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Design and Optimization of Eco-Friendly Biocomposite Films for Packaging Applications Using Response Surface Methodology

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Abstract

The use of synthetic polymers as packaging materials constitutes environmental pollution due to the accumulation of plastic waste after they are discarded. This study aimed at preparing and optimizing an environmental-friendly carboxymethyl starch/PVA/kaolin composite film using response surface methodology to develop potential solutions for replacing synthetic packaging and optimize the formulation of the biocomposite films. The biocomposite films were prepared by solution casting method. The interactive effect of carboxymethyl starch (CMS) (2.0-5.0 g), poly(vinylalcohol) (PVA) (0.0-3.0 g) and kaolin (0.00-0.22 g) on the ultimate tensile strength (UTS), percentage elongation at break (%EB) and water vapour permeability (WVP) were determined. The central composite design (CCD) was used to optimize the compositions of the composite films to yield best properties. The results showed that the interaction of PVA and kaolin with the carboxymethyl starch had a positive increasing effect on the tensile mechanical and barrier properties of the composite films. The optimal compositions of the composites obtained at 95.4% desirability were 3.33 g CMS, 2.39 g PVA and 0.22 g kaolin. Also, the predicted optimal values of the ultimate tensile strength, %EB and WVP of the composites were 5.71 MPa, 23.57% and 1.08 g/m·s.Pa.

Keywords: Carboxymethyl starch; Biocomposite; Water vapour permeability; Response surface methodology; Tensile mechanical properties

Introduction

The production and consumption of plastics have greatly expanded globally over the last several years. This has also brought about a rising incidence of environmental problems emanating from plastic waste disposal (Avella et al. 2005). Among plastic packaging, plastic films alone account for 34% of the total demand for plastics and offer one of the largest market in the plastic industry (Horodytska et al. 2018). Plastics on account of their non-biodegradability and derivability from non-renewable sources are associated with environmental pollution (Perumal et al. 2018). Recently, the development of biodegradable packaging materials from natural polymers such as starch, chitosan, cellulose, gelatin, lignin and many others is gaining overwhelming interest in the field of research (Perumal et al. 2018). Among these renewable polymers, starch stands out due to its extensive availability, low cost, excellent biocompatibility, non-toxicity, and renewability, making it a valuable resource (Omoike and Okieimen 2022, Souza et al. 2010).

Several studies have investigated native starch-based films. However, major limitation in the use of starch is its poor tensile strength and high water vapour

permeability (Yang et al. 2021). To enhance the application of native starch-based films, its properties could be modified by blending starch with other biopolymer (e.g. PVA, gelatin, chitosan etc.) (Patil et al. 2021), addition of reinforcing fillers (e.g. bentonite, kaolin, cellulose, keratin) (Hazrol et al. 2022) or by use of chemically modified starch (Yang et al. 2021). Chemically modified starches include oxidized starch, cross-linked starch, etherified starch, esterified starch and grafted starch.

Carboxymethyl starch is an etherified starch (modified starch) use in medicine, pharmacy, cosmetics, food industry, packaging and many other applications (Spychaj et al. 2013). It is produced through the Williamson reaction, where native starch reacts with monochloroacetic acid or its sodium salt to introduce carboxymethyl groups into the starch structure, especially at C1, C2, and C3 positions (Yanli et al. 2009). Unlike native starch, carboxymethyl starch has a lower gelatinization temperature and does not tend retrodegrade. Addtionally, it has good thermal stability and film-forming properties which increases significantly with its degree of substitution (Spychaj et al. 2013). Limited studies have been reported on CMS-based films. Yang et al. (2021) prepared cross-linked CMS-based composite films and studied the effect of cross-linking agents and additives on the properties of the composite films. Wilpiszewska et al. (2015) produced CMS/montmorillonite nanocomposite films and examined the effects of calcium montmorillonite on the physico-mechanical properties of the films. However biodegradable films from pure carboxymethyl starch are still limited in the field of packaging because of its moisture absorption and low flexibility. High moisture absorption in carboxymethyl starch can compromise its structural integrity and shelf-life by causing swelling, loss of mechanical strength and degradation, ultimately leading to a reduction in its performance. Therefore, it is extremely appropriate to blend CMS with other polymers such as poly(vinyl alcohol), poly(ethylene glycol). These polymers possess the ability to enhance flexibility, boost mechanical strength and reduce sensitivity to moisture, thereby improving their overall performance and durability.

