2 (0.965–0.999), Herschel-Bulkley model was found to be an inappropriate rheological model. Emadzadeh and Razavi (2011) and Taghizadeh and Razavi (2009) reported negative yield stress values for pistachio butter which is not acceptable and has no physical meaning [22, 23].

All linear terms demonstrated significant effect on Bingham and Casson apparent yield stress followed by xanthan-starch interaction. Since data analysis did not show obvious results for Bingham and Casson consistency coefficients, the ANOVA table relevant to these two rheological

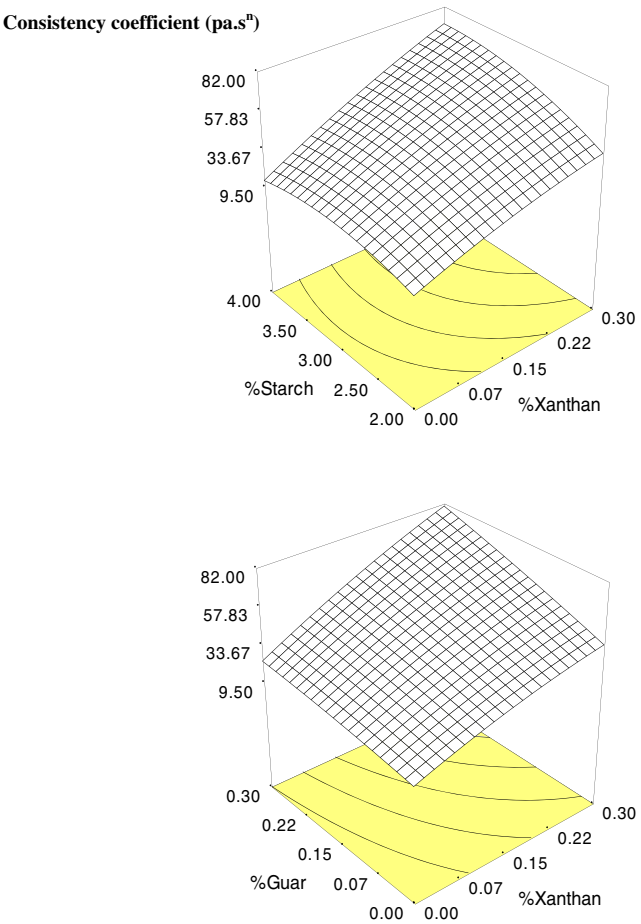

Fig. 1 Response surface plot for power law consistency coefficient obtained by modeling the data measured for mayonnaise samples as a function of xanthan, guar and pre gel corn starch

models is omitted. Therefore, Power law model turned out to be the best rheological model fitted on the experimental rheological data.

All linear effects were highly significant ($p<0.001$) on consistency coefficient of Power law followed by the interaction terms of xanthan-starch and xanthan-guar (Table 2). On the basis of sum of squares, among all statistical terms xanthan linear effect was found to be the most effective term as compared to the other hydrocolloids. The relationship between Power law consistency coefficient and used hydrocolloids is demonstrated in Fig. 1 that shows increase in xanthan concentration from 0 up to 0.3 % had considerably positive influence on consistency coefficient. These results are in agreement with those reported about high ability of xanthan to enhance viscosity by Dolze et al. (2007), Sanchezs et al. (1995) and Thomareis and Chatziantoniou (2011) [11, 24, 25]. The high molecular weight of xanthan gum and formation of aggregates via hydrogen bonding are the reasons why its solutions exhibit high viscosity [26–28]. Comparison of p-values as a way of searching significance of model terms implied that Power law consistency coefficient was dependent on the interactions between xanthan-starch and xanthan-guar. These results are in accordance with those found by previous researchers who observed synergistic effect between xanthan-starch [11, 28, 29] and also between xanthan-guar [29–31]. In the research conducted by Weber et.al (2009), no covalent bonds were found between starch-xanthan; therefore they reported that probably the only interactions occurring between them were hydrogen bonds [33]. Besides, comparing sum of squares (Table 2) showed that the interaction between xanthan and guar was also significant, but not as significant as the interaction between xanthan and starch. Xanthan interacts with galactomannans (e.g. locust bean gum or guar gum); therefore the viscosity of the mixture increases synergistically [30]. Results also showed that most of the samples had higher consistency value compared to the controls (Table 1).

