Formulation of Physical Properties of Methyl Glucoside Polyester by Mixture Response Surface Methodology

Yu-Fu Lai and Chwen-Jen Shieh*

Department of Food Engineering, Dayeh University, 112 Shan-Jiau Road, Da-Tsuen, Chang-Hua 51505, Taiwan

Methyl glucoside polyester (MGPE), consisting of a methyl glucoside molecule esterified with four fatty acids, is a potential fat substitute. A mixture response surface methodology was employed to model the physical properties (melting point, density, and viscosity) of MGPE prepared from composite blends of fatty acid methyl esters (FAME). The measured physical properties were similar to those of soybean oil, except for a higher viscosity. The physical properties correlated significantly with the degree of saturation of their composite fatty acids. Results showed that the physical properties of MGPE prepared from a FAME mixture derived from high oleic acid safflower oil and soybean oil (molar ratio 1:1) was similar to those of soybean oil. The physical properties of MGPE can be adjusted by modifying the saturated fatty acids of synthesized MGPE to simulate the physical properties of soybean oil.

Keywords: *Formulation; methyl glucoside polyester; mixture RSM; optimization; physical properties*

INTRODUCTION

Reduced- or zero-calorie fat substitutes have been introduced into the food industry as food ingredients. Most fat substitutes are limited by heat stability, texture, taste, and marketing; however, Olestra (sucrose polyester, SPE) exhibits functional and physical properties that resemble those of conventional triglycerides but contributes no calories to the diet (*1*). The U.S. Food and Drug Administration approved the use of Olestra—a fat-based substitute for conventional fats—in certain snack foods, such as potato chips (*2*). In addition, Olestra exhibits potential for reducing blood cholesterol and body weight in obese individuals (*3*).

Methyl glucoside polyester (MGPE), a potential fat substitute consisting of a methyl glucoside molecule with four fatty acids esterified to the hydroxyl groups, is a possible low-calorie oil replacement for conventional edible oils (*4*). The use of MGPE as a fat substitute in the diet is safe and may be useful for weight reduction (*5*).

Thus far, MGPE is chemically synthesized by transesterification of methyl glycoside with fatty acid methyl esters or by direct esterification with fatty acids. Albano-Garcia et al. (*6*) reported a solventless synthesis of methyl glucoside esters of coconut fatty acids in the presence of catalysts. Akoh and Swanson (*4*) synthesized MGPEs by a solvent-free system of methyl glucoside with fatty acid methyl esters (FAMEs) of long-chain fatty acids. Boutte and Swanson (*7*) modified the soap method using a rotary evaporator in a laboratory scale experiment. Recently, Shieh and Lai (*8*) employed response surface methodology (RSM) to evaluate the effects of synthesis parameters, including reaction time, temperature, and substrate molar ratio, and the optimum synthesis of MGPE was suggested.

The physical properties of SPE have been reported by several researchers (*9*−*11*). The physical properties of SPE can be adjusted by varying the degree of saturation and chain length of the component fatty acids (*9*). The physical properties and functions of SPE are similar to those of conventional triacylglycerols; however, the measured viscosity of SPE is significantly greater than that of vegetable oil. The physical properties of MGPE have been investigated by several researchers (*4*); however, the effect of fatty acid composition on the physical properties of MGPE needs to be studied further.

Table 1. Composition of MGPEs Reactant FAME Prepared from Palm, Safflower, and Soybean Oils[a]

	components of FAME (%)		
formula	palm oil	safflower oil	soybean oil
1	100	0	0
2	0	100	0
3	0	0	100
4	50	50	0
5	50	0	50
6	0	50	50
7	33.3	33.3	33.3

[a] Mixture design resulted in seven formulations.

Our objectives were to model the physical properties of MGPE synthesized from composite FAME blends of palm oil, high oleic acid safflower oil, and soybean oil by using mixture RSM and to determine the FAME composition yielding MGPE with physical characteristics comparable to those of 100% soybean oil. A triangular contour plot and superimposing technique were employed to reach the objectives.