Poly(vinyl alcohol) is a semicrystalline, non-toxic and environmental-friendly polymer. It is biodegradable under certain conditions, particularly in the presence of specific microbial environments (Alexy et al. 2002). Its outstanding thermal stability (Tudorachi et al. 2000), excellent barrier properties, biocompatibility and superior film-forming capabilities (Yun et al. 2008) make it an ideal candidate for blending in biocomposite films (Omoike and Okieimen 2022). Many studies have reported the properties, applications and modification of starch/PVA composite films (Patil et al. 2021, Hazrol et al. 2022). In order to further enhance the properties and applications of starch/PVA films reinforcing agents, such as nanoclays, cellulose nanofibers, and montmorillonite, are employed.

The incorporation of reinforcing fillers has been reported as a good approach to improve properties of starch-based films. Various fillers which have often been used include silver nanoparticles, zinc oxide and montmorillonite clay. Clay is a non-toxic and environmentally friendly natural mineral which finds useful applications in the industry (Chen and Evans 2005). Several kinds of clay exist, with montmorillonite and kaolinite being among the most popular. In this study, kaolin clay was selected as a reinforcement material due to its cost effectiveness, widespread availability and good reinforcing properties. The improvement in material properties of starch-based composites on incorporation of montmorillonite clay has been widely reported. There are only a few reports on the use of kaolin clay as a reinforcing filler for improving properties of CMS-based films (Kwa´sniewska et al. 2020).

The purpose of this study is to prepare and optimize the composition of biocomposite films based on CMS/PVA/kaolin with potential application as packaging. Various factors that contribute individually or synergistically to the properties of CMS-based composite films were examined.

Response surface methodology was used to optimize the composition of the film. CMS, PVA and kaolin were considered as independent variables to obtain desired optimum properties: ultimate tensile strength, percentage elongation at break and water vapour permeability as the responses

Materials and Methods

Materials

Carboxymethyl starch of degree of substitution of 0.71), poly(vinyl alcohol) (PVA) and glycerol were obtained in analytical grades from a chemical store in Benin City. Kaolin clay, known for its high purity, was obtained from a factory in Auchi, Edo State. All other chemicals and reagents were of analytical grade.

Preparation of carboxymethyl starch/PVA/kaolin composites

Carboxymethyl starch/PVA film reinforced with kaolin clay was prepared by solution casting method (Hejri et al. 2013); a process that involves pouring a liquid solution into a mold, followed by controlled evaporation, which enables the formation of a solid film. First, PVA was dissolved in 60 ml of distilled water at 90 ^{o}C for 30 mins with stirring to achieve complete dissolution. After the dissolution of PVA, a dispersion of CMS was added to the PVA solution and was followed by addition of glycerol (30% of the total dry weight of starch and PVA). The whole mixture was stirred in a magnetic stirrer for 30mins at 50-60 ^{o}C for gelatinization, which involves the swelling of starch granules and the subsequent release of amylose and amylopectin into the solution, enhances film properties; and finally homogenization of the mixture. Thereafter a suspension of kaolin clay was introduced into CMS/PVA filmogenic solution with constant stirring in a magnetic stirrer for 20 mins. The homogenized mixture was poured on a glass plate of dimensions 10 cm x 10 cm. It was dried in an oven at 60 ^{o}C for 16 hours. Thereafter, the glass plate was removed. On cooling, the dried films were peeled off the glass plate and stored in a desiccator prior to further analysis. The thickness of the films was controlled by measuring a known volume of the film solution in the glass plate.

Optimization of carboxymethyl starch/PVA/kaolin composites by response surface methodology (RSM)

Central Composite Design (CCD) based on Response Surface Methodology (RSM) was used to optimize the composition of CMS-based composite. A three-factor at five levels CCD was employed to evaluate the effects of the independent variables considered on the responses. The independent variables were starch (X_1), PVA (X_2) and kaolin (X_3). The levels of independent variables and the code of variables are presented in Table 1.

Table 1: Coded levels of variables

Independent Variables	Symbols	Coded Levels				
		-∝	**-1**	**0[a]**	**+1**	**+∝**
Starch (g)	X_1	2.00	2.61	3.50	4.39	5.00
PVA (g)	X_2	0.00	0.61	1.50	2.39	3.00
Kaolin (g)	X_3	0.00	0.06	0.14	0.22	0.275

[a]center points, k=3 (independent variables), $\propto$ = 1.6818

The mathematical relationship between the process variables and response were calculated and fitted to the quadratic polynomial expression given in Equation 1 (Myers and Montgomery 1995)

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ij} X_i^2 + \sum_{\substack{i=1 \\ i<j}}^{3} \beta_{ij} X_i X_j + e \qquad (1)$$

Figure 1: Schematic illustration of the preparation of the optimized films

Evaluation of properties of carboxymethyl starch-based composite film

The following properties of CMS/PVA/kaolin films were determined as described below:

Tensile mechanical properties

Prior to the tensile testing, the films were cut into strips of dimensions 3 cm x 15 cm and conditioned in a desiccator for 48 hours. The tensile mechanical properties of the films including ultimate tensile strength and percentage elongation at break were determined using a universal testing machine (TecQuipment, India), which applied tensile forces to materials in accordance with standard procedures outlined in ASTM D882-91 and as described in earlier publication by Noshirvani et al. (2016). This allows for accurate measurement of their tensile mechanical behaviour.

