Effects of Glycerol and Ethylene–Acrylic Acid on Composition Optimization of PVOH/Starch-Blended Biodegradable Resin Using Response Surface Methodology

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ABSTRACT: Response surface methodology was used to analyze the effect of glycerol (X_1) and ethylene–acrylic acid (EAA) level (X_2) on the objective (water solubility index (WSI), water absorption index (WAI), and tensile strength) attributes of a poly(vinyl alcohol) (PVOH)/starch-blended plastic resin. A rotable central composite design was used to develop models for the objective responses. The experiments were run with different barrel temperatures, such as zone 1: 100°C, zone 2: 100°C, zone 3: 105°C, and zone 4: 105°C, respectively, with a feed rate of 20 g/min and screw speed of 25 rpm. Responses were most affected by changes in glycerol level (X_1) and to a lesser extent by EAA level (X_2). Individual contour plots of the different responses were overlaid, and regions meeting the optimum WSI of 6.10%, WAI of 5.57 g gel/g dry wt, and tensile strength of 62.14 MPa were identified at the glycerol level of 72.41 mL and the EAA level of 36.03 g, respectively. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2915–2921, 2009

Key words: biodegradable plastic; ethylene–acrylic acid copolymers (EAA); glycerol; optimization

INTRODUCTION

Most of the synthetic plastics are nonbiodegradable, such as polystyrene, polypropylene, and polyethylene, which are used widely in daily life, in packaging and food industry, medical field, and agriculture. A heavy environmental pollution accompanies their uses, because of their nonbiodegradability. The disposal of waste plastics has become a serious problem.[1] Therefore, in the past 2 decades, biodegradable materials have been paid attention as alternatives to the petroleum-derived plastics.[1–9] Natural biopolymers including starch, cellulose, and chitosan were tested, alone or combined with synthetic polymers, for the possibility to form a fully or partially biodegradable film or resin.[1] Of these materials, starch is the most attractive candidate because of its low cost, easy availability, and high production from annually renewable resources.[7]

As a matter of fact, the low water resistance and high brittleness of starch films or resins limited their extensive application.[6,8,10] Therefore, many attempts have been made to overcome these problems by blending starch with synthetic polymers. However, the biodegradability of starch film or resin decreased with addition of the nondegradable synthetic polymers. Therefore, much interest lies in blending starch with biodegradable synthetic polymers.[11–15]

Poly(vinyl alcohol) (PVOH) is a hydrophilic biodegradable polymer, which is mainly composed of C—C bonds.[6] However, its water solubility is related to its degree of hydrolysis, molecular weight, and the modification while blending with other processing additives,[16] with a maximum value at the degree of hydrolysis of 88%.[17] From the cost and practicality points, it is preferable that the blend contains as much starch as possible. However, the properties of the blend films deteriorated as starch proportion in the film formulation increased. This might result from a poor compatibility between starch and PVOH[18] and phase separation during film preparation.[19] Moreover, the water resistance of the native starch/PVOH film deteriorated compared to that of the PVOH film.

The influence of starch sources, starch components, starch molecular mass, and plasticizer, such as water and polyols (glycerol), has been studied to

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improve the mechanical properties of starch plastics. However, poor mechanical properties constitute one of the major unresolved problems. Although their tensile strength may be rather high (30–60 MPa), these materials are fragile with low elongation at break and poor in water resistance. After absorbing water, they are too weak to be used.[20–22] Ethylene vinyl acetate copolymer or ethylene–acrylic acid (EAA) copolymer, which form thermodynamically heterogeneous system with other polymer and show uniformly dispersed particles, can be used as modifier. The increase in adhesive properties of other polymer because of addition of polymer modifier is based on the mechanism suggestive of modification mechanism by low-molecular plasticizers.[23]

The effectiveness of response surface methodology (RSM) in the development and optimization of cereal products has been highlighted by different authors.[24–28] The basic principle of RSM is to relate product properties of regression equations that describe interrelations between input parameters and product properties. Some of the good examples of appropriate applications of this technique in food extrusion are the optimization of complex products or properties or of many process variables.[29]

In this study, investigations were undertaken to formulate a glycerol (X_1) and EAA level (X_2) additive-based PVOH/starch-blended resin by extrusion technology. The well-established functional property of amylose acts as a chain attacker of the alpha-1,4-link of starch, whereas the glycerol acts as a good destructuring–plasticizing agent.[30,31] The objective of this study was to optimize the formulation of raw compositions, that is, glycerol (X_1) and EAA level (X_2) for production of a PVOH/starch-blended resin by RSM. Therefore, the effects of the extruder's operating conditions were neglected during this experiment.