The flow behavior indices of Power law (Table 1) confirmed high shear thinning and non-Newtonian behavior for all mayonnaise samples over the entire range of shear rate used. Pseudo-plastic flow behavior has already been reported for mayonnaise by previous researchers who used different types of polysaccharides in mayonnaise formulation [7, 8, 10, 11, 33]. This behavior results in easy pumping and flowing through pipes and containers [32]. Fig. 2 (viscosity as a function of shear rate) indicates that viscosity decreased approximately up to shear rate of 150 (1/s). In fact, viscosity decreases from a high value at low shear stresses to a low constant value at high shear stresses [35]. It is obvious that viscosity curve of control 1 overlaps the curve of the second control, showing that substitution of 50 % of egg with soy milk would not change viscosity of mayonnaise.

Similar rheological behavior was observed for other samples containing different levels of hydrocolloids. The most shear thinning behavior was observed for samples 9 and 3 with higher levels of xanthan and guar. Also, higher flow behavior indices which mean weak pseudo-plastic behavior

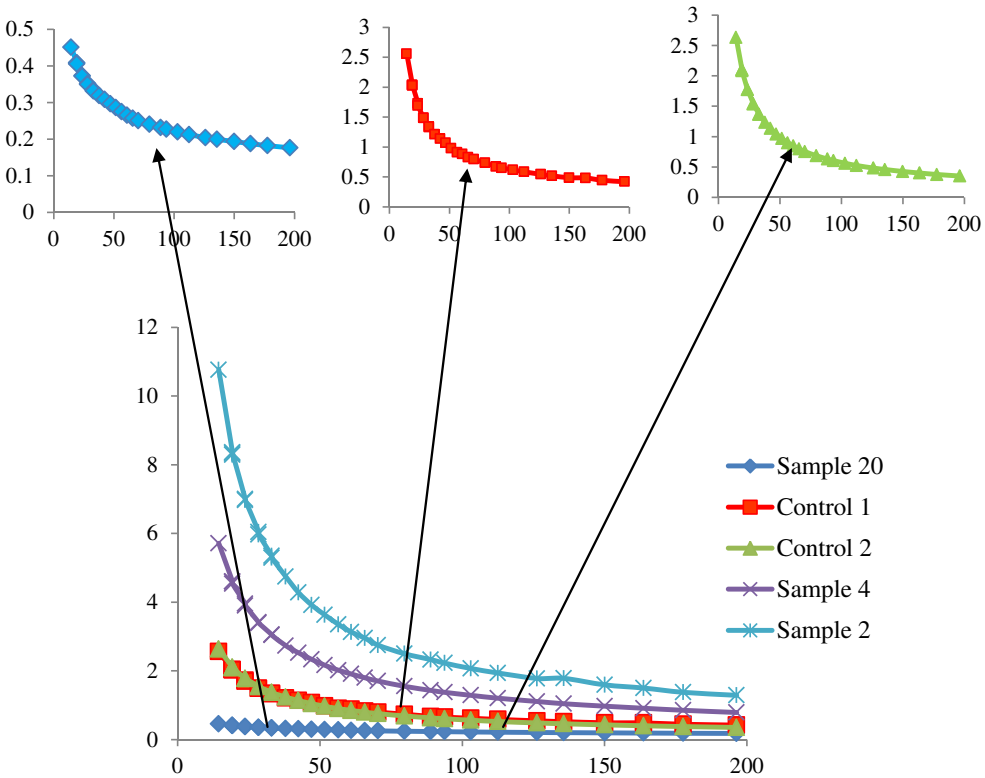

Fig. 2 Viscosity versus shear rate rheograms of mayonnaise samples

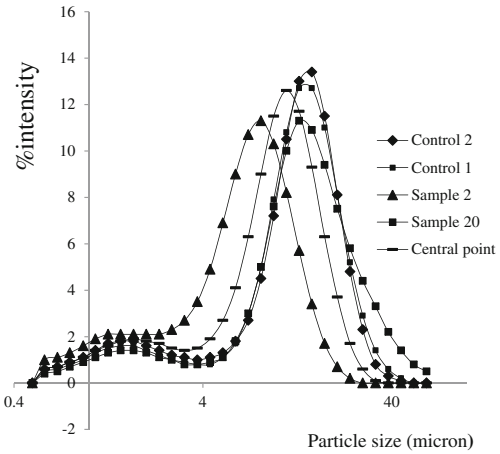

Fig. 3 Particle size distribution curves for mayonnaise samples including sample 2 (4 % pre gel corn starch, 0.3 % xanthan and 0.3 % guar), sample 20 (2 % pre gel corn starch), sample 4 (3 % pre gel corn starch, 0.15 % xanthan and 0.15 % guar gum), control 1 and control 2

were related to the samples 20 and 7 containing just starch as fat replacer. These results are in accordance with those explained by previous researchers who observed shear thinning behavior for xanthan and guar [26, 27, 30–32]. Likewise, in agreement with the present results, Thaiudoma and Khantarat (2011) reported an increase in n value of mayonnaise samples with increasing starch content as fat replacer [34].

Particle Size, Specific Surface Area and Span

According to the results (given in Table 2), starch and xanthan linear terms and the interaction between xanthan and starch were found to be significant parameters in the model fitted for particle size.

Figure 3 shows droplet size distribution curves for the mayonnaise emulsions prepared with different concentrations of xanthan, guar and pre gel corn starch. Bio modal (double peaked) distribution curves were observed, in the presence of used hydrocolloids, for all mayonnaise samples with a smooth first peak in the range of 0.4–4 micron. As can be seen, increasing the amount of gums and pre gel corn starch changed the pattern of droplet size distribution. It is obvious from the figure that using higher contents of different hydrocolloids, irrespective of their type, shifted the curves to the left. It is inferred from this result that higher contents of hydrocolloids prevented droplet flocculation and coalescence after emulsion preparation that consequently resulted in smaller particle size and narrower distribution curve for mayonnaise samples.

