Optimization of the Process Variables for the Synthesis of Starch-Based Biodegradable Resin Using Response Surface Methodology

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ABSTRACT: Response surface methodology (RSM) was used to analyze the effect of different additives glycerol level (X1) and plasticizer level (X2) on the objective (water solubility index, water absorption index, and Max. loading) attributes of a cornstarch/PHBV blended composite. A rotatable central-composite design (CCD) was used to develop models for the objective responses. The experiments were run at barrels temperatures 160, 160, 165, and 165°C, respectively, with screw speed 40 rpm and complete feeding (filling ratio = 1). Responses were most affected by changes in plasticizer level (X2) and to a lesser extent by glycerol level (X1). Individual contour plots of the different responses were overlaid, and regions meeting the predicted optimum water solubility index of 4.34%, water absorption index of 4.55 g gel/g dry wt, and Max. loading of 370.06 *N* were identified at the plasticizer level of 21.06 g, and the glycerol level of 96.11 mL, respectively. These predicted values for optimum process conditions were in good agreement with experimental data. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1797–1804, 2011

Key words: plasticizer; glycerol; corn starch; poly (β-hydroxybutyrate-*co*-valerate) (PHBV); optimal composition

INTRODUCTION

Huge amounts of generated waste have made acquiring sufficient areas for landfill sites more difficult. Lack of capacity of waste landfills has become a serious problem, especially in urban areas, and effective reduction or decomposition of waste is now necessary to secure adequate landfill capacity. Among several compounds in waste landfill sites, plastics are estimated to make up ~ 20–30% of the volume of municipal solid waste landfill sites.[1] Because plastics are recalcitrant to microbial degradation, they would remain in landfill sites semipermanently. Plastic waste is recognized as one of the most troublesome categories of waste, and disposal of plastic waste has been blamed for shortening the life of landfill sites. In response to this problem of plastic waste in landfills, biodegradable plastics (BPs), which have been designed to be easily degraded by microorganisms and to be absorbed by the natural environment or by waste landfills, are gaining public endorsement as a possible alternative to petroleum-derived plastic.

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Poly(hydroxyl alkanoates), or PHAs, have received considerable attention in recent years as biodegradable alternatives to synthetic thermoplastics Copolymers of hydroxybutyrate and hydroxyvalerate, commonly referred to as PHBVs, have been produced and marketed by Zeneca Biopolymers. Because of the high cost of PHBV relative to commodity thermoconsiderable attention in recent years as biodegradable-plastics, various attempts have been made to incorporate starch and other low-cost components into PHBV-based composites.[2–7] Starch is an attractive filler for PHBV because of its low cost and inherent biodegradability.

The use of starch in PHBV composites is hampered by the low degree of adhesion between the starch granules and the polymer matrix. The resulting loss in tensile strength and elongation compared to the unfilled polymer limits the maximum amount of starch which can be incorporated.[3,6] Shogren has shown that precoating the starch with polyethylene oxide (PEO) improves tensile strength and elongation, presumably due to improved adhesion from PEO-PHBV interactions.[4] Kotnis et al. showed that the degree of adhesion between starch granules and PHBV was poor but could be mitigated via appropriate formulation and processing techniques to obtain materials with commercially useful properties.[5]

Another approach to improving adhesion between starch filler and PHBV is by grafting a functional monomer onto the starch. Starch graft copolymers have been extensively studied and are easily prepared by free radical polymerization with unsaturated monomers.[8] On the other hand, the external plasticization is more efficient to apply to polymers because it could provide a relatively simple route to improve some mechanical properties of polymer as well as to lower costs. However, plasticizers for biodegradable polymers should preferably also be biodegradable. In this respect, most of the plasticizers used in synthetic polymer processing are not suitable for PHB.

