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Evaluation of the Sorption, Solubility, Mechanical Property and Predictive Behaviour of Kaolinite-Reinforced Dual-Modified Cassava Starch Films

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Abstract

Growing environmental concerns associated with petroleum-based plastics have intensified the search for biodegradable alternatives derived from renewable resources. Cassava starch is widely recognized as a promising biopolymer; however, its inherent hydrophilicity and poor mechanical strength limit its direct application in packaging materials. As a result, chemical modification and filler reinforcement are necessary to improve starch-based film performance. This study examined the absorptive behaviour, solubility characteristics, structural properties, mechanical performance, and predictive modelling of biodegradable films produced from a kaolinite-reinforced dual-modified cassava starch matrix. Acetylated and carboxymethylated cassava starches were blended in a 50:50 ratio to enhance structural stability and compatibility with glycerol plasticizer and kaolinite filler. Films were prepared with varying glycerol (2–5 g) and kaolinite (0–1 g) concentrations and characterized using Fourier Transform Infrared (FTIR) spectroscopy, absorption tests (water, moisture, and acid), solvent solubility analysis, and mechanical testing. FTIR spectra confirmed successful chemical modification, evidenced by the appearance of an ester carbonyl peak around 1740 cm^{-1} in acetylated starch and carboxylate bands near 1600 and 1410 cm^{-1} in carboxymethylated starch, indicating the incorporation of functional groups that altered intermolecular bonding within the starch network. Increasing glycerol content significantly elevated moisture, water, and acid absorption to approximately 43–45%, while kaolinite incorporation reduced absorption due to its barrier-forming layered structure. All films were soluble in alkaline medium, suggesting susceptibility to alkaline hydrolysis, but remained insoluble in ethanol, confirming resistance to organic solvents. Mechanical analysis revealed enhanced tensile strength with kaolinite reinforcement and increased elongation at break at higher glycerol levels due to improved polymer chain mobility. Regression modelling demonstrated a strong predictive relationship ($R^2 \approx 0.93$) between tensile strength, elongation, and moisture content, with ANOVA confirming statistical significance ($P < 0.05$). Overall, the developed films exhibited tunable physicomechanical properties and reliable predictive behaviour, highlighting their potential as sustainable packaging materials requiring controlled solubility and structural integrity.

Keywords: Absorption; Dual-Modified Cassava Starch; Kaolinite; Mechanical Properties; Regression Modelling.

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1.0 Introduction

Plastic pollution remains one of the most pressing global environmental challenges, with conventional petroleum-based plastics contributing to persistent waste in terrestrial and marine ecosystems [1]. As awareness of plastic accumulation increases, research efforts have shifted toward biodegradable alternatives derived from renewable natural polymers. Starch-based materials have gained significant attention due to their low cost, abundance, biodegradability, and versatility in forming films and composites suitable for packaging and related applications [2, 3].

Cassava (*Manihot esculenta*) starch is widely recognized as an excellent source of biopolymers, particularly in tropical regions where cassava production is abundant. Despite its advantages, native cassava starch exhibits limitations, including high water sensitivity, poor mechanical strength, and limited thermal stability as reported by Yang *et al.,* (2021) [4]. Chemical modification methods such as acetylation and carboxymethylation have been successfully used to overcome these shortcomings. Acetylation introduces hydrophobic acetyl groups that improve flexibility and reduce retrogradation [5], while carboxymethylation introduces negatively charged carboxymethyl groups that enhance swelling, solubility, and interaction with additives [6]. Combining both functional groups in a dual-modified starch matrix provides improved compatibility, greater structural versatility, and enhanced performance in film applications.

In addition to chemical modification, reinforcement with inorganic fillers plays an important role in determining film performance. Kaolinite, a naturally occurring aluminosilicate clay, has been extensively studied as a reinforcing agent due to its plate-like structure, thermal stability, and ability to enhance mechanical strength and reduce permeability in polymer composites [7, 8]. When incorporated into starch-based matrices, kaolinite enhances interfacial bonding and creates a tortuous path for molecular movement, thereby influencing both the mechanical and absorptive behaviors of the resulting films.

Moisture absorption, water uptake, acid absorption, and solubility characteristics are critical properties governing the functional performance of biodegradable starch films. These properties determine how the material behaves under humid, acidic, or solvent-exposed environments, significantly influencing its stability, packaging suitability, and degradation behaviour. Mechanical properties such as tensile strength and elongation at break are equally important, reflecting the structural integrity and flexibility required for film handling and application. Understanding how dual modification, plasticization, and kaolinite reinforcement jointly influence these properties is therefore essential to optimizing film performance.

Statistical modelling using regression and analysis of variance (ANOVA) provides an efficient approach for predicting mechanical performance and identifying the most influential formulation variables. Such modelling improves formulation design, reduces experimental cost, and helps establish structure–property relationships within modified starch composites [9].

Despite growing interest in modified starch-based films, limited studies have integrated absorptive behaviour, solubility characteristics, mechanical properties, and predictive modelling into a single systematic evaluation. This study addresses this gap by investigating the absorptive, solubility, mechanical, and statistical predictive performance of kaolinite-reinforced films prepared from a dual-modified cassava starch blend. This study aims to provide a comprehensive material performance profile and establish predictive relationships that are useful for designing environmentally friendly packaging materials.

