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RESEARCH ARTICLE

BIODEGRADABILITY AND THERMAL PROPERTIES OF DUAL-MODIFIED STARCH FILMS REINFORCED WITH KAOLINITE CLAY.

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ABSTRACT

This study evaluates bioplastic films produced from a 50:50 blend of acetylated and carboxymethylated cassava starch reinforced with kaolinite. The films were formulated with varying concentrations of glycerol (2–5 g) and kaolinite (0–1 g) which were subjected to soil burial test and thermal analysis (TGA/DTA). Unreinforced films with highest glycerol concentrations degraded fastest, showing up to 44.0% weight loss within one week owing to enhanced hydrophilicity and weaker intermolecular bonding while reinforced films recorded lower degradation, with values ranging between 20.00–36.50% depending on filler level. At constant glycerol content, biodegradability decreased with increasing kaolinite loading due to reduced microbial accessibility and improved structural integrity. Thermogravimetric analysis revealed three characteristic decomposition phases: initial moisture loss at 50–100 °C, major polymer degradation at 170–225 °C, and final carbonaceous residue formation. Differential thermal analysis indicated glass transition temperatures (Tg) between 55–90 °C, decreasing with increasing glycerol content and slightly increasing with kaolinite incorporation. Reinforced films also displayed higher residual mass, confirming improved thermal stability. Overall, the acetylated and carboxymethylated starch blend exhibited high biodegradability and moderate-to-high thermal stability, with properties tunable through plasticizer and filler levels. The findings highlight the potential of dual-modified cassava starch films as promising eco-friendly alternatives to petroleum-based packaging materials.

KEYWORDS

Cassava starch; Acetylation; Carboxymethylation; Biodegradable films; Thermal properties; Soil burial biodegradation.

1. INTRODUCTION

The increasing global concern over plastic pollution has intensified the demand for biodegradable alternatives that can replace conventional petroleum-based materials. Traditional plastics persist in the environment for centuries, fragmenting into microplastics that pose significant ecological and human health risks, as reported by (Jambeck et al.,2015) and UNEP (2018). As a result, biopolymers derived from renewable resources have garnered considerable attention, with starch emerging as one of the most promising candidates due to its biodegradability, abundance, low cost, and non-toxicity, as demonstrated by (Le et al., 2019 and Tokiwa et al., 2009).

Cassava (*Manihot esculenta*) starch is particularly suitable for bioplastic development because of its high carbohydrate content, ease of modification, and wide availability in tropical regions. However, the native starch presents challenges, including brittleness, high hydrophilicity, and poor thermal stability, which limit its direct application in packaging and related industries as reported by (Yang et al., 2021). To address these limitations, chemical modification techniques such as acetylation and carboxymethylation have been widely explored. Acetylation introduces hydrophobic acetyl groups, which reduce intermolecular bonding and enhance flexibility and water resistance, as demonstrated by (Wu et al., 2020). In contrast, carboxymethylation introduces carboxymethyl groups that improve solubility, swelling behavior, and compatibility with additives, as reported by (Sadeghi et al., 2021).

Blending chemically modified starches provides a pathway for enhancing the functional performance of starch-based films. Dual modification has been reported to improve mechanical, thermal, and barrier properties beyond those achievable through single modification routes. In addition to chemical modification, incorporating formulation components such as plasticizers and fillers plays a crucial role in tailoring the biodegradability and stability of the material. Glycerol is widely used to improve flexibility and reduce brittleness. In contrast, kaolinite clay serves as a reinforcing filler that enhances structural rigidity and thermal resistance, as reported by (Le et al., 2019 and Kwaśniewska et al.,2020).

Despite significant progress, there remains limited research on the biodegradability and thermal behaviour of films produced from a blend of acetylated and carboxymethylated cassava starch. Most existing studies focus on either single modification pathways or unmodified starch matrices. Understanding how dual modification interacts with the incorporation of plasticizer and filler is essential for designing composites with targeted environmental and functional performance.

Therefore, this study focuses on producing biodegradable films from a 50:50 blend of acetylated and carboxymethylated cassava starch and evaluating their biodegradability and thermal properties. Emphasis is also placed on understanding how glycerol plasticization and kaolinite reinforcement influence environmental degradation behavior and thermal transitions. The findings aim to contribute to the development of sustainable, functional, starch-based materials that can replace petroleum-derived packaging films.

2. MATERIALS AND METHODS

2.1 Sample Collection/Sample Area:

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Cassava tuber were purchased from a farm in Ekosodin community Benin City, Edo State. It is located along the longitude 5o 451 and 6o 151 east and latitude 5o 151 and 6o 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), Ethylene glycol (SRL-99% Purity), Glycerol (WARCHEM-85% Purity), 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 the method described by (Ezeoha and Ezenwanne 2013). 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:

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

2.3 Preparation of Acetylated Starch

The native starch was modified via acetylation using methodology reported by (Henry 2007) with slight modification. 20 g of starch was dispersed in 100 cm^3 of distilled water and then stirred constantly for 30 minutes. The slurry was adjusted to pH 8.0 with 3% NaOH, and 1.2 g 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 0.5 M 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:

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

2.4 Preparation of Carboxymethylated Starch

The native starch was modified via carboxymethylation using the methodology demonstrated by (Adeyanju and Olatoyinbo 2019). 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 100mm-mesh sieve. The yield was calculated using:

$$(\%)Yield = \frac{weight\ of\ modified\ \ starch\ (g)}{weight\ of\ native\ starch\ (g)} x100 \quad (3)$$

Table 1: Experimental Design for Biodegradable Plastic Film Formulation

	Glycerol (g)	Kaolinite (g)
	2	0
		0.5
		1.0
	3	0
50:50 blend of Acetylated Starch and Carboxymethylated Starch		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). 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 50 ^{0}C, and stored at room temperature.

2.6 Physicochemical Properties

The physicochemical properties of the acetylated starch were determined using standard methods. Parameters like moisture content, pH, gelatinization temperature and degree of substitution.

2.6.1 Moisture Content and pH

Using the AOAC method, a crucible was dried in an oven at 105 °C, then cooled in a desiccator and weighed as (W_0). 2 g of the starch sample was added to the crucible, and the weight was recorded as (W_1). The crucible was then placed in the oven at 105 °C for 6 hours. After drying, it was transferred to a desiccator to cool and subsequently weighed as (W_2). The crucible was returned to the oven for another 6 hours to ensure complete drying. After the second drying period, the crucible was weighed again to confirm weight consistency. The pH was measured by dissolving 2 g of starch in 50 mL of distilled water and using a pH meter.

%Moisture content was calculated using:

$$(\%)Moisture = \frac{W1-W2}{W1-W0} x100 \quad (4)$$

2.6.2 Gelatinization Temperature

1 g of dried starch sample was weighed into a beaker filled with 10 mL of distilled water; the pH of the starch was recorded using a calibrated FP20 Mettler Toledo pH meter before it was subjected to heat using a magnetic stirrer with hot plate. The mixture was continuously stirred while the temperature was monitored. The gelatinization temperature was recorded using a thermometer.