MATERIALS AND METHODS

Experimental Design. A three-variable simplex centroid design was used, in which the number of points was $2^q - 1$, q being equal to the number of variables, that is, three in this study (*11*, *12*). This design resulted in seven FAME mixtures (Table 1). The molar ratio (percentage) of composite blends of

* Corresponding author (telephone 886-4-853-0421; fax 886-4-853-4845; e-mail cjshieh@mail.dyu.edu.tw).

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Table 2. Experimental and Predicted Fatty Acid Profiles and Physical Properties of MGPE Prepared from FAME of Palm, Safflower, and Soybean Oils

	fatty acid profiles						properties properties		
formula[a]	saturated fatty acid (%)	unsaturated fatty acid[b] (%)	MUFA (%)	PUFA[c] (%)	mean chain length	molecular weight	specific gravity (40 °C/40 °C)	viscosity (40 °C) (cP)	melting point (°C)
1	50.00	50.00	44.35	5.65	17.00	1265.5	0.942	133.10	28.55
	51.11[d]	*50.46*	*45.61*	*7.41*	*16.98*	*1265.6*	*0.942*	*133.30*	*28.36*
2	7.11	92.89	83.54	9.35	17.86	1309.9	0.935	94.50	4.40
	7.33	*92.05*	*84.24*	*10.45*	*17.85*	*1310.0*	*0.935*	*94.72*	*4.65*
3	14.91	85.09	34.36	50.73	17.70	1297.5	0.937	83.25	4.15
	15.10	*86.61*	*35.62*	*50.59*	*17.70*	*1297.5*	*0.937*	*83.47*	*4.40*
4	30.89	69.11	58.99	10.12	17.38	1285.1	0.940	104.25	7.35
	29.22	*71.25*	*57.36*	*8.93*	*17.42*	*1284.4*	*0.940*	*103.40*	*8.11*
5	38.16	71.67	44.52	27.15	17.32	1281.9	0.940	99.00	8.10
	33.11	*68.53*	*40.62*	*28.00*	*17.34*	*1281.6*	*0.940*	*98.11*	*8.86*
6	10.49	89.86	76.67	13.19	17.79	1310.0	0.937	86.00	4.65
	11.22	*89.33*	*73.90*	*16.36*	*17.78*	*1309.4*	*0.937*	*85.11*	*4.53*
7	24.60	75.41	51.76	23.64	17.51	1290.5	0.938	90.75	7.10
	24.51	76.36	58.00	16.52	17.51	1291.9	0.938	92.75	5.40
soybean oil	12.60	87.40	26.09	61.31	17.75	921.2	0.910	11.24	6.38

[a] Components of composite FAME formulas are shown in Table 1. [b] Unsaturated fatty acid includes mono- and polyunsaturated fatty acid (MUFA and PUFA, respectively). [c] PUFA includes two and three double bonds of fatty acid. [d] Italic type indicates predicted value from model listing in Table 3.

FAME ranges from 0 to 100%. Two replications of the study were conducted.

Materials. High oleic acid safflower oil, palm oil, and soybean oil were purchased locally (Chang-Hua, Taiwan). α-Methyl glucoside was purchased from Aldrich Chemical Co. (Milwaukee, WI). All organic solvents, sodium hydroxide, hydrochloric acid, potassium hydroxide, and potassium carbonate were purchased from Merck Chemical Co. (Darmstadt, Germany).

