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Effect of glycerol and coating weight on functional properties of biopolymer-coated paper

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ABSTRACT

The effects of glycerol concentration and coating weight on biopolymer-coated paper properties were investigated using response surface methodology. Tests were run on the coated papers to determine water vapor barrier and mechanical properties. Coating weight was the most important parameter affecting water vapor permeability (WVP). Conversely, increasing coating weight led to a decrease in WVP and to an increase in tensile strength (TS) of the resulting coated papers. The papers coated with sodium caseinate (NaCAS) exhibited lower WVP values than those coated with other biopolymers. The TS of the papers coated with hydroxypropylmethylcellulose (HPMC) and chitosan was not affected by the glycerol concentration. HPMC-coated papers were higher in TS and %*E* than the other coated papers. For all types of coated paper, a maximum level of coating weight and level of glycerol concentration within range of 18.72–26.11% were found to be optimum for minimum WVP and maximum TS and %*E*.

1. Introduction

Nowadays, paper is reported to be the most widely used material in packaging applications thanks to its characteristics of printability, recyclability and biodegradability. However, since paper is hygroscopic and porous, its barrier properties against water-vapor, gases and aromas are poor. To improve its barrier properties, paper is often impregnated with coatings from synthetic polymers such as polyethylene, polyvinyl alcohol, rubber latex and fluorocarbon. Theses polymers fill the paper pores and form a dense layer at the paper surface. Unfortunately, the use of such synthetic polymers leads to the loss of the paper's biodegradability. In an effort to produce more environmentally friendly and renewable materials, biodegradable polymers have been investigated as surface-coating materials on paper or paperboard (Han & Krochta, 2001; Lin & Krochta, 2003; Park et al., 2000).

Biopolymer-based packaging materials originated from naturally renewable resources such as polysaccharides, proteins, and lipids or combinations of those components have the potential to replace current synthetic paper coatings, since they offer favorable environmental advantages of recyclability and reutilization. Agriculturally derived alternatives to polyolefin packaging materials reduce importation of petroleum and its derivates and provide an opportunity to strengthen the agricultural economy. Moreover, biodegradable polymers developed for packaging materials have suitable application properties and can be disposed of after use in an economically and ecologically acceptable way.

Natural polymer coatings on paper packaging materials can serve as moisture, grease, and oxygen barriers in many food packaging applications. Moreover, they are potential inclusion matrices of antimicrobial agents to develop biodegradable active packaging (Ben Arfa, Chakrabandhu, Presiozi-Belloy, Chalier, & Gontard, 2007; Khwaldia, Tehrany, & Desobry, 2010; Vartiainen et al., 2004).

Agropolymers such as proteins and polysaccharides have drawn attention for their good film-forming capacity and gas barrier properties and have been used to make biodegradable films and coatings. Biopolymers investigated as paper-coating materials include milk proteins (Gastaldi, Chalier, Guillemin, & Gontard, 2007; Han & Krochta, 1999, 2001; Khwaldia, 2010; Khwaldia, Linder, Banon, & Desobry, 2005), isolated soy protein (Park et al., 2000; Rhim, Lee, & Hong, 2006), wheat gluten (Gällstedt, Brottman, & Hedenqvist, 2005), corn zein (Parris, Vergano, Dickey, Cooke, & Craig, 1998; Trezza & Vergano, 1994), chitosan (Despond, Espuche, Cartier, & Domard, 2005; Ham-Pichavant, Sèbe, Pardon, & Coma, 2005; Kjellgren, Gällstedt, Engström, & Järnström, 2006), carrageenan (Rhim, Hwang, Park, Kang, & Jung, 1998); alginate (Rhim et al., 2006), and starch (Matsui et al., 2004).

Milk proteins, such as caseinates, have been formulated into coatings and films, owing to their effectiveness in enhancing the shelf life by serving as selective barriers combined with their environmental compatibility and nutritional value (Brault, D'Aprano, & Lacroix, 1997; Chen, 1995; Vachon et al., 2000). Sodium caseinate

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(NaCAS) is commercially available and can easily form cohesive films from aqueous solutions because of its random coil nature and its ability to form extensive intermolecular hydrogen, electrostatic, and hydrophobic bonds. The oxygen permeability of NaCAS films has been reported to be lower than that of nonionic polysaccharide films (Khwaldia, Perez, Banon, Desobry, & Hardy, 2004). This may be related to their more polar nature and more linear (nonring) structure, leading to higher cohesive energy density and lower free volume (Miller & Krochta, 1997). Moreover, NaCAS films have better tensile and optical properties than calcium caseinate films (Fabra, Talens, & Chiralt, 2009). These properties make NaCAS an attractive polymer for the coating of cellulose-based materials for food packaging purposes. Khwaldia (2010) indicated that water vapor barrier and mechanical properties of paper are improved by coating with NaCAS.

Among many polysaccharides available for forming coatings on paper packaging materials, chitosan is one of the most interesting and the most studied (Bordenave, Grelier, Pichavant, & Coma, 2007; Ho, An, Park, & Lee, 2003; Kjellgren et al., 2006; Vartiainen et al., 2004). Chitosan is a cationic polysaccharide obtained from partial deacetylation of chitin, the main constituent of the crustacean skeleton and the second most abundant naturally occurring biopolymer after cellulose (No & Meyers, 1995). Chitosan has been documented to possess film-forming properties for use as edible films or coatings and also bioactive properties either in its polymeric or oligomeric form (Begin & Van Calsteren, 1996; Coma, Deschamps, & Martial-Gros, 2003). By being antifungal and antimicrobial, chitosan-based films and coatings formulations have additional value addition. Chitosan-based films and coatings have good mechanical properties (Arvanitoyannis, Nakayama, & Aiba, 1998) and can act as excellent oxygen and grease barriers (Kittur, Kuman, & Tharanathan, 1998). Chitosan has been used as a papermaking additive and for the surface treatment of paper for decades due to its high retention and good compatibility with cellulose-based substrates.