2.6.3 Degree Substitution of Acetylated Starch (Ds)

The acetyl group (AG expressed as percentage on dry basis) and the degree of substitution (DS) of cassava starch were determined as demonstrated by (Mark and Mehltretter, 1972). 5 g of starch sample was weighed, transferred to a 250 mL conical flask and dispersed in 50 mL distilled water. Few drops of phenolphthalein indicator were added and titrated with 0.1N sodium hydroxide to permanent pink colour. Then 25 mL of 0.45N NaOH was added to it and shaken vigorously for half an hour. The stopper and neck of flask was flushed with little distilled water and then the excess alkali was titrated with 0.2N HCl to disappearance of pink colour. A total of 25 mL of 0.45N NaOH was titrated as blank. Acetyl group and degree of substitution were calculated as follows:

$$(\%)AD = \frac{(Blank-sample)\ mLx\ M(HCl)\ x\ 0.43\ x100}{\text{weight of sample}} \quad (5)$$

$$DS = \frac{162\ X\ \%Acetyl}{4300-(42\ x\ \%Acetyl)} \quad (6)$$

2.6.3 Degree Substitution of Carboxylmethylated Starch (Ds)

The DS of carboxymethylated starch was determined as reported by (Stojanovic et al., 2005). The carboxymethyl groups in the CMS were first converted to an acid with hydrochloric acid. The acidified starch was then recovered by precipitation with methanol, filtration, washing with methanol and drying. Then, 0.2 M NaOH (10ml) was added to a suspension of accurately 1g weighed carboxylmethylstarch in 10 mL of purified water. The mixture was transferred to a 100-mL volumetric flask and adjusted to the mark with purified water. 25 mL of the solution was transferred to an Erlenmeyer flask and titrated with 0.04M HCl using phenolphthalein as the indicator. The titration was repeated three times, and the average value of HCl volume was used for the calculations. A blank was also titrated.

The DS was calculated using:

$$DS = \frac{162\ x\ nCOOH}{mds-58\ x\ nCOOH} \quad (7)$$

$$mds = \frac{(1-Wwater)}{100} xms \quad (8)$$

$$nCOOH = (V - V_n)\ x\ C_{HCl}\ x\ 4 \quad (9)$$

Where 162 is the molar mass of anhydrous glucose unit (g/mol); nCOOH (mol) is the amount of COOH; mds (in g) is the mass of dry sample; ms (g) is sample mass; Wwater (%) is water content; V (mL) is the volume of HCl used for the titration of the blank; Vn (mL) is the volume of HCl used for the titration of the sample; CHCl (mol/L) is the HCl concentration; and 4 is the ratio of the total solution volume (100mL) and the volume taken for titration (25 mL).

2.7 Characterization

2.7.1 Fourier Transform Infrared (FTIR) Spectroscopy and Thickness of The Film

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. The spectra were recorded (16 scans) in the transparent mode from 4000 to 400 cm-1, as demonstrated by (Bernardino-Nicanor et al., 2017)

The thickness of the bioplastic film was determined using the micrometer screw gauge. Each sample was recorded at five different points. The mean value was recorded as the thickness of the bioplastic.

2.8 Biodegradability Test

The biodegradable behavior of the bioplastic film samples was determined using soil burial decomposition test as proposed by (Nwaka et al., 2025) with slight modifications. Bioplastic films (3 inches by 3 inches) were weighed (W1), buried in moist soil at a 3-inch depth for one week, and reweighed (W2). The percent weight loss was calculated using:

$$(\%)Weight\ Loss = \frac{W1 - W2}{W1} x100$$

2.9 Thermogravimetric/Differential Thermal Analysis (TGA/DTA)

TGA/DTA was conducted using the PerkinElmer TGA 4000 (Netherlands) to assess the thermal stability and decomposition behavior of the bioplastic film. This test provided insights into the materials resistance to heat and the efficiency of the composite's formulation and filler reinforcement.

3. Results and Discussion

Table 2: The Yield, Moisture, pH and Gelatinization Temperature of Native Starch

Yield (%)	Moisture (%)	pH	Gelatinization temperature(oC)
62.3	12.3	6.0	65

From Table 2, the starch yield of 62.3% indicates efficient extraction and minimal processing losses. A moisture content of 12.3% was recorded, which falls within the acceptable range for starch storage stability typically below 13% as reported by (Chisenga *et al.,* 2019), suggesting that the starch can be preserved without significant microbial growth or deterioration. A pH value of 6.0 indicates a slightly acidic nature, consistent with most starch derived from plant sources. This mild acidity can influence starch retrogradation and its suitability for further modification.

Gelatinization temperature is a key indicator of the starch quality, as it reflects the degree of crystallinity and the strength of intermolecular hydrogen bonding within the granules. The gelatinization temperature of 65°C is the temperature at which starch granules begin to swell and lose their crystalline structure upon heating in water. This value is within the expected range (60–70 °C) for cassava starch as reported by (Santos et al., 2016) confirming typical starch behavior with good thermal stability. The observed value thus suggests that the extracted cassava starch possesses a balanced structural integrity, making it suitable for subsequent chemical modifications such as acetylation and carboxymethylation.

Table 3: Degree of Substitution (Dos), Yield and Gelatinization Temperature of Modified Starch.

Sample	Yield (%)	DOS	Gelatinization temp(oC)
Acetylated Starch	61	0.34	51
Carboxymethylated Starch	59	0.27	50
50:50 blend of Carboxymethylated and Acetylated Starch			50

From Table 3, the chemical modification of native starch through acetylation and carboxymethylation was successfully achieved, as reflected in the percentage yield, degree of substitution. The percentage yield serves as a direct indication of the efficiency of the modification process. In this study, the recovered yields were 61% for acetylated starch and 59% for carboxymethylated starch. These values, although slightly below the theoretical maximum, are consistent with the expected recovery range for chemically modified starches. The slight loss in yield can be attributed to multiple factors such as material loss during washing and filtration, dissolution of low molecular fragments in the reaction medium, and partial hydrolysis of starch granules under alkaline conditions. This outcome shows that while some starch chains were degraded, the main polymer backbone remained intact, resulting in a reasonable balance between modification efficiency and product recovery.

DOS values obtained were 0.34 for acetylated starch and 0.27 for carboxymethylated starch, representing moderate substitution levels. These results imply that approximately one in every ten hydroxyl groups was successfully replaced by acetyl or carboxymethyl groups. A moderate DOS of this nature is desirable because it introduces sufficient functional changes to improve the starch's physical and chemical behavior without completely destroying its granular structure or crystalline order. Excessive substitution would make the starch too soluble and reduce its film-forming and structural integrity, while too little substitution might not significantly alter its performance. Therefore, the DOS values reported here suggest that the modification reactions were well controlled and effective in tuning the starch properties toward the desired balance of hydrophilicity, flexibility, and processability.

