Effects of Mica, Carnauba Wax, Glycerol, and Sodium Caseinate Concentrations on Water Vapor Barrier and Mechanical Properties of Coated Paper

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ABSTRACT: The combined effects of mica (0% to 1.2% [w/w]), carnauba wax (0% to 0.8% [w/w]), glycerol (0% to 6% [w/w]), and sodium caseinate (10% to 13% [w/w]) concentrations on water vapor barrier and mechanical properties of coated paper were studied. A Doehlert matrice was used to investigate the main effects of these factors and their different interactions. The results were analyzed using the response surface methodology. Carnauba wax and glycerol concentrations were the most important parameters affecting water vapor permeability (WVP). Glycerol enhanced WVP as its concentration increased. Carnauba wax and mica factors decreased WVP of coated paper. Conversely, increasing the amount of glycerol led to a decrease in tensile strength (TS) and to an increase in elongation (%E) of the resulting coated papers.

Keywords: sodium caseinate, paper, coating, mechanical strength, water vapor permeability, Doehlert-matrix

Introduction

Environmental concerns over the use of certain synthetic packaging and coatings have prompted research in the area of alternative packaging materials. Considerable interest in edible films due to their environmentally friendly nature and their potential use in the food industry has been renewed (Kester and Fennema 1986; Gennadios and Weller 1990; Gontard and Guilbert 1994; Guilbert and others 1996; Krochta and De-Mulder-Johnston 1997; Khwaldia and others 2004). Edible films and coatings are natural polymers obtained from agricultural productions such as casein, whey protein, corn zein, wheat, and other materials. They are perfectly biodegradable and therefore perfectly safe for the environment. These natural polymers provide possibilities for improving the quality of heterogeneous foods by limiting the migration of moisture, lipids, flavors/aromas, and colors between food components; carrying food ingredients, such as antioxidants, antimicrobials, or flavors; and/or improving the mechanical integrity or handling characteristics (Krochta 1992).

Natural polymers can also be used as barrier coatings on paper packaging materials. Such coatings have the potential to replace current synthetic paper and paperboard coatings, such as polyethylene, polyvinyl alcohol, rubber latex, and fluorocarbon in food packaging applications (Chan and Krochta 2001a, 2001b). These coatings also have potential advantages for some food applications. They may be used to retard unwanted mass transfer in food products (Trezza and Vergano 1994; Han and Krochta 2001). They have potential environmental advantages over conventional polymer films. They are biodegradable and may improve the recyclability of some packaging applications by reducing the need for complicated multilayer structures.

Han and Krochta (1999) showed that whey-protein–coated paper improves packaging material performance of paper by increasing oil resistance and reducing water-vapor permeability. Milk proteins, such as casein, have several key physical characteristics for effective performance in edible films and coatings, such as their solubility in water and ability to act as emulsifiers (Southward 1985). Sodium caseinate (NaCAS) is highly soluble and can be dispersed rapidly in aqueous mixtures and homogenized in the presence of fat or oil (Kinsella 1984). NaCAS can easily form films from aqueous solutions because of its random coil nature and its ability to form extensive intermolecular hydrogen, electrostatic, and hydrophobic bonds, resulting in an increase of the interchain cohesion (Avena Bustillos and Krochta 1993; McHugh and Krochta 1994; Brault and others 1997). Caseinate films exhibit resistance to thermal denaturation and/or coagulation, which means that the protein film remains stable over a wide range of pH values, temperatures, and salt concentrations (Kinsella 1984).

Paper, which consists of porous cellulose network, is often coated to improve its barrier properties to water vapor, oxygen, and aromas. Generally, protein coatings provide limited resistance to moisture transmission due to the substantial inherent hydrophilicity of proteins and to the high amounts of hydrophilic plasticizers incorporated into protein coatings to impart adequate flexibility (Gennadios and others 1994). Composite protein-lipid coatings have been prepared to combine the good structural and oxygen-barrier properties of protein coatings with the good moisture-barrier characteristics of lipids such as long-chain fatty acids and waxes.