Chitosan is selected as a paper coating material in this study because it is readily compatible with paper and is therefore a good comparison when analysing the other biopolymer-paper systems.

Alginate, another naturally occurring polymer, is an anionic polysaccharide composed of mannuronic acid and guluronic acid residues and is extracted from seaweed. Alginates are resistant to solvents, oil, and grease and exhibit interesting film-forming properties. They are widely used in encapsulation applications due to their ability to form gels in the presence of cerain divalent cations such as calcium, barium, and strontium (Braccini & Perez, 2001) by ionotropic gelation. Also, alginate-based films are good oxygen barriers, can improve the flavor and the texture of foods, and can delay lipid oxidation (Kester & Fennema, 1986). In addition, alginates are nontoxic, biodegradable, and biocompatible (Shapiro & Cohen, 1997) and are generally used in sizing and/or coating paper to produce surface uniformity. Rhim et al. (2006) reported that water barrier properties of paperboards increased by alginate coating with $CaCl_2$ posttreatment.

Polysaccharide-based polymer such as hydroxypropylmethylcellulose (HPMC) is used in food industries as an emulsifier, protective colloid, suspending agent, and film former (Tharanathan, 2003). HPMC presents excellent film-forming properties that enable the production of a tough and protective coating (Nisperos-Carriedo, 1994; Villabos, Hernández-Muñoz, & Chiralt, 2006), with very efficient oxygen, carbon dioxide and lipid barriers. This polysaccharide is available in a wide range of degree of substitution, molecular weight, viscosity, and particle size influencing the properties of the subsequent film coatings (Capan, 1989; Rowe, 1986). In addition, its nontoxic property, ease of handling, and relatively simple manufacturing technology (Shah et al., 1996) make HPMC a promising coating material for paper to improve some of its functional properties. Sothornvit (2009) showed that HPMC-based coatings improved paper flexibility and durability and reduced WVP and further reduction was obtained when beeswax was incorporated in the HPMC-lipid composite coated paper.

In this study, it is aimed to investigate the effects of glycerol concentration and coating weight on the water vapor barrier and mechanical properties of biopolymer-coated papers and to find the optimum conditions for each biopolymer investigated as paper-coating material that maximize tensile strength and elongation and minimize water vapor permeability.

2. Materials and methods

2.1. Coatings materials and papers

Sodium caseinate (NaCAS, molecular weight ~25,000 Da, Sigma Aldrich, Steinheim, Germany), Sodium alginate (NaAlg, molecular weight ~80,000 Da, Sigma Aldrich, Steinheim, Germany), Hydroxypropylmethylcellulose (HPMC, Methocel E-19, Food grade, molecular weight ~50,000 Da, Dow Chemical Co. Midland, USA) and chitosan (deacetylation degree >75%, viscosity ≤200 mPa s in 1% acetic acid, molecular weight ~150,000 Da, Sigma Aldrich, Steinheim, Germany) were used as coatings materials. Glycerol (>97% purity) was used as a plasticizer and was purchased from Sigma Aldrich (Steinheim, Germany). Paper packaging having a grammage of $79.15 \pm 0.89\ g/m^2$ and a thickness of $99.2 \pm 1.40\ \mu m$ at 23 °C and 50% RH, was provided from SOTEFI (Soukra, Tunisia).

2.2. Coating solutions

Biopolymer-coating solutions were prepared according to the experimental plan (Table 1).

Preparation of NaCAS-based coating solution was adapted from Khwaldia (2010). NaCAS powder was dispersed in distilled water at 60 °C while stirring for 30 min. Next, selected amounts of glycerol were added during heating and stirring. NaAlg coating solutions were prepared with the same method used for alginate film

Table 1
Experimental domain and level distribution of the variables used to evaluate the effect of glycerol concentration (%, w/w) and coating weight (g/m^2) on biopolymer-coated paper properties.

Biopolymer	Variable levels	Independent variables	
		Glycerol concentration (%, w/w)	Coating weight (g/m^2)
NaCAS	−1.41	0	2.79
	−1	8.79	4.89
	0	30	9.96
	+1	51.21	15.03
	+1.41	60	17.13
NaAlg	−1.41	0	2.50
	−1	8.79	3.02
	0	30	4.27
	+1	51.21	5.52
	+1.41	60	6.04
HPMC	−1.41	0	3.40
	−1	8.79	4.66
	0	30	7.70
	+1	51.21	10.74
	+1.41	60	12
Chitosan	−1.41	0	2.43
	−1	8.79	2.77
	0	30	3.58
	+1	51.21	4.39
	+1.41	60	4.73

preparation (Rhim, 2004). 5 g of alginate powder was added to a constantly stirred mixture of 100 ml of distilled water. Selected amounts of glycerol were then added into the polymer solution. The mixture was heated on a hot plate with constant stirring until completely dissolved and clear

HPMC coating solutions were prepared using the procedure described by Imran, El-Fahmy, Revol-Junelles, and Desobry (2010). 7 g of HPMC powder was dissolved in a mixture of distilled water (65 ml) and ethanol (35 ml) heated at 65 °C with constant agitation, until all particles were thoroughly dispersed. Then, appropriate amounts of glycerol were added to the film forming solutions. Chitosan coating solutions were prepared by dissolving chitosan 2% (w/v) in 1% (v/v) acetic acid solution with agitation using a magnetic stirrer at 45 °C (Vartiainen et al., 2004). Next, glycerol was added in concentrations between 8.79 and 60% (w/w). For the four biopolymers raw materials studied, coating solutions were degassed to remove the entrapped air bubbles during mixing.

2.3. Coating method

A control coater (model KCC 101, RK Print-Coat Instuments Ltd., Hertz, UK) was used to deposit the coating solutions on the paper at ambient temperature. This automatic machine uses standard wire wound bars to produce a uniform and repeatable coating. For each biopolymer coating solution, five coat weights were applied, where the coat weight was varied by varying the diameter of the wire on the rod. Coated papers were then dried at 40 °C for 30 min (dryer model 400, TECHPAP, Gières, France). Before properties testing, all samples were conditioned for two days in an environmental chamber at 50% RH and 23 °C.