MATERIALS AND METHODS

Materials

Edible corn starch (a white fine powder with 10 wt % moisture content containing 30 wt % amylose and 70 wt % amylopectin) was obtained from the Hong Chi Company (Taiwan, ROC). Polyvinyl alcohol (product name code BF-17, complete alkalization PVOH, degree of polymerization average 1700–1800, molecular weight 75,000–80,000) was purchased from the Chang Chun Petroleum Chemistry Incorporated Company (Taiwan, ROC). Ethylene–acrylic acid copolymers, EAA 459 containing 8 wt % of acrylic acid, ρ 23°C = 0.93 g/cm^3, MFI = 9 g/10 min, and glycerol (AR grade) were obtained from Sigma Chemical (St. Louis, MO). All the materials were mixed by a mixer according to the formulas (Table I) homogeneously.

TABLE I
The Levels of the RSM Design with Different Operating Conditions

Treatments	Coded		Uncoded	
	X_1	X_2	Glycerol level (mL)	EAA level (g)
1	1	1	60.25	10.13
2	−1	1	60.25	34.87
3	−1	−1	109.75	10.13
4	1	−1	109.75	34.87
5	0	1.414	85	5
6	0	−1.414	85	40
7	1.414	0	50	22.5
8	−1.414	0	120	22.5
9	0	0	85	22.5
10	0	0	85	22.5
11	0	0	85	22.5
12	0	0	85	22.5
13	0	0	85	22.5

Extruder

A single-screw extruder made by Yea Jing Machinery (Taiwan, ROC) with screw compression ratio 2.8, $\psi = 2.8$, $L/D = 32$ was used. Electrical-resistive heater (220 V, 1700 W) heated the temperature zone at die. A single-screw volumetric feeder fed the formulas (Table I). A 19.1 mm × 2.93 mm rectangular-shaped single-outlet die was used to give continuous extrudates. The experiments were run with different barrel temperatures, such as zone 1: 100°C, zone 2: 100°C, zone 3: 105°C, and zone 4: 105°C, respectively, with a feed rate of 20 g/min and screw speed of 25 rpm.

Experimental design

This study is based on the hypothesis that water solubility index (WSI), water absorption index (WAI), and tensile strength are functionally related to specific composition, and attempts to fit multiple-regression equations describing quality composition responses.[32,33] Table I lists the levels of the RSM design with different glycerol and EAA levels.

WAI and WSI were measured using a technique developed for cereals.[13] The ground extrudate was suspended in water at room temperature for 30 min, gently stirred during this period, and then centrifuged at 3000 *g* for 15 min. The supernatant was decanted into an evaporating dish of known weight. The WSI is the weight of dry solids in the supernatant expressed as a percentage of the original weight of sample. The WAI is the weight of gel obtained after removal of the supernatant per unit weight of original dry solids. Determinations were made in triplicate.

Tensile strength was carried out on the tension test specimens. A total of 5 mm/min was used for the biodegradable plastics, and the tests were carried out in conformity with ISO 294, ISO 527 (TS 1396), and TS 720.[34–36] The tests were carried out at least five times for each specimen, and the results were averaged arithmetically.

The design is depended on the symmetrical selection of variation increments about the centre composition. These levels of variation were chosen to be within the range of reasonable formulations, and the increments were carefully selected, because interpretation of the results was valid only within the experimental limits.[32,33] The levels selected were also based on the conclusions of a previous study,[2,4,7,8,10] which are important for PVOH/starch-blended resin, whereas the optimum processing variables for each response did not fall exactly in the same region in the two-dimensional space formed by the compositions levels. Moreover, those constraints were set such that all responses (WSI, WAI, and tensile strength) met their optimum acceptable region with the same composition levels. Therefore, it was assumed that a WSI should be more than 5.9% but less than 6.3%, WAI should be more than 5.4 g gel/g dry wt but less than 5.8 g gel/g dry wt, and tensile strength should be more than 62 MPa but less than 64 MPa.

