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Effect of Glycerol and Hydrophobic Silica on the Mechanical and Surface Properties of Starch-based Films: A Response Surface Methodology Approach

ABSTRACT

Starch-based films are promising biodegradable alternatives to conventional polymeric materials. However, their poor mechanical properties and high affinity for water limit their practical applications. The combined effects of plasticizer and hydrophobic nanoparticle content on the mechanical and surface properties of starch-based films remain insufficiently understood. In this study, potato starch films containing glycerol and hydrophobic nano-silica were prepared and characterized for their mechanical properties and surface free energy. Response Surface Methodology (RSM) was used to evaluate the effects of film composition and identify a formulation that balances mechanical and surface properties, with potential applications in printing technologies.

KEY WORDS
Starch films, mechanical properties, surface free energy, design of experiment, response surface methodology

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1. Introduction

Starch is a readily available, biodegradable, inexpensive, and renewable polysaccharide and can be harvested without destroying the plant (Ray, Narayan Das & Das, 2021; Ojogbo, Ogunsona & Mekonnen, 2020). It is well known that starch exhibits filmogenic properties and, upon processing, can form films that are green, environmentally friendly, and biodegradable alternatives to plastic materials intended for various applications (Colivet & Carvalho, 2017; Freitas, González-Martínez & Chiralt, 2023). Films formed from starch are isotropic, odorless, tasteless, colorless, non-toxic, and biodegradable (A'yun & Bintoro, 2021; Castro et al., 2022).

Among the many disadvantages of these materials, the most significant are their poor mechanical properties and affinity for water. These limitations hinder their widespread commercial application. Therefore, various strategies have been developed to overcome these limitations and improve the overall performance of starch-based materials. For example, modifications to starch can be performed to improve its final properties. For example, UV-B irradiation or cold plasma to modify the properties of corn and potato starches (Kurdziel et al., 2022; da Fonseca de Albuquerque et al., 2022). Another solution is to develop various blends or enhance the properties of starch-based films with nanoparticles, such as micro- or nanocellulose (Żołek-Tryznowska et al., 2023), nanoclays (Muangmala et al., 2026), or metal oxide nanoparticles (Dhiman et al., 2025).

Response surface methodology (RSM) can be successfully applied for the optimization of starch-based materials. Tessema et al. have applied a Box-Behnken experimental design from response surface methodology to optimize the levels of anchote starch, glycerol, and acetic acid for the development of edible films (Tessema, Admassu & Dereje, 2023). The optimum level results in a film with maximum tensile strength (10.076 MPa) and elonga-

tion at break (33.95%) at 3.801% w/v anchote starch, 28.566% w/w glycerol, and 0.1% w/v acetic acid concentration (Tessema, Admassu & Dereje, 2023), which are values comparable to low-density polyethylene (tensile strength ~ 10MPa) (Szlachetka et al., 2021). Furthermore, Gupta et al. combined RSM methodology along with an artificial neural network coupled with a genetic algorithm to predict the effect of the concentration of independent variables on the responses (Gupta, Guha & Srivastav, 2026). However, the tensile strength of taro starch optimized with the combined RSM model was much lower (~2.45 MPa) than that of anchote starch. Tafa et al. used the RSM approach to optimize tef starch films, reporting tensile strength of 17.97–24.25 MPa, elongation at break of 1.21–2.03%, and elastic modulus of 17.58–108.69 MPa (Tafa, Satheesh & Abera, 2023).

In this study, hydrophobic nano-silica was incorporated into starch-based films to simultaneously modify their surface and mechanical properties. The effects of hydrophobic nano-silica content (up to 0.5) and glycerol concentration, used as a plasticizer, on the surface and mechanical properties of the resulting starch/silica composites were systematically investigated. A Design of Experiments (DoE) approach, with some modifications, combined with Response Surface Methodology (RSM), was employed to evaluate the effects and interactions of these formulation variables and to determine the optimal composition of the composite films. The optimized formulation is expected to provide a promising starch-based material with properties suitable for printing applications.