The moderate DOS values directly influenced several key material

properties. The substitution of hydroxyl groups by acetyl or carboxymethyl groups reduces the extensive hydrogen bonding network that holds the starch granules together, resulting in a looser, more open structure. This structural change increases water affinity, swelling power, and solubility, particularly for the carboxymethylated starch due to the presence of ionic carboxylate groups. Similarly, the introduction of acetyl groups enhances the hydrophilic–hydrophobic balance, improving film flexibility while slightly reducing intermolecular cohesion. These molecular alterations explain the improved gelatinization and swelling behaviors observed for the modified starches.

One of the outcomes of the modification process was the reduction in gelatinization temperature. The native starch gelatinized at 65°C, whereas the acetylated and carboxymethylated starches gelatinized at approximately 51°C and 50°C respectively. The reduction in gelatinization temperature indicates that the structural order of the starch granules was partially disrupted by chemical substitution. Gelatinization involves the unwinding of double helices and the breakdown of crystalline regions within the granules as they absorb water and swell. In native starch, these regions are stabilized by strong hydrogen bonds between hydroxyl groups. Substitution with acetyl or carboxymethyl groups weakens these interactions, making the crystalline zones less stable and easier to disrupt. Consequently, less heat energy is required to achieve gelatinization. The increased hydrophilicity and partial fragmentation of the granules further facilitate this process, allowing water to penetrate the structure more easily and trigger gelatinization at a lower temperature.

The 50:50 blend of starch acetate and carboxymethyl starch also exhibited a gelatinization temperature of about 50 °C, closely aligning with the carboxymethyl starch. This suggests that the blend inherits the combined characteristics of both components. The ionic groups in the carboxymethyl starch promote water absorption and thermal mobility, while the acetylated fraction contributes flexibility and improved film-forming ability. The interaction between these two modified starches results in a material that gelatinizes easily at lower temperatures, displays good water compatibility, and possesses improved mechanical balance. This makes the blend especially attractive for bioplastic formulations where low-temperature processing and moderate mechanical flexibility are required.

Figure 1: Acetylated Starch

Figure 2: Carboxymethylated Starch

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 3, 4 and 5 respectively. Distinct differences in absorption bands among the samples provide evidence of successful chemical modification of the starch molecules.

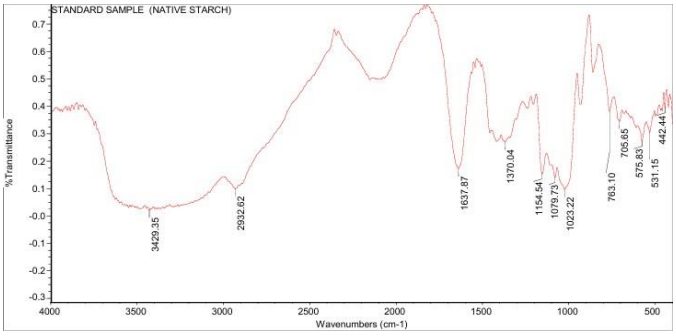

Figure 3: FTIR for Native Starch

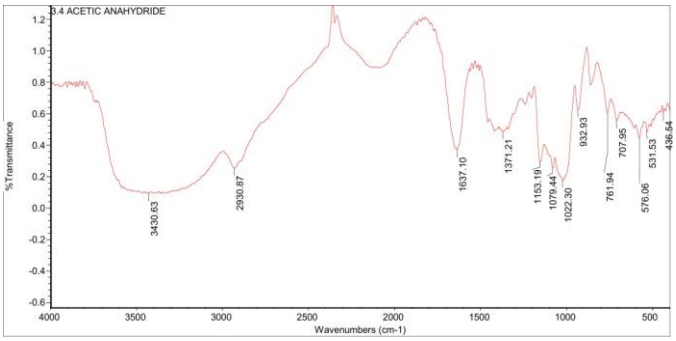

Figure 4: FTIR for Acetylated Starch

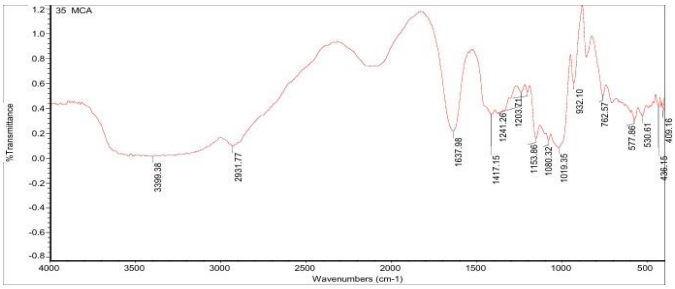

Figure 5: FTIR for Carboxymethylated Starch

From Figure 3, 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. 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 the glycosidic linkages. A weak band around 1640 cm^{-1} is attributed to bound water molecules.

From figure 4, there is a distinct absorption peak around 1740 cm^{-1}, which is attributed to the carbonyl (C=O) stretching vibration of ester groups, confirming acetylation. 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, reducing intermolecular hydrogen bonding. Slight intensity variations in the 1000–1150 cm^{-1} region also indicate modifications to the starch backbone.

From Figure 5, there are notable spectral changes with new absorption peaks appearing at approximately 1600 cm^{-1} and 1410 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations of the carboxylate ($–COO^-$) groups, respectively. These bands confirm the successful introduction of carboxymethyl substituents on the starch backbone. Additionally, a 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.

Comparative analysis of the spectra clearly demonstrates that the chemical modifications carboxymethylation and acetylation were successfully achieved.

Table 4: Bioplastic Formulation, Colour and Thickness				
	Glycerol (g)	**Kaolinite(g)**	**Colour**	**Average Thickness (mm)**
	2	0	White	0.413
		0.5	Off white	0.512
		1.0	Off white	0.518
	3	0	White	0.412
		0.5	Off white	0.520
		1.0	Off white	0.525
50:50 blend of Carboxymethylated and Acetylated Starch	4	0	White	0.420
		0.5	Off white	0.521
		1.0	Off white	0.522
	5	0	White	0.421
		0.5	Off white	0.530
		1.0	Off white	0.531

From Table 4, a 50:50 blend of acetylated starch and carboxymethylated starch shows that the addition of glycerol (plasticizer) and kaolinite (filler) affects both the color and thickness of the films. As the amount of glycerol and kaolinite increases, the colour shifts from white to off- white, indicating changes in the material's structure. The thickness of the films also increases with more glycerol and filler, because glycerol adds flexibility and kaolinite enhances structural integrity. These variations suggest that both ingredients play a key role in customizing the bioplastic's properties for different applications.