Coating weights (g/m^2) were obtained by subtracting from the weight of a defined area of coated paper, the weight of the same area of the uncoated paper.

2.4. Paper thickness measurements

Paper thickness was measured using a ProGage thickness tester (Thwing-Albert Instrument company, Philadelphia, PA) in accordance with ISO 534-2005. Ten replicates were done on each sample.

2.5. Water vapor permeability

Water vapor permeability (WVP) measurements were 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) to maintain a RH 0% in the cell. The permeation cells were 6.4 cm (internal diameter) by 8.9 cm (external diameter) by 4.8 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 fitted with a variable-speed fan to provide a strong driving force across the film for water vapor diffusion. Unsteady-state periods of 30 min were demonstrated in preliminary tests. The water vapor transport was determined from the weight gain of the cell. Changes in the weight of the cell were recorded as a function of time. Slopes were calculated by linear regression (weight changes vs. time) and the correlation coefficient for all reported data was >0.99. The water vapor transmission rate (WVTR) was defined as the slope (g d^{-1}) divided by the transfer area (m^2). After the permeation tests, film thickness was measured and WVP was calculated as follows (McHugh & Krochta, 1994):

$$\mathrm{WVP} = \frac{\mathrm{WVTR} \cdot X}{\Delta p} \, [\mathrm{g\,\mu m\ m^{-2}\,d^{-1}\,kPa^{-1}}] \tag{1}$$

where X is the coated paper thickness, Δp is the difference of partial water vapor pressure across the film ($\Delta p = p(RH_2 - RH_1) = 5.942$ kPa, where p is the saturation vapor pressure of water at 38 °C, $RH_2 = 90\%$, $RH_1 = 0\%$). Four replicates were made from each type of paper.

2.6. Tensile properties

Tensile strength (TS) and elongation at break (%E) in the machine direction of the papers were evaluated using a material testing machine (Lloyd LRX, Lloyd Instruments Ltd., Royston, UK), according to a standard method of ISO 1924-2-1994. The experiments were performed under controlled conditions, at 23 °C and 50% RH. Ten rectangular paper samples (15 mm wide × 100 mm long) were cut from each type of paper and were tested using a double clamp with a separation of 30 mm at a test speed of 20 mm/min. The clamp separation was 100 mm and the strain rate was 20 mm/min. The curve load vs. extension was recorded until the elongation at break was reached. The TS was expressed in MPa and was calculated by dividing the maximum load (N) by the cross-sectional area (m^2). Maximum elongation at break or percent elongation at break (%E) was determined by dividing the extension at the moment of breakage by the initial gauge length of the samples and multiplying by 100.

2.7. Experimental design

For each biopolymer used to make coating formulations, a central composite design using the response surface methodology was performed to evaluate the effects of glycerol concentration and coating weight on coated paper properties.

Glycerol concentration (X_1) and coating weight (X_2) were independent variables (factors) that were modulated according to a two factor, five level central composite design, as reported in Table 1 while thickness (Y_1), WVP (Y_2), TS (Y_3), and E (Y_4) were dependent variables (responses). The lowest and highest levels of independent variables studied were chosen from results of preliminary laboratory tests.

For each biopolymer, 11 experiments were carried out; experiment 9 was performed at the center of the experimental domain and repeated 2 times (10, 11) to estimate residual variance (Table 2).

Fitting the data to a second-order polynomial function provided the following regression model:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}{X_1}^2 + b_{22}{X_2}^2 + b_{12}X_1X_2 \tag{2}$$

where Y is the dependent variable; b_0 is the constant coefficient; b_1 and b_2 are the linear regression coefficients; b_{11} and b_{22} are the quadratic regression coefficients; b_{12} is the interaction coefficient, and X_1 and X_2 are the coded independent variables.

2.8. Statistical analysis

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

ANOVA and canonical analysis were used to characterize the validity of the 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) was accurately predicted by the second-order polynomial models, as shown by coefficients of determination ($R^2 \geq 90\%$).

For each biopolymer used, the optimum values of the selected variables were obtained by solving the regression equation at desired values of the responses as the optimization criteria. Optimization of responses was performed by desirability function

Table 2
Central composite design and experimental responses.

Biopolymer	Exp no.	Variables[a]		Responses[b]			
		X_1	X_2	Thickness (Y_1) (μm)	WVP (Y_2) (g μm m^{-2} d^{-1} kPa^{-1})	TS (Y_3) (MPa)	%E (Y_4)
NaCAS	1	8.79	4.89	104.60	318	26.85	5.06
	2	51.21	4.89	104.20	410	26.44	5.52
	3	8.79	15.03	111.60	192	28.11	5.37
	4	51.21	15.03	114.10	202	26.88	5.89
	5	0.00	9.96	106.70	142	27.88	5.50
	6	60.00	9.96	110.60	320	26.77	5.91
	7	30.00	2.79	104.00	378	26.64	5.26
	8	30.00	17.13	114.67	152	28.22	5.74
	9	30.00	9.96	106.60	299	26.81	5.71
	10	30.00	9.96	106.90	327	27.14	5.69
	11	30.00	9.96	106.75	299	26.97	5.71
NaAlg	1	8.79	3.02	103.82	460	28.56	4.81
	2	51.21	3.02	103.93	535	28.40	5.40
	3	8.79	5.52	104.69	420	29.95	5.13
	4	51.21	5.52	104.80	459	28.51	5.85
	5	0.00	4.27	103.79	430	29.70	4.74
	6	60.00	4.27	104.43	506	27.78	5.47
	7	30.00	2.50	103.33	590	27.37	4.61
	8	30.00	6.04	104.84	480	28.97	5.74
	9	30.00	4.27	104.07	541	27.82	5.34
	10	30.00	4.27	104.11	501	27.66	5.23
	11	30.00	4.27	104.07	521	27.74	5.28
HPMC	1	8.79	4.66	102.93	447	33.02	5.36
	2	51.21	4.66	102.93	490	31.55	5.48
	3	8.79	10.74	104.50	361	36.24	5.68
	4	51.21	10.74	107.00	387	34.09	5.99
	5	0.00	7.70	102.30	477	34.31	5.20
	6	60.00	7.70	103.47	491	32.02	5.73
	7	30.00	3.40	102.30	522	31.92	5.22
	8	30.00	12.00	107.50	298	36.84	5.94
	9	30.00	7.70	103.85	426	34.51	5.69
	10	30.00	7.70	104.21	454	33.88	5.76
	11	30.00	7.70	104.03	454	34.19	5.72
Chitosan	1	8.79	2.77	102.42	406	29.35	4.88
	2	51.21	2.77	103.04	468	28.03	5.22
	3	8.79	4.39	103.54	325	30.30	5.04
	4	51.21	4.39	103.86	316	30.28	5.32
	5	0.00	3.58	102.29	271	30.35	4.92
	6	60.00	3.58	103.17	418	29.13	5.26
	7	30.00	2.43	102.22	491	29.24	4.92
	8	30.00	4.73	103.94	284	30.74	5.25
	9	30.00	3.58	103.25	357	29.60	5.12
	10	30.00	3.58	103.00	354	29.27	5.04
	11	30.00	3.58	103.00	354	29.43	5.08