The increments of variation for each variable spaced around the centre point levels, along with the responses, are presented in Table II. Feed compositions were coded for solutions of the multiple regression (prediction) equations.[32,33]

A central composite design (CCD) (Table II) was adopted.[32,33] In this design, for two variables, the size of the experiment was reduced by using the 2^k, factorial (2^2), thus making the total number of experiments equal to 13 instead of 50 with full factorial design.[32,33] Experiments were randomized to minimize the effects of unexplained variability in the observed responses due to external factors. The function was assumed to be approximated by a second-degree polynomial equation:

$$Y_k = b_{k0} + \sum_{i=1}^{2} b_{ki}X_i + \sum_{i=1}^{2} b_{ii}X_i^2 + \sum_{i\neq j=1}^{2} b_{kij}X_iX_j, \quad (1)$$

where b_{k0} was the value of the fitted response at the centre point of the design, that is, point (0, 0), b_{ki}, b_{ii}, and b_{kij} were the linear, quadratic, and cross-product regression terms, respectively.

Analysis of data

The regression analysis was conducted using the "stepwise variable selection backward elimination" procedure[32,33] for fitting the model represented by eq. (1) to the experimental data. Optimization of the polynomial thus fitted was performed by numerical techniques, using the mathematical optimizer procedure of the Minitab 14.2 software package that deals with constraints. The mapping of the fitted response surfaces was achieved using the internal microprogram of the Minitab 14.2. The response surfaces and contour plots for these models were plotted as a function of two variables. The overlapping of the contour plots was done to take into account the three responses for their optimum values corresponding to two variables at a time.

RESULTS AND DISCUSSION

Diagnostic checking of the fitted model

Regression analyses for different models indicated that the fitted quadratic models accounted for more than 90% of the variations in the experimental data, which were highly significant. Multiple regression equations were generated relating WSI, WAI, and tensile strength to coded levels of the variables.[32] The developed models were indicated as follow, whereas terms in those equations are based on the P-values evaluation in Tables III–VIII:

$$\text{Water solubility index}(Y_1) = 14.6571 - 0.2412X_1 + 0.0019X_1^2 + 0.0073X_2^2 - 0.0034X_1X_2 (R^2 = 0.767)$$

$$\text{Water absorption index}(Y_2) = -4.69380 + 0.22927X_1 + 0.1488X_2 - 0.00145X_1^2 - 0.00401X_2^2 (R^2 = 0.899)$$

$$\text{Tensile strength}(Y_3) = 112.753 - 1.174X_1 + 0.006X_1^2 - 0.017X_2^2 (R^2 = 0.885)$$

All the main effects including linear and quadratic and interaction of effects were calculated for each

TABLE II
The Box-Behnken Arrangement and Responses

Treatments	Responses		
	Water solubility index Y_1 (%)	Water absorption index Y_2 (g gel/g dry wt)	Tensile strength Y_3 (MPa)
1	4.98 ± 0.52	5.22 ± 0.67	72.45 ± 1.42
2	8.05 ± 0.13	5.33 ± 0.46	70.13 ± 3.23
3	7.19 ± 0.45	4.51 ± 0.07	56.87 ± 2.01
4	6.11 ± 0.91	5.15 ± 0.29	50.82 ± 1.14
5	6.79 ± 0.75	5.16 ± 0.25	53.37 ± 2.96
6	5.07 ± 0.51	5.00 ± 0.39	55.85 ± 2.54
7	5.83 ± 0.30	4.79 ± 0.72	75.03 ± 2.66
8	6.18 ± 0.23	4.26 ± 0.14	58.39 ± 2.01
9	4.07 ± 0.86	6.24 ± 0.37	60.68 ± 1.97
10	3.98 ± 0.72	6.43 ± 0.26	61.15 ± 2.14
11	3.99 ± 0.27	6.14 ± 0.23	61.31 ± 1.89
12	3.95 ± 0.86	6.72 ± 0.19	60.71 ± 2.24
13	3.99 ± 0.43	6.62 ± 0.44	60.33 ± 2.03

TABLE III
The Regression Model of Variance of Process Variables to Extrudate's Water Solubility Index

Term	Coef.	SE Coef.	T	P
Constant	14.6571	3.82479	3.832	0.006
X_1	−0.2412	0.07615	−3.170	0.016
X_2	−0.0459	0.12215	−0.376	0.718
X_1*X_1	0.0019	0.00042	4.508	0.003
X_2*X_2	0.0073	0.00168	4.362	0.003
X_1*X_2	−0.0034	0.00111	−3.064	0.018
S = 0.6777				
R-Sq = 86.4%				
R-Sq(adj) = 76.7%				

X_1, glycerol level; X_2, EAA level; S, the coefficient of variation.