2 Materials and Method

2.1 *Sample Collection/Sample Area:*

Cassava tuber were purchased from a farm in Ekosodin community Benin City, Edo State. It is located along the longitude 5° 451 and 6° 151 east and latitude 5° 151 and 6° 451 north of the central province of Edo state. Additional materials such as HCl (ReAgent 36%- WW), Sodium hydroxide pellets (MOLYCHEM-98% Purity), Acetic Anhydride (APC- 98% Purity), 2- Propanol (WARCHEM-99.7% Purity), Monochloroacetic acid (ACS reagent-99% Purity), Glycerol (WARCHEM-85%) and Kaolinite were sourced from Pyrex-IG Scientific company Benin City, Edo State Nigeria.

2.2 Preparation of Native Starch

Extraction of cassava starch was carried out using methodology demonstrated by Ezeoha, and Ezenwanne, (2013) [10]. The cassava tubers were mechanically grated after being manually peeled and cleaned with distilled water—three times as much water as the shredded cassava was added to the mixture. A coarse sieve and a filter cloth were used to sieve and filter the mixture, respectively. The filtrate was allowed to settle for six hours, then mixed with an equal amount of water and left to settle for a day. At the end of 24 hours, the wet starch was decanted, manually dewatered, and then oven-dried at 105°C for 4 hours to reduce its moisture content.

%Starch yield was calculated using:

$$(\%)Starch\ Yield = \frac{weight\ of\ extracted\ starch\ (g)}{weight\ of\ cassava\ tubers} x100 \text{ ----------(1)}$$

2.3 Preparation of Acetylated Starch

The native starch was modified via acetylation using methodology reported by Henry, (2007) [11] with slight modification. 20g of starch was dispersed in 100cm³ of distilled water and then stirred constantly for 30 minutes. The slurry was adjusted to pH 8.0 with 3% NaOH, and 1.2g of acetic anhydride was added to the slurry. After the

addition of acetic anhydride, the reaction was allowed to proceed for an additional five minutes. The pH of the slurry was adjusted to 4.5 with 0.5M HCl, and then it was filtered through Whatman No. 1 filter paper. The residue obtained was washed four times with distilled water to remove acids that may be present in the product, and finally air-dried at room temperature.

%Yield was calculated using:

$$(\%)Yield = \frac{weight\ of\ acetylated\ starch\ (g)}{weight\ of\ native\ starch\ (g)}\ x\ 100 \text{---------- (2)}$$

2.4 Preparation of Carboxymethylated Starch

The native starch was modified via carboxymethylation using the methodology demonstrated by Adeyanju, and Olatoyinbo, (2019) [12]. 10 g of native starch was suspended in 100mL of 2-propanol. Aqueous sodium hydroxide solution was added (3% W/v (10mL)). The mixture was stirred at a controlled temperature (30 °C) for 10 minutes. Monochloroacetic acid was added, and stirring was continued for up to 30 minutes. The pH of the mixture was adjusted to 5.0 by adding 50% glacial acetic acid. The carboxymethylated starch was filtered and washed with an aqueous ethanol solution. Finally, the starch was dried at 50 °C for 6 hours, and the dried starch was passed through a 100 mm-mesh sieve.

The yield was calculated using:

$$(\%)Yield = \frac{weight\ of\ modified\ starch\ (g)}{weight\ of\ native\ starch\ (g)} x100$$

---------(3)

Table 1: Experimental Design for biodegradable plastic film formulation

	Glycerol (g)	**Kaolinite (g)**
50:50 blend of Acetylated Starch and Carboxymethylated Starch	2	0
		0.5
		1.0
	3	0
		0.5
		1.0
	4	0
		0.5
		1.0
	5	0
		0.5
		1.0

2.5 Preparation of Biodegradable Plastic Film

The preparation was conducted following a refined modification of the method proposed by Nwaka *et al.,* (2025) [9]. 10 g of (50:50) of acetylated and carboxymethylated starch powder was weighed in a beaker, to which 100 mL of distilled water was added. The mixture was stirred at 350 rpm for 10 minutes on a magnetic stirrer. Kaolinite powder was then added at different weights: 0g (0% w/w), 0.5 g (5% w/w), and 1g (10% w/w), and stirred. Glycerol was also added at different weights (2, 3, 4, 5 g) and stirred at 350 rpm for 15 minutes. The solution was heated to approximately 80°C with continuous stirring to form a gel. The slurry was then poured onto a mold, dried in a hot air oven at 50ºC, and stored at room temperature.

2.6 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of native and modified starch were acquired on a Perkin Elmer FTIR spectrophotometer (Perkin Elmer, Inc., MA, USA) using a potassium bromide (KBr) disc prepared from powdered samples mixed with dry KBr to determine the changes in the functional groups in the starch samples. The spectra were recorded (16 scans) in the transparent mode from 4000 to 400 cm^{-1}, as demonstrated by Bernardino-Nicanor *et al.,* (2017) [13].

2.7 Sorption Analysis

The adsorption properties of biodegradable plastic films are critical in determining their interaction with moisture, and other environmental substances. These films can adsorb water and other polar molecules onto their surface or within their polymer matrix, which affects their mechanical performance and degradation behavior.

The methodology for assessment of water sorption was adopted from previous study demonstrated by Nwaka et al. (2025) [9].