Water vapor permeability

Water Vapour Permeability (WVP) of films was determined gravimetrically in accordance with the ASTM E96-95 desiccant method as described by Kashiri et al. (2017). Permeation cup of dimensions 4 cm diameter and 3.5 cm depth was used for this experiment. The cup contained 7.0 g of anhydrous silica gel to serve as desiccant. The test film was cut into circular disc (diameter 5.5 cm) and mounted on the top surface of the cup. The cup with its contents was initially weighed in an analytical balance before placing in a desiccator containing saturated solution of NaCl. The saturated solution of NaCl maintains a constant relative humidity of 75%. The test cup was periodically weighed every 24 hours for 5 days under room temperature conditions. The amount of water vapour permeated through the film was calculated from the weight gain of the cup. The water vapour transmission rate (WVTR) through the film was calculated from the slope of the plot (S) divided by the exposed film area (A) (Eqn. 2). This was multiplied by the thickness of the film and divided by partial pressure difference across the two sides of the film to obtain the WVP, as shown in equation 2 and equation 3.

$$\text{WVTR} = \frac{S}{A} \quad (2)$$

$$\text{WVP} = \frac{WVTR}{S_{vp}(R_1 - R_2)} X\, h \quad (3)$$

Where h is the mean film thickness (in m), S_{vp} is the saturated vapour pressure (in Pa) at the tested temperature, R_1 is the relative humidity at the test chamber expressed as a

fraction, and R_2 is the relative humidity at the vapour sink expressed as a fraction.

Results and Discussion

Optimization of CMS-based composites based on response surface methodology (RSM)

The results of the 20 conducted experiments used to determine the tensile strength, percentage elongation at break and WVP of the CMS-based composite films based on the central composite design are presented in Table 2.

Table 2: Independent variables and responses of central composite design of composites

Runs	Actual Variables			Responses					
	CMS (X_1) (g)	PVA (X_1) (g)	Kaolin (X_1) (g)	Tensile strength (Y_1) (MPa)		Elongation at break (Y_2) (%)		WVP × 10^{-11} (Y_3) (gm/m^{2}sPa)	
				Actual	Predicted	Actual	Predicted	Actual	Predicted
1	2.61	2.39	0.22	6.04	5.91	21.48	22.61	1.44	1.73
2	3.50	1.50	0.14	3.82	3.84	30.45	31.99	2.32	2.38
3	3.50	1.50	0.00	2.52	2.33	28.78	29.22	2.57	2.72
4	4.39	2.39	0.06	2.95	3.11	33.09	34.14	2.59	2.59
5	3.50	1.50	0.14	4.00	3.84	31.84	31.99	2.34	2.38
6	2.61	0.61	0.22	3.98	3.95	25.10	23.59	2.88	2.92
7	3.50	3.00	0.14	5.46	5.34	28.35	28.92	1.07	1.30
8	4.39	0.61	0.06	2.12	2.38	42.65	41.07	4.25	4.00
9	2.00	1.50	0.14	3.82	3.98	24.66	25.01	3.73	3.53
10	3.50	1.50	0.28	4.95	4.94	20.23	20.43	1.35	1.14
11	2.61	2.39	0.06	3.56	3.63	30.85	29.03	2.86	2.53
12	5.00	1.50	0.14	3.26	2.91	40.33	40.62	3.45	3.59
13	3.50	1.50	0.14	3.98	3.84	33.05	31.99	2.52	2.38
14	3.50	0.00	0.14	3.15	3.08	35.48	35.56	3.78	3.48
15	3.50	1.50	0.14	3.88	3.84	34.23	31.99	2.31	2.38
16	4.39	2.39	0.22	4.86	5.07	27.35	25.66	1.44	1.12
17	4.39	0.61	0.22	3.14	3.20	35.68	37.04	2.54	2.92
18	3.50	1.50	0.14	3.58	3.84	32.00	31.99	2.05	2.38
19	3.50	1.50	0.14	3.75	3.84	30.50	31.99	2.74	2.38
20	2.61	0.61	0.06	2.88	2.81	24.33	25.56	2.95	3.32

The independent variables considered in the experiment were CMS, PVA and kaolin. The tensile strength, percentage elongation at break (%EB) and WVP were found to be in the range of 2.12 MPa to 6.04 MPa, 20.23% to 42.65% and 1.07 g/m·s.Pa to 4.25 g/m·s.Pa respectively. The highest tensile strength was 6.04 MPa which was obtained with 2.61 g CMS, 2.39 g PVA and 0.22 g kaolin. The highest %EB of 40.33% was obtained with 4.39 g CMS, 0.61 g PVA and 0.06 g kaolin while the lowest value of WVP was 1.07 g/m·s.Pa and was found at 3.50 g CMS, 3.00 g PVA and 0.14 g kaolin. The tensile strength, % EB and WVP of the prepared films were analyzed using RSM-CCD to determine the effects of the independent variables on the responses.