[a] Factors: X_1, glycerol concentration (%, w/w); X_2, coating weight (g/m^2).
[b] WVP, water vapor permeability; TS, tensile strength; %E, elongation at break.

method, which is one of the most widely used methods for optimization of multiple response processes in diverse field of applied science and engineering (Chakraborty & Bordoloi, 2006). The desirability function combines all the responses into one measurement and is defined as the geometric mean of individual desirability functions. Higher the desirability value more desirable is the system (Srinivasa, Ravi, & Tharanathan, 2007).

3. Results and discussion

3.1. Thickness

The thickness of coated papers varied significantly ($p < 0.001$) with the coating weight (Table 4). The thickness of coated paper increased as the coating weight increased.

From analysis of the isoresponse contours, it is possible to observe that the increase in thickness was more important in the NaCAS-coated papers than in the other coated papers (Fig. 1). Considering that the uncoated papers have thickness value of 99.2 ± 1.4 μm, NaCAS could form coating layers of 4.8–15.5 μm thickness on the surface of paper. Therefore, most of the NaCAS content formed a continuous layer on the surface of the paper, which is a porous, with rough surface, material leading to an increase of measurable paper thickness. Khwaldia (2010) demonstrated through microscopic observations that NaCAS produced a homogeneous film on the paper with a regular and smooth surface. Likewise, Gastaldi et al. (2007) reported that calcium caseinate solutions presented a low impregnation rate, due to the formation of a gel structure for calcium caseinate concentration higher than 10%, leading to a rapid immobilization of caseinate molecules on paper surface.

The range of thickness values for alginate- and chitosan-coated papers was approximately 102.2–104.8 μm. The deposition of the alginate and chitosan solutions onto the cellulosic substrate led to a low thickness increase. Therefore, most of chitosan and alginate coating solutions penetrated into the porous paper structure during casting and drying. In the present study, the alginate and chitosan solutions penetrated into the cellulosic substrate to a greater extent

Table 3
Analysis of variance for studied experimental responses.

Biopolymer	Source of variation	Sum of square				Degrees of freedom	Mean square[a]			
		Y_1	Y_2	Y_3	Y_4		Y_1	Y_2	Y_3	Y_4
NaCAS	Regression	146.9859	76118.6	3.5388	0.6425	5	29.3972***	15223.7**	0.7078**	0.1285***
	Residual	2.1829	5463.59	0.2799	0.0609	5	0.4366	1092.72	0.0560	0.0122
	Lack of fit	2.1379	4940.92	0.2254	0.0606	3	0.7126*	1646.97	0.0751	0.0202**
	Pure error	0.0450	522.667	0.0545	0.0003	2	0.0225	261.333	0.0272	0.0001
	Total	149.1688	81582.2	3.8187	0.7034	10				
NaAlg	Regression	2.0679	22990.7	6.6587	1.4050	5	0.4136**	4598.15*	1.3317**	0.2810*
	Residual	0.1696	3178.89	0.5610	0.1510	5	0.0339	635.778	0.1122	0.0302
	Lack of fit	0.1685	2378.89	0.5482	0.1450	3	0.0562*	792.964	0.1827*	0.0483
	Pure error	0.0011	800	0.0128	0.0061	2	0.0005	400	0.0064	0.0030
	Total	2.2375	26169.6	7.2197	1.5561	10				
HPMC	Regression	28.9018	38753.5	28.1212	0.6712	5	5.7804**	7750.70*	5.6242***	0.1342**
	Residual	0.9218	4192.52	0.4006	0.0417	5	0.1844	838.505	0.0801	0.0083
	Lack of fit	0.8570	3669.86	0.2021	0.0392	3	0.2857	1223.29	0.0674	0.0131
	Pure error	0.0648	522.667	0.1985	0.0025	2	0.0324	261.333	0.0992	0.0012
	Total	29.8236	42946	28.5218	0.7129	10				
Chitosan	Regression	3.1525	46826.4	5.3292	0.2194	5	0.6265*	9365.27***	1.0658*	0.0439**
	Residual	0.2758	3776.18	0.4997	0.0125	5	0.0552	755.235	0.0999	0.0025
	Lack of fit	0.2341	3770.18	0.4453	0.0093	3	0.0780	1256.73**	0.1484	0.0031
	Pure error	0.0417	6	0.0545	0.0032	2	0.0208	3.000	0.0272	0.0016
	Total	3.4083	50602.5	5.8289	0.2319	10				

[a] Y_1, thickness; Y_2, water vapor permeability; Y_3, tensile strength; Y_4, elongation at break.
* $1\% < \alpha < 5\%$.
** $1‰ < \alpha < 1\%$.
*** $\alpha < 1‰$.

Table 4
Regression coefficients of predicted second-order polynomial models.