Figure 6: Bioplastic Film

Table 5: Bioplastic Film Degradability					
	Glycerol(g)	**Kaolinite(g)**	**Degradability (%) Week 1**	**Degradability (%) Week 2**	**Degradability (%) Week 3**
	2	0	32.5	73.0	Degraded
		0.5	27.0	62.0	Degraded
		1.0	20.0	50.1	Degraded
50:50 blend of Carboxymethylated and Acetylated Starch	3	0	35.5	79.0	Degraded
		0.5	28.6	65.2	Degraded
		1.0	22.0	52.0	Degraded
	4	0	41.0	88.0	Degraded
		0.5	32.0	72.0	Degraded
		1.0	27.0	62.0	Degraded
	5	0	44.0	91.0	Degraded
		0.5	36.5	80.0	Degraded
		1.0	33.5	75.0	Degraded

From Table 5, the biodegradability of the bioplastic films was examined through a three-week soil burial test. Each film contained a 50:50 blend of acetylated starch and carboxymethylated starch, plasticized with 2–5 g glycerol and reinforced with 0–1 g kaolinite. Weight loss was used to determine the percentage degradation, reflecting microbial and moisture activity within the soil as demonstrated by (Tokiwa et al., 2009).

After two weeks, bioplastic weight loss rose from 73 % with (2 g) to 91 % with (5 g) of glycerol. Glycerol's hydrophilic and plasticizing nature enhances water absorption, increases chain mobility, and promotes microbial access to the starch matrix as reported by (Shah et al., 2008), (Ma and Kennedy 2005). Films with higher glycerol degraded faster due to greater moisture uptake and lower crystallinity.

Raising the kaolinite content reduced the degradation rate, at 2 g glycerol from 73% to 62% to 50% as the filler increased from 0 g to 1 g. Kaolinite strengthens and densifies the matrix, restricting water diffusion and microbial penetration as demonstrated by (Ray and Okamoto, 2003; Arrieta et al., 2014). Although this improves stability, it slows down biodegradation because kaolinite is an inorganic and non-degradable material.

A clear trade-off exists, glycerol promotes flexibility and rapid degradation, while kaolinite enhances rigidity and stability. All films completely degraded by week 3, confirming full biodegradability. The best balance occurred at 4 g glycerol with 0.5 g kaolinite, giving moderate degradation (72 %) and adequate strength ideal for packaging.

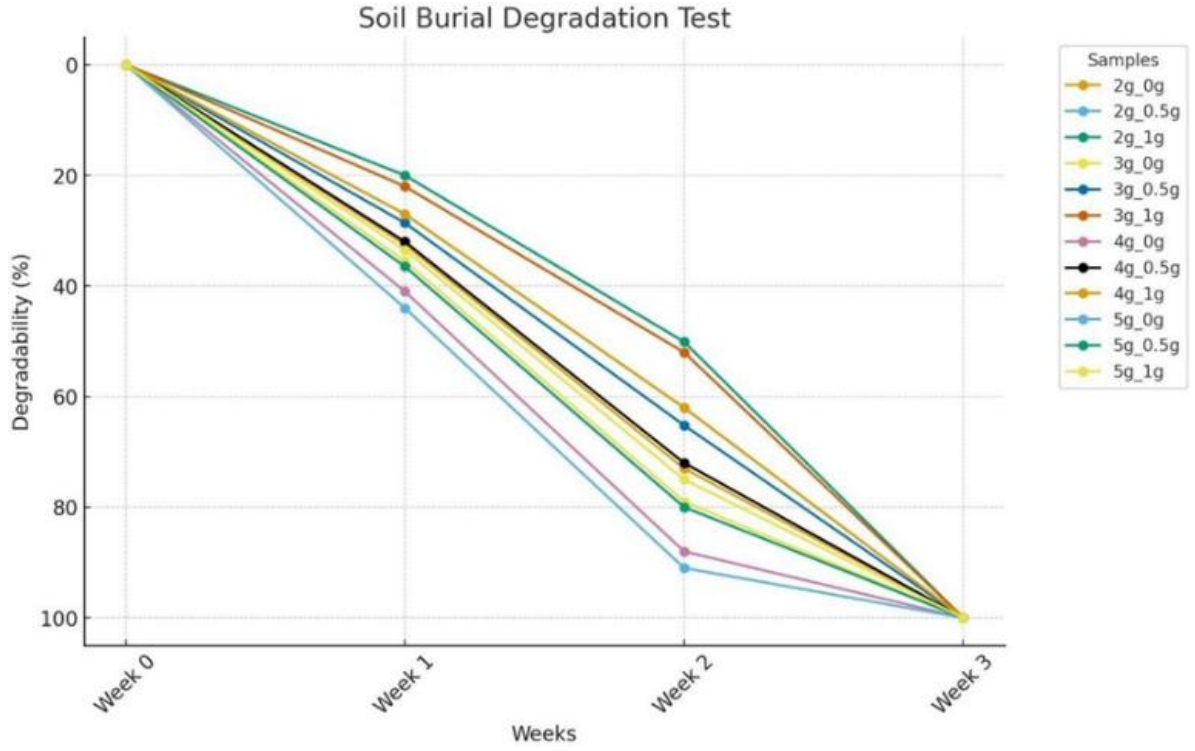

Figure 7: Soil Burial Degradation Test

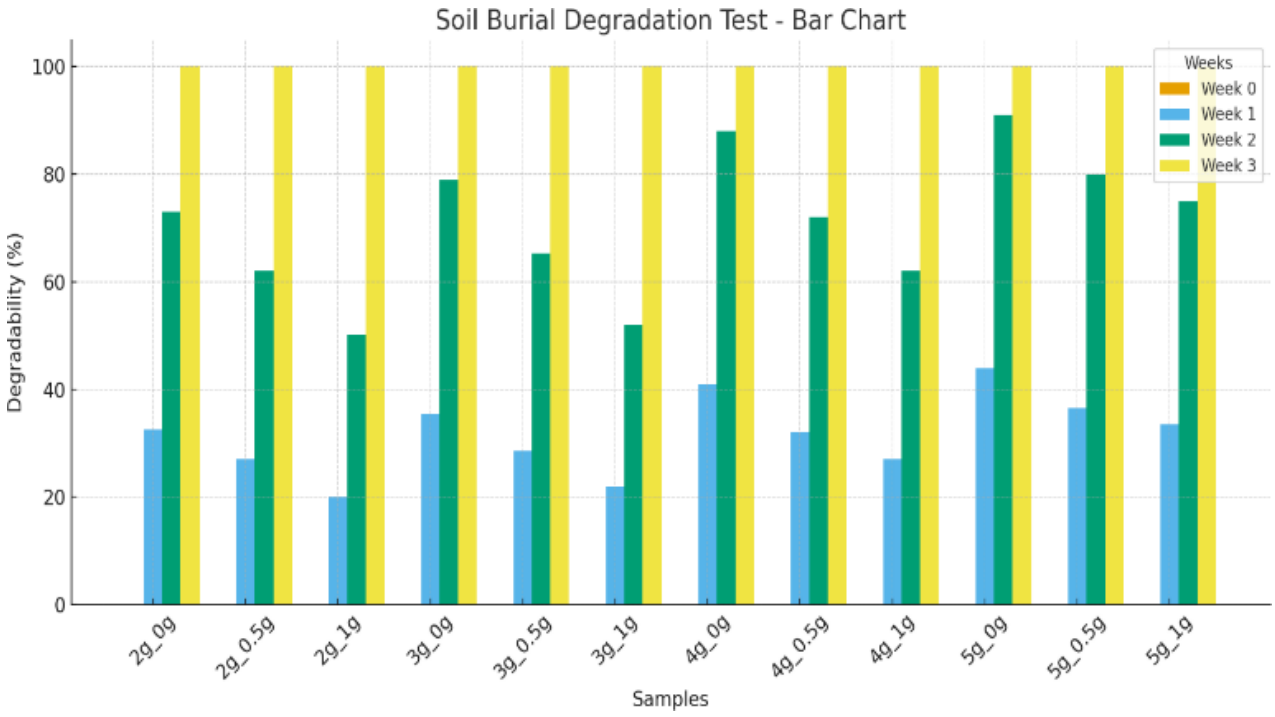

Figure 8: Bar chart of biodegradability of bioplastic film at different concentrations of glycerol and kaolinite.