The effectiveness of response surface methodology (RSM) in the development and optimization of cereal products has been highlighted by different authors.[9–13] 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.[14]

In this study, investigations were undertaken to formulate a plasticizer level (X2) and glycerol level (X1) additive based cornstarch/PHBV blended composite by extrusion technology. The well-established functional properties of plasticizer act as a good destructuring-plasticizing agent as well as the glycerol.[15,16] The objective of this study was to optimize the formulation of raw compositions, i.e., plasticizer level (X2) and glycerol level (X1) for production of a cornstarch/PHBV blended composite by RSM.

MATERIALS AND METHODS

Materials

Corn starch (a white fine powder with 10 wt % moisture content containing 30 wt % amylase and 70 wt % amyl pectin) was obtained from the Hong Chi Company Limited, Taiwan, R.O.C. Poly(β-hydroxybutyrate-*co*-valerate) (PHBV), [Y1000, D300P (5% HV), from Chinese Tianan Biology Material Company Limited] was purchased from the Ming Guan Instrument Company Limited, Taiwan, R.O.C. Triethyl citrate (TEC) were used as biodegradable plasticizer for PHBV from Sigma Chemical, St. Louis, MO. Glycerol (AR grade) was obtained from Sigma Chemical, St. Louis, MO.

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 hole die was used to give continuous extrudates. The experiments were run at barrels temperatures 160, 160, 165, and 165°C with a feed rate 25 g min^{-1}, and screw speed 40 rpm.

TABLE I
Coded and Actual Levels for the Independent Variables

	Coded		Actual	
Treatments	X1	X2	Glycerol level (mL)	TEC level (g)
1	−1	−1	80	10
2	−1	1	80	40
3	1	−1	110	10
4	1	1	110	40
5	0	−1.414	95	3.79
6	0	1.414	95	46.21
7	−1.414	0	73.79	25
8	1.414	0	116.21	25
9	0	0	95	25
10	0	0	95	25
11	0	0	95	25
12	0	0	95	25
13	0	0	95	25

Experimental design

This study is based on the hypothesis that water solubility index, water absorption index, and Max. loading are functionally related to specific composition, and attempts to fit multiple-regression equations describing quality composition responses.[17,18] Table I lists the levels and levels of the RSM design with different plasticizer and glycerol levels.

Water absorption index (WAI) and water solubility index (WSI) were measured using a technique developed for cereals.[19] The ground extrudates 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.

Max. loading were carried out on the tension test specimens. About 5 mm min^{-1} was used for the biodegradable plastics, and the tests were carried out in conformity with ISO 294, ISO 527 (TS 1396) and TS 720.[20–22] The tests were carried out at least five times for each specimen and the results were averaged arithmetically.

TABLE II
Responses of Different Treatments

Treatments	Responses		
	Water solubility index (%)	Water absorption index (g gel/g dry wt)	Max. loading (*N*)
1	1.93 ± 0.29	4.93 ± 0.11	323.80 ± 6.20
2	2.13 ± 0.55	5.06 ± 0.03	237.20 ± 6.25
3	5.48 ± 0.17	4.24 ± 0.14	364.20 ± 5.11
4	5.77 ± 0.47	4.3 ± 0.08	260.67 ± 6.82
5	2.27 ± 0.28	4.44 ± 0.16	416.05 ± 8.82
6	3.29 ± 0.21	5.13 ± 0.14	293.54 ± 5.37
7	3.43 ± 0.13	4.96 ± 0.05	263.70 ± 1.55
8	3.05 ± 0.21	4.14 ± 0.08	267.92 ± 5.54
9	4.46 ± 0.09	4.4 ± 0.05	347.20 ± 5.42
10	4.28 ± 0.21	4.42 ± 0.08	377.16 ± 5.32
11	4.16 ± 0.19	4.49 ± 0.02	358.69 ± 7.82
12	4.33 ± 0.23	4.48 ± 0.01	388.62 ± 5.95
13	4.53 ± 0.22	4.56 ± 0.29	372.16 ± 6.77