2.7.1 Water absorption resistance:

Samples of the bioplastic films were evaluated by soaking them in water at room temperature for one hour, drying them with cotton pieces, and weighing them. The percentage of water absorption was calculated using:

$$(\%)Water\ absorption = \frac{wet\ \ weight - dry\ weight}{dry\ weight} x100 \quad \text{----------(4)}$$

2.7.2 Acid absorption resistance:

Samples of the bioplastic films were soaked in 1M hydrochloric acid solution, and their weights were recorded after one hour. The percentage of acid absorption was calculated using:

$$(\%)Acid\ absorption = \frac{wet\ \ weight - dry\ weight}{dry\ weight} x100 \text{----------(5)}$$

2.7.3 Base absorption resistance

Bioplastic samples were soaked in 1M sodium hydroxide solution and weighed at regular intervals. The percentage of base absorption was calculated using**:**

2.9 Mechanical Properties

Mechanical Testing: The mechanical properties of the composites were evaluated using standardized testing methods. Tensile strength and elongation at break were determined using the Tensile Strength Test Machine TM 2101-T7, following ASTM D638, with a maximum force of 10N. The percentage elongation was also calculated using:

$$\%Elongation = \frac{(L-Lo)}{Lo} x100 \text{ ----------(8)}$$

Where L is the final length and Lo is the initial length. Tensile Strength, Elongation at Break, Ultimate Elongation, Toughness, Yield Point were obtained from the stress – strain curve.

3 Results and Discussion

3.1 FTIR

Fourier Transform Infrared (FTIR) spectroscopy was used to identify and confirm the functional groups present in the native, acetylated and carboxymethylated starch samples. The spectra for these samples are in Figures 1, 2 and 3 respectively. Distinct differences in absorption bands among the samples provide evidence of successful chemical modification of the starch molecules.