Synthesis and Purification. MGPE was synthesized in a solvent-free system based on our previous investigation (*8*), in which the optimum parameters were as follows: reaction time, 6.3 h; synthesis temperature, 123.8 °C; substrate molar ratio, 5.9:1 (FAME/methyl glucoside). The mean molecular weight of MGPE was calculated on the basis of the fatty acid composition as determined by gas chromatography (GC) (*9*). In a typical synthesis, 0.167 mol of methyl glucoside (32.88 g) and 1.00 mol of FAME (288.21 g of FAME of palm oil, 294.11 g of FAME of safflower oil, and 294.32 g of FAME of soybean oil) were reacted in a 2 L three-neck round-bottom flask attached to an evaporator; a magnetic stirring bar was used for mixing. The heat was supplied by an external electrically heated and thermostatically controlled heating mantle to maintain a constant temperature. The amount of potassium hydroxide was 2.5% and of methanol, 40 wt % of FAME plus methyl glucoside. The potassium hydroxide was milled, and the FAMEs were added to the 2 L three-neck round-bottom flask and stirred at room temperature for 30 min, after which time the methyl glucoside was added. The reactants were heated to 85 °C for 15 min at atmospheric pressure to form soap. Then, the mixture was heated to 123.8 °C to promote the transesterification reaction at a full vacuum (∼100 mmHg). After heating to 123.8 °C, 0.5% (w/w) potassium carbonate was added to catalyze the MGPE reaction. When the reaction temperature was reached after 6.3 h, the reaction was cooled to 80 °C and terminated with 2−3 mL of concentrated acetic acid. The crude product was washed three times with 95% ethanol at 60 °C and five times with 1.5 L of water (70 °C). The MGPE was dissolved in hexane, stirred, and bleached with decolorizing carbon (∼20%, w/w) twice at 100 °C for 1.5 h under a vacuum of ∼100 mmHg in a rotary evaporator. The MGPE solution was dissolved in hexane, and charcoal particles were removed by filtering the mixture through a 0.5 μm filter. A KDL-4 short-path distillation apparatus (UIC, Joliet, IL) was used to remove excess FAMEs and methyl glucoside esters with a low degree of substitution. The MGPE was not steam deodorized.

Analysis and Measurements. The fatty acid profile of MGPE was obtained by transesterification of MGPE with 1.0 M methanolic NaOH, and the resulting methyl esters were analyzed by GC. The theoretical molecular weight of synthesized MGPE was calculated under the assumption that the MGPE had four long-chain fatty acids attached ($C_{14:0}$−$C_{18:3}$), as determined from the fatty acid composition by GC analysis (*9*). The specific gravity of MGPE was calculated by using the density of MGPE at 40 °C divided by the density of water at 40 °C (*11*). The melting point of MGPE was measured by using the standard AOCS (*13*) method Cc 1-25. The viscosity of MGPE was measured with a Brookfield viscometer (model LVDV II+; Stoughton, MA), and the viscosity values were expressed in centipoises (cP) at 40 °C.

Statistical Analysis. The Statistical Analysis System (*14*) was employed to analyze the experimental data (Table 2). Multiple regression analysis (Proc Reg) with stepwise elimination option was used to fit a quadratic canonical polynomial model described by Scheffé (*15*) as follows:

$$Y = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_1\beta_2 X_1 X_2 + \beta_1\beta_3 X_1 X_3 + \beta_2\beta_3 X_2 X_3$$

where Y is a predicted dependent variable (each property of MGPE); β_1, β_2, β_3, $\beta_1\beta_2$, $\beta_1\beta_3$, and $\beta_2\beta_3$ are the corresponding parameter estimates for each linear and cross-product term produced for the prediction models; X_1 is the FAME prepared from palm oil; X_2 is the FAME prepared from safflower oil; and X_3 is the FAME prepared from soybean oil. The intercept and quadratic terms of the model were removed from the models in accordance with the procedures (*12*). A stepwise option was employed to eliminate insignificant ($p < 0.15$) variables in a model.