Analysis of variance of the tensile strength, %EB and WVP

Analysis of variance (ANOVA) was employed in fitting the quadratic response surface models by the least squares method and to test the extent of suitability of the models at a confidence level of 95% (5% significance level). The quadratic regression

models for tensile strength, %EB and WVP of the composite materials were found to be highly significant with large F-values of 38.47, 23.81 and 11.62 respectively and very low p-values of < 0.0001, < 0.0001 and 0.0003 respectively. The lack of fit for tensile strength, %EB and WVP was insignificant. The insignificant lack of fits of the models indicates that all three models fit the process, which is a desirable outcome (Fitriani et al. 2022).

Fit statistics of the models

The features of the models were further described using the fit statistics as given in Table 3. From Table 7, the coefficient of variation (C.V.) of 5.87, 5.50 and 13.42% respectively for TS, %EB and WVP of the composite materials are within acceptable range, since C.V. describes the amount of variability in a data set relative to its mean value. A smaller coefficient of variation (C.V.) indicates better reproducibility, as it represents a lower standard deviation relative to the mean. Conversely, a high C.V. suggests higher variability in the data, indicating that the mean value is less reliable and more susceptible to fluctuations (Daniel 1991).

Table 3: Fit Statistics of TS, %EB and WVP of the models

Parameters	TS	%EB	WVP
Standard deviation	0.22	1.68	0.34
Mean	3.78	30.52	2.56
Coefficient of variation, C.V. (%)	5.87	5.50	13.42
R^2	0.9719	0.9554	0.9127
Adjusted R^2	0.9467	0.9153	0.8342
Predicted R^2	0.8273	0.7259	0.4062
Adequate Precision	22.7623	17.3726	11.8763

The suitability of the models was tested using the coefficient of determination (R^2). The high values of the R^2 for tensile strength, %EB and WVP of 0.9719, 0.9554 and 0.9127 respectively are close to unity (1), indicating that the fitted models could predict reasonably precise outcome (Suwanthai et al. 2016). The Predicted R^2 values of 0.8273 and 0.7259 for TS and %EB respectively are in reasonable agreement with the Adjusted R^2 values of 0.9467 and 0.9153 (i.e. their difference is less than 0.2) while for WVP, the predicted R^2 value of 0.4062 did not reasonably agree with the adjusted R^2 value of 0.8342. Adequate precision is a measure of how well a model can predict responses across the entire design space. It is calculated as the ratio of the range of predicted values to the average prediction interval. A ratio greater than 4 is generally considered sufficient. The adequate precision values obtained for tensile strength, %EB and WVP are 22.7623, 17.3726 and 11.8763 respectively indicating adequate signals. The signal-to-noise ratio compares the magnitude of the signal (response variable) to the magnitude of the noise (experimental error). High signal-to-noise ratio leads to high adequate precision indicating that the predictions are more reliable and trustworthy. This shows that the models can be used to navigate the design space.

Regression models of composite process

The empirical models obtained for the tensile strength, %EB and WVP are given in equation 4-6 in terms of the coded values. It is important to note that this equation is only valid within the limits of the experimental conditions stated in this study. The value of the coefficients indicates the strength of the relationship while the sign of the coefficients indicates the direction of the relationship. The positive coefficients indicated a favourable effect while the negative coefficients suggest a diminishing effect on the responses (Fitriani et al. 2022).

$Y_1 = 3.84 – 0.3172X_1 + 0.6718X_2 + 0.7759X_3 – 0.0238\ X_1X_2 – 0.0813\ X_1X_3 + 0.2837X_2X_3 – 0.1402X_1^2 + 0.1302X_2^2 – 0.0713\ X_3^2$ (4)

$Y_2 = 31.99 + 4.64X_1 - 1.98X_2 - 2.61X_3 – 2.60X_1X_2 – 0.5137X_1X_3 – 1.11X_2X_3 + 0.2916X_1^2 + 0.0865X_2^2 – 2.53X_3^2$ (5)

$Y_3 = 2.38 + 0.0160X_1 – 0.6479X_2 - 0.4688X_3 – 0.1537X_1X_2 – 0.1712X_1X_3 - 0.0987X_2X_3 + 0.4159X_1^2 + 0.0040X_2^2 – 0.1604X_3^2$ (6)