TABLE V
The Regression Model of Variance of Process Variables to Extrudate's Water Absorption Index

Term	Coef.	SE Coef.	T	P
Constant	−4.69380	1.47996	−3.172	0.016
X_1	0.22927	0.02947	7.781	0.000
X_2	0.14880	0.04727	3.148	0.016
X_1*X_1	−0.00145	0.00016	−8.961	0.000
X_2*X_2	−0.00401	0.00065	−6.170	0.000
X_1*X_2	0.00043	0.00043	1.011	0.346
S = 0.2622				
R-Sq = 94.1				
R-Sq(adj) = 89.9				

X_1, glycerol level; X_2, EAA level; S, the coefficient of variation.

model. The regression coefficients are shown in Tables III, V, and VII, as well as the analysis of variances obtained for all the models are shown in Tables IV, VI, and VIII. The correlation coefficient for WSI, WAI, and tensile strength (R^2 = 0.767, 0. 899, and 0. 885, respectively) are high for a response surface.

First of all, Table III indicates that the glycerol level has negative linear but a positive quadratic effects on WSI. The EAA level has a negative quadratic effect on WSI. The interaction effect of the variables was significant. Table IV shows that the multiple regression analysis of the WSI model was significant but the interaction of variables of the model was also significant.

Second, Table V shows that the glycerol level has a positive linear but negative quadratic effect on WAI. Meanwhile, the EAA level has a positive linear but negative quadratic effect on WAI. The interaction effect of the variables was not significant. Table VI shows that the multiple regression analysis of the WAI model was significant but the interaction of variables of the model was not significant.

Finally, Table VII illustrates that the glycerol level has negative linear and quadratic effect on tensile strength. The EAA level has negative quadratic effect on tensile strength. The interaction effect of the variables was not significant. Table VIII shows that the multiple regression analysis of the tensile strength model was significant but the interaction of variables of the model was not significant.

Analysis of variance

Once a model was selected, an analysis of variance was calculated to assess how well the model represents the data. The analyses of variances for different responses are presented in Tables IV, VI, and VIII. To evaluate the goodness of the model, the coefficient of variation (the level of the standard error of estimate to the mean value expressed as a percentage) and F-value tests were conducted. As a general regulation, the coefficient of variation should be not greater than 10%.[32,33]

In this study, the coefficients of variation for WSI, WAI, and tensile strength were 0.6777, 0.2622, and 2.439%, respectively. Also, the F-value for both responses was significant at the 95% level, as shown in Tables IV, VI, and VIII. The contour and response surface plots for both responses are shown in Figures 1–3. From analyses of residuals (data not

TABLE IV
The Analysis of Variance of Process Variables to Extrudate's Water Solubility Index

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	20.3902	20.3902	4.07804	8.88	0.006
Linear	2	0.0976	4.8397	2.41985	5.27	0.040
Square	2	15.9870	15.9870	7.99349	17.40	0.002
Interaction	1	4.3056	4.3056	4.30562	9.37	0.018
Residual error	7	3.2151	3.2151	0.45931		
Lack-of-fit	3	3.2072	3.2072	1.06908	539.94	0.000
Pure error	4	0.0079	0.0079	0.00198		
Total	12	23.6354				

DF, degrees of freedom; Seq SS, sequential sums of squares; Adj SS, adjusted sums of squares; Adj MS, adjusted mean squares; F, significance; P, P-value.

TABLE VI
The Analysis of Variance of Process Variables to Extrudate's Water Absorption Index

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	7.71313	7.71313	1.54263	22.43	0.000
Linear	2	0.37030	4.19117	2.09558	30.47	0.000
Square	2	7.27261	7.27261	3.63630	52.88	0.000
Interaction	1	0.07022	0.07022	0.07022	1.02	0.346
Residual error	7	0.48138	0.48138	0.06877		
Lack-of-fit	3	0.24670	0.24670	0.08223	1.40	0.365
Pure error	4	0.23468	0.23468	0.05867		
Total	12	8.19451				

DF, degrees of freedom; Seq SS, sequential sums of squares; Adj SS, adjusted sums of squares; Adj MS, adjusted mean squares; F, significance; P, P-value.