RESULTS AND DISCUSSION

Table 2 presents the fatty acid profiles and physical properties of MGPE and soybean oil. The theoretical molecular weights of MGPE were between 1260 and 1310, on the basis of its fatty acid composition and the assumption that MGPE contains four long-chain fatty acids. Both the theoretical molecular weights and the specific gravity of MGPE were larger than those of soybean oil. The reason is that MGPE contains four fatty acids, whereas the triacylglycerols of soybean oil comprise three fatty acids per molecule. The range of melting points was wide, from 4.15 to 28.55 °C, varying with different fatty acid compositions. The viscosities of all formulations were greater than that of soybean oil (11.24 cP). The MGPE prepared from 100% palm oil was solid at ambient temperatures. The MGPEs of

Table 3. Parameter Estimates for Variables Used in Prediction Models for Fatty Acid Profiles and Physical Properties of MGPE Using Composite of FAME of Palm (PM), Safflower (SF), and Soybean Oils (SB)[a]

	fatty acid profiles						physical properties		
FAME	saturated fatty acid	unsaturated fatty acid	MUFA	PUFA	mean chain length	molecular weight	specific gravity	melting point	viscosity
PM	51.110++	50.457++	45.609++	7.405+	16.978++	1265.576++	0.942++	28.361++	133.322++
SF	7.328++	92.050++	84.235++	10.449+	17.854+	1310.014++	0.934++	4.651++	94.722++
SB	15.104++	86.606++	35.623++	50.592++	17.698++	1297.544++	0.937++	4.401++	83.472++
PM × SF			−30.242+			−13.387	0.007+	−33.593	−42.643++
PM × SB								−30.093	−41.143++
SF × SB			55.875+	−56.646+		22.415+	0.005+		−15.943++
R^2	0.993	0.998	0.995	0.972	0.999	0.999	0.999	0.995	0.999

[a] +, $p < 0.05$; ++, $p < 0.01$.