3.2 Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of Bioplastic Films

The TGA/DTA analysis confirms that through chemical modifications and the incorporation of fillers and plasticizers, the thermal properties of cassava starch films can be tuned to optimize performance for specific applications, particularly in biodegradable plastic production.

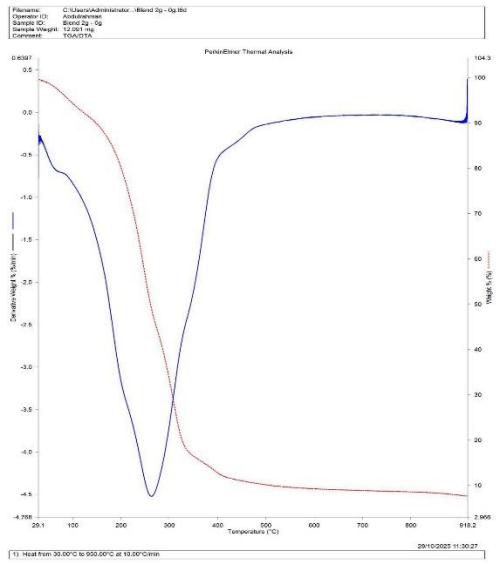

Figure 9: Bioplastic from a modified starch blend with 2 g glycerol and 0 g kaolinite

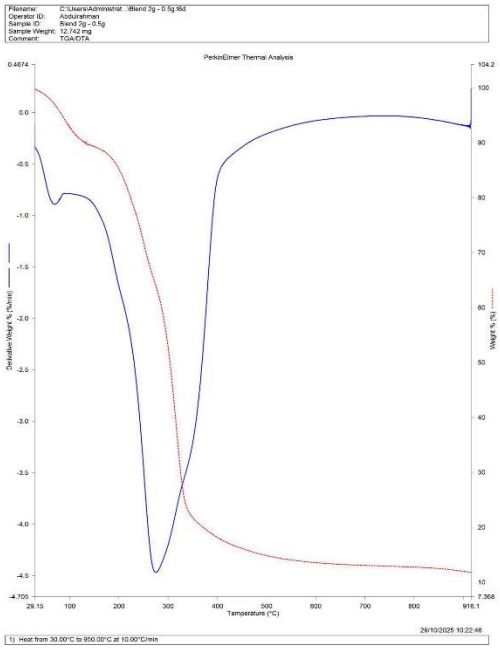

Figure 10: Bioplastic from a modified starch blend with 2 g glycerol and 0.5 g kaolinite

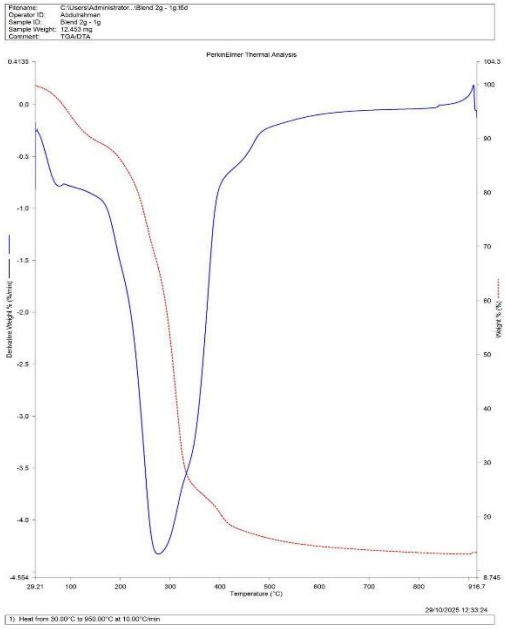

Figure 11: Bioplastic from a modified starch blend with 2 g glycerol and 0.5 g kaolinite

Figures 9, 10 and 11 show the TGA curve for the bioplastic with 2 g glycerol and 0 g filler, which exhibits a typical thermal degradation profile for a starch-based film with high plasticizer content. The initial weight loss observed between 50 °C and 150 °C corresponds to the evaporation of moisture absorbed by the film, which is expected due to the hygroscopic nature of glycerol.

Second Degradation Phase (200 °C – 350 °C): The second weight loss phase occurs at a relatively low temperature, between 200 °C and 350 °C, indicating reduced thermal stability his weight loss is typical of high-glycerol films because the plasticizer weakens the starch matrix, making it more susceptible to degradation at lower temperatures.

Residual Mass: The absence of significant residual mass after 350 °C further highlights the lower thermal resistance of this composite. The starch matrix decomposes more rapidly, suggesting that glycerol does not significantly reinforce the film, which leads to faster breakdown at elevated temperatures.

For the 2 g glycerol, 0 g filler sample, the low thermal stability and rapid decomposition indicate a highly flexible but thermally unstable film.

The DTA thermograms for the 2 g glycerol samples show an endothermic peak between 65 °C and 75 °C, corresponding to the evaporation of moisture and softening of the plasticized starch matrix. The relatively low glycerol content limits the degree of molecular mobility, which results in lower plasticity but a more compact starch structure.

At 0 g kaolinite, the endothermic peak at 75 °C and exothermic peak near 250 °C indicate that the film undergoes rapid heat-induced transitions with lower thermal stability.

At 0.5 g kaolinite, the endothermic peak shifts slightly to 70 °C, and the exothermic peak moves to around 240 °C. This shift demonstrates that kaolinite reinforces the starch matrix, improving heat absorption and delaying degradation.

At 1g kaolinite, the endothermic peak drops to 65 °C. However, the exothermic peak shifts downward to 230 °C, indicating that at higher filler loading, increased rigidity restricts molecular mobility and enhances thermal resistance, albeit at the expense of reduced flexibility. The DTA results for 2 g glycerol compositions indicate that films with low glycerol content exhibit high rigidity and low flexibility. At the same time, the incorporation of kaolinite enhances thermal stability by promoting heat dispersion within the starch matrix.