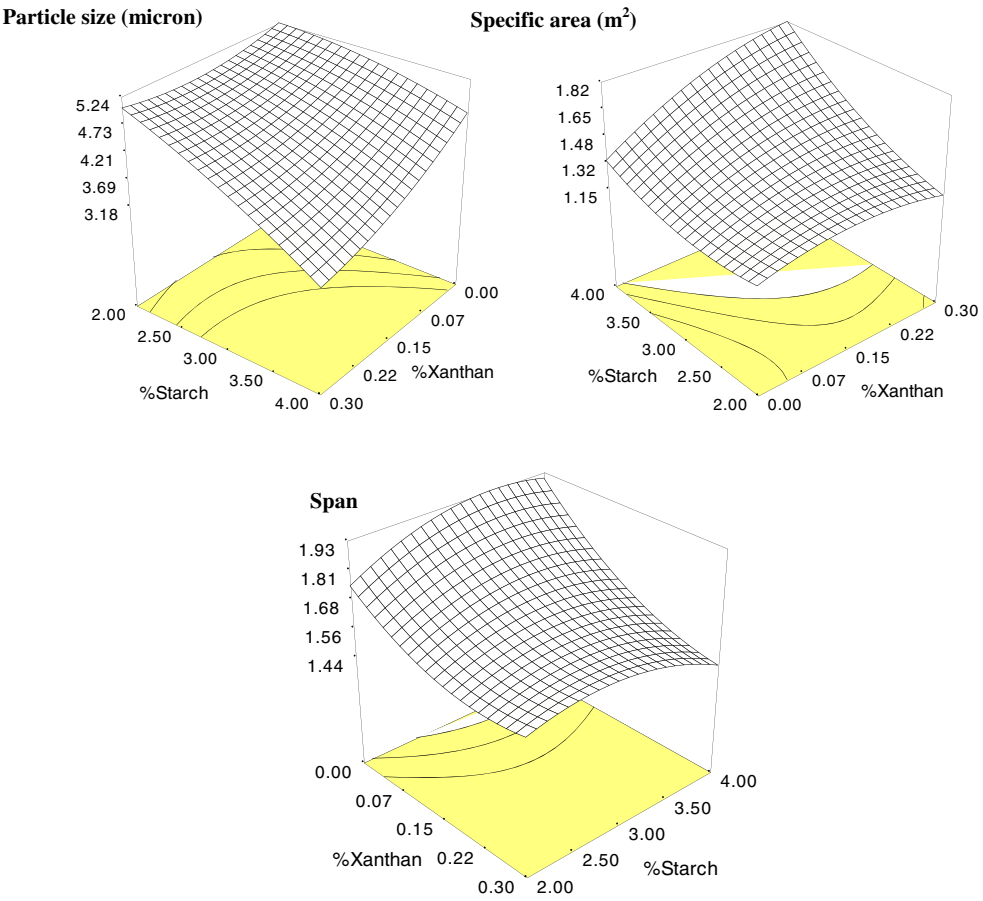

Fig. 4 Surface plots for particle size, specific surface area and span obtained by modeling the data measured for mayonnaise samples

Surface plots for particle size as a dependent variable (Fig. 4) demonstrated that increasing starch and xanthan led to a decrease in droplet size. However, based on the sum of squares (Table 2) increasing guar gum concentration did not change oil droplet size statistically. Generally smaller droplet sizes were observed in samples with higher concentrations of hydrocolloids. This can be interpreted as polysaccharides, via water absorption, result in more viscous continuous phase which limits movements of oil droplets. Therefore the collisions among droplets would decrease, resulting in smaller size for dispersed droplets [5, 36, 37]. Similar results were reported by previous researchers who observed smaller particle sizes for samples with higher viscosity [36, 38]. However, in some studies [39, 40] there is a report of limited breaking up of oil droplets in a viscous continuous phase, leading to larger particle size.

Although higher viscosity was observed for samples containing higher concentrations of xanthan, the order of significant coefficients in the particle size model showed that xanthan was the second significant parameter that affected droplet sizes. This is likely due to its negatively-charged structure. In general, if sufficient charged biopolymer is added to an emulsion containing oppositely charged droplets it may completely saturate the droplet surfaces and form a stable system since the droplets are completely coated with polymer [35]. pH values for mayonnaise samples are reported in Table 1. In the pH value lower than isoelectric pH, proteins are positively charged (isoelectric points for soy glycin, soy beta conglycin, egg white and egg yolk proteins are 4.64, 4.90, 