The protein-based coating solution also can contain regular paper pigments such as clay and mica to improve oil-based ink absorption and surface smoothness. Therefore, the protein may work as a binding agent (adhesive) as well as a surface sizing agent after it is coated on the paper (Han and Krochta 1999).

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Table 1—Experimental domain and level distribution of the variables used for the evaluation of the influence of mica, carnauba wax, glycerol, and sodium caseinate concentrations (% w/w) on coated paper barrier and mechanical properties. Bolded column shows the center of the experimental domain (where experiment 21 was performed).

Variables		Experimental values							Levels
X1:	Mica concentration								
	Natural values		0	0.3	**0.6**	0.9	1.2		5
	Coded values		–1	–0.5	**0**	0.5	1		
X2:	Carnauba wax concentration								
	Natural values	0	0.14	0.27	**0.4**	0.53	0.66	0.8	7
	Coded values	–0.866	–0.577	–0.288	**0**	0.288	0.577	0.866	
X3:	Glycerol concentration								
	Natural values	0	0.73	2.25	**3**	3.74	5.24	6	7
	Coded values	–0.816	–0.612	–0.204	**0**	0.204	0.612	0.816	
X4:	NaCAS concentration								
	Natural values			10	**11.5**	13			3
	Coded values			–0.790	**0**	0.790			

The objective of this study was to determine the relative influence of mica, carnauba wax, glycerol, and NaCAS concentrations on water vapor permeability and the mechanical properties of the coated paper.

Materials and Methods

Coatings materials and papers

Sodium caseinate (NaCAS, Sigma Chemical Co., Steinheim, Germany), synthetic mica (Somasif ME-100, CO-OP Chemical CO., Ltd, Tokyo, Japan), and carnauba wax (MICHEM LUBE 160PF.E, Michelman Chemicals SA, Villeneuve Saint Germain, France) were used as coatings materials. Glycerol (>97% purity) was used as a plasticizer and was obtained from Merck (Darmstadt, Germany). Standard paper packaging (Rocal 400, 37 g/m^2) was provided by Ahlstrom Paper Group Research and Services (Pont-évêque, France).

Coating dispersion and coating methods

Coating dispersions were prepared according to the experimental plan (Table 1) by dispersing the appropriate NaCAS powder and mica in distilled water at 60°C while stirring for 30 min. Next, selected amounts of glycerol and carnauba wax were added during heating and stirring. After lipid melting, the whole mixture was homogenized at 24000 rpm in a homogenizer (Ultra-Turrax Model T25 IKA, Labortechnik GmbH. Munich, Germany) for 2 min and cooled at 23 °C.

Amounts of mica, carnauba wax, glycerol and NaCAS were calculated to prepare 100 g of coating dispersion.

The papers were coated at 23 °C using a control coater (model KCC 101, R K Print-Coat Instruments Ltd., Herts, U.K.). This automatic machine uses standard wire wound bars to produce a uniform and repeatable coating. Wired bars consist of a pattern of identically shaped grooves. These grooves precisely control the coating weight. A standard bar is chosen in this study to obtain a coating of 10 g/m^2 and a dry coating thickness of 10 μm. The coating process was performed at a speed of 6 m/min. After wet coating, the papers were dried at 40 °C for 30 min (dryer model 400, TECHPAP, Gières, France).

Before properties testing, all coated papers were conditioned for 2 d in an environmental chamber at 50% RH and 23 °C.

Water vapor permeability

Water vapor permeability of the films was determined with the gravimetric method described in the AFNOR NF H00-030 standard (AFNOR 1974). The test film was sealed in a permeation cell containing a desiccant (silica gel). The permeation cells were 5.8 cm (internal dia) by 7.8 cm (external dia) by 3.6 cm deep with an exposed area of 26.42 cm^2. The permeation cells were placed in a controlled temperature (38 ± 1°C) and relative humidity (90% ± 3%) chamber via ventilation. The water vapor transport was determined from the weight gain of the cell. After 30 min, steady-state conditions were reached and weighings were made. Six replicates were made from each film composition.