Biopolymer	Variables		Thickness (μm)	WVP (g μm m^{-2} d^{-1} kPa^{-1})	TS (MPa)	%E
NaCAS	Intercept Linear		106.750***	308.3***	26.973***	5.703***
	Glycerol concentration	b_1	0.952**	44.2*	−0.401**	0.195***
	Coating weight	b_2	3.999***	−81.7**	0.492**	0.170***
	Quadratic	b_{11}	0.858**	−30.500	0.099	−0.035*
		b_{22}	1.201**	−13.500	0.151	−0.137***
	Interaction	b_{12}	0.725**	−20.500	−0.205	0.015
	R^2		0.985	0.933	0.927	0.913
	Adjusted R^2		0.971	0.866	0.853	0.827
	Intercept Linear		104.083***	521.0***	27.740***	5.283***
NaAlg	Glycerol concentration	b_1	0.141**	27.7*	−0.539**	0.293**
	Coating weight	b_2	0.484***	−33.9*	0.470**	0.296**
	Quadratic	b_{11}	0.066*	−34.8*	0.600**	−0.050
		b_{22}	0.054*	−1.3	0.315**	−0.015
	Interaction	b_{12}	−0.000	−9.0	−0.320*	0.032
	R^2		0.924	0.879	0.922	0.903
	Adjusted R^2		0.848	0.757	0.845	0.806
	Intercept Linear		104.030***	444.7***	34.193***	5.723***
HPMC	Glycerol concentration	b_1	0.519*	11.1	−0.857***	0.147**
	Coating weight	b_2	1.624***	−63.2**	1.590***	0.231**
	Quadratic	b_{11}	−0.461	13.2	−0.526**	−0.103*
		b_{22}	0.547*	−23.8	0.081	−0.045
	Interaction	b_{12}	0.625*	−4.3	−0.170	0.048
	R^2		0.969	0.902	0.986	0.941
	Adjusted R^2		0.938	0.805	0.972	0.883
	Intercept Linear		103.083***	355.0***	29.433***	5.080***
Chitosan	Glycerol concentration	b_1	0.273*	32.6***	−0.383*	0.138***
	Coating weight	b_2	0.547**	−65.7***	0.665**	0.091**
	Quadratic	b_{11}	−0.099	−2.1	0.060	0.012
		b_{22}	0.076	19.4***	0.185	0.009
	Interaction	b_{12}	−0.075	−17.8**	0.325	−0.015
	R^2		0.919	0.925	0.914	0.946
	Adjusted R^2		0.838	0.851	0.829	0.892

* $1\% < \alpha < 5\%$.
** $1‰ < \alpha < 1\%$.
*** $\alpha < 1‰$.

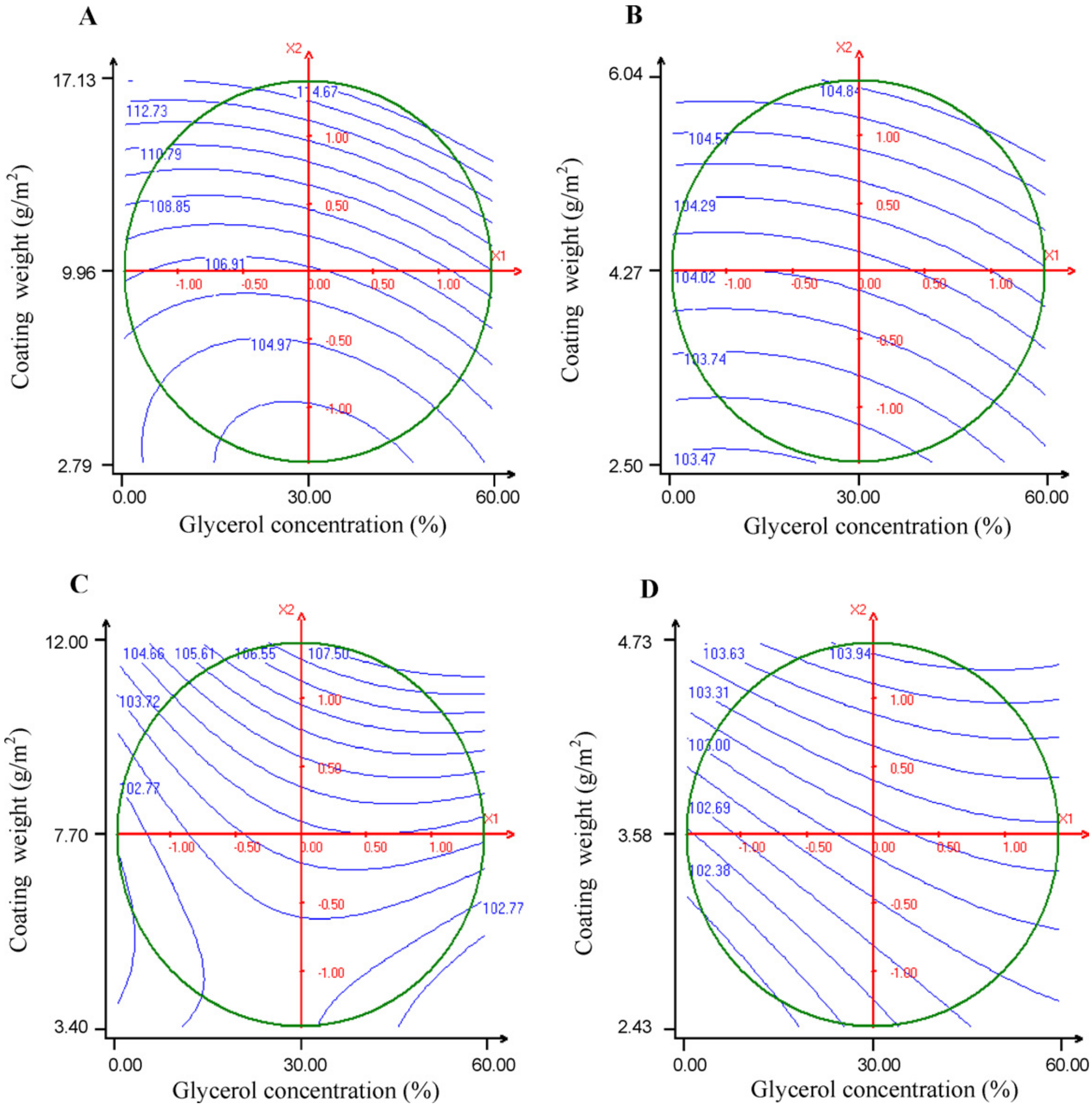

Fig. 1. Response surface contours for thickness of paper coated with (A) NaCas, (B) NaAlg, (C) HPMC, and (D) chitosan, as a function of glycerol concentration (X_1) and coating weight (X_2).