5.4 and 5.3, respectively). Due to the presence of proteins and lipoproteins of egg and soy, xanthan molecule as an anionic gum, may be adsorbed at the interface via attractive electrostatic forces that consequently results in thicker protective coating layer. Therefore, larger particle sizes will produce. In these multi layer emulsions the internal part of the layer is built by protein and the outer section is built by polysaccharide [41]. This result was exactly in accordance with that of observed by Bouyer et al. (2011) who reported that in the dispersion of beta-lactoglobulin and gum arabic, beta-lactoglobulin adsorbed at the interface and gum arabic electrostatically bound to it, leading to the formation of a bi-layer stabilized emulsion [42]. It is also possible that xanthan bridges droplets. If an anionic biopolymer is added to an emulsion containing cationic droplets, a single biopolymer may link two or more droplets together through an electrostatic attraction [35]. Therefore, larger particle sizes may be observed.

The concentration dependence of specific surface area on the different hydrocolloids is presented in the surface plots, shown in Fig. 4. Statistical results (Table 3) showed that linear effects of independent variables (except for the effect of guar) were found to be significant on the variation in specific surface area model.

Results exhibited more dependency of specific surface area on the starch concentration compared with those of xanthan and guar. The mutual term responsible for variation in specific surface area model was the interaction between xanthan-starch (Table 3). Generally, higher specific surface area values were obtained for samples with smaller particle sizes. It is well known that smaller particle size results in increase in the specific surface area of droplets [19], which is also obvious in Fig. 5 for control samples.