Water vapor permeability (WVP) of the film was calculated as follows (McHugh and Krochta 1994):

$$WVP = \frac{\delta q \cdot X}{A \cdot \delta t \cdot \Delta p} \text{ [g μm/m}^2\text{/d/kPa]}$$

where δq is the weight gain of the cup over time (δt), A is the area of packaging exposed to water vapor transport, Δp is the vapor pressure differential across the film, and X is the coated paper thickness.

Tensile testing

Tensile strength (TS) and elongation at break (%E) were determined on rectangular paper samples (15 mm wide × 200 mm long) with a dynamometer SYNERGY 100 (Adamel-Lhomargy, Ivry, France) according to a standard method of ISO 1924-2-1994. The experiments were performed under controlled conditions, at 23°C and 50% RH. Before the testing, paper thicknesses were measured at 5 points with a micrometer (MI 20, Adamel-Lhomargy, Ivry, France), and the mean value was recorded (44 ± 1 μm). Ten paper samples were cut from each preconditioned film (50% RH, 23°C) and uniaxially stretched at a constant rate of 25 mm/mn until breaking. Stress-strain measurements were carried out to determine TS and %E at break value.

Experimental design and statistics

An experimental design using a Doehlert matrix was performed to study the combined effect of mica, carnauba wax, glycerol, and NaCAS concentrations on coated paper properties (Doehlert 1970). This mathematical tool was selected to replace the traditional experiments to quantify the effects of each parameter and interaction between factors and to obtain maximum information and precision from a reduced number of experiments (Linder and others 1995). This matrix displays a uniform distribution of the experimental points within the space of the coded variables; it allows attribution of different levels to the selected variables.

The total number of points (N = k^2 + k + 1, where k is the num-

Table 2—Doehlert plan and experimental responses

	Variables (%)[a]				Responses		
Exp no.	X1	X2	X3	X4	WVP (Y1) (g μm/m²/d/kPa)	TS (Y2) (kN/m)	%E (Y3) (%)
1	1.20	0.40	3.00	11.50	938	3.12	2.16
2	0.00	0.40	3.00	11.50	955	2.83	2.49
3	0.90	0.80	3.00	11.50	858	3.08	2.56
4	0.30	0.00	3.00	11.50	955	3.43	2.69
5	0.90	0.00	3.00	11.50	1165	3.27	2.45
6	0.30	0.80	3.00	11.50	938	3.2	2.21
7	0.90	0.53	6.00	11.50	990	2.88	2.42
8	0.30	0.27	0.00	11.50	1007	3.41	2.47
9	0.90	0.27	0.00	11.50	1060	3.44	2.27
10	0.60	0.66	0.00	11.50	1060	3.46	2.48
11	0.30	0.53	6.00	11.50	1262	2.88	2.58
12	0.60	0.14	6.00	11.50	1165	2.91	2.77
13	0.90	0.53	3.74	13.00	1165	3.06	2.35
14	0.30	0.27	2.25	10.00	1183	3.12	2.47
15	0.90	0.27	2.25	10.00	1157	3.19	2.35
16	0.60	0.66	2.25	10.00	1122	3.25	2.55
17	0.60	0.40	5.24	10.00	1144	2.7	2.48
18	0.30	0.53	3.74	13.00	1148	3.22	2.76
19	0.60	0.14	3.74	13.00	1192	3.03	2.59
20	0.60	0.40	0.73	13.00	1117	3.66	2.62
21	0.60	0.40	3.00	11.50	1148	2.4	1.82
21a	0.60	0.40	3.00	11.50	1157	2.17	1.74
21b	0.60	0.40	3.00	11.50	1148	2.27	1.41

[a]WVP = water vapor permeability; X1 = mica concentration; X2 = carnauba wax concentration; X3 = glycerol concentration; X4 = NaCAS concentration.

ber of factors) for 4 factors is 21 (Mathieu and Phan-Than-Luu 1997a). Twenty-three experiments were carried out: Experiment 21 was performed at the center of the experimental domain and repeated 2 times (21a, 21b) to estimate residual variance (Table 2).