TABLE VII
The Regression Model of Variance of Process Variables to Extrudate's Tensile Strength

Term	Coef.	SE Coef.	T	P
Constant	112.753	13.7658	8.191	0.000
X_1	−1.174	0.2741	−4.284	0.004
X_2	0.984	0.4396	2.239	0.060
X_1*X_1	0.006	0.0015	3.692	0.008
X_2*X_2	−0.017	0.0060	−2.851	0.025
X_1*X_2	−0.003	0.0040	−0.765	0.469
$S = 2.439$				
R-Sq = 93.3%				
R-Sq(adj) = 88.5%				

X_1, glycerol level; X_2, EAA level; S, the coefficient of variation.

shown), it is possible to conclude that they were randomly distributed around zero, and there is no evidence of outliers (no point lying away from the mean more than four times the means).[32,33]

Conditions for optimum responses

The direction in which to change variables to optimize WAI, WSI, tensile strength was usefully indicated by the models. The multiple regression equation Y_1 was solved for the optimum WSI (6.10%), Y_2 was solved for the optimum WAI (5.57 g gel/g dry wt), and Y_3 was solved for the optimum tensile strength (62.14 MPa). The optimum conditions to achieve the above responses are presented in Figure 5. Optimum values of WSI, WAI, and tensile strength for all the variables lie close to the middle of the experimental range, indicating the validity of the selection of the variables range, and the models were accepted because of theirs significance at $P < 0.01$. The response surface models were obtained by selecting three variables, and the one remaining has the value which leads to the optimum response in the equations of Y_1, Y_2, and Y_3. Some selected surfaces are presented in Figures 1–3.

TABLE VIII
The Analysis of Variance of Process Variables to Extrudate's Tensile Strength

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	581.361	581.361	116.2722	19.54	0.001
Linear	2	429.609	197.479	98.7394	16.60	0.002
Square	2	148.274	148.274	74.1369	12.46	0.005
Interaction	1	3.478	3.478	3.4782	0.58	0.469
Residual error	7	41.648	41.648	5.9496		
Lack-of-fit	3	41.028	41.028	13.6760	88.30	0.000
Pure error	4	0.620	0.620	0.1549		
Total	12	623.008				

DF, degrees of freedom; Seq SS, sequential sums of squares; Adj SS, adjusted sums of squares; Adj MS, adjusted mean squares; F, significance; P, P-value.

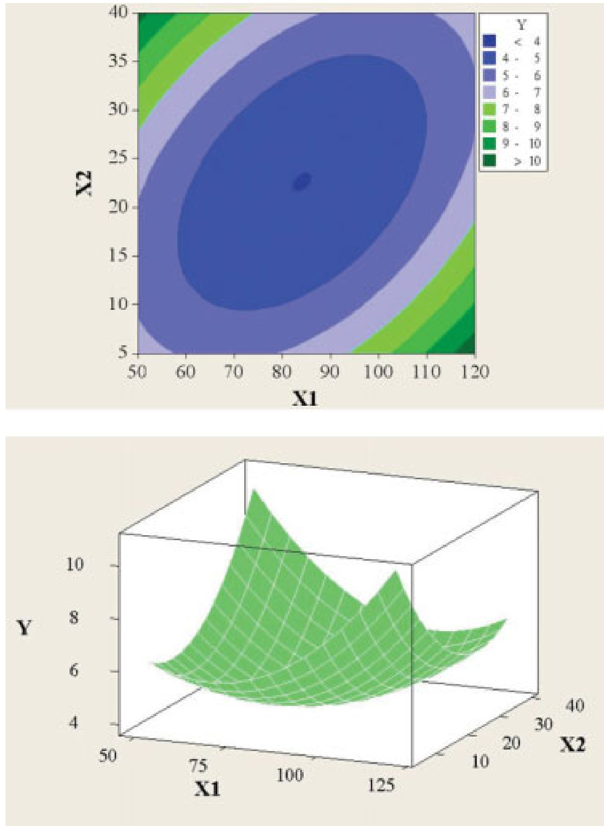

Figure 1 The contour and response surface plots of extrudate's water solubility index (WSI). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In moving along the horizontal axis in Figure 1, it can be seen that with the increase of glycerol level had a positive parabolic effect on WSI. However, the EAA level has a negative parabolic effect on WSI. The optimum value of WSI lies very close to the middle low of experimental region.