The design is depended upon the symmetrical selection of variation increments about the center composition. These levels of variation were chosen to be within the range of reasonable formulations, and the increments were carefully selected, since interpretation of the results was valid only within the experimental limits.[17,18] The levels selected were also based on the conclusions of a previous study,[23–27] which are important for cornstarch/PHBV blended composite. Whereas, the optimum processing variables for each response did not fall exactly in the same region as in the two dimensional space formed by the compositions levels. Moreover, those constraints were set such that all responses (water solubility index, water absorption index, and Max. loading) met their optimum acceptable region with the same composition levels. Therefore, it was assumed that a water solubility index should be more than 4.2 but less than 4.5, water absorption index more than 4.4 but less than 4.5, and Max. loading should be more than 360 but less than 380*N*.

The increments of variation for each variable spaced around the center point levels, along with the responses are presented in Table II. Feed compositions were coded for solutions of the multiple regression (prediction) equations.[17,18]

A central composite design (CCD) (Table II) was adopted.[17,18] 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.[17,18] 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, i.e., 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[17,18] 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 micro program 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 water solubility index, water absorption index, and Max. loading to coded levels of the variables.[17] The developed models were indicated as follow, whereas, terms in those

TABLE III
Coefficient of Variables in the Predictive Model for Extrudate's Water Solubility Index

Term	Coef	SE Coef	*T*	*P*
Constant	5.093	0.859	5.928	0.001**
X1	2.352	1.061	2.216	0.062
X2	0.451	0.13	3.459	0.011*
X1*X1	0.232	0.386	0.6	0.568
X2*X2	−0.031	0.007	−4.549	0.003*
X1*X2	−0.019	0.068	−0.284	0.784
$S = 0.5097$				
R-Sq = 90.4%				
R-Sq(adj) = 83.6%				

X1: glycerol level; X2: plasticizer level; S: the coefficient of variation.
* Significant at $P < 0.05$.
** Significant at $P < 0.01$.

TABLE IV
Analysis of Variance Results for Fitted Models of Extrudate's Water Solubility Index

Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Regression	5	17.14	17.14	3.428	13.2	0.002*
Linear	2	11.366	6.701	3.35	12.9	0.004*
Square	2	5.753	5.753	2.876	11.07	0.007*
Interaction	1	0.021	0.021	0.021	0.08	0.784
Residual error	7	1.819	1.819	0.260		
Lack-of-fit	3	1.804	1.804	0.601	168.46	0
Pure error	4	0.014	0.014	0.004		
Total	12	18.958				

* Significant at $P < 0.05$. **Significant at $P < 0.01$.

TABLE VI
Analysis of Variance Results for Fitted Models of Extrudate's Water Absorption Index

Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Regression	5	1.177	1.177	0.235	15.52	0.001**
Linear	2	1.021	0.093	0.047	3.07	0.11
Square	2	0.155	0.155	0.077	5.11	0.043*
Interaction	1	0.001	0.001	0.001	0.08	0.784
Residual error	7	0.162	0.162	0.015		
Lack-of-fit	3	0.09	0.09	0.03	7.51	0.04*
Pure error	4	0.016	0.016	0.004		
Total	12	1.283				

* Significant at $P < 0.05$.
** Significant at $P < 0.01$.

equations are based on the *P*-values evaluation in Tables III–VIII:

Water solubility index (Y_1)

$$= 5.09305 + 0.45117X_2 - 0.0313X_2^2$$
$$(R^2 = 0.904)$$

Water absorption index (Y_2)

$$= 4.12216 + 0.00529X_2^2$$
$$(R^2 = 0.917)$$

Max. loading (Y_3)

$$= 307.174 - 199.111X_1 - 101.349X_1^2$$
$$(R^2 = 0.945)$$

These models could be adequately used as predictor models, regardless of low coefficient of determinations. Only coefficients making a significant contribution to the model are included in the model. Hence, it can be concluded that the proposed models approximates the response surfaces and can be used suitably for prediction at any values of the parameters within experimental range.

All the main effects including linear and quadratic, and interaction of effects were calculated for each 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 water solubility index, water absorption index, and Max. loading ($R^2 = 0.904$, $R^2 = 0.917$, and $R^2 = 0.945$, respectively) are very high for a response surface.