A higher value of regression coefficient indicates a greater effect of the independent variable on the response. Kaolin (X_3) had the greatest significant effect on the tensile strength, CMS (X_1) showed the most significant effect on the %EB while PVA had the most dominant effect on WVP. From Eqn. 4, among the main factors, CMS (X_1) had negative effect on the tensile strength of the composite film (i.e. an increase or decrease in CMS will lead to a corresponding decrease or increase in the tensile strength of the composite films) while PVA and kaolin (X_2 and X_3) had positive effects on the tensile strength of the composite film (i.e. increase or decrease in PVA or kaolin will lead to a corresponding increase or decrease in the tensile strength of the composite films). Equation 5 shows that all the three independent variables (X_1, X_2 and X_3) have negative effects on the percentage elongation at break of the composite films. In equation 6, CMS(X_1) has a negative effect, while PVA (X_2) and kaolin (X_3) have positive effects on the water vapour permeability of the composite films. In other words, increasing CMS (X_1), decreases water vapour permeability; while increasing PVA (X_2) and kaolin (X_3) increases water vapour permeability. The results obtained showed the composites were satisfactorily fit by quadratic models for tensile strength, % EB and WVP.

Effects of interaction of factors on tensile strength, %EB and WVP of composite material

Figure 2, 3 and 4 shows the 3D response surface and contour plots of the effects of CMS, PVA and kaolin as independent variables on the tensile strength, %EB and WVP respectively using equation 4-6. The 3D response surfaces were generated by holding one variable at its average value while systematically varying the other two variables thus creating a visual representation of the relationships between the variable and the response.

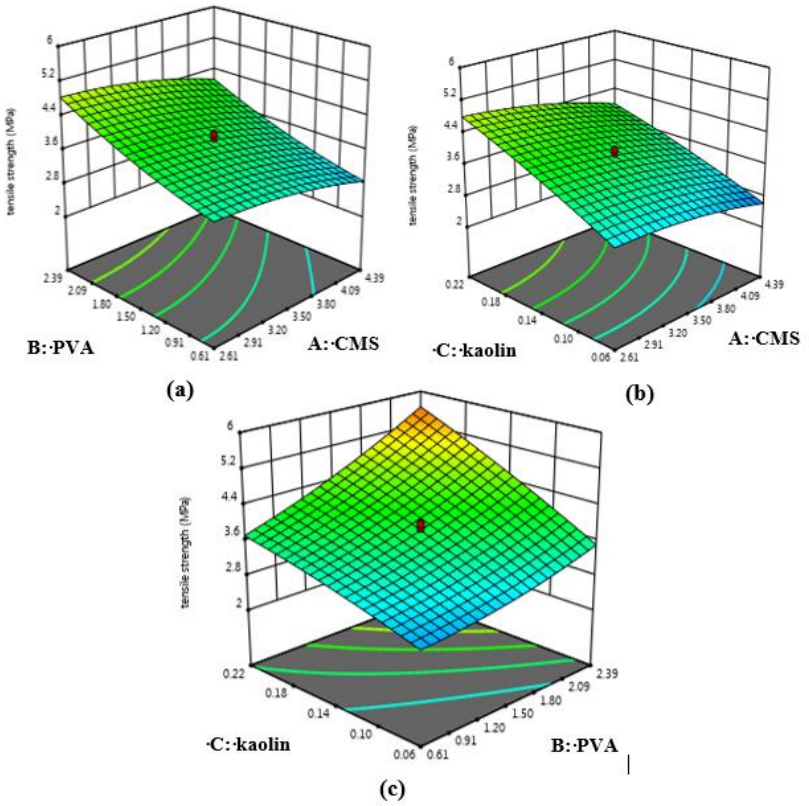

Figure 2: Response surface plots showing the effects of (a) CMS and PVA composition (b) CMS and kaolin composition and (c) PVA and kaolin composition on the tensile strength of the composite material

Figure 2 reveals a quadratic effect of CMS, PVA, and kaolin on tensile strength. This means that the relationships between these variables and tensile strength are non-linear. Upon examining Figures 2a and 2b, it is evident that increasing PVA and kaolin leads to a significant increase in tensile strength. In contrast, increasing CMS slightly decreases tensile strength. This suggests that PVA and kaolin have a synergistic effect on enhancing tensile strength, while CMS has a negative impact. Furthermore, the analysis reveals that kaolin has the most significant effect on tensile strength, followed by PVA. This indicates that kaolin is the primary driver of tensile strength, while PVA also plays a crucial role. The optimal values for tensile strength were identified in each figure. In Figure 2a, the highest tensile strength of 4.82 MPa was achieved at 2.61g CMS and 2.37g PVA. In Figure 2b, the highest tensile strength of 4.79 MPa was obtained at 2.62g CMS and 0.22g kaolin. Notably, Figure 2c shows the highest tensile strength of 5.60 MPa at 2.37g PVA and 0.22g kaolin.