Figure 2 shows that with the increase of glycerol level had a negative parabolic effect on WSI. Meanwhile, the glycerol level also has a negative parabolic effect on WSI. The optimum value of WAI lies very near to the top of experimental region. Gomez and Aguilera[37] reported that the increase of the starch level will increase the amount of the —OH functional group, which resulted in the increase of water absorption.

In Figure 3, the glycerol level has a negative parabolic effect on tensile strength. Meanwhile, the EAA level also has a negative parabolic effect on tensile strength. The optimum value lies near the middle value of the level.

Superimposition of contour plots of responses

Areas of optimum performance were located by superimposing contour graphs for WSI, WAI, and

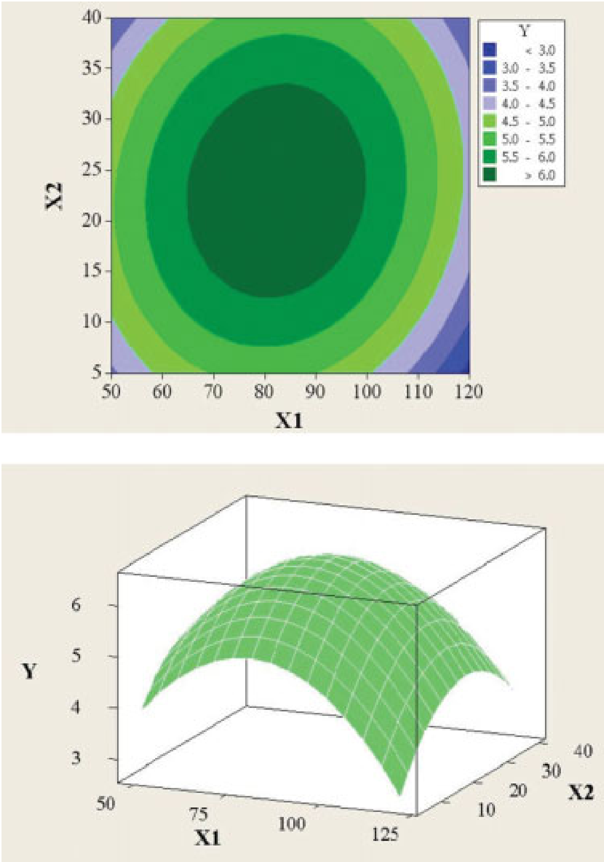

Figure 2 The contour and response surface plots of extrudate's water absorption index (WAI). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tensile strength for compositions levels, which established limits of acceptable quality for each factor. Because the optimum processing variables for each response did not fall exactly in the same region in the two-dimensional space formed by the compositions levels, constraints were set such that all responses (WSI, WAI, and tensile strength) met their optimum acceptable region with the same composition levels. It was assumed that a WSI should be more than 5.9% but less than 6.3%, WAI should be more than 5.4 g gel/g dry wt but less than 5.8 g gel/g dry wt, and tensile strength should be more than 62 MPa but less than 64 MPa.[10,11,17,19] Superimposing the individual contour plots for the response variables resulted in the identification of a region (shown by the white colored area), which satisfied all constraints and runs with different barrel temperatures, such as zone 1: 100°C, zone 2: 100°C, zone 3: 105°C, and zone 4: 105°C, respectively, with a feed rate of 20 g/min and screw speed of 25 rpm as shown in Figure 4. However, it may not be advisable to set the experimental conditions very rigid and, therefore, a moderation level has been given to each process variable and response as shown in Figure 5.