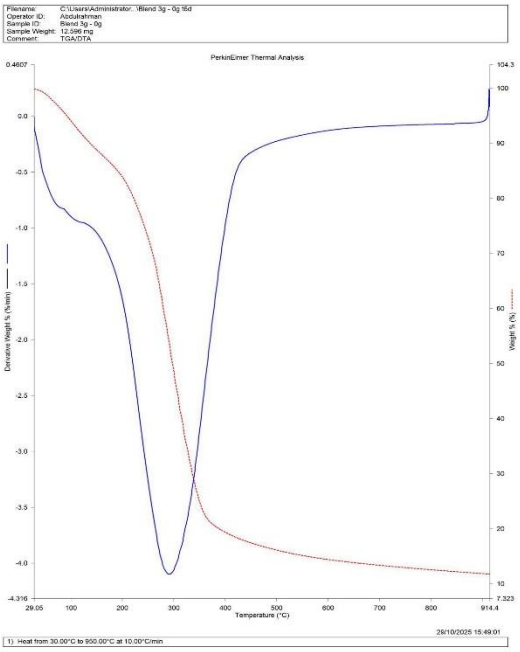

Figure 12: Bioplastic from a modified starch blend with 3 g glycerol and 0 g kaolinite

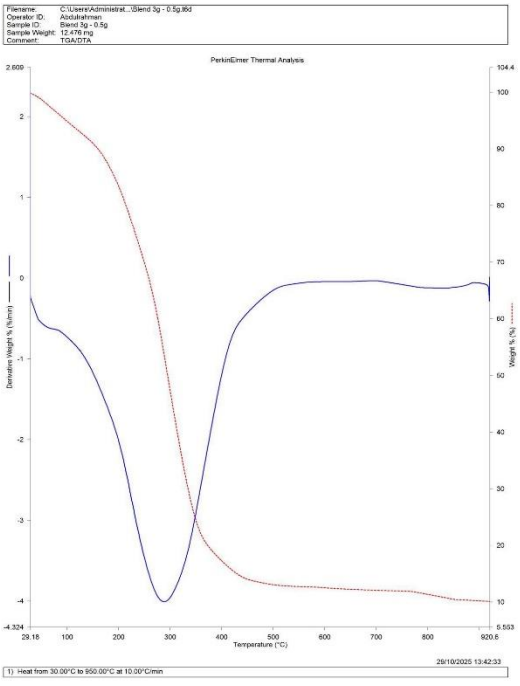

Figure 13: Bioplastic from a modified starch blend with 3 g glycerol and 0.5 g kaolinite

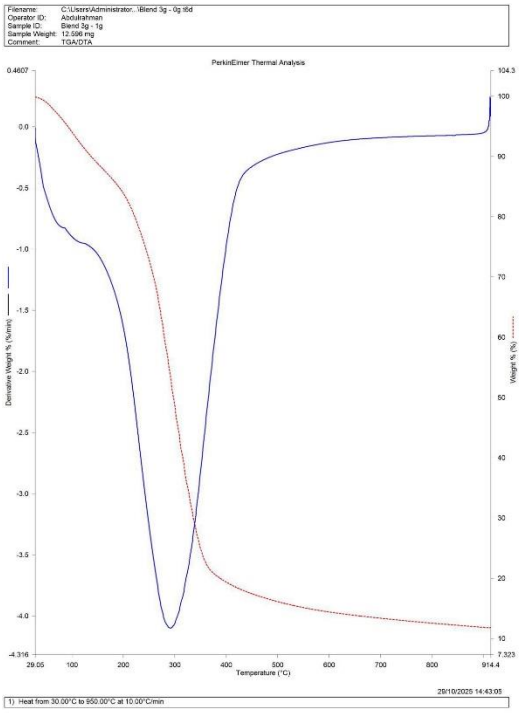

Figure 14: Bioplastic from a modified starch blend with 3 g glycerol and 1 g kaolinite

From Figures 12, 13 and 14, the glycerol content increases to 3 g. The TGA curve reveals similar behavior to the 2 g glycerol sample, but with slightly higher thermal stability.

Initial Weight Loss: The initial weight loss between 50 °C and 150 °C still corresponds to the evaporation of moisture. However, due to the higher glycerol concentration, this sample exhibits higher moisture absorption, as the hygroscopic nature of glycerol increases.

Second Degradation Phase (200 °C – 350 °C): With 3 g glycerol, the degradation temperature shifts slightly higher compared to the 2 g glycerol sample. The onset of degradation occurs at a temperature closer to 200 °C, indicating better thermal stability. However, this phase still occurs at relatively low temperatures, suggesting that glycerol continues to lower the thermal resistance of the starch matrix.

Filler Addition (0.5 g and 1 g kaolinite): The addition of kaolinite at 0.5 g and 1 g increases the thermal stability of the film. The onset of degradation moves closer to 75 °C for the 1 g kaolinite sample. Kaolinite acts as a thermal insulator, enhancing the thermal resistance of the film by stabilizing the matrix, thereby delaying thermal degradation.

Residual Mass: Even with the addition of kaolinite, the residual mass after 350 °C remains quite low, indicating that the glycerol-plasticized starch remains prone to rapid degradation once the initial stages of moisture loss are complete.

3 g glycerol, 0.5 g or 1g kaolinite results in a film that exhibits improved thermal stability due to the presence of kaolinite, but the glycerol still limits the film's overall heat resistance.

With an increase to 3 g glycerol, the films become more flexible, as glycerol effectively disrupts starch–starch hydrogen bonds, increasing chain mobility. The DTA curves reflect this increased flexibility through lower Tg values and smoother endothermic transitions.

At 0 g kaolinite, the endothermic peak at 80 °C corresponds to higher moisture release, while the exothermic peak at 260 °C signifies moderate thermal degradation. This composition is highly flexible but exhibits reduced thermal resistance.

At 0.5 g kaolinite, Tg is at 75 °C, while the exothermic peak moves to 250 °C, indicating that kaolinite improves heat tolerance without severely affecting flexibility.

At 1 g kaolinite, Tg increases to 78 °C, and the exothermic peak at 240 °C suggests that filler addition further stabilizes the film, improving rigidity and heat resistance.

The DTA analysis confirms that 3 g glycerol formulations exhibit a balanced combination of flexibility and moderate thermal stability, especially at 0.5 g kaolinite filler, where molecular motion and thermal insulation are optimally balanced.