Overall, the analysis demonstrates that kaolin and PVA are critical variables in enhancing tensile strength, while CMS has a limited negative impact. The optimal combinations of these variables result in varying levels of tensile strength, with the highest value achieved at 2.37g PVA and 0.22g kaolin. These insights are important for future material development and optimization strategies.

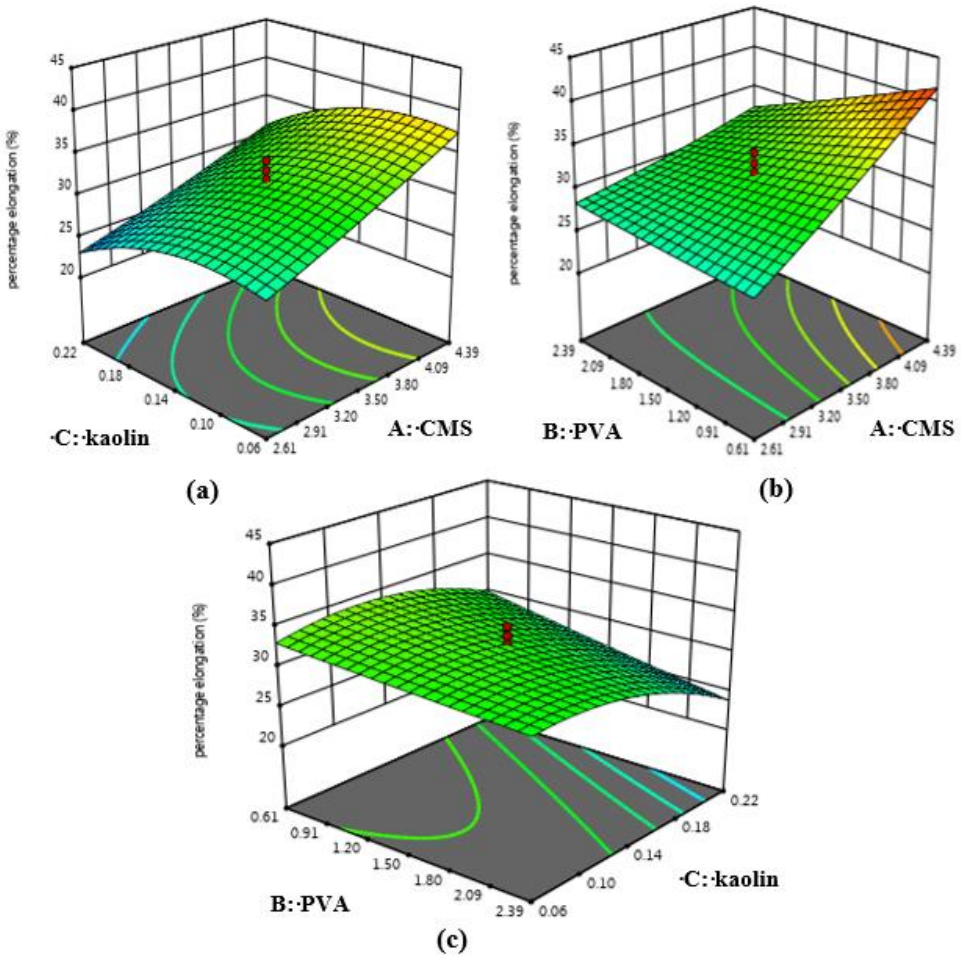

Figure 3: Response surface plots showing the effects of (a) CMS and PVA (b) CMS and kaolin and (c) PVA and kaolin on the %EB of the composite material.

Figure 3 demonstrates that the %EB increases significantly with increase in CMS but decreases with increase in PVA or kaolin. CMS demonstrated the most significant effect on the %EB. In Figure 2a, the lowest %EB of 27.13% of the composites was obtained at 2.61 g CMS and 0.61 g PVA. The %EB rises with higher CMS (Figure 3a). The highest value of the %EB (i.e. 41.41%) was obtained at 4.38 g CMS and 0.63 g PVA. In Figure 3b, %EB increases significantly with increase in CMS while it decreases slightly with kaolin. The highest value of %EB was 37.84% at 4.39 g CMS and 0.078 g kaolin while the lowest value of % EB was 23.18% at 2.63 g CMS and 0.22 g kaolin. In Figure 3c, the lowest value of %EB was found to be 24.10% at 2.36 g PVA and 0.22 g kaolin, while the highest value was 34.14% at 0.68 g PVA and 0.11 g kaolin.