The variables investigated were mica (X1), carnauba wax (X2), glycerol (X3), and NaCAS (X4) amounts. The 1st was a 5-level variable; the last was a 3-level; and all the others had 7 levels (Table1). Responses were as follows: water vapor permeability (Y1), tensile strength (Y2), and elongation (Y3).

A full quadratic model with 15 coefficients, including interaction terms, was assumed to describe relationships between responses and experimental factors:

$$\eta_k = f_k\,(X1, X2, X3, X4) \text{ where } k = 1, 2, 3,4 \text{ for } f_k$$

$$\eta_k = b_{ii} + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} b_{ij} X_i X_j$$

where η_k is the dependant variable; b_0 is the constant coefficient; X_i and X_j are the coded independent variables; b_i is the linear coefficient; b_{ij} is the second-order interaction coefficient, and b_{ii} is the quadratic coefficient.

Data analysis

Data analysis was performed with the NEMROD® software (Mathieu and Phan-Than-Luu 1997b) including analysis of variance (ANOVA) and multiple regression analysis to obtain interactions between the variables and responses.

ANOVA and canonical analysis were used to characterize the validity of proposed polynomial models. The adequacy of each polynomial model was tested by the lack of fit, the coefficient of determination, R^2, and adjusted R^2. Statistical analysis of responses (Table 3) were accurately predicted by the quadratic model, as shown by coefficients of determination ($R^2 \geq 90\%$).

Results and Discussion

Water vapor permeability

Water vapor permeability (WVP) of coated papers varied with significant effect ($P \leq 0.01$) due to carnauba wax (b_2) and glycerol (b_3) concentrations (Table 4). Significant interactions at $0.001 < P \leq 0.01$ between all experimental factors were observed.

The linear coefficient values showed that WVP decreased with the concentrations of carnauba wax (–67.2) and mica (–13.2), in contrast to glycerol (+52.42) and sodium caseinate (+2.53) coefficient values, which enhanced WVP as their concentrations increased. The strong quadratic coefficient values of mica (–204.5) and carnauba wax (–161.18) indicated that these variables responses were not linear. The mica-wax (167.44) and glycerol-caseinate (142.41) interactions coefficients were greater than the mica-glycerol (139.82), wax-glycerol (31.01), mica-caseinate (124.43), and wax-caseinate (32.94) interactions coefficients.

A series of response surfaces was generated by plotting WVP as a function of mica and carnauba wax concentrations (glycerol and caseinate concentrations were kept at fixed value of X3 = 3.00% and X4 = 11.50%). For example, the values of WVP as a function of mica and carnauba wax concentrations are represented by contour surfaces (Figure 1).

From analysis of the isoresponse contours, mica and carnauba wax amounts are apparent prevailing factors affecting WVP, which ranged from 858 to 1151 g μm/m²/d/kPa (Figure1). At mica concentrations <0.6%, the WVP was the lowest at very low carnauba wax concentration (near 0.2%). At mica concentrations >0.6%, the lowest WVP value was observed for films containing high wax concentrations (between 0.6% and 0.8%). The WVP of coated papers decreased as the amount of wax in the coating increased. Indeed, the hydrophilic nature of proteins (NaCAS) incorporated into coatings induces interaction with water, causing swelling (Banker and others 1966; Swarbrick and Amann 1968; Biquet and Labuza 1988; McHugh and others 1993) and deviation from Fick's law (Barrer 1951; Crank 1975).

Table 3—Analysis of variance for studied experimental responses: WVP (Y1), TS (Y2), and %E (Y3)

Source of variation	Sum of square			Degrees of freedom	Mean square[a]		
	Y1	Y2	Y3		Y1	Y2	Y3
Regression	221845	2.98	2.21	14	15846**	0.21**	0.15**
Residual	22521.1	0.2	0.18	8	2815.14	0.02	0.02
Lack of fit	22467.1	0.18	0.09	6	3744.52*	0.03	0.01
Pure error	54.00	0.02	0.09	2	27.00	0.01	0.04
Total	244366	3.18	2.4	22	18661.14	0.23	0.18

[a]*1% < α <5%; **1‰ < α <1%; WVP = water vapor permeability.