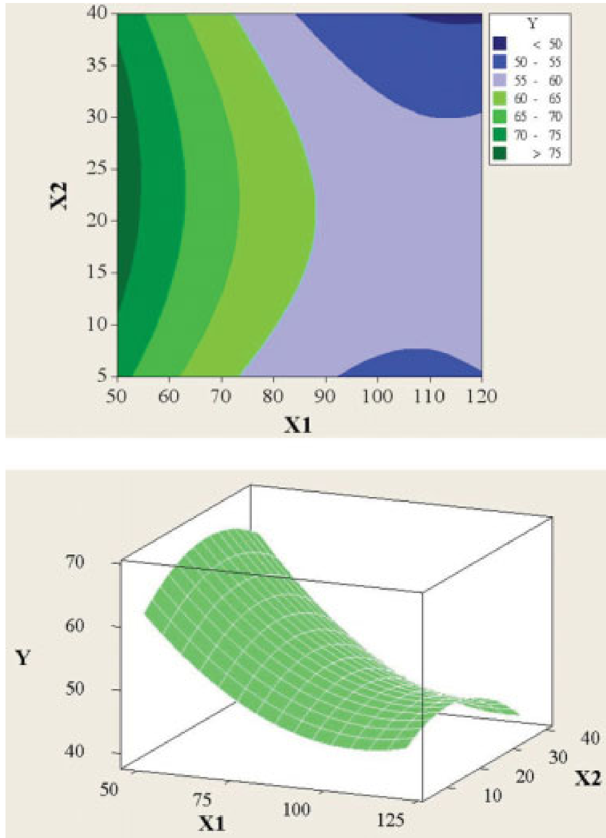

Figure 3 The contour and response surface plots of extrudate's tensile strength. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Hence, the final optimum conditions, for example, WSI of 6.10%, WAI of 5.57 g gel/g dry wt, and tensile strength of 62.14 MPa identified at the glycerol

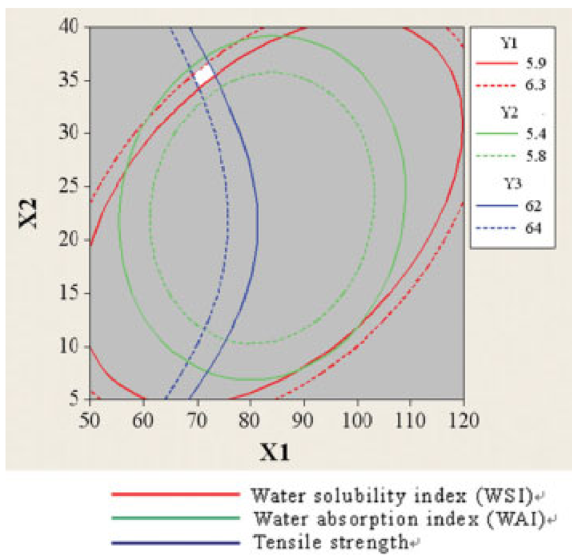

Figure 4 The optimum operating condition from the contour plots. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

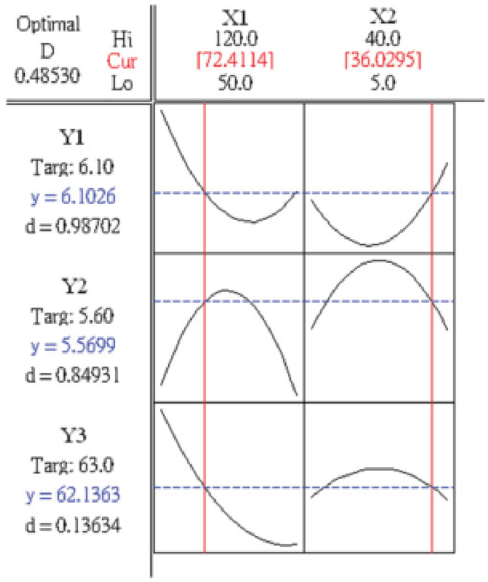

Figure 5 The predicted responses values by the optimum formula. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

level of 72.41 mL and the EAA level of 36.03 g, respectively, were computed as shown in Figure 5. The optimum conditions were experimentally tested, obtaining a WSI of 6.431%, WAI of 5.628 g gel/g dry wt, and tensile strength of 64.51 MPa.

CONCLUSIONS

This could be concluded that the system of WSI, WAI, and tensile strength of PVOH/starch-blended resin can be effectively optimized using RSM and with a minimum number of experiments. Also, computerized computations, model building, and generation of three-dimensional graphs and contours will be effective in simplify the complexity of the preparation of PVOH/starch-blended resins with different variables used. According to the optimum conditions given for the variables, the process can be scaled up for industrial production, and the PVOH/starch-blended resins are suitable for biodegradable plastics application.