2. Methods

2.1. Materials

Potato starch (CAS 9005-25-8), glycerin (purity ≥ 99%, CAS 56-81-5) as a plasticizer, and diiodomethane (purity ≥ 99%, CAS 75-11-6) for contact angle measurements, and ethanol (purity ≥ 96%, CAS 64-17-5) for silica solubilization were purchased from Sigma-Aldrich. Amorphous, hydrophobic silica, Aerosil R 972 (CAS 68 611-44-9) with a BET specific surface area of 90–130 $m^2 \cdot g^{-1}$, an average particle size of 16 nm, and a carbon content of 0.6–1.2 wt.%, was purchased from Evonik. All reagents were used as received.

2.2. Experiment design

Response surface methodology (RSM) was applied to evaluate the combined effects of glycerol and hydrophobic silica content on the mechanical and surface properties of starch-based films. The experimental design was based on a central composite design (CCD) geometry with two formulation factors. The initial design comprised four factorial and four axial points and was subsequently supplemented with an independently prepared center-point formulation and independent replicates of two axial formulations. The two independent variables were glycerol (28.28–91.72%) and silica (0.25–0.50 g) content, while the thickness, tensile strength, and SFE properties of the composite film were evaluated. The ranges of independent parameters were selected based on our previous results (Żołek-Tryznowska et al., 2024). The experimental dataset comprised the initial eight formulations (Z1–Z8) and three additional independently prepared films, including repeated formulations at 28.28% glycerol/0.375 g SiO_2 and 91.72% glycerol/0.375 g SiO_2, as well as an additional formulation at the design center (60% glycerol/0.375 g SiO_2).

2.3. Film production

The film production description was shown in our previous works (for example, see (Żołek-Tryznowska et al., 2024)).

All reagents (starch, plasticizer, and water) were heated up to 95 °C upon stirring with a mechanical stirrer. The silica was dissolved in 20 mL of ethanol, homogenized, and added to the starch suspension, and mixed. Next, the starch suspension was cast onto the Teflon® plates and dried in the climate room for one week under controlled conditions (23 ± 0.5°C; 50 ± 1% RH). When the samples dried, they were carefully torn off. The mechanical and surface free energy measurements were conducted one week after film preparation to ensure repeatability.

2.4. Film properties

The thickness for the mechanical measurements was measured with a hand-held micrometer with 0.001 mm resolution and an error of ±0.5 mm. The mechanical properties were determined using a Z010 tensiometer (Zwick-Roell, Germany) in accordance with ISO 527-1. The measurements were performed using specimens with dimensions of 15 mm in width and 100 mm in length. The initial grip separation was set to 50 mm, while the stretching rate was maintained at 100 $mm \cdot min^{-1}$. The tensile strength (TS), elongation at break (EaB), and Young's modulus (YM) were determined from the corresponding stress–strain curves.

The surface free energy was determined using the Drop Shape Analysis System (DSA 30E, Krüss, Germany) from the contact angles of formamide and diiodomethane using the Owens-Wendt method (Owens & Wendt, 1969). Due to the hydrophilic properties of the starch film and its affinity for water, we eliminate water contact angle measurements.

2.5. Statistical analysis

The experimental data were analyzed using STATGRAPHICS Centurion 19.1.3. Quadratic models containing linear effects (A, B), interaction (AB), and quadratic terms (A^2, B^2) were initially considered. Model reduction was performed by removing unsupported higher-order terms while maintaining model hierarchy. The final models were selected based on analysis of variance (ANOVA), coefficient significance, model complexity, coefficients of determination (R^2 and adjusted R^2), predicted R^2, prediction error sum of squares (PRESS), and the physical interpretability of the response.

3. Results and discussion

In this work, we apply response surface methodology to investigate the synergistic effect of glycerol and hydrophobic silica content on several parameters of starch-based films. The experimental design was performed using CCD with some modifications. Table 1 presents the experimental design and responses used in modeling. The RSM was used to study the linear, quadratic, and interaction effects of glycerol and silica content on the studied responses.