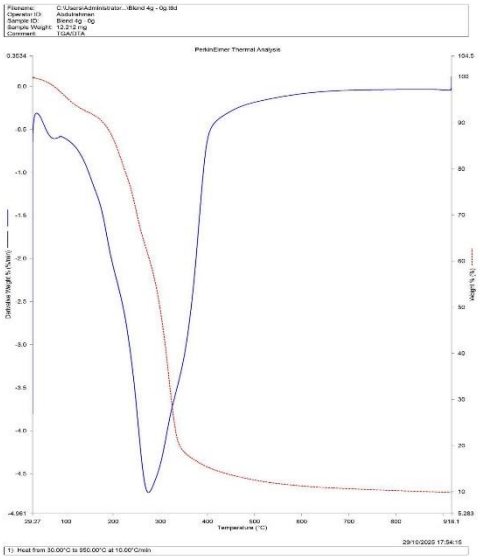

Figure 15: Bioplastic from a modified starch blend with 4 g glycerol and 0 g kaolinite

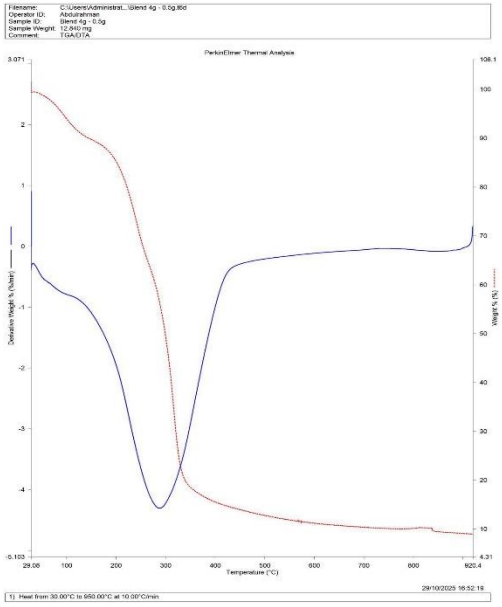

Figure 16: Bioplastic from a modified starch blend with 3 g glycerol and 0.5 g kaolinite

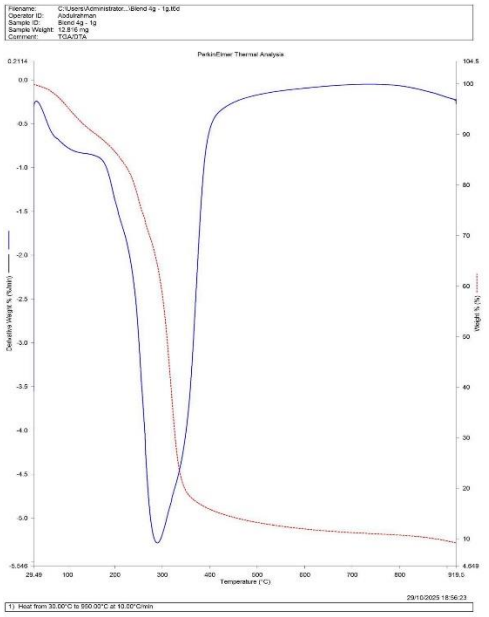

Figure 17: Bioplastic from a modified starch blend with 3 g glycerol and 1.5 g kaolinite

From Figures 15, 16 and 17, the TGA curve for 4 g glycerol indicates even greater flexibility compared to the previous samples, but moisture absorption remains high.

Initial Weight Loss: The initial weight loss is still primarily due to moisture evaporation. With 4 g glycerol, the moisture absorption is more significant, making the film more hygroscopic and prone to higher moisture retention.

Second Degradation Phase (200 °C – 350 °C): The onset of degradation is observed at 55 °C, indicating low thermal stability, primarily due to the high glycerol content. This film is highly flexible, but it degrades relatively quickly under heat, indicating that glycerol's effect of increasing plasticity compromises the film's ability to withstand high temperatures.

Filler Addition (0.5 g and 1 g kaolinite): The addition of kaolinite (0.5 g and 1 g) improves the thermal stability of the film, shifting the onset degradation temperature to 70 °C and 75 °C, respectively. The presence of kaolinite slows down the thermal decomposition, indicating that the filler enhances the rigidity and thermal resistance of the film while maintaining flexibility at moderate levels. However, the film still decomposes relatively quickly in comparison to films with lower glycerol content.

Residual Mass: Despite the presence of kaolinite filler, the residual mass after 350 °C remains low, indicating that while kaolinite improves thermal resistance, glycerol continues to compromise the film's structural integrity at higher temperatures.

The 4 g glycerol, 0 g kaolinite sample is highly flexible but prone to rapid degradation. However, adding kaolinite (0.5 g or 1 g) increases the film's rigidity and thermal resistance, making it better suited for moderate temperature applications.

At 4 g glycerol, the DTA profiles exhibit pronounced endothermic behavior around 70–85 °C, consistent with increased molecular mobility and higher moisture retention due to glycerol's hydrophilic properties. This concentration of plasticizer imparts excellent flexibility but compromises the film's structural stability under heat.

At 0 g kaolinite, an endothermic peak at 85 °C reflects high moisture release and chain mobility, while the exothermic peak at 270 °C indicates poor thermal stability.

At 0.5 g kaolinite, the endothermic transition occurs at 72 °C, with an exothermic peak near

255 °C. The DTA pattern suggests improved heat absorption and slower degradation, highlighting the filler's stabilizing influence.

At 1g kaolinite, the Tg increases to 70 °C, with an exothermic transition at 240 °C, indicating that the addition of kaolinite increases rigidity and enhances thermal insulation, albeit at the expense of ductility.

The DTA results for 4 g glycerol indicate optimal flexibility with moderate thermal reinforcement at 0.5 g kaolinite. This combination maintains the film's integrity at moderate temperatures, making it suitable for biodegradable packaging applications.

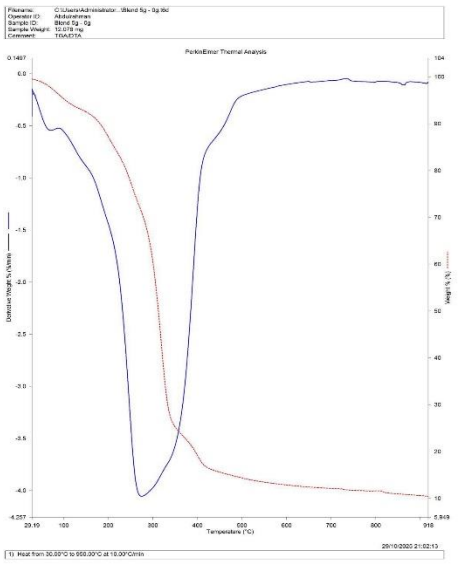

Figure 18: Bioplastic from a modified starch blend with 5 g glycerol and 0 g kaolinite

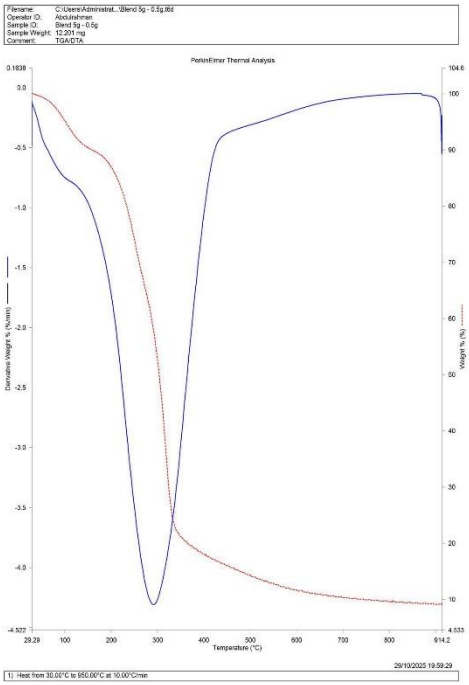

Figure 19: Bioplastic from a modified starch blend with 5 g glycerol and 0.5 g kaolinite