The addition of hydrophobic substances (carnauba wax) to this hydrophilic matrix provides the moisture barrier properties. The substantial reduction in WVP of paper by incorporation of carnauba wax was expected because waxes are considerably more resistant to moisture transport than most other lipid or nonlipid biopolymers. Kester and Fennema (1986) found that water vapor permeability decreased with the increase in the hydrophobicity of the components: waxes were found to be the most effective.

Optimal conditions were established according to the 4 factors and were shown to minimize WVP (Figure 2). WVP ranged from 858 to 1368.7 g μm/m²/d/kPa. To minimize WVP, the left pathway should be analyzed. The optimal pathway indicates that optimization of WVP should be obtained by increasing mica and carnauba wax amounts. The glycerol amount should be slightly increased and the sodium caseinate amount should be slightly decreased. The concentrations of mica, carnauba wax, glycerol, and sodium caseinate to obtain optimum WVP were 0.9%, 0.7%, 3.8%, and 11.3%, respectively. Indeed, the incorporation of mica in the coating dispersions decreased the WVP of coated paper. This could be explained by 2 factors: First, the mica, which is a hydrophilic pigment, smoothed the paper surface and made it more homogeneous because the empty pores of cellulose structure, which contained nonpolar air, were filled with mica particles, thus, reducing transmission of water vapor. Han and Krochta (1999) showed that the paper containing hydrophilic fillers and pigments has small and few empty pores, as well as reduced depth of surface ridges and valleys (roughness) compared with the pulp paper. Second, the presence of these pigments in the coating increases the "film tortuosity," which further decreases diffusion and thus WVP.

Mechanical properties

The glycerol factor with a negative sign (–0.396) had the most significant effect ($P < 0.001$) on the tensile strength of coated paper, which decreased as the glycerol concentration increased (Figure 3). Conversely, increasing the amount of glycerol led to a decrease in

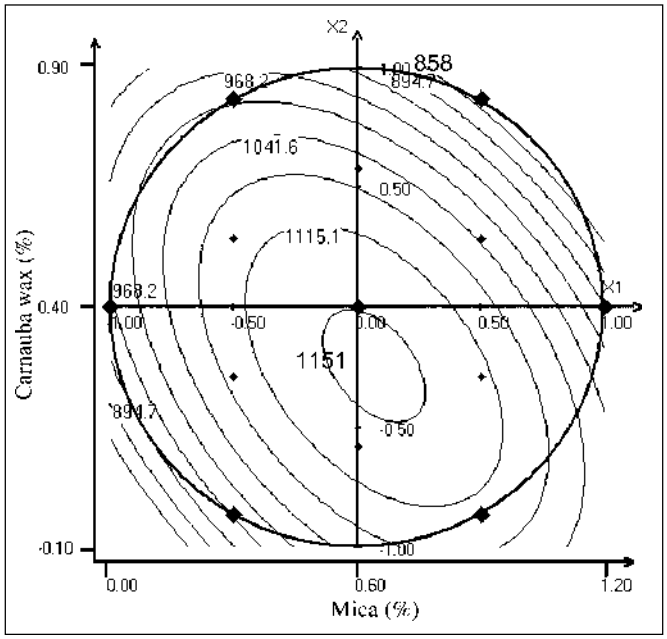

Figure 1—Response surface contours for water vapor permeability (Y1) as a function of mica (X1) and carnauba wax (X2) concentrations. Glycerol (X3) and NaCAS (X4) concentrations were fixed at their central value of the experimental domain (X3 = 3.00%; X4 = 11.50%).