First of all, the multiple regression model for predicting the water solubility index could explain 90.4% of the observed variations. Table III indicates that the plasticizer level has a significant effect and positive correlation with the water solubility index. However, it was negatively affected by the quadratic coefficient of plasticizer level. Table IV shows that the multiple regression analysis of the water solubility index model was significant; however, the interaction of variables of the model was not significant.

Second, the multiple regression model for predicting the water absorption index could explain 91.7%

TABLE V
Coefficient of Variables in the Predictive Model for Extrudate's Water Absorption Index

Term	Coef	SE Coef	*T*	*P*
Constant	4.122	0.208	19.856	0**
X1	−0.281	0.256	−1.096	0.309
X2	−0.053	0.032	−1.676	0.138
X1*X1	0.063	0.093	0.669	0.525
X2*X2	0.006	0.002	3.186	0.015*
X1*X2	−0.005	0.016	−0.284	0.784
$S = 0.1232$				
R-Sq = 91.7%				
R-Sq(adj) = 85.8%				

X1: glycerol level; X2: plasticizer level; S: the coefficient of variation.
* Significant at $P < 0.05$.
** Significant at $P < 0.01$.

TABLE VII
Coefficient of Variables in the Predictive Model for Extrudate's Max. Loading

Term	Coef	SE Coef	*T*	*P*
Constant	307.174	28.026	10.96	0**
X1	−199.111	34.609	−5.753	0.001**
X2	−8.437	4.254	−1.983	0.088
X1*X1	−101.349	12.607	−8.039	0**
X2*X2	−0.22	0.224	−0.981	0.359
X1*X2	−3.129	2.217	−1.411	0.201
$S = 16.63$				
R-Sq = 94.5%				
R-Sq(adj) = 90.7%				

X1: glycerol level; X2: plasticizer level; S: the coefficient of variation.
* Significant at $P < 0.05$.
** Significant at $P < 0.01$.

TABLE VIII
Analysis of Variance Results for Fitted Models of Extrudate's Max. Loading

Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Regression	5	33554.9	33554.9	6710.99	24.28	0**
Linear	2	15139.2	14398.2	7199.11	26.04	0.001**
Square	2	17865.2	17865.2	8932.58	32.32	0**
Interaction	1	550.6	550.6	550.61	1.99	0.201
Residual error	7	1934.9	1934.9	276.42		
Lack-of-fit	3	1897.7	1897.7	632.58	68.07	0.001**
Pure error	4	37.2	37.2	9.29		
Total	12	35489.9				

*Significant at $P < 0.05$.
** Significant at $P < 0.01$.

of the observed variations. Table V indicates that the water absorption index was positively affected by the quadratic coefficient of plasticizer level. Table VI shows that the multiple regression analysis of the water absorption index model was significant, however, the linear and interaction of variables of the model was not significant.

Finally, the multiple regression model for predicting the Max. loading could explain 94.5% of the observed variations. Table VII indicates that the glycerol level has a significant effect and negative correlation with the Max. loading. Moreover, it was negatively affected by the quadratic coefficient of glycerol level. Table VIII shows that the multiple regression analysis of the Max. loading model was significant; however, 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%.[17,18]

In this study, the coefficients of variation for water solubility index, water absorption index, and Max. loading, were 0.5097, 0.1232, and 16.63%, respectively. Also, the *F*-value for both responses was significant at the 95% level, as shown in Table 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 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).[17,18]

Conditions for optimum responses

The direction in which to change variables to optimize water absorption index, water solubility index, Max. loading were usefully indicated by the models. The multiple regression equation Y_1 was solved for the optimum water solubility index (4.34%), Y_2 was solved for the optimum water absorption index (4.55 g gel/g dry wt), and Y_3 was solved for the optimum Max. loading (370.06*N*). The optimum conditions to achieve the above responses are presented in Figure 5. Optimum values of water solubility index, water absorption index, and Max. loading 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 was accepted due to theirs significance at $P < 0.01$. The response surface models were obtained by selecting three variables and the one remaining have the value which