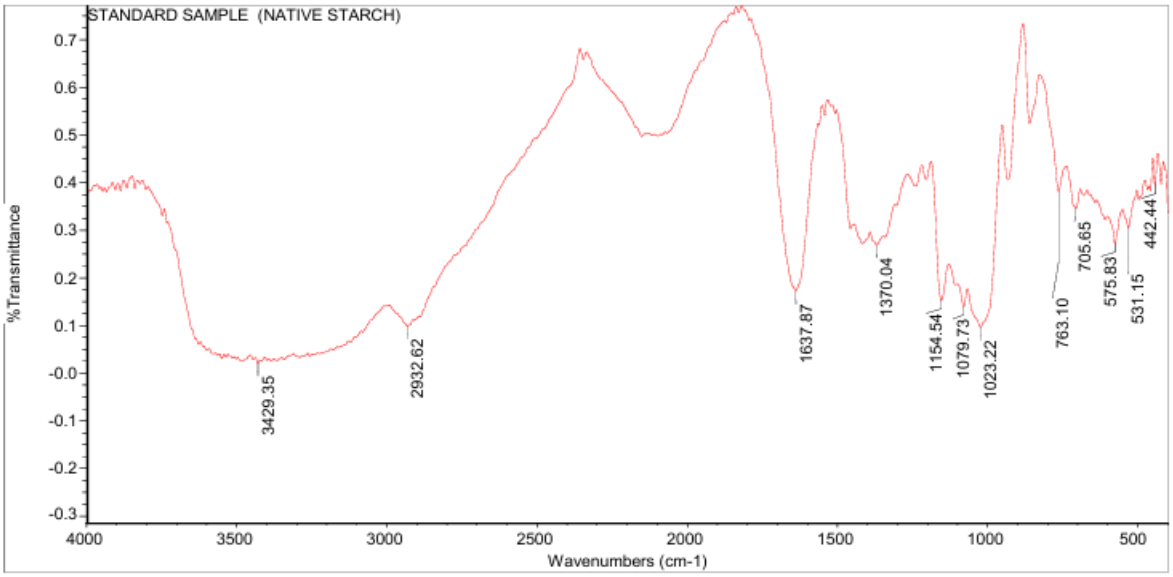


Figure 1: FTIR Spectrum for Native Starch

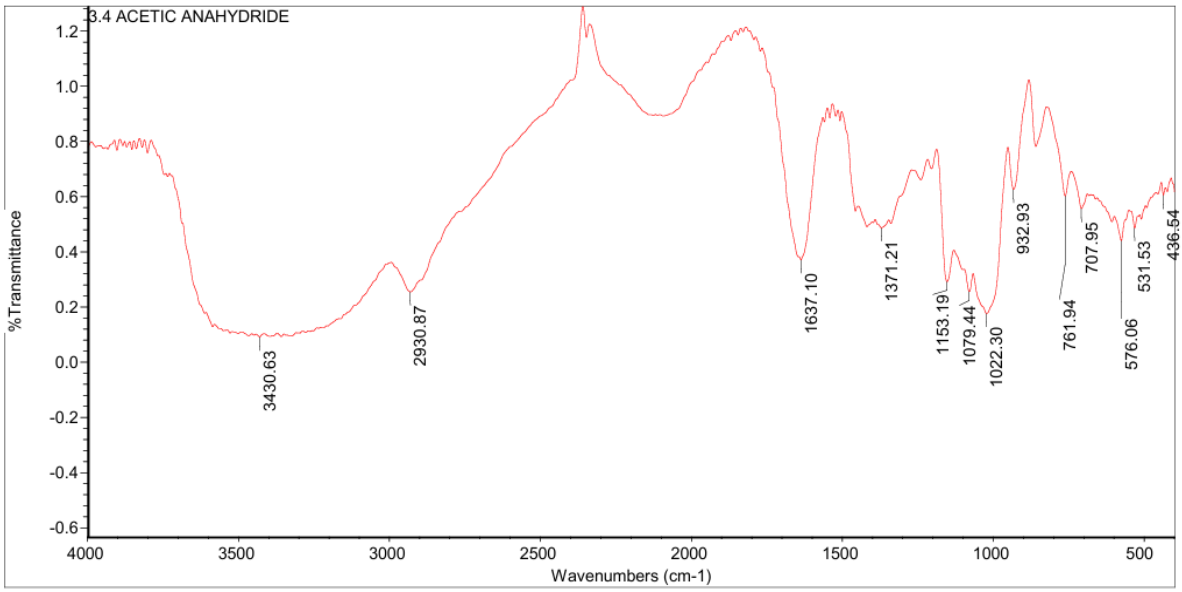


Figure 2: FTIR Spectrum for Acetylated Starch

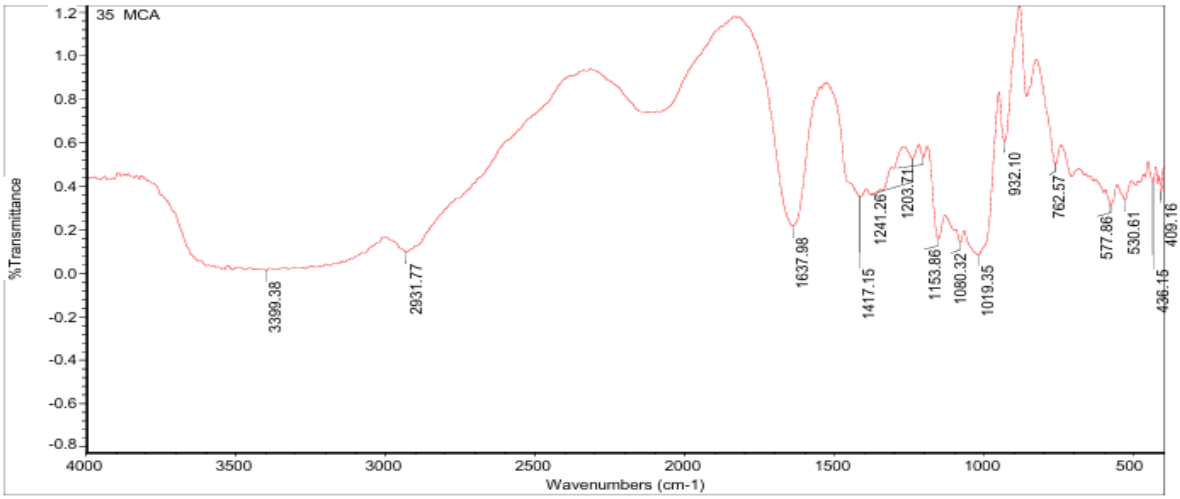


Figure 3: FTIR Spectra for Carboxymethylated Starch

The spectra for native, carboxymethylated, and acetylated starch are presented in Figures 1–3, respectively. Distinct differences in absorption bands among the samples provide strong evidence of successful chemical modification of the starch molecules, consistent with previous studies that reported noticeable spectral changes following starch derivatization.[14,15] From Figure 1, the native starch exhibited characteristic absorption bands typical of polysaccharides. A broad band around 3400 cm^{-1} corresponds to O–H stretching vibrations of hydroxyl groups involved in intra- and intermolecular hydrogen bonding. Similar broad hydroxyl peaks have been widely reported

for native starches due to their highly hydrogen-bonded structure. [16] The weak band near 2920 cm^{-1} arises from C–H stretching vibrations of methylene groups, while the strong absorption in the 1150–1000 cm^{-1} region represents C–O–C and C–O stretching of glycosidic linkages. A weak band around 1640 cm^{-1} is attributed to bound water molecules, a feature commonly observed in hydrophilic starch materials [14]. From Figure 2, a distinct absorption peak around 1740 cm^{-1} is attributed to the carbonyl (C=O) stretching vibration of ester groups, confirming acetylation. This observation agrees with earlier reports where the emergence of a carbonyl band near 1740 cm^{-1} served as clear evidence of acetyl group incorporation into the starch backbone [17, 18]. An additional peak at 1230–1260 cm^{-1} corresponds to C–O stretching of the acetyl ester linkage. The observed decrease and narrowing of the O–H stretching band intensity around 3400 cm^{-1} reflects the replacement of hydroxyl groups by acetyl moieties, thereby reducing intermolecular hydrogen bonding. Slight intensity variations in the 1000–1150 cm^{-1} region further indicate modifications to the starch backbone. From Figure 3, notable spectral changes were observed with new absorption peaks appearing at approximately 1600 cm^{-1} and 1410 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations of carboxylate ($–COO^-$) groups, respectively. These bands confirm the successful introduction of carboxymethyl substituents on the starch backbone and align with findings from previous studies on carboxymethylated starch by Bhattacharyya *et al.,* (1995) [19] and Stojanović *et al.,* (2005) [20].

Additionally, the reduction in the broad O–H stretching band intensity near 3400 cm^{-1} suggests substitution of hydroxyl groups by carboxymethyl groups, leading to decreased hydrogen bonding. Minor shifts within the fingerprint region (1200–1000 cm^{-1}) further indicate structural modification of the polysaccharide network. Overall, the comparative spectral analysis clearly demonstrates that the chemical modifications, carboxymethylation and acetylation were successfully achieved, with the observed band patterns closely matching those reported in the literature for chemically modified starches.