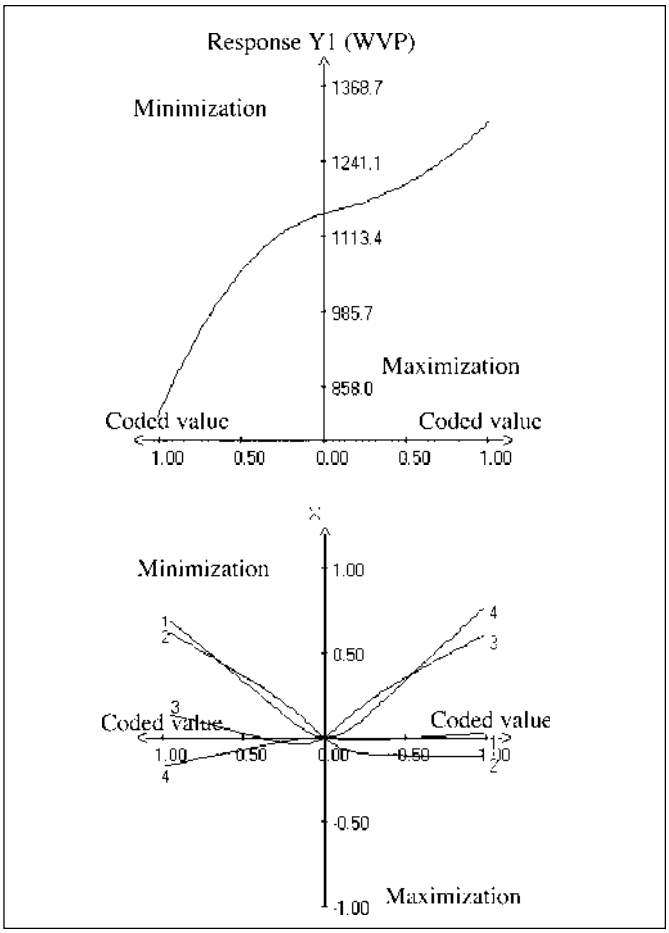

Figure 2—Optimal pathway for water vapor permeability (WVP) response minimization (Y1) in coded variables. Mica (X1), carnauba wax (X2), glycerol (X3), and NaCAS (X4) concentrations.

Table 4—Regression coefficient of predicted quadratic polynomial models[a]

Variables		WVP (g μm/m²/d/kPa)	TS (kN/m)	%E
Intercept		1151.00***	2.280***	1.657***
Linear				
Mica concentration	b1	–13.20*	0.024	–0.144
Wax concentration	b2	–67.20***	–0.048	–0.070
Glycerol concentration	b3	52.42**	–0.396***	0.086*
NaCAS concentration	b4	2.53	0.112	0.074
Quadratic	b11	–204.50***	0.695**	0.668**
	b22	–161.18***	1.055***	0.872***
	b33	0.93	0.887***	0.877***
	b44	76.95**	0.870***	0.900***
Interaction	b12	–167.44***	0.023	0.341
	b13	–139.82**	–0.027	–0.096
	b23	–31.01*	0.081	–0.197
	b14	124.43**	–0.147	–0.283
	b24	32.94*	0.121	–0.003
	b34	142.41**	–0.048	–0.004
R^2	0.90	0.93	0.92	
Adjusted R^2	0.74	0.82	0.78	

[a]*1% < α <5%; **1‰ < α <1%; ***α <1‰; %E = increase in elongation; TS = tensile strength; WVP = water vapor permeability.

tensile strength and to an increase in elongation of the resulting coated papers. This hydrophilic plasticizer decreases the intermolecular forces along polymer chains and increases the free volume and chain mobility, imparting increased film flexibility and stretchability.

Carnauba wax content (X2) had a negative effect on tensile strength and elongation responses. This may be related to the weakening effect of these hydrophobic substances on the protein network, due to the lack of structural integrity of the wax. The presence of carnauba wax in the coating matrix affects the interactions between the polar polymer molecules (NaCAS). Because the interactions between polar polymer and nonpolar lipid molecules are believed to be much lower than those between the polar polymer molecules, the tensile strength of coated paper is decreased.

In a previous study, tensile strength decreases have been documented for NaCAS edible films due to the addition of anhydrous milk fat (Khwaldia and others 2004). Debeaufort and Voilley (1995) reported that when lipids were mixed to hydrocolloid as an emulsion, mechanical properties were strongly affected by the presence of lipid and by film thickness.