than did the HPMC and NaCAS solutions. It was reported that the penetration of biopolymer into paper was related to the nature of biopolymer, the coating weight, and the intrinsic properties of the cellulosic substrate (affinity toward biopolymer-coating solutions, topography and porosity) (Gastaldi et al., 2007; Guillaume, Pinte, Gontard, & Gastaldi, 2010).

3.2. Water vapor permeability (WVP)

Water vapor is a critical compound that can penetrate the packaging materials and degrade food quality. To avoid the moisture transfer that can affect food quality, WVP control is important to assure stability and safety during distribution and storage.

Fig. 2 shows the surface response plot of WVP vs. the investigated independent variables. As can be inferred from the above figure, WVP values of biopolymer-coated papers were positively affected by the glycerol concentration (X_1), while negatively influenced by the coating weight (X_2).

The coating weight factor had the most important effect on the WVP of coated paper, which decreased as the coating weight increased (Table 4). Indeed, biopolymer-coating materials impregnated the paper structure, filled pores of the cellulose structure, thus, reducing transmission of water vapor. In agreement with present findings, WVP decreased have been documented for NaCAS-coated paper (Khwaldia, 2010) and HPMC-lipid composite coated paper (Sothornvit, 2009).

On the other hand, increasing the amount of glycerol led to an increase in WVP of the paper sheets coated with NaCAS, NaAlg, and chitosan (Fig. 2A, B, and D). An increase in the interchain spacing caused by inclusion of glycerol molecules between the polymer chains may promote water vapor diffusivity through the film and, hence, accelerate the water vapor transmission. The high hydrophilicity of glycerol molecules, which is favorable to the adsorption of water molecules, could also contribute to the increase in the WVP. The increases in WVP arising from increases in plasticizer concentration reported in this study were consistent with the findings of Khwaldia, Banon, Desobry, and Hardy (2004) and Chillo et al. (2008) who reported that increasing plasticizer concentration increased film WVP.

However, glycerol content did not have an impact on the WVP of HPMC-coated paper. Sothornvit and Krochta (2005) pointed out that the plasticizer effect depends on the nature of the plasticizer