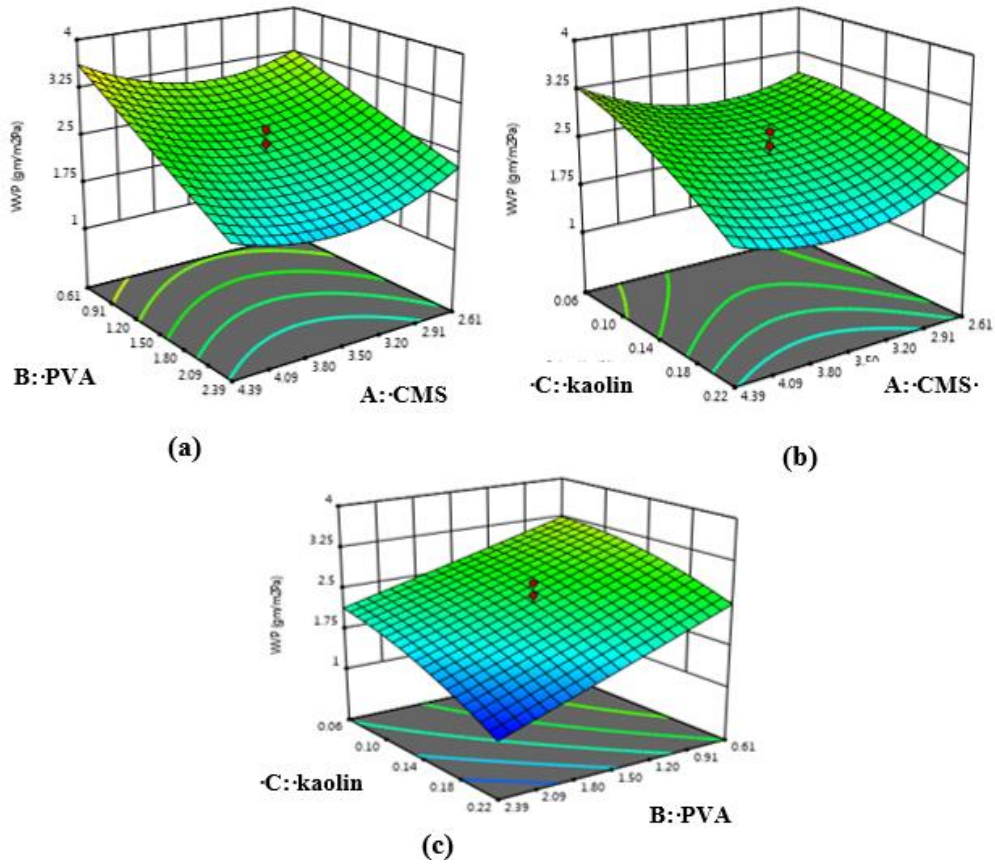

Figure 4: Response surface plots showing the effects of (a) CMS and PVA (b) CMS and kaolin and (c) PVA and kaolin on the WVP of the composite material

Figure 4 shows the 3D response surface plot demonstrating the effect of CMS, PVA and kaolin on the WVP. The plot illustrates that CMS and kaolin had a quadratic effect on the response-WVP.

The water vapor permeability (WVP) value exhibited a significant decrease with increasing concentrations of PVA and kaolin, whereas it slightly increased with increasing CMS concentration. Kaolin had the most pronounced decreasing effect on WVP, followed by PVA, while CMS demonstrated a minor increasing effect. This suggests that incorporating kaolin and PVA into the CMS polymer matrix enhances its water vapor barrier properties. The notable decrease in WVP with increasing kaolin content can be attributed to the good interfacial interaction and layered arrangement of kaolin microparticles within the CMS polymer chains. This creates a more tortuous pathway for water vapor molecules to travel, reducing the rate of water vapor diffusion through the polymer matrix and resulting in lower permeability. This finding aligns with a previous study on composite films of thermoplastic starch incorporated with kaolin (Chen and Evans 2005).

The optimal WVP values were achieved at specific concentrations: 1.73 g/m·s.Pa at 3.66g CMS and 2.39g PVA (Figure 4a), 1.75 g/m·s.Pa at 3.62g CMS and 0.22g kaolin (Figure 4b), and 1.06 g/m·s.Pa at 2.33g PVA and 0.22g kaolin (Figure 4c).

Optimization of the CMS-based composites

Response surface methodology (RSM) was used to optimize the formulations for the preparation of the CMS/PVA/kaolin composites. In the optimization selection, there were three variables namely CMS, PVA and kaolin which were used to make the desired composition.