According to the sum of squares (Table 3) and as exhibited in Fig. 4 (the variation in span values as a nonlinear function of polysaccharides), xanthan gum was the only significant parameter that affected span values. It seems that multi layer and concentrate structure, produced by xanthan, resulted in more uniform droplets in size. Actually it is due to the higher viscosity of the samples containing higher levels of xanthan prevented flocculation of droplets. Uniform sizes result in narrower particle size distribution range and smaller span values. Usually larger particle size results in higher span value (Fig. 4 and 5).

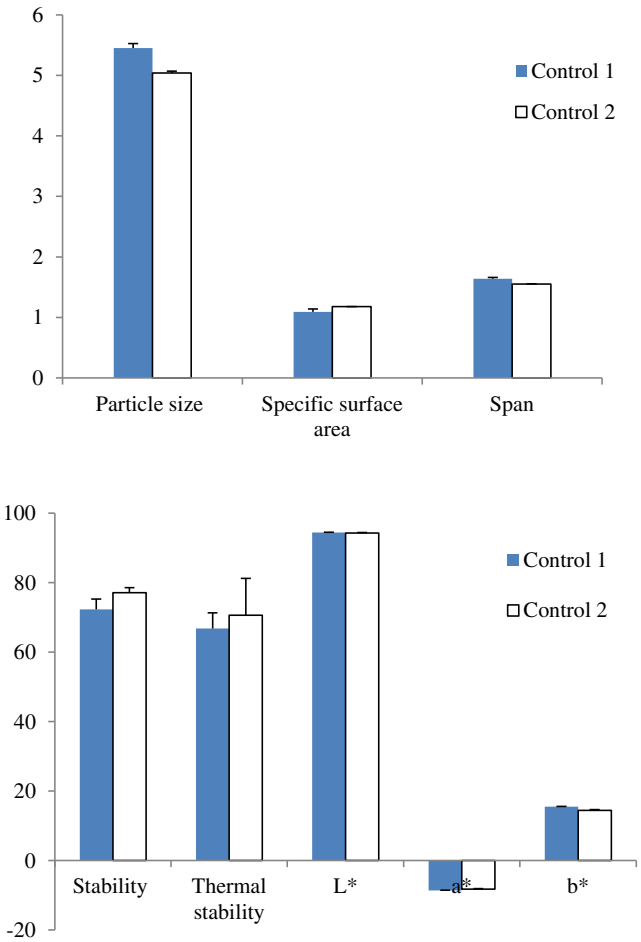

Fig. 5 Experimental data measured for control samples

Stability and Thermal Stability

With respect to the sum of squares and model coefficients (Table 3), stability and thermal stability were positively proportional to the linear, quadratic and interaction terms. The most significant term affecting stability and thermal stability was shown to be the linear effect of xanthan, followed by the linear effects of starch and guar and then the interaction term of xanthan-starch (more significant than xanthan-guar). As shown in Fig. 6 (that presents stability and thermal stability as functions of xanthan, guar and pre gel corn starch concentrations), increasing concentration of all hydrocolloids improved stability and thermal stability of emulsions.

With increasing concentration of xanthan from 0 to 0.3 %, the rate of stability was observed to increase considerably. But addition of guar gum and pre gel corn starch resulted in linear positive influence on stability and thermal stability. This observation can be contributed to the thicker protective layer produced by xanthan at the interface (multilayer coating layer). This kind of emulsion may be highly stable to environmental stresses, such as pH, salt, heating, chilling, freezing and dehydration [35].

The highest response for stability and thermal stability was observed when the emulsion was produced with 0.3 % xanthan, 0.3 % guar and 4 % starch. According to the Stoke's law, the sedimentation or creaming velocity is inversely proportional to the viscosity of the water phase [19] which means higher viscosity of continuous phase and smaller particle size are the main reasons leading to the reduction in creaming rate. Thus, high stability of samples was attributed to their both particle size and fat replacer content. Similar result has been observed by Worrasinchai et al. (2006) [7].