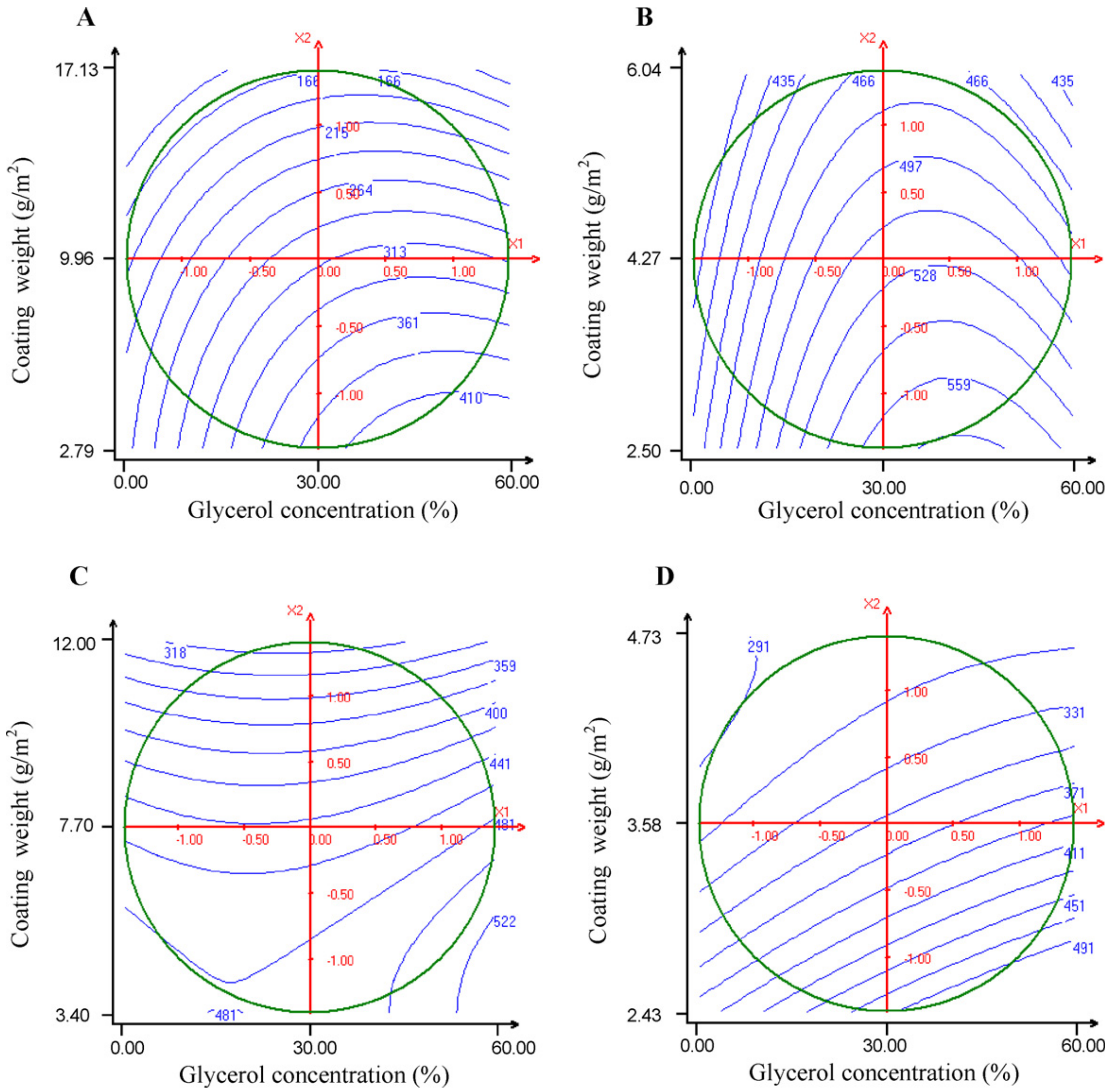

Fig. 2. Response surface contours for WVP of paper coated with (A) NaCas, (B) NaAlg, (C) HPMC, and (D) chitosan, as a function of glycerol concentration (X_1) and coating weight (X_2).

and the polymer, and the same trend in permeability properties might not be found for different polymer–plasticizer pairs.

For all studied biopolymers, the highest water-vapor barrier properties are obtained at the highest coating weights and at the lowest concentrations of glycerol. For example, the lowest WVP value of chitosan-coated papers was observed for 6.4% of glycerol and 4.3 g/m^2 of coating weight.

Overall, WVP values for biopolymer-coated papers increased in the following order of NaCAS (166–410 g μm m^{-2} d^{-1} kPa^{-1}), chitosan (291–491 g μm m^{-2} d^{-1} kPa^{-1}), HPMC (318–502 g μm m^{-2} d^{-1} kPa^{-1}), and NaAlg (420–574 g μm m^{-2} d^{-1} kPa^{-1}). WVP values were different depending on the type of coating biopolymer used which reflected the difference of interaction between the biopolymer and cellulose fiber structures.

Table 5
Optimization parameters for each biopolymer used and the overall desirability.

Biopolymer	Independent variable	Actual levels of variables	WVP (g μm m^{-2} d^{-1} kPa^{-1})	TS (MPa)	%*E*	Overall desirability
NaCAS	Glycerol (%) Coating weight (g/m^2)	26.11 16.58	174	28.00	5.65	0.9864
NaAlg	Glycerol (%) Coating weight (g/m^2)	18.72 5.92	456	29.59	5.46	0.9533
HPMC	Glycerol (%) Coating weight (g/m^2)	19 11.30	337	36.60	5.80	0.9636
Chitosan	Glycerol (%) Coating weight (g/m^2)	20.42 4.55	299	30.50	5.15	0.9854

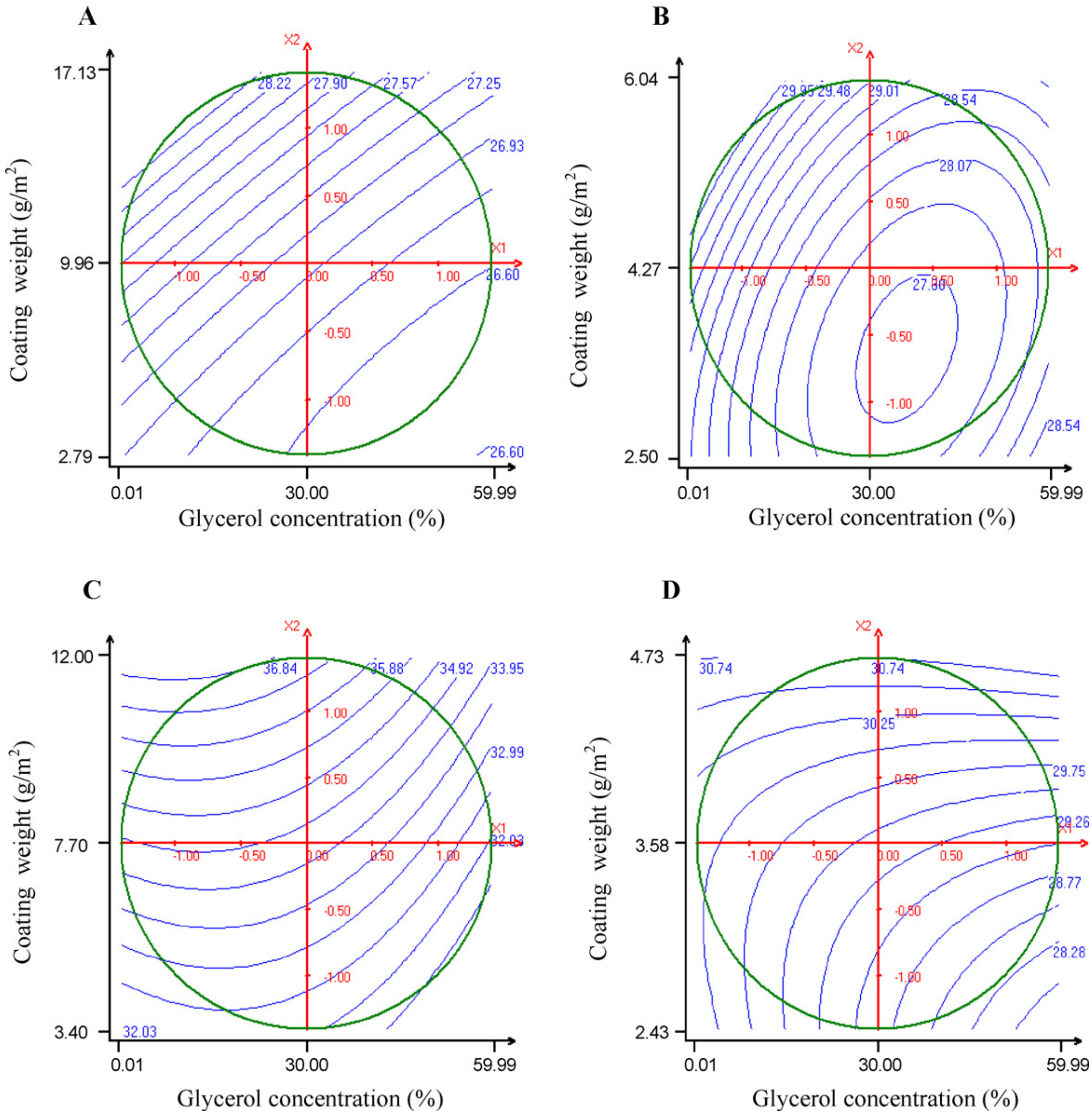

Fig. 3. Response surface contours for TS of paper coated with (A) NaCas, (B) NaAlg, (C) HPMC, and (D) chitosan, as a function of glycerol concentration (X_1) and coating weight (X_2).