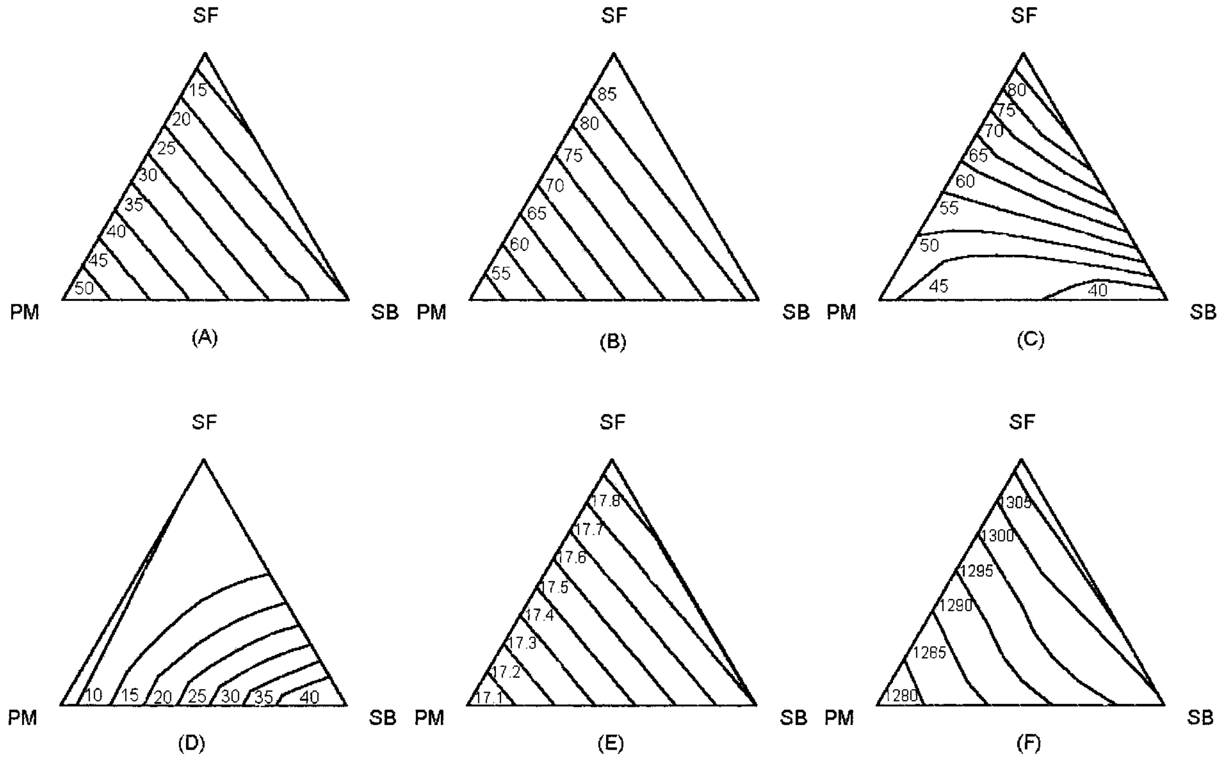

Figure 1. Triangular contour plots for fatty acid profiles for blends containing composite FAME prepared from palm oil (PM), safflower oil (SF), and soybean oil (SB): response contour plots for (A) percentage of saturated fatty acid, (B) percentage of unsaturated fatty acid, (C) percentage of monounsaturated fatty acid, (D) percentage of polyunsaturated fatty acid, (E) chain length, and (F) mean molecular weight.

formulas 4 and 5 (prepared from 50% palm oil) were semisolid, and the others were liquid at ambient temperature. MGPE containing >70% unsaturated fatty acid is a form of liquid at ambient temperature. The MGPE was yellow oil at room temperature, similar to the color of soybean oil. Overall, the measured properties of MGPE were similar to those of soybean oil, except for the viscosity. The viscosity of SPE was significantly higher than that of soybean oil (*11*) and the viscosity of MGPE closer to that of soybean oil.

The results of the multiple regressions with stepwise elimination are presented in Table 3, which lists estimates of parameters and the coefficient of determination (R^2) for the prediction models for the fatty acid profiles and the physical properties of MGPE. The stepwise regression option was specified to eliminate the insignificant variable in a full model. The final prediction models were employed to generate triangular contour plots (Figure 1). The composite fatty acid blend is better understood through the triangular contour plots. The MGPE prepared from palm oil FAME was higher (∼50%) in saturated fatty acids (Figure 1A) than the others. The MGPE prepared from safflower oil was high in monounsaturated fatty acids (Figure 1C), and the MGPE prepared from soybean oil was high in polyunsaturated fatty acids (Figure 1D). The higher mean molecular weight of MGPE was produced from the FAME of safflower oil (Figure 1F).

The triangular contour plots of the physical properties of MGPE are presented in Figure 2. The contour behavior of the specific gravity (Figure 2A) exhibited no relationship with the degree of saturation or the chain length of the fatty acid composition of MGPE. The contour behaviors of the melting point and the viscosity (Figure 2B,C) were similar to those of the degree of saturated fatty acids (Figure 1A) and somewhat related to the mean chain length (Figure 1E). Figure 3, produced from the prediction model, indicates that the melting points and viscosities of MGPE were affected by the degree of saturation and average chain length. Parts A and B of Figure 3 reveal that the melting point and viscosity of MGPE were significantly affected by the degree of saturation of MGPE but only slightly affected by the average chain length. The greater the saturated