Table 2: Absorption and solubility test on bioplastic film

	Glycerol	Kaolinite	Water Absorption	Moisture Absorption	Acid Absorption	Solubility in NaOH	Solubility in Ethanol
	2g	0g	24.0%	10.0%	20.0	Soluble	Insoluble
		0.5g	38.5%	8.5%	12.0	Soluble	Insoluble
		1.0g	35.0%	8.0%	8.0	Soluble	Insoluble
	3g	0g	39.1%	22.1%	21.5	Soluble	Insoluble
50:50 blend of		0.5g	41.0%	10.3%	15.7	Soluble	Insoluble
Acetylated and		1.0g	30.0%	10.0%	10.0	Soluble	Insoluble
Carboxymethyl	4g	0g	39.3%	28.0%	25.6	Soluble	Insoluble
ated Starch		0.5g	41.7%	17.0%	15.9	Soluble	Insoluble
		1.0g	30.5%	12.0%	11.1	Soluble	Insoluble
	5g	0g	42.8%	30.0%	32.6	Soluble	Insoluble
		0.5g	50.0%	21.4%	21.25	Soluble	Insoluble
		1.0g	36.1%	14.0%	17.9	Soluble	Insoluble

Table 2 shows the influence of glycerol and kaolinite on the water, moisture, and acid absorption characteristics, as well as the solubility profile, of bioplastic films produced from a 50:50 blend of acetylated and carboxymethylated starch. These parameters provide insight into the film's stability, dimensional behavior, and its suitability for biodegradable or packaging applications.