3.3. Mechanical properties

High mechanical properties are usually required to maintain packaging integrity during shipping, handling and storage. Tensile strength (TS) and elongation at break (%*E*) are the most commonly reported responses to describe mechanical properties of paper-based packaging materials. TS is a measure of the ability of a film to resist breaking under tension, which is dependent on the strength of fibers, their surface area, and length, and also the bonding strength between them. %*E* shows the ability of a film to stretch before it breaks (Rabinovitch, 2003).

The TS values of biopolymer-coated papers were positively affected by the linear terms of coating weight, while negatively influenced by the glycerol concentration (Table 4). A series of response surfaces were generated by plotting TS as a function of glycerol concentration and coating weight (Fig. 3). From analysis of the isoresponse contours, it can be seen that the TS of coated papers increased with increasing the coating weight. These results are in accordance with those of Gällstedt et al. (2005) who reported that the TS increased with increasing coating weight for paper sheets coated with chitosan, whey protein isolate, whey protein concentrate, and wheat gluten protein. In a previous study, TS and ductility increases have been documented for coated paper, consisting of cellulose, NaCAS, mica, carnauba wax, and glycerol (Khwaldia et al., 2005). Conversely, Han and Krochta (2001) reported that whey protein coating decreased the TS of the paper, because the coated paper structure has smaller interaction force between fibers because of coating interference.

Increasing the amount of glycerol led to a decrease in TS of the NaCAS- and NaAlg-coated papers. On the other hand, a negligible effect of the glycerol amount on the TS of HPMC- and chitosan-coated papers was measured (Fig. 3C and D).

From Fig. 3, it is possible to observe that the highest TS values of papers coated with NaCAS, NaAlg, HPMC, and chitosan are obtained at the lowest concentrations of glycerol and at the highest coating weights. For example, the highest TS value of NaAlg-coated papers was observed for 0% of glycerol and 4.6 g/m^2 of coating weight.

On the other hand, glycerol content (X_1) had a positive effect on elongation responses of the resulting coated papers (Table 4). This hydrophilic plasticizer decreases the intermolecular forces along polymer chains and increases the free volume and chain mobility, imparting increased film flexibility and stretchability.

Elongation of papers coated with NaAlg and HPMC increased with increasing coating weight, as shown in Table 4. This may be caused by a stress relaxation in the base paper during the coating process when the base paper was exposed to the water in the coating solution. Elongation increases have been documented for NaCAS-paraffin wax coated paper (Khwaldia, 2010) and greaseproof paper coated with chitosan (Kjellgren et al., 2006).

The range of TS and %*E* values of all biopolymer-coated papers were approximately 26.60–36.88 MPa and 4.72–5.99%, respectively. HPMC-coated papers were higher in TS and E than the other coated papers. The TS and E of coated papers were greater than that of uncoated paper (23.84 ± 1.33 MPa; 4.13 ± 0.25%), which means that biopolymer coating improved paper strength and ductility. Our results are in agreement with those of Vartiainen et al. (2004) who reported that chitosan coating improved the tensile properties of paper and could be regarded as a reinforcement layer. Overall, the TS and E values for coated papers in this study are similar to those reported for alginate- or soy protein-coated paperboards (Rhim et al., 2006).

3.4. Optimization using the desirability functions

Optimum conditions for paper coating were determined to obtain minimum WVP and maximum TS and %*E*. For all types of coated paper, a maximum level of coating weight and level of glycerol concentration within range of 18.72–26.11% were found to be optimum for minimum WVP and maximum TS and %*E* (Table 5). For chitosan-coated paper, desirability score of 0.9854 was obtained when WVP, TS and %*E* values were 299 g μm m^{-2} d^{-1} kPa^{-1}, 30.50 MPa and 5.15%, respectively. These values were obtained when the independent variables, i.e., glycerol concentration and coating weight were 20.42% and 4.55 g/m^2, respectively.

Kjellgren et al. (2006) studied the conditions necessary to obtain good barrier and surface properties of chitosan-coated greaseproof paper. A coating weight of 5.2 g/m^2 was required to obtain a packaging material with good barrier properties against oxygen, nitrogen, carbon dioxide and grease as well as high fracture strain.

For each biopolymer used, the obtained value of desirability (>0.95) shows that the estimated function may represent the experimental model and desired conditions (Table 5).

The results of simultaneous optimization parameters, for each biopolymer used, were validated by repeating the experiment at the conditions predicted. The comparison between predicted and experimental values showed excellent correlation. The predicted and experimental responses were not significantly different at 5% significance level.

4. Conclusion

The properties of biopolymer-coated papers were influenced by biopolymer type, glycerol concentration, and coating weight. With regards to WVP data, the coating weight had a negative effect while the glycerol had a positive effect. The glycerol concentration had a positive influence on the %*E* values and a negative effect on the TS of the papers coated with NaCAS and NaAlg; whereas, the coating weight affected positively both TS and %*E*. For all types of coated paper, the optimum conditions that yield minimum WVP and maximum TS and %*E* correspond to a maximum level of coating weight and level of glycerol concentration within range of 18.72–26.11%.

Biopolymer-coating on paper packaging materials are very promising systems for the future improvement of food packaging. The use of such biopackagings will open up potential economic benefits to farmers and agricultural processors. However, further investigation is still needed to verify the properties of coated paper with specific products.

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