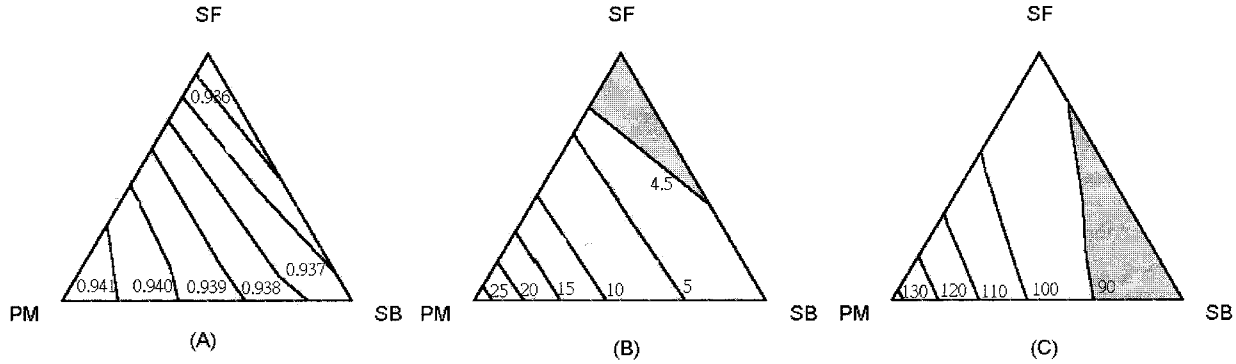

Figure 2. Triangular contour plots for physical properties for blends containing composite FAME prepared from PM, SF, and SB: response contour plots for (A) specific gravity, (B) melting point, and (C) viscosity. Shaded regions represent accepted area. See Figure 1 for abbreviations.

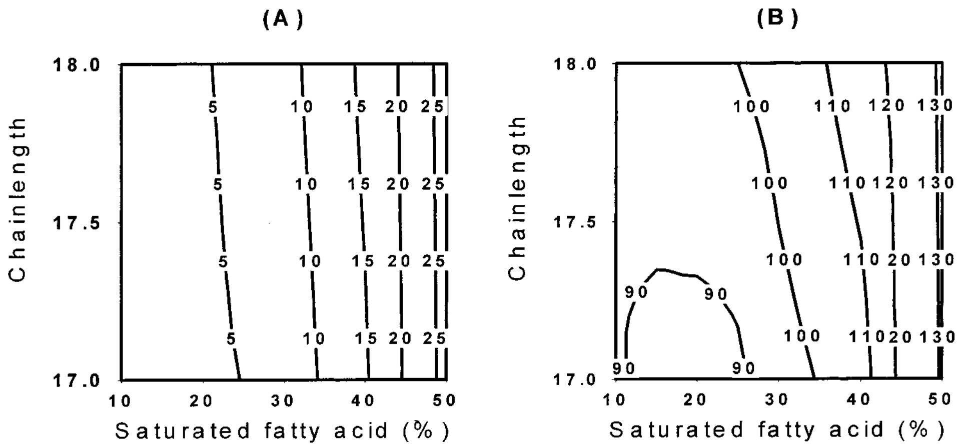

Figure 3. Contour plots of physical properties affected by degree of saturation and average chain length of their fatty acid composition: (A) melting point (°C); (B) viscosity (cP).

fatty acid content, the higher the melting point and viscosity. Overall, the physical properties of MGPE can be adjusted by modifying the degree of saturation to simulate the physical properties of soybean oil.

Table 2 also presents the observed and predicted values from the prediction models for both the fatty acid profile and the physical properties of MGPE, with an $R^2 > 0.95$. The chi-square tests indicated that the measured values were not significantly different (p value > 0.95, df = 6) from the predicted values for all models, indicating that parameter estimates can be used to predict the actual properties of MGPE (Table 3) (*16*).

The physical properties of MGPE were optimized to simulate those (Table 2) of soybean oil and obtain the optimum ratio of FAME for MGPE synthesis. The acceptable properties of MGPE for simulating soybean oil were designated as follows: melting point < 4.5 °C and viscosity < 90 cP. The optimum areas for the physical properties were outlined on surface contour plots and are indicated by the shaded region in Figure 2. Figure 4, obtained by superimposing parts B and C of Figure, presents the acceptable regions for formulations producing values within the optimum criteria range. The shaded area in Figure 4 represents the region in which soybean oil can be replaced with synthesized MGPE. Furthermore, a FAME mixture derived from safflower oil and soybean oil (molar ratio 1:1) is suggested as the optimum formula in this study.

Mixture RSM was employed to determine the effects of variations in FAME prepared from palm oil, high oleic acid safflower oil, and soybean oil with regard to the fatty acid profiles and physical properties of seven formulations in this study. The measured physical properties were similar to those of soybean oil, except for a higher viscosity. The physical properties of MGPE were affected by the degree of saturated fatty acid composition. A mixture of 1:1 FAME (prepared from high oleic acid safflower oil and soybean oil) reacted with methyl glucoside can be used to synthesize an MGPE with physical properties most similar to those of soybean oil.