Storage at 2 ˚C for 3 months showed that almost all mayonnaise samples were highly stable at low temperature and no oil or cream separation occurred (except for sample 20). Generally, results derived from temperature-dependency examines of stability exhibited more stable emulsions in lower temperatures. This result shows that emulsions are temperature sensitive; therefore creaming rate of all samples was considerably higher in high temperature. This may be due to the stronger emulsion structure, as a consequence of increase in the viscosity of continuous phase, produced by used polysaccharides in low temperature. This network limits mobility of oil droplets and prevents them from coming into coalescence and reduces droplet growth rate. High temperature can reduce viscosity of both continuous and oil phases. Therefore, oil drops tend to move up ward and higher degree of coalescence and creaming would occur. Another reason to this result

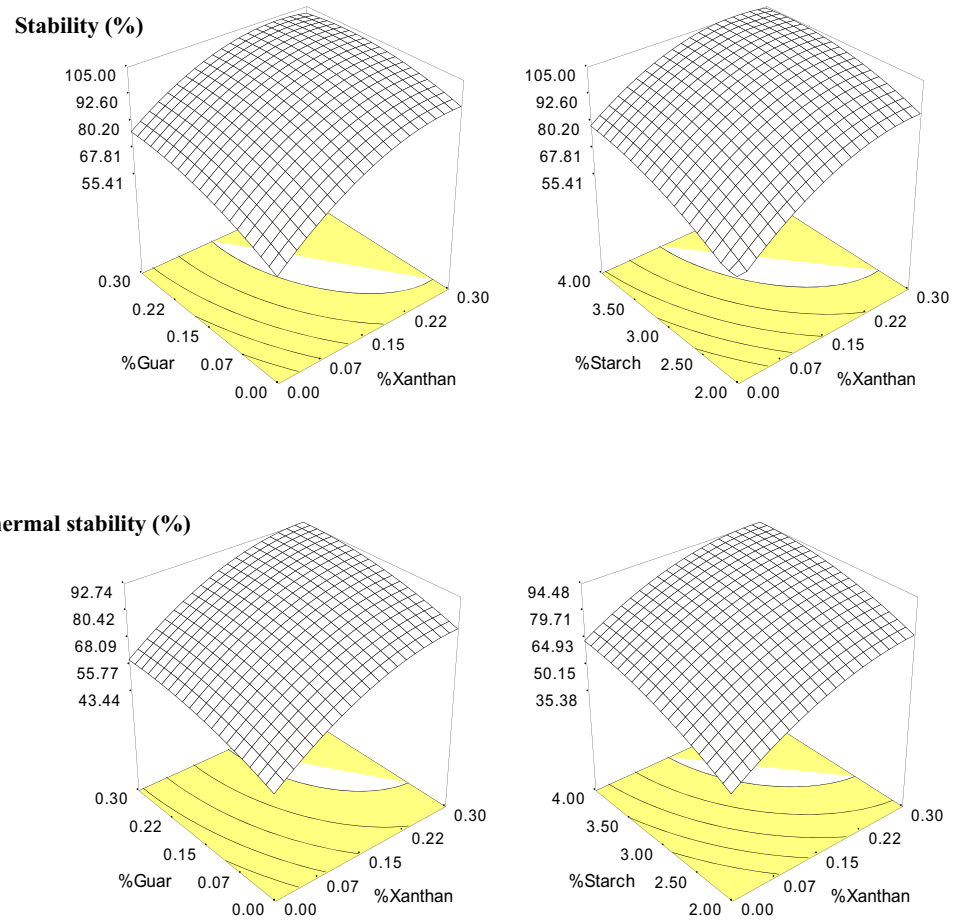

Fig. 6 Response surface plots for stability and thermal stability obtained by modeling the data measured for mayonnaise samples as functions of xanthan, guar and pre gel corn starch

has been stated by Depree and Savage (2001) who reported that when mayonnaise is stored at elevated temperatures, increase in Brownian motion of the droplets decreases the viscosity of the continues phase and solubilization of the surfactants contributes to the breakdown of the emulsion [43]. Also Goush et al. (2008) observed more stable mayonnaise emulsions in low temperatures. They believed in the rapid flocculation in higher temperatures that was well correlated with the data derived from experiments in the present study [44].