The decrease in elongation when lipids are dispersed in the protein matrix of the paper coating is due to a lower continuity of the protein network because of the presence of lipid globules.

The tensile strength and elongation of coated paper having a 10 g/m² coating weight (Table 2) were greater than that of uncoated paper (2.39 ± 0.15 kN/m; 1.48% ± 0.15%), which means that coating increased paper strength and ductility. Conversely, Han and Krochta (2001) noticed that whey protein coating decreased the tensile strength of the paper. During the coating process, whey protein isolate solution swells the cellulose fiber structure and penetrates into spaces between fibers. After drying, whey protein remains in the cellulose structure and interfere with fiber-to-fiber interaction. Because the coated paper structure has smaller interaction force between fibers because of coating interference, the tensile strength is decreased after coating.

Optimal conditions were established according to the 4 factors

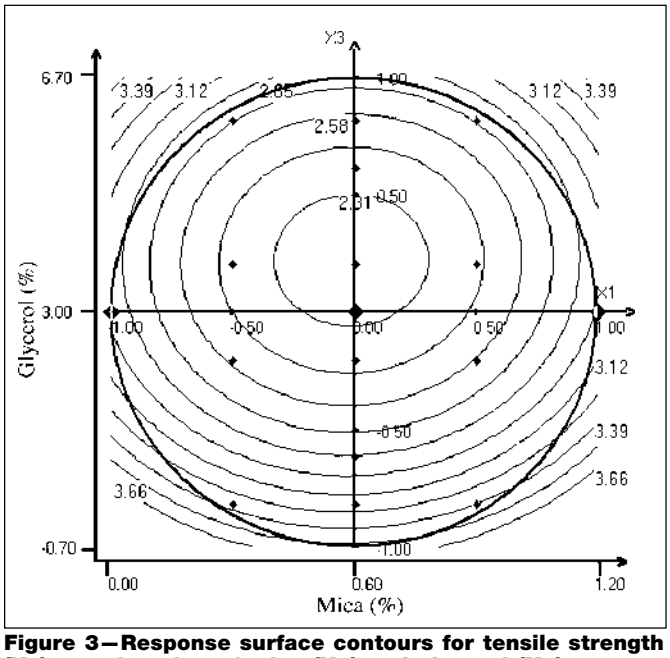

Figure 3—Response surface contours for tensile strength (Y2) as a function of mica (X1) and glycerol (X3) concentrations. Carnauba Wax (X2) and NaCAS (X4) concentrations were fixed at their central value of the experimental domain (X2 = 0.40%; X4 = 11.50%).