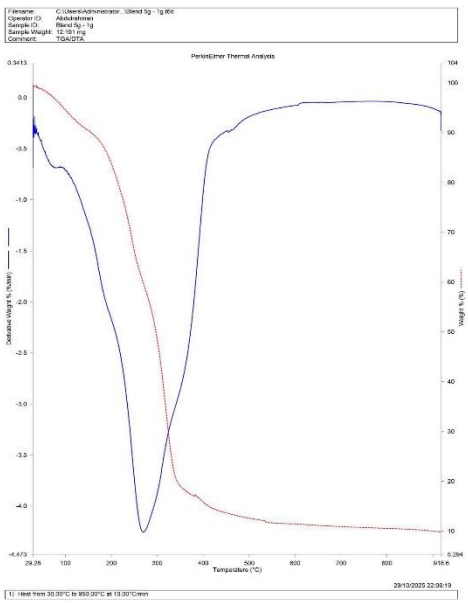

Figure 20: Bioplastic from a modified starch blend with 5 g glycerol and 1 g kaolinite

In all samples with 5 g glycerol, the TGA curve shows the highest flexibility but the lowest thermal stability among all the samples.

Initial Weight Loss: The initial weight loss resulting from moisture evaporation is significant, and the film remains highly hygroscopic due to the large amount of glycerol present. The moisture absorption is at its highest (42.8%), indicating that glycerol is causing the film to absorb and retain more moisture.

Second Degradation Phase (200 °C – 350 °C): The degradation temperature for the 5 g glycerol sample begins at 55 °C, which is the lowest among all samples. The film degrades rapidly under heat, indicating that a high glycerol content significantly reduces thermal resistance and accelerates thermal degradation.

Filler Addition (0.5 g and 1g kaolinite): The addition of kaolinite improves the thermal stability of the film. With 0.5 g kaolinite, the onset degradation temperature increases to 65 °C, and with 1 g kaolinite, the degradation temperature shifts further to 70 °C. However, even with the kaolinite filler, the film remains less thermally stable than other combinations due to the high glycerol content. The kaolinite reinforces the film but does not entirely counteract the plasticizing effects of glycerol, which reduce the film's overall thermal stability.

Residual Mass: The residual mass after 350 °C remains low, indicating that the glycerol- plasticized starch remains highly susceptible to thermal breakdown despite the presence of kaolinite.

5 g glycerol, 0 g kaolinite results in high flexibility, but very low thermal stability. Adding kaolinite (0.5 g or 1 g) helps increase rigidity and thermal resistance; however, the film remains less thermally stable than films with lower glycerol content.

The DTA profiles of 5 g glycerol samples exhibit the highest endothermic peaks (75–90 °C) due to increased water absorption and molecular freedom within the polymer matrix. The films are highly flexible but thermally unstable.

At 0 g kaolinite, an endothermic peak at 90 °C and an exothermic peak at 280 °C indicate significant energy absorption during phase transitions, leading to rapid degradation.

At 0.5 g kaolinite, the Tg increases to 58 °C, and the exothermic peak at 260 °C shows slight improvement in thermal resistance, suggesting effective filler dispersion.

At 1 g kaolinite, the Tg further increases slightly to 60 °C. At the same time, the exothermic peak near 250 °C indicates that excessive kaolinite limits chain flexibility and increases brittleness, despite the composite exhibiting higher resistance to heat flow. At 5 g glycerol, DTA results demonstrate a trade-off between flexibility and thermal endurance. While kaolinite enhances heat resistance, the overall stability remains lower than in lower-glycerol films.

Table 6: Thermal Properties of Biodegradable Plastic Film

Glycerol (g)	Kaolinite (g)	Onset (°C)	Max Degradation (°C)	Tg (°C)	Thermal Stability	Observation
2	0	65	200	80	Low	Flexible but thermally weak
2	0.5	70	210	85	Moderate	Improved stability, reduced moisture
2	1	75	220	90	High	High rigidity, good heat resistance
3	0	60	190	72	Low	Flexible, low stability
3	0.5	70	210	75	Moderate	Balanced stability and flexibility
3	1	72	215	78	High	Rigid, thermally stable
4	0	58	180	65	Low	High flexibility, low stability
4	0.5	70	220	68	High	Stable and flexible (optimal)
4	1	75	225	70	Very high	Rigid, improved heat resistance
5	0	55	170	55	Very low	Very flexible, unstable
5	0.5	65	200	58	Moderate	Moderately stable, flexible
5	1	70	210	60	High	Brittle, more heat-resistant

Recommended Combination for Packaging:

4 g Glycerol, 0.5 g Kaolinite provides a good balance of flexibility (from glycerol) and rigidity/thermal stability (from kaolinite), which is ideal for packaging applications that require:

Flexibility for wrapping or covering products.

Thermal stability to ensure the packaging doesn't degrade under typical environmental conditions (temperature fluctuations).

Moisture resistance, especially if the packaging is intended to protect food or other moisture- sensitive goods.

Performance for Packaging:

Thermal Stability: The onset degradation temperature at 70 °C is sufficient for most packaging conditions where high heat resistance is not needed.

For instance, food packaging typically does not require materials to withstand very high temperatures, so this is an optimal range.

Moisture Resistance: The moisture absorption of 41.7% is relatively low, which is important for ensuring the packaging remains durable and does not degrade or lose integrity in humid environments.

Flexibility: The 4 g glycerol provides enough flexibility for the film to be used in a wide range of packaging applications, from food wraps to more rigid packaging, without compromising its structural integrity.

4. Conclusion

This study confirmed that biodegradable films produced from a 50:50 blend of acetylated and carboxymethylated cassava starch reinforced with kaolinite clay possess highly tunable biodegradability and thermal properties suitable for eco-friendly packaging applications. The moderate degrees of substitution obtained for starch acetate (DS 0.34) and carboxymethyl starch (DS 0.27) confirmed successful chemical modification, which reduced gelatinization temperature, enhanced water interaction, and improved the processability of the starch matrix. FTIR analysis further validated the introduction of acetyl and carboxymethyl functional groups, confirming the structural transformation of native starch into a more reactive and thermally responsive biopolymer.

Biodegradation tests revealed that all films were fully biodegradable within three weeks, with degradation rates strongly influenced by glycerol and kaolinite contents. Increasing glycerol concentration significantly enhanced biodegradability, with weight-loss values rising from 73% at 2 g glycerol to 91% at 5 g after two weeks. This behaviour resulted from glycerol- induced hydrophilicity, which enhanced water uptake, microbial colonization, and enzymatic hydrolysis. Conversely, kaolinite slowed down degradation, reducing the two-week weight loss to values as low as 50–62% at a 1 g filler. This reduction reflects the barrier effect and structural reinforcement imparted by kaolinite, which reduced matrix porosity