Color Factors

Values of color variables obtained by image processing technique are indicated in Table 1. Analysis of variance (not shown) exhibited that hydrocolloids did not have a significant influence on color factors. Similar results were achieved by Thaiudom and Khantarat (2011) who reported that there was no considerable difference in color parameters of reduced fat mayonnaise samples containing 50 % oil and different levels of starch [34]. Results shown in Fig. 5 indicate that replacement of 50 % of egg with soy milk would not affect mayonnaise color.

Optimization

Optimum level for independent variables was determined by numerical optimization using response optimizer (Design expert software) to obtain minimum particle size, minimum span, maximum specific surface area, maximum stability and thermal stability values. The optimization procedure indicated the overall optimum region to be at the combined level of 0.29 % xanthan, 0.23 % guar and 4 % preglatinized corn starch.

The corresponding response values for characteristics predicted under the recommended optimum conditions were particle size: 3.26, specific surface area: 1.80, span: 1.48, stability: 100 % and thermal stability: 96.42 %.

Conclusions

Results and comparison between predicted and actual values for the response variables indicated that the RSM and polynomial regression models were satisfactorily appropriate for predicting the responses and determining optimum formulation of mayonnaise. In addition pre gelatinized corn starch, as a fat replacer and thickener, showed high adequacy to improve mayonnaise characteristics. Synergistic interaction between xanthan and pre gel corn starch, stronger than the interaction between xanthan and guar, occurred and improved physicochemical properties of the product. As a consequence of this interaction, xanthan and preglatinized corn starch can be used as appropriate and potential fat replacers and thickening agents in mayonnaise and other food products.

References

1. K. M. Garcia, *Quality characterization of cholesterol-free mayonnaise-type spreads containing rice bran oil*, MSc thesis (Louisiana State University, Louisiana, 2006)
2. 3. S. S. Jonnalagadda, J. M. Jones, *J American Dietetic Association*. (), 266–275 (2005)
3. A.M. Miraglio, American Journal Clinical Nutrition **62**(5), 1175–1179 (1995)
4. D.J. McClements, K. Demetriades, Critical Reviews in Food Science and Nutrition **38**(6), 511–536 (1998)
5. S. Maghsoudi, *The technology of sauces producing* (Marzedanesh, Tehran, 2004)
6. C.F. Ognean, N. Darie, M. Ognean, Journal of Agroaliment Processes Technology **7**(2), 433–442 (2006)
7. S. Worrasinchai, M. Suphantharika, S. Pinjai, P. Jamnong, Food Hydrocolloids **20**(1), 68–78 (2006)
8. H. Liu, X.M. Xu, S.D. Guo, LWT **40**(6), 946–954 (2005)
9. H. Su, C. Lien, T.A. Lee, R.S. Ho, Journal Science of Food and Agriculture **90**(5), 806–812 (2010)
10. S. Mun, Y.L. Kim, C.G. Kang, K.H. Park, Inter Journal of Biol Macromol **44**(5), 400–407 (2009)
11. M. Dolz, M.J. Hernandez, J. Delegido, M. Alfaro, J. Munoz, Journal of Food Engineering **81**(10), 179–186 (2007)
12. A. Farahnaki, M. Majzoobi, G. Mesbahi, *Properties of hydrocolloids* (Agricultural science of Iran, Tehran, 2009)
13. R.E. Igoe, Y.H. Hui, *Dictionary of food ingredients* (Aspen publisher, Gaithersburg, 2001)
14. J.D. Firebaugh, *Characterization and application of a derivatized whey ingredient, MSc thesis* (North California state university, California, 2004)
15. P. Murphy, Starch, in *Hand book of hydrocolloids*, ed. by G.O. Phillips, P.A. Williams (Wood head publishing Ltd, Cambridge, 2000), pp. 41–65
16. N. Seyhun, G. Sumnu, S. Sahin, Food Bioproducts Processes **83**(1), 1–5 (2005)
17. J. Rodríguez-Miranda, E. Delgado-Licon, B. Hernández-Santos, D. Reyes-Jaquez, E. Aguilar-Palazuelos, H. Medrano-Roldan, R.O. Navarro-Cortez, J. Castro-Rosas, C.A. Gómez-Aldapa, J Anim Prod Adv **2**(7), 335–344 (2012)
18. A. Anastasiades, S. Thanou, D. Loulis, A. Stapatoris, T.D. Karapantsios, Journal of Food Engineering **52**, 57–66 (2002)
19. K. Rahmati, M. Mazaheri Tehrani, K. Daneshvar, *J Food Sci Technol*. DOI 10.1007/s13197-012-0806-9 (2012)
20. W. Pabst, E. Gregorova, *Characterization of particles and particle systems* (ICT Prague, 2007)
21. S.M.T. Gharibzahedi, S.M. Mousavi, M. Hamedi, M. Ghasemlou, Food Hydrocolloids **26**(1), 293–301 (2012)
22. B. Emadzadeh, S.M.A. Razavi, M. Hashemi, Inter J Nuts & Relat Sci **2**(1), 37–47 (2011)
23. M. Taghizadeh, S.M.A. Razavi, Inter J Food Prop **12**(2), 331–340 (2009)
24. V.E. Sanchez, G.B. Bartholomai, A.M.R. Pilosof, LWT **28**(4), 380–385 (1995)
25. A.S. Thomareis, S. Chatziantoniou, Proced Food Sci **1**, 1997–2002 (2011)
26. B. Katzbauer, Polymer Degradation Stability **59**(1–3), 81–84 (1998)