Table 1

Data values of variables and responses: Young's modulus (YM), tensile strength (TS), elongation at break (EaB), thickness (h), total surface free energy (SFE), and its polar and dispersive components

Entry	Sample	Independent variables		Responses						
		Glycerol (%)	Silica (g)	YM (MPa)	TS (MPa)	EaB (%)	h (µm)	SFE total (mN/m)	SFE polar (mN/m)	SFE dispersive (mN/m)
1	Z1	40.00	0.250	6.16	0.96	40.90	181.00	53.42	22.82	30.61
2	Z2	80.00	0.250	86.79	2.98	48.38	166.75	51.88	10.37	41.51
3	Z3	40.00	0.500	138.83	3.84	46.67	116.22	55.68	21.86	33.82
4	Z4	80.00	0.500	30.30	2.24	36.20	165.70	35.89	1.13	34.76
5	Z5	28.28	0.375	1073.10	18.05	9.43	118.50	53.29	20.46	32.83
6	Z6	91.72	0.375	13.75	1.47	43.10	183.80	46.96	9.15	37.81
7	Z7	60.00	0.250	86.17	3.23	59.10	115.20	53.04	14.73	38.31
8	Z8	60.00	0.500	60.50	2.95	48.00	127.70	56.13	22.32	33.80
9	Z5	28.28	0.375	312.00	6.32	34.00	138.80	52.14	13.29	38.85
10	Z6	91.72	0.375	5.02	0.80	–	198.40	52.31	13.79	38.52
11	Z9	60.00	0.375	14.60	1.50	54.00	202.50	52.59	12.28	40.31

Table 2

Summary of the fitted RSM models for mechanical properties, film thickness, and surface free energy: A – glycerol content; A^2 – quadratic effect of glycerol content; 2FI – two-factor interaction model

Response	Model	p-value	R^2	Adj. R^2	Significant terms
Et	Linear	0.1803	0.3484	0.1855	*p > 0.05*
σM	Linear	0.1713	0.3566	0.1958	*p > 0.05*
εtB	Quadratic	0.0648	0.6757	0.5136	*A^2: p < 0.05*
h	Linear	0.1440	0.3840	0.2300	*p > 0.05*
Total SFE	2FI	0.1192	0.5444	0.3492	*p > 0.05*
Polar SFE	Linear	0.1278	0.4021	0.2526	*A: p < 0.05*
Dispersive SFE	2FI	0.1446	0.5161	0.3087	*p > 0.05*

The adequacy of the fitted response surface models was evaluated using analysis of variance (ANOVA), model p-values, coefficients of determination (R^2 and adjusted R^2), standard error, and the prediction error sum of squares (PRESS). The experimental responses and the statistical parameters of the fitted models are summarized in Table 2. Depending on the response, reduced linear, interaction, or quadratic models were selected after eliminating unsupported higher-order terms while preserving the model hierarchy. R2 ranged from 0.3484 to 0.6757 for the mechanical properties and from 0.4021 to 0.5444 for the surface free energy components. Although the overall models did not reach statistical significance at the 0.05 level (p = 0.0648–0.1803), individual model terms revealed significant formulation effects. In particular, the quadratic effect of glycerol content on elongation at break was significant (A^2, p=0.0293), while glycerol content significantly affected the polar component of SFE (p=0.0495). Therefore, the fitted models were used primarily to describe response trends within the investigated experimental domain and to support multi-response desirability analysis rather than for unrestricted prediction outside the studied factor ranges.

After model reduction, the final regression equations, expressed in terms of the actual factor levels, were obtained to describe the effects of glycerol and silica contents on the mechanical properties, film thickness, and surface free energy components, as shown in Eqs 1–7.:

$$YM = 609.132 - 7.8046A + 67.3467B \quad (1)$$

$$TS = 10.4893 - 0.123139A + 2.48B \quad (2)$$

$$EaB = -30.6074 + 2.88338A - 23.3467B - 0.0224156A^2 \quad (3)$$

$$h = 132.757 + 0.829641A - 71.1067B \quad (4)$$

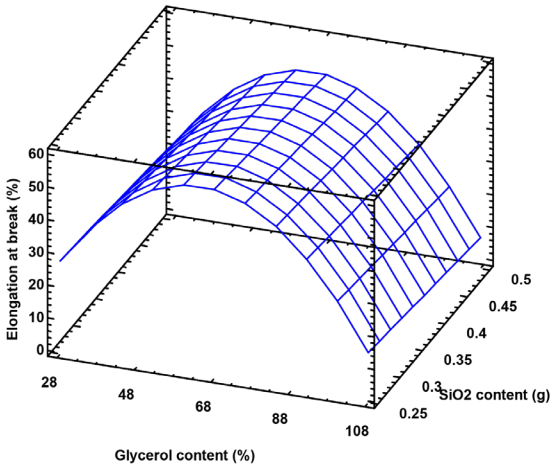
$$SFE_{total} = 22.1044 + 0.5738A + 95.3133B - 1.8250AB \quad (5)$$