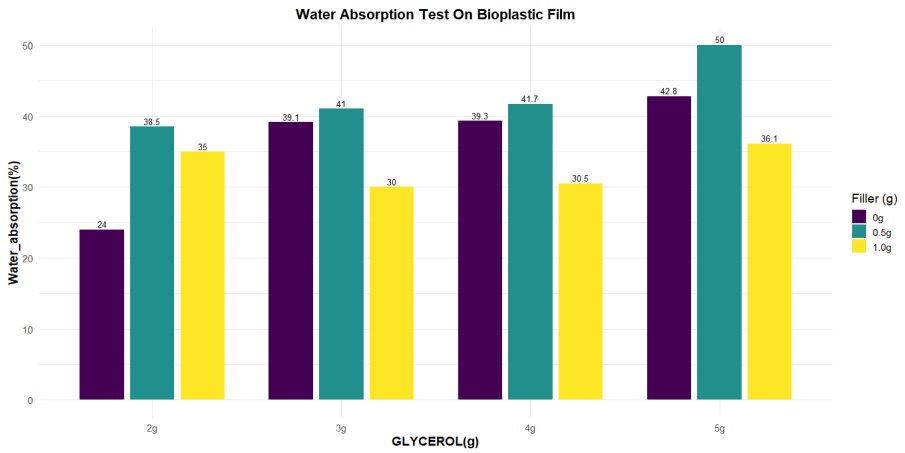


Figure 4: Water Absorption Test on Bioplastic Film

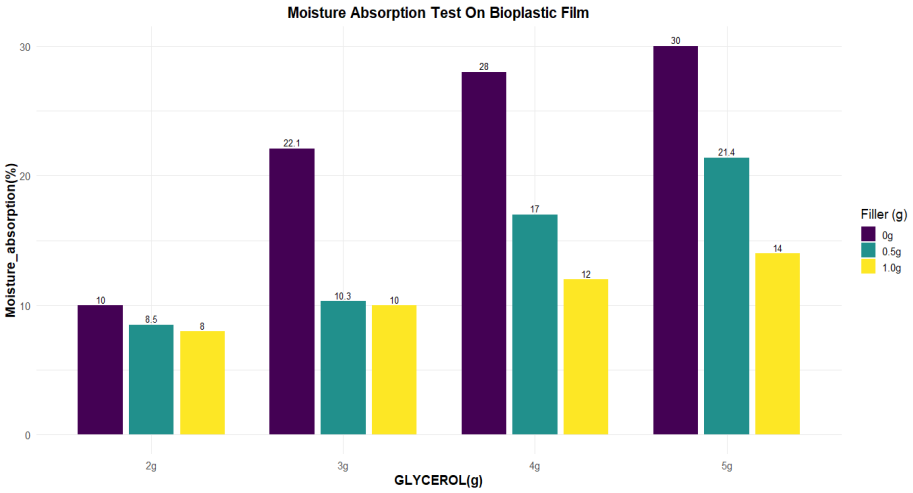


Figure 5: Moisture Absorption Test on Bioplastic Film

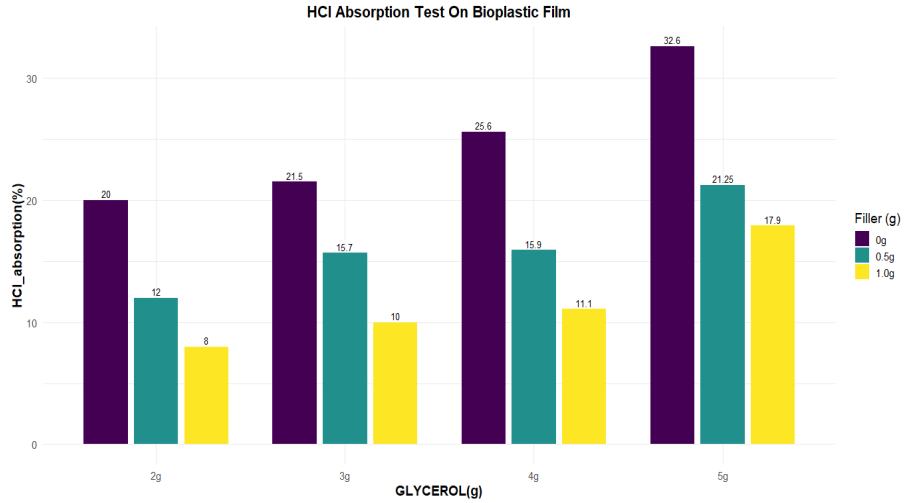


Figure 6: Acid Absorption Test on Bioplastic Film

3.2 Effect of Glycerol Concentration on Absorption and Solubility

An overall rise in both water and moisture absorption was observed as glycerol concentration increased from 2 g to 5 g. This increase is attributed to the hygroscopic nature of glycerol, which contains multiple hydroxyl groups capable of forming hydrogen bonds with water molecules. By inserting itself between starch chains, glycerol disrupts the native hydrogen-bonding network, loosens chain packing, and creates additional free volume, thereby making the matrix more permeable to water. Similar behaviour has been widely reported in plasticized starch films, where

glycerol enhances hydrophilicity and water diffusion through the polymer structure [21, 22].

At 2 g glycerol, the films exhibited relatively low water absorption (≈24%), consistent with a denser polymer network. In contrast, films produced with 5 g glycerol showed markedly higher water uptake (up to 42.8%), reflecting increased flexibility and greater hydrophilicity. Moisture absorption followed a similar trend, with values reaching around 30% at the highest glycerol loading. High plasticizer levels may promote partial phase separation and surface tackiness, further increasing moisture retention and weakening film integrity [23, 24].

Acid absorption also tended to rise with increasing glycerol content. Films with higher plasticizer levels exhibited greater uptake in 1 M HCl, likely due to enhanced porosity and reduced matrix cohesion. Moderate glycerol levels (3–4 g), however, produced more stable behaviour, suggesting an optimal plasticizer range that balances flexibility with resistance to excessive acid penetration. Comparable observations have been reported, indicating that excessive plasticizer reduces intermolecular forces and facilitates liquid diffusion into starch matrices [25].

All films dissolved completely in 1 M NaOH, irrespective of glycerol content. This solubility is expected, as the ester (acetyl) and ether (carboxymethyl) linkages are susceptible to alkaline hydrolysis [15]. In contrast, none of the films dissolved in ethanol, indicating strong incompatibility with the solvent due to the hydrophilic nature of the starch matrix and the insufficient polarity of ethanol to disrupt the hydrogen-bonded polymer network.[21]

3.3 Effect of Kaolinite on Absorption and Solubility

Kaolinite concentration (0, 0.5, and 1.0 g) also influenced absorption behaviour. At 0.5 g, many samples showed increased water absorption compared to the unfilled films. This water absorption may occur when low filler amounts lead to poor dispersion, weak particle–matrix adhesion, or micro void formation, which facilitates water ingress.

At the higher filler loading (1.0 g), water and acid absorption values generally decreased. The improved kaolinite distribution at this concentration creates a more continuous barrier throughout the matrix, thereby restricting diffusion pathways for water and acid molecules. This barrier effect arises from kaolinite's layered structure, which increases tortuosity and limits molecular transport.

Moisture absorption followed the same trend: films containing 1.0 g kaolinite exhibited the lowest moisture uptake. This finding aligns with previous research by Le *et al*. (2019) [8] that clay minerals enhance moisture resistance in starch composites by impeding vapor diffusion and improving dimensional stability.

Acid absorption also declined with increased kaolinite loading. Besides creating a physical barrier, kaolinite's slight basicity may partially neutralize acidic medium, reducing acid-mediated hydrolysis of the starch chains and enhancing overall resistance.

3.4 Combined Influence of Plasticizer–Filler Interaction

The interaction between glycerol and kaolinite demonstrates a clear combined influence on absorption and solubility. At lower glycerol levels (2–3 g) and higher kaolinite content (1.0 g), the films exhibited balanced performance, characterized by moderate water absorption, good flexibility, and enhanced resistance to moisture. Within this range, glycerol contributes to softness, while kaolinite reinforces the matrix, preventing significant swelling or structural collapse.

However, when the glycerol content was high (≥4 g) and the filler loading was low (0–0.5 g), the films became highly permeable to water and moisture due to excessive chain mobility and reduced matrix compaction. The high permeability suggests that plasticizer effects dominate when filler reinforcement is insufficient.

The films' insolubility in ethanol supports their potential use in packaging applications where resistance to non-aqueous solvents is important. Their solubility in alkaline medium suggests favourable environmental degradability and compatibility with composting environments.

Overall, the results show that both additives significantly modulate the films' physicochemical behaviour. Glycerol enhances processability but increases hydrophilicity, while kaolinite strengthens the matrix, reduces water and acid penetration, and improves stability. The best balance was achieved at moderate glycerol levels (3–4 g) combined with a higher kaolinite loading (1.0 g), resulting in films with desirable flexibility, reduced moisture sensitivity, and improved resistance in acidic environments properties well-suited for biodegradable packaging and agricultural applications.