27. C. Viebke, P.A. Williams, Food Hydrocolloids **14**(3), 265–270 (2011)
28. F. Wang, Z. Su, Y.J. Wang, Food Hydrocolloids **15**(4–6), 575–581 (2001)
29. V. Krstonosic, L. Dokic, J. Milanovic, Food Hydrocolloids **25**(3), 361–367 (2011)
30. F. Garcia–Ochoa, V.E. Santos, J.A. Casas, E. Gomez, Biotechnology Advances **18**(7), 549–579 (2000)
31. H.D. Belitz, W. Grosch, P. Schieberle, *Food chemistry* (Springer, Berlin, 2009)
32. L. N. Sadar, *Rheological and textural characteristics of copolymerized hydrocolloidal solutions containing curdlan gum,* MSc thesis (University of Maryland, Maryland, 2004)
33. F.H. Weber, M.T.P.S. Clerici, F.P. Collares-Queiroz, Y.K. Chang, Starch-Starke **61**(1), 28–34 (2009)
34. S. Thaiudom, K. Khantarat, Procedia Food Sci **1**, 315–321 (2011)
35. D. J. McClements, in *Modern Biopolymer Science,* ed. by S. Kasapis, I. T. Norton, J. B. Ubbink (Springer, Oxford, 2009), pp. 129–166
36. B. Wang, D. Li, L.J. Wang, B. Adhikari, J. Shi, Journal of Food Engineering **100**(3), 417–426 (2010)
37. H. Torabizadeh, *Food emulsions and emulsifiers* (Ayeej, Tehran, 2002)
38. R.E. Aluko, T. McIntosh, Innov Food Sci & Emerg Technol **6**(2), 195–202 (2005)
39. O. Behrend, K. Ax, H. Schubert, Ultrasonics Sonochem **7**, 77–85 (2000)
40. A.R. Taherian, P. Fustier, H.S. Ramaswamy, Food Engineering **77**, 687–696 (2005)
41. E. Dickinson, Food Hydrocolloids **25**(8), 1966–1983 (2011)
42. E. Bouyer, G. Mekhloufi, I. Le Potier, T. Kerdaniel, J. Grossiord, V. Rosilio, F. Agnely, Journal of Colloid and Interface Science **354**(2), 467–477 (2011)
43. J.A. Depree, G.P. Savage, Trends in Food Science and Technology **12**(5–6), 157–163 (2001)
44. M.A. Ghoush, M. Samhourim, M. Al-Holy, T. Herald, Journal of Food Engineering **84**(2), 348–357 (2008)