The objective was to optimize the formulation process to achieve a dual goal: maximizing tensile strength while minimizing both elongation at break (%EB) and water vapor permeability (WVP) values. Maximizing tensile strength is crucial for ensuring material durability and performance in various applications. Similarly, minimizing elongation at break (%EB) is essential for maintaining material rigidity and resistance to deformation. Additionally, reducing water vapor permeability (WVP) is vital for preventing moisture ingress, which can compromise material integrity. However, optimizing this process involves navigating trade-offs between these competing factors. Therefore, a balanced approach is necessary to achieve a synergistic combination that meets the desired material properties. Therefore, the target value of the responses was the highest value (for tensile strength) and lowest values (for %EB and WVP) obtained from the experimental values. Figure 5 presents a graphical representation of the optimized formulations of the variables: CMS, PVA and kaolin, along with the achieved optimal responses for tensile strength (TS), percentage elongation at break (%EB) and water vapour permeability (WVP). The goal for each response is also indicated-Tensile strength (maximize), percentage elongation at break (constant) while water vapour permeability (minimize). After optimization, several solutions for tensile mechanical and WVP properties of the composites were obtained. A value of one or close to one (100%) is an acceptable value for the desirability function. The desirability function sets perimeters to find the optimal value for all the responses during the optimization procedure. In this study, a desirability of 95.4% was obtained for the tensile mechanical and WVP properties of the composites containing 3.33 g CMS, 2.39 g PVA and 0.22 g kaolin. This level of the independent variables gave the optimum responses of tensile strength, %EB and WVP values of 5.71 MPa, 23.57% and 1.08 gm/m^{2}sPa respectively.

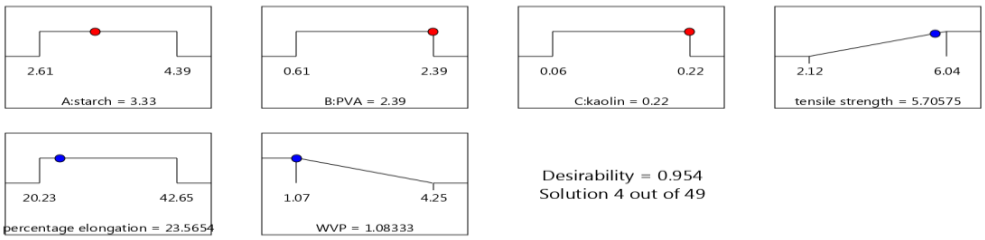

Figure 5: Optimum conditions of the independent variables and the responses of the CMS/PVA/kaolin composites

This study demonstrated that the addition of PVA and kaolin to CMS improved the tensile mechanical properties (i.e. tensile strength and % EB) and barrier properties (i.e. lowered WVP) of the composites films.

Validation of the optimized carboxymethyl starch/PVA/kaolin composites

To verify the model's accuracy, CMS-based composites were prepared using the predicted optimal formulations of CMS, PVA, and kaolin. The resulting composites were then tested in triplicate to measure their ultimate tensile strength, percentage elongation at break (%EB), and water vapor permeability (WVP). The comparison between the actual results and the predicted values, detailed in Table 4, demonstrated that the experimental outcomes were within the

anticipated range. This supports the reliability of the model for predicting the process and outcomes, making it a dependable tool for future formulation work.

Table 4: Actual and predicted responses of the prepared optimized composite films

	Tensile strength (MPa)	**Percentage elongation (%)**	**WVPx10^{-11} (g/m·s.Pa)**
Actual	6.24	22.67	1.25
Predicted	5.71	23.57	1.08

Conclusions

In this study, Response Surface Methodology (RSM) was successfully employed to design and optimize tensile mechanical and water vapour permeability properties of CMS-based biocomposite films for packaging applications. RSM's application enabled the investigation of individual and interactive effects of CMS, PVA, and kaolin as independent variables on tensile strength (TS), percentage elongation at break (%EB), and water vapor permeability (WVP). The optimal composition, 3.33g CMS, 2.39g PVA, and 0.22g kaolin, yielded maximum TS (5.71 MPa) and minimum WVP (1.08 g/m·s.Pa), with a corresponding %EB of 23.57%. This optimal composition signifies a crucial balance between mechanical strength and barrier properties. Statistical validation through Analysis of Variance (ANOVA) and regression models confirmed the significance of PVA and kaolin in enhancing tensile strength and barrier properties. Comparative analysis with a control sample demonstrated the superiority of the optimized CMS/PVA/kaolin composite. The optimized biocomposite films offer promising potential for packaging applications due to their enhanced mechanical and barrier properties. These eco-friendly films can replace synthetic materials, reducing environmental impact. Future studies can explore scalability, biodegradability, and functionalization for specific packaging needs.

Declaration of interest

The authors declare there are no known conflicting financial interests or personal relationships in this work

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