Table 3: Mechanical properties of bioplastic film

Blend	Tensile Strength (MPa)	Elongation at Break (mm)	Ultimate Elongation (%)	Toughness (MJ/m³)	Yield Point (MPa)
2 g Glycerol – 0 g Filler	14.20	3.80	7.50	0.58	12.10
2 g Glycerol – 0.5 g Filler	15.00	3.60	7.00	0.60	12.80
2 g Glycerol – 1 g Filler	15.80	3.40	6.70	0.62	13.40
3 g Glycerol – 0 g Filler	13.10	4.20	8.50	0.63	11.20
3 g Glycerol – 0.5 g Filler	13.90	4.00	8.10	0.65	11.90
3 g Glycerol – 1 g Filler	14.60	3.80	7.60	0.67	12.40
4 g Glycerol – 0 g Filler	12.00	4.70	9.40	0.70	10.40
4 g Glycerol – 0.5 g Filler	12.80	4.40	8.90	0.71	11.20
4 g Glycerol – 1 g Filler	13.50	4.20	8.50	0.73	11.80
5 g Glycerol – 0 g Filler	11.00	5.10	10.40	0.78	9.60
5 g Glycerol – 0.5 g Filler	11.90	4.80	9.90	0.80	10.30
5 g Glycerol – 1 g Filler	12.70	4.60	9.50	0.82	11.00

3.5 Effect of Glycerol (Plasticizer)

Glycerol acted as a classical plasticizer by weakening intermolecular hydrogen bonding and increasing molecular mobility within the polymer matrix. As glycerol content increased from 2 g to 5 g (in the absence of filler), a progressive reduction in tensile strength was observed (14.20 → 11.00 MPa), indicating greater softness and diminished structural resistance. Correspondingly, the yield point decreased (12.10 → 9.60 MPa), confirming a reduction in stiffness and an earlier onset of plastic deformation.

In contrast, elongation at break increased substantially (3.80 → 5.10 mm) with rising plasticizer concentration, demonstrating enhanced ductility. Toughness also improved (0.58 → 0.78 MJ/m³), showing that the films absorbed more energy before failure as plasticization increased. These trends are consistent with observations by Jumaidin et al., (2024) [26], who reported that glycerol promotes

extensibility but weakens tensile performance when present at high levels due to excessive softening of the polymer network. Overall, glycerol imparted flexibility and improved energy absorption but compromised tensile strength and rigidity—effects that intensify with increasing dosage.

3.6 Effect of Kaolinite (Filler)

The addition of kaolinite imparted a clear reinforcing effect across all glycerol concentrations. Increasing filler content from 0 g to 1.0 g enhanced tensile strength due to the rigidity and high aspect ratio of the clay particles. For instance, at 5 g of glycerol, the tensile strength increased from 11.00 MPa to 12.70 MPa upon the addition of 1.0 g of kaolinite. This reinforcement arises from improved interfacial adhesion and the ability of kaolinite layers to restrict polymer mobility. However, this increased stiffness limited deformability, as elongation at break decreased with increasing filler amounts, reflecting reduced chain movement and increased brittleness. The yield point also increased with kaolinite loading, confirming improved resistance to plastic flow and higher rigidity. Toughness exhibited modest improvements when filler was well dispersed (e.g., 0.78 → 0.82 MJ/m³ at 5 g glycerol), suggesting that kaolinite can enhance energy absorption when particle distribution is uniform. However, excessive rigidity or poor particle–matrix compatibility may introduce micro voids or stress concentration points that reduce extensibility. These behaviours align closely with earlier findings by Mbey**,** et al., (2022) [27] and Meité *et al*. (2018) [28], who reported that mineral fillers increase stiffness while reducing ductility in starch-based composites.

3.7 Combined Effect and Optimal Composition

The results reveal a competitive interplay between plasticization and reinforcement.

Glycerol softens the matrix, increasing ductility and toughness but lowering tensile strength.

Kaolinite reinforces the matrix, increasing tensile strength and yield point but reducing elongation.

The best mechanical balance was obtained with moderate glycerol levels (3–4 g) combined with 0.5 g kaolinite, where the films exhibited adequate strength, improved flexibility, and acceptable toughness. These formulations retained the structural benefits of filler reinforcement while avoiding excessive stiffness. Higher filler content (**≥1 g**) substantially increased rigidity but reduced elongation too sharply, while excessive glycerol (**5 g**) lowered tensile strength beyond desirable limits for structural or packaging applications.

3.8 Analysis of Variance (ANOVA)

3.8.1 Influence of EB percentage and moisture percentage

From Table 4, A two-way Analysis of Variance (ANOVA) was conducted to determine how effectively elongation at break (EB%) and moisture content predict the tensile strength of the dual-modified starch films. The models were fitted using the least squares method, and their adequacy was assessed at a 95% confidence level ($\alpha = 0.05$)**.** The quadratic model was found to be statistically robust, with both EB% and moisture content exerting significant individual effects.

ANOVA results revealed that EB% was the most influential factor, producing a very high F-value of 102.74 and an extremely small p-value (7.67×10^{-6}). The data indicate a highly significant contribution of EB% to the variation in tensile strength. The strength of this effect aligns with the established inverse relationship between elongation and tensile performance, where greater ductility generally corresponds to reduced stiffness and tensile resistance.

Moisture content also had a significant effect, though to a lesser extent. It generated an F-value of 11.42 with a p-value of 0.00965, confirming that its influence is statistically meaningful. Moisture likely contributes to changes in matrix cohesion and internal hydrogen bonding, thereby modifying tensile strength in predictable ways.

The interaction between EB% and moisture content was found to be statistically insignificant, with an F-value of 0.03 and a p-value of 0.86707. This data suggests that the influence of moisture on tensile strength is independent of the level of elongation, and vice versa. In other words, the effects of both variables are additive rather than synergistic, and each operates independently within the studied range.