References

1. Wu, C.-S. Polym Degrad Stab 2003, 80, 127.
2. Thakore, I. M.; Desai, S.; Sarawade, B. D.; Devi, S. Eur Polym J 2001, 37, 151.
3. Yang, H.-S.; Yoon, J.-S.; Kim, M.-N. Polym Degrad Stab 2005, 87, 131.
4. Kiatkamjornwong, S.; Thakeow, P.; Sonsuk, M. Polym Degrad Stab 2001, 73, 363.
5. Ishiaku, U. S.; Pang, K. W.; Lee, W. S.; Ishak, Z. A. M. Eur Polym J 2002, 38, 393.
6. Zhang, X.; Burgar, I.; Lourbakos, E.; Beh, H. Polymer 2004, 45, 3305.
7. Demirgoz, D.; Elvirs, C.; Mano, J. F.; Cunha, A. M.; Piskin, E.; Reis, R. L. Polym Degrad Stab 2000, 70, 161.
8. Kim, M. Carbohydr Polym 2003, 54, 173.
9. Kim, M.-N.; Lee, A.-R.; Yoon, J.-S.; Chin, I.-J. Eur Polym J 2000, 36, 1677.
10. Santayanon, R.; Wootthikanokkhan, J. Carbohydr Polym 2003, 51, 17.
11. Avella, M.; Errico, M. E.; Lauriennao, P.; Martuscelli, E.; Raimo, M.; Rimedio, R. Polymer 2000, 41, 3875.
12. Bhatnagar, S.; Hanna, M. A. Cereal Chem 1996, 73, 601.
13. Bhatnagar, S.; Hanna, M. A. Trans ASAE 1995, 38, 567.
14. Willett, J. L.; Shogren, R. L. Polymer 2002, 43, 5935.
15. Yang, J. H.; Park, J.; Kim, D.; Lee, D. J Appl Polym Sci 2004, 93, 1762.
16. Alexy, P.; Bakos, D.; Crkon ova, G.; Krama rova, Z.; Hoffmann, J.; Julinova, M. Polym Test 2003, 22, 811.
17. Coffin, D. R.; Fishman, M. L.; Ly, T. V. J Appl Polym Sci 1996, 61, 71.
18. Lawton, J. W. Carbohydr Polym 1996, 29, 203.
19. Lawton, J. W.; Fanta, G. F. Carbohydr Polym 1994, 23, 275.
20. Hulleman, S. H. D.; Janssen, F. H. P.; Feil, H. Polymer 1998, 39, 2043.
21. Lourdin, D.; Valle, G. D.; Colonna, P. Carbohydr Polym 1995, 7, 261.
22. Soestvan, J. J. G.; Benes, K.; Witde, D. Polymer 1996, 7, 3543.
23. Novák, I.; Florián, Š. J Mater Sci Lett 1994, 13, 1211.
24. Malcolmson, L. J.; Matsuo, R. R.; Balshaw, R. Cereal Chem 1993, 70, 1.
25. Saxena, D. C.; Rao, P. H. Int J Food Sci Technol 1996, 31, 345.
26. Shelke, K.; Dick, J. W.; Holm, Y. F.; Loo, K. S. Cereal Chem 1990, 67, 572.
27. Sushma, T.; Saxena, D. C. Lebensm-Wiss u-Technol 2000, 33, 354.
28. Vaisey-Genser, M.; Ylimaki, G.; Johnson, B. Cereal Chem 1987, 64, 50.
29. Vainionpaa, J.; Malkki, Y. 7th World Congress of Food Science and Technology; Singapore Institute of Food Science and Technology: Singapore, 1987.
30. Colonna, P.; Doublier, J. L.; Melcion, J. P.; Monredon, F. D.; Mercier, C. Cereal Chem 1984, 61, 538.
31. Linko, P.; Mattson, C.; Linko, Y. Y.; Antila, J. J Cereal Sci 1984, 2, 43.
32. Chatterjee, S.; Price, B. Regression Analysis by Example; Wiley: New York, 1977.
33. Cocharan, W. G.; Cox, G. M. Experimental Designs, 2nd ed.; Wiley: New York, 1957.
34. ISO 294. ISO: Switzerland, 1995.
35. ISO 527 (TS 1396). ISO: Switzerland, 1966.
36. ISO 180 (TS 1005). ISO: Switzerland, 1982.
37. Gomez, M. H.; Aguilera, J. M. J Food Sci 1983, 48, 378.