$$SFE_{polar} = 26.7871 - 0.1789A - 3.4800B \quad (6)$$

$$SFE_{dispersive} = 13.9819 + 0.4418A + 49.0267B - 0.9960AB \quad (7)$$

where A is glycerol content (%), and B is silica content (g).

The fitted linear model showed a negative relationship between glycerol content and YM and TS, while the effect of silica on YM and TS is positive. However, there is no statistical significance (p < 0.05). Furthermore, the EaB initially increases at lower-to-intermediate glycerol content and then decreases at higher glycerol levels (see Figure 1). This is related to the fact that glycerol exhibited a significant quadratic effect on EaB (A^2, p = 0.0293). In contrast, silica showed a negative but non-significant effect on EaB. This tendency corresponds to the expected plasticizing effect of glycerol, which increases molecular mobility by spreading the starch chains and consequently lowers the stiffness of the polymer matrix. Finally, glycerol and silica have positive and negative effects on film thickness, respectively.



» **Figure 1:** *Response surface plot for EaB*

The glycerol-silica formulation had a markedly greater influence on the SFE components than on the total surface free energy. Increasing glycerol content significantly decreased the polar SFE component (p<0.05). This effect has been observed in other studies and is related to the presence of hydroxyl groups in glycerol. Increasing the hydrophobic silica content up to 0.50 g did not significantly (p>0.05) lower the polar component of the film surface free energy, indicating that the increase in hydrophobicity of the film was not significant. The dispersive component showed opposite trends, increasing with glycerol and decreasing with SiO_2 content, although these effects were not statistically significant (p>0.05).

Numerical optimization was performed to determine the compromise between the mechanical and surface performance. Therefore, Young's modulus, tensile strength, and elongation at break were maximized, while film thickness and the total surface free energy were targeted at 150 µm and 52 mN/m, respectively. Considering the hydrophobic nature of the silica filler, the polar component of surface free energy was minimized, whereas the dispersive component was maximized. The optimum composition was obtained at approximately 52.88% glycerol and 0.3745 g silica, with an overall desirability of ~0.592 (see Table 3). Furthermore, the predicted composition lies within the experimental factor space, close to the central point, increasing its practical relevance as a candidate for formulation for further validation. Unfortunately, the predicted R2 values for individual models were low; the predicted composition should not be treated as a global optimum; and a validation experiment with a film containing approximately 53% glycerol and 0.375 silica should be performed.

Table 3
Multi-response desirability optimization of glycerol and silica contents and predicted properties of the starch-based films.

Response	Optimization goal	Criterion	Predicted value	Individual desirability
YM (MPa)	Maximize	Max. = 300	221.66	0.739
TS (MPa)	Maximize	Max. = 6.5	4.91	0.755
EaB (%)	Maximize	Max. = 60	50.44	0.841
h (µm)	Target	150	150.00	1.000
Total SFE (mN/m)	Target	52	52.00	1.000
Polar SFE (mN/m)	Minimize	—	16.02	0.303
Dispersive SFE (mN/m)	Maximize	—	35.98	0.498

Overall desirability: D = 0.592

4. Conclusions

This study investigated the combined effects of glycerol and hydrophobic nano-silica on the mechanical and surface properties of starch-based films. Glycerol content significantly affected elongation at break and the polar component of surface free energy, whereas the effect of silica was less pronounced within the investigated concentration range. Despite the limited predictive ability of the fitted models, Response Surface Methodology enabled the identification of formulation trends and supported multi-response optimization. A formulation containing approximately 53% glycerol and 0.375 g silica was identified as a promising balance between mechanical and surface properties. Further studies should validate this formulation experimentally and evaluate its printability.

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