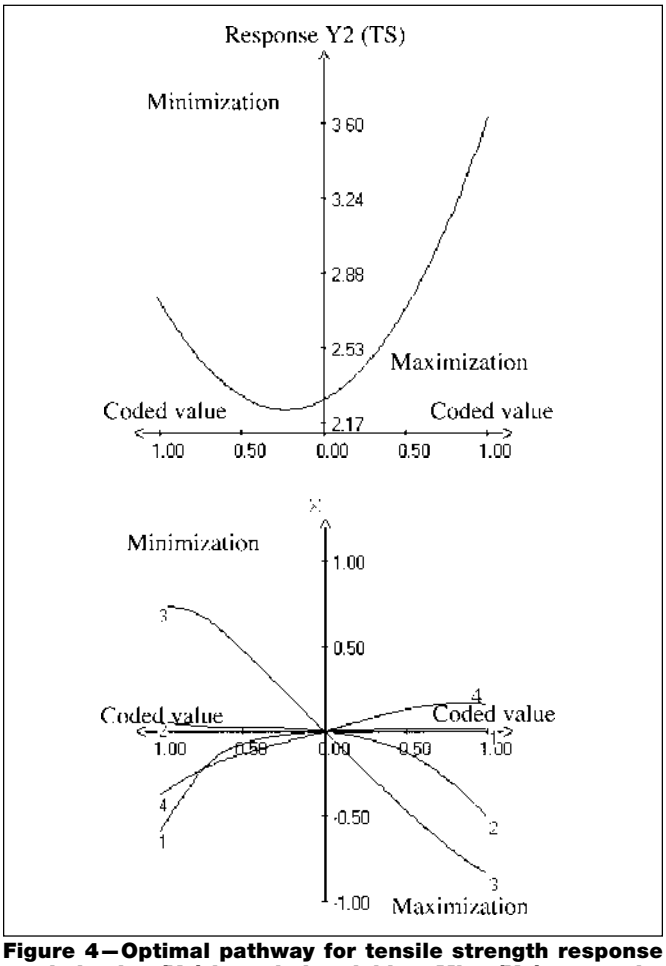

Figure 4—Optimal pathway for tensile strength response maximization (Y2) in coded variables. Mica (X1), carnauba wax (X2), glycerol (X3), and NaCAS (X4) concentrations.

and were shown to maximize tensile strength (Figure 4) and elongation (Figure 5). To maximize TS and %E, the right pathway of each figure should be analyzed. Starting from the center of the experimental domain, the optimal pathway (Figure 4) indicates that optimization of tensile strength should be obtained by decreasing the glycerol and carnauba wax amounts and increasing the NaCAS amount. However, optimization of elongation should be obtained by decreasing the mica and carnauba wax amounts and increasing the glycerol amount.

Conclusions

This study has shown that optimization conditions to minimize WVP and maximize TS and %E should be obtained by increasing mica, carnauba wax, and sodium caseinate amounts and decreasing the glycerol amount. Coating increased both paper strength and ductility. The coated paper is biodegradable, consisting of cellulose, NaCAS, mica, carnauba wax, and glycerol. It is an environmentally friendly material compared with any synthetic packaging. Response surface methodology permitted a predictive experimental model to be developed. The resulting quadratic polynomial equation proved valuable through the initial Doehlert network. The results will enable development of large-scale experiments through characterization of important parameters.

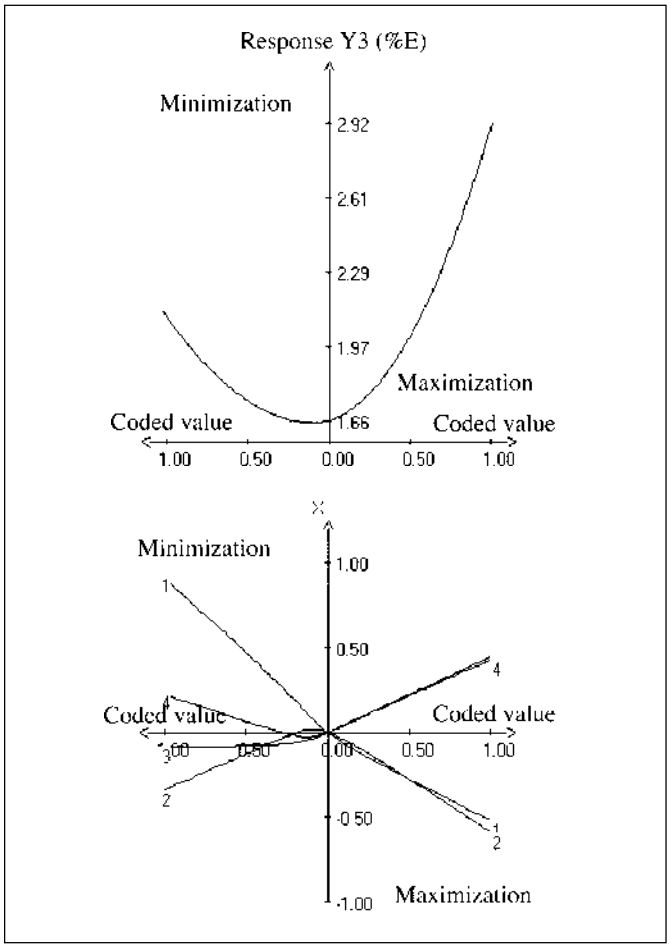

Figure 5—Optimal pathway for elongation response maximization (Y3) in coded variables. Mica (X1), carnauba wax (X2), glycerol (X3), and NaCAS (X4) concentrations.

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