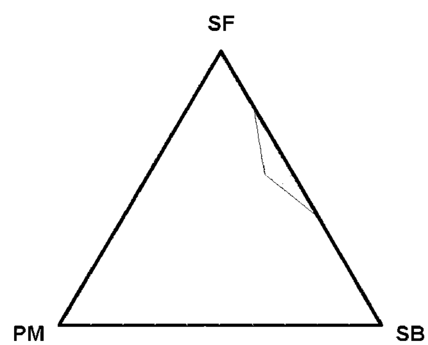

Figure 4. Optimum region (shaded) obtained by superimposing contour plots of major physical properties (melting and viscosity) for blends containing composite FAME from PM, SF, and SB. See Figure 1 for abbreviations.

LITERATURE CITED

(1) Bernhardt, C. A. Olestra—a non-caloric fat replacement. *Food Technol. Int. Eur.* **1988**, 176–178.

(2) Klis, J. B. FDA approves fat substitute, Olestra. *Food Technol.* **1996**, *51*, 124.
(3) Jandacek, R. J. Developing a fat substitute. *CHEMTECH* **1991**, *21*, 398−402.
(4) Akoh, C. C.; Swanson, B. G. Synthesis and properties of alkyl glycoside and stachyose fatty acid polyesters. *J. Am. Oil Chem. Soc.* **1989**, *66*, 1295−1301.
(5) Akoh, C. C.; Swanson, B. G. Absorbability and weight gain by mice fed methyl glucoside fatty acid polyesters: potential fat substitutes. *J. Nutr. Biochem.* **1991**, *2*, 652−655.
(6) Albano-Garcia, E.; Lorica, R. G.; Pama, M.; de Leon, L. Solvent-less synthetic methods for methyl glucoside and sorbitol esters of coconut fatty acid. *Philipp. J. Coconut Stud.* **1980**, *5*, 51.
(7) Boutte, T. T.; Swanson, B. G. Supercritical fluid extraction and chromatography of sucrose and methyl glucose polyester. In *Carbohydrate Polyesters as Fat Substitute*; Akoh, C. C., Swanson, B. G., Eds.; Dekker: New York, 1994; pp 65−93.
(8) Shieh, C.-J.; Lai, Y.-F. Application of response surface methodology to the study of methyl glucoside polyester synthesis parameters in a solvent-free system. *J. Agric. Food Chem.* **2000**, *48*, 1124−1128.
(9) Akoh, C. C.; Swanson, B. G. Optimized synthesis of sucrose polyesters: comparison of physical properties of sucrose polyesters, raffinose polyesters and salad oils. *J. Food Sci.* **1990**, *55*, 236−243.
(10) Hamm, D. J. Preparation and evaluation of trialkoxytricarballylate, trialkoxycitrate, trialkoxyglyceryl ether, jojoba oil and sucrose polyester as low-calorie replacements of edible fats and oil. *J. Food Sci.* **1984**, *49*, 419−428.
(11) Shieh, C.-J.; Akoh, C. C.; Koehler, P. E. Formulation and optimization of sucrose polyester physical properties by mixture response surface methodology. *J. Am. Oil Chem. Soc.* **1996**, *73*, 455−460.
(12) Cornell, J. A. Experiments with mixtures: a review. *Technometrics* **1973**, *15*, 437−455.
(13) AOCS. Method Cc 1-25, In *Official Methods and Recommended Practices of the American Oil Chemists' Society*; Firestone, D., Ed.; American Oil Chemists' Society: Champaign, IL, 1994.
(14) SAS. *SAS User's Guide*; SAS Institute: Cary, NC, 1990.
(15) Scheffé, H. Experiments with mixtures. *J. R. Statis. Soc.* **1958**, *20*, 344−360.
(16) Ott, L. *An Introduction to Statistical Methods and Data Analysis*; PWS-Kent Publishing: Boston, MA, 1988.

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