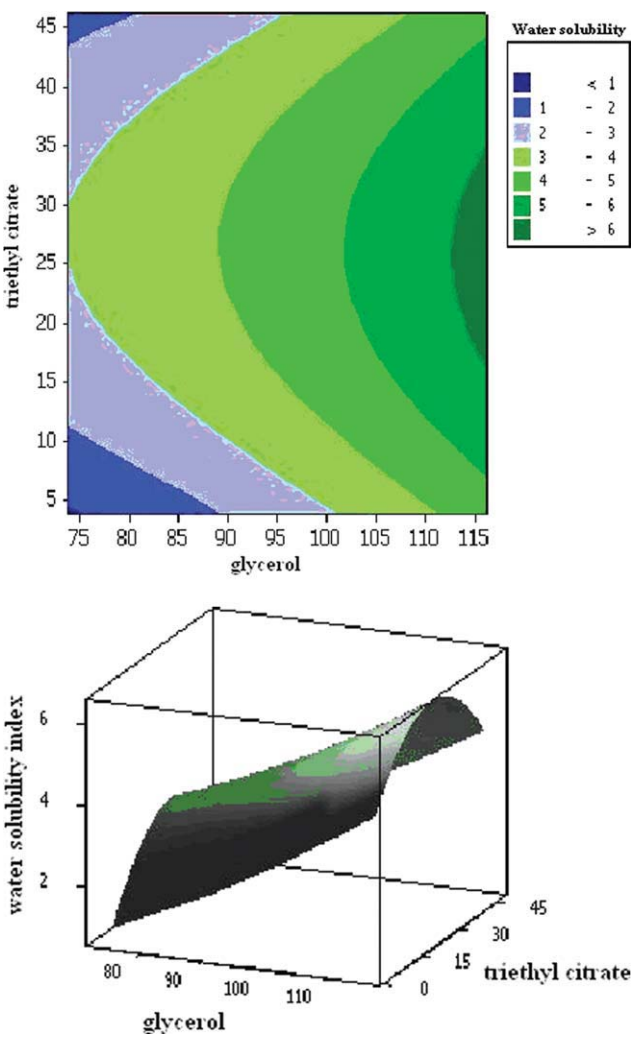

Figure 1 Contour and response surface plots of extrudate's water solubility index (WSI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

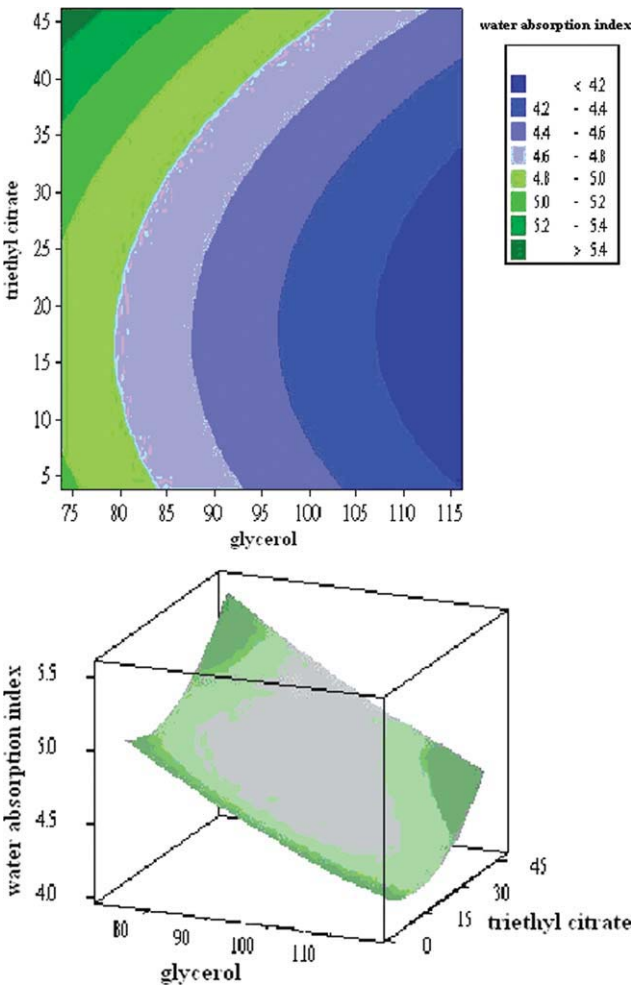

Figure 2 Contour and response surface plots of extrudate's water absorption index (WAI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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.

In moving along the horizontal axis in Figure 1, it can be seen that with the increase of plasticizer level had a positive parabolic effect on water solubility index. Meanwhile, the glycerol level has a positive linear effect on water solubility index as well. The optimum value of water solubility index lies very close to the middle of experimental region. The greatest WSI values may due to disintegration of starch granules and low molecular compounds from extrudate melt during extrusion process, this may cause in an increase in soluble material.[28]

Figure 2 show that with the increase of plasticizer level had a negative parabolic effect on water absorption index. However, the glycerol level has a negative parabolic effect on water absorption index. The optimum value of water absorption index lies very near to the bottom of experimental region. Gomez and Aguilera reported that the increase of the starch level will increase of the amount of the —OH functional group, which resulted in the increase of water absorption.[27] Increase in the value of WAI may probably be caused by uncovering of hydrophilic groups in extrudates and greater availability and easier penetration of structures by water molecules.[28]

In Figure 3, the plasticizer level has a negative parabolic effect on Max. loading as well as the glycerol level and the optimum 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 water solubility index, water absorption index, and Max. loading for compositions levels which established limits of acceptable quality for each factor. Since the optimum processing variables for each response did not fall exactly in the same region in the two dimensional

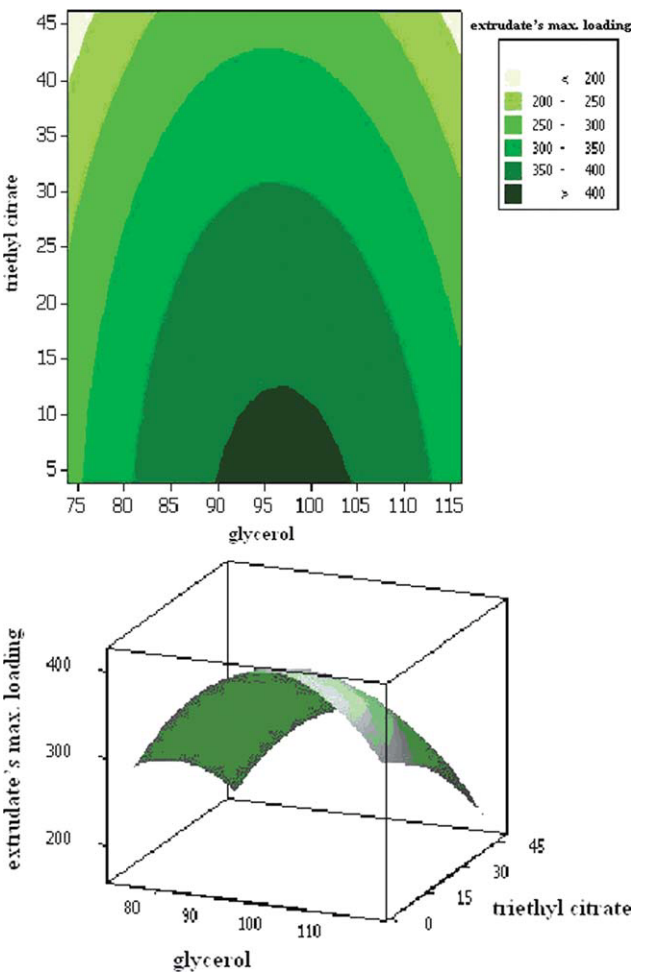

Figure 3 Contour and response surface plots of extrudate's Max. loading. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

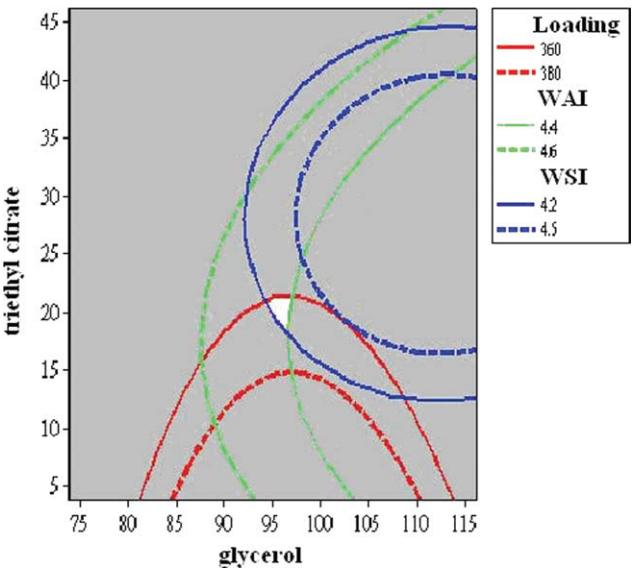

Figure 4 Optimum operating condition from the contour plots. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

space formed by the compositions levels, constraints were set such that all responses (water solubility index, water absorption index, and Max. loading) met their optimum acceptable region with the same composition levels. It was assumed that a water solubility index should be more than 4.2 but less than 4.5, water absorption index more than 4.4 but less than 4.5, and Max. loading should be more than 360 but less than 380*N*.[27,29–31] 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 at barrels temperatures 160, 160, 165, and 165°C with a feed rate 25 g min^{-1}, and

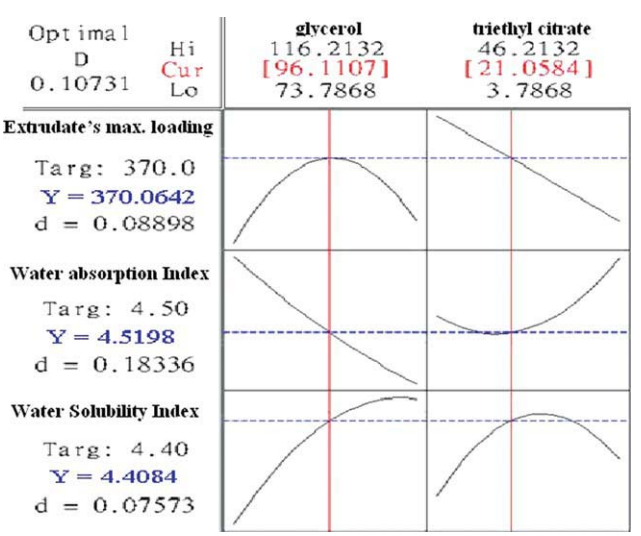

Figure 5 Predicted responses values by the optimum formula. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

screw speed 40 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. Hence, the final optimum conditions, for, water solubility index of 4.34%, water absorption index of 4.55 g gel/g dry wt, and Max. loading of 370.06*N* were identified at the plasticizer level of 21.06 g and the glycerol level of 96.11 mL, respectively, were computed as shown in Figure 5. The optimum conditions were experimentally tested, obtaining a water solubility index of 4.34%, water absorption index of 4.55 g gel/g dry wt, and Max. loading of 378.07*N*. Hence, the above predicted values for optimum process conditions were in good agreement with experimental data.

CONCLUSION

This could be concluded that the system of water solubility index, water absorption index, and Max. loading of cornstarch/PHBV blended composite 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 cornstarch/PHBV blended composites with different variables used. According to the optimum conditions given for the variables, the process can be scaled up for industrial production and the cornstarch/PHBV blended composite are suitable for biodegradable plastics application.

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