3.8.2 Model Adequacy

The lack-of-fit test was insignificant**,** indicating that the quadratic model adequately captured the relationship between tensile strength and the predictor variables. The absence of significant deviation between observed and predicted values confirms that the model is appropriate and reliable for describing tensile behaviour within the experimental region.

The ANOVA results clearly demonstrate that both EB% and moisture content are significant predictors of tensile strength, with EB% exerting the stronger influence. The statistically insignificant interaction term shows that the predictors do not modify each other's effects. Collectively, these findings validate the use of the quadratic model for predicting tensile strength based on formulation-dependent parameters and support its application for optimizing the mechanical performance of dual-modified starch films.

3.9 Linear Regression

A multiple linear regression model was developed to predict tensile strength using elongation at break (EB%) and moisture content as predictor variables. The model, fitted using the least squares method, demonstrated strong explanatory power and statistical significance.

3.9.1 Model Fit and Predictive Strength

The model achieved a multiple R^2 of 0.9343 (adjusted R^2 = **0.9197**), indicating that approximately 93% of the variability in tensile strength was accounted for by the two predictors. The overall F-statistic **(**63.98**, p =** 4.78×10^{-6}**)** confirmed that the regression equation was highly significant at the 95% confidence level. The residual spread (range: −0.43 to 1.05) showed no large discrepancies between observed and predicted values, further supporting good model adequacy.

3.9.2 Significance of Predictor Variables

Both EB% and moisture content significantly contributed to predicting tensile strength.

EB% had a coefficient of **1.76537** and was statistically significant (p = **0.01346**), showing that increases in elongation correspond to increases in tensile strength within this model structure.

Moisture content exhibited a coefficient of **0.11446** with a highly significant p-value (**0.00595**), indicating a positive but smaller effect on tensile strength relative to EB%.

The intercept (2.17821) was not significant (p > 0.05), meaning it has limited physical relevance beyond model formality.

3.9.3 Regression Equation

The final regression model is expressed as:

Tensile Strength=2.17821+
(1.76537×EB Percentage) +
(0.11446×Moisture Percentage)

Where:

Tensile Strength is the predicted tensile strength.

EB Percentage is the Elongation at Break percentage.

Moisture Percentage is the moisture content percentage.

This equation provides a straightforward predictive tool for estimating tensile strength from measurable film parameters.

3.9.4 Model Adequacy

The lack-of-fit test was insignificant, confirming that the model adequately describes the relationship between the variables without systematic deviation. Together with high R^2 and strong predictor significance, this validates the model's suitability for formulation optimization.

The regression results demonstrate that both EB% and moisture content are reliable predictors of tensile strength, with EB% exerting the stronger influence. The high model accuracy ($R^2 > 0.93$) indicates that tensile behavior in these bioplastic

Table 4: Analysis of Variance (ANOVA) for tensile strength

Source of Variation	Degrees of Freedom (Df)	Sum of Squares (Sum Sq)	Mean Square (Mean Sq)	F-Value	P-Value	Significance
EB Percentage	1	24.233	24.233	102.74	7.67e-06	***
Moisture Percentage	1	2.693	2.693	11.42	0.00965	**
EB Percentage: **Moisture Percentage**	1	0.007	0.007	0.03	0.86707	
Residuals	8	1.887	0.236	-	-	

***: p-value < 0.001 (Highly Significant), **: p-value < 0.01 (Significant)

films can be effectively forecasted from simple measurable parameters, making the model useful for design and quality control in starch-based bioplastic development.

This study demonstrated that the absorptive, solubility, mechanical, and predictive behaviours of kaolinite-reinforced dual-modified cassava starch films are strongly governed by the balance between plasticizer and filler content. Increasing glycerol improved flexibility, elongation, and toughness but also enhanced water, moisture, and acid absorption due to increased matrix mobility and hydrophilicity. In contrast, kaolinite provided measurable reinforcement, increasing tensile strength and reducing moisture uptake, with the strongest improvements observed at higher filler loadings.

4.0 Conclusion

The films exhibited complete solubility in alkaline medium but remained insoluble in ethanol, confirming their hydrophilic nature and potential for environmentally responsive degradation. Optimal property enhancement occurred at moderate glycerol levels (3–4 g) combined with 1.0 g kaolinite, yielding films with improved mechanical balance and reduced moisture sensitivity.

Statistical analysis further validated these observations. ANOVA identified elongation at break and moisture content as significant independent predictors of tensile strength, while regression modelling produced a highly accurate predictive equation ($R^2 \approx 0.93$). The insignificant lack of fit affirmed the reliability of the model for estimating film strength from simple physical parameters. This findings highlight the effectiveness of dual chemical modification combined with mineral reinforcement in tuning the performance of starch-based bioplastics. The demonstrated structure–property–prediction relationships provide a practical framework for optimizing biodegradable film formulations for packaging and related applications.

5.0 Recommendation

Future studies should explore the incorporation of nanofillers such as nanoclay, cellulose nanocrystals, or graphene oxide to further enhance the mechanical strength, barrier properties, and thermal stability of dual-modified cassava starch films. Investigation into alternative plasticizers or mixed plasticizer systems is also recommended to optimize the balance between flexibility and moisture resistance. Additionally, advanced morphological analyses using techniques such as Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) could provide deeper insight into filler dispersion and structural interactions within the polymer matrix. Finally, real-world packaging trials, biodegradation kinetics under diverse environmental conditions, and scalability assessments are necessary to evaluate the commercial viability of these films as sustainable alternatives to conventional plastics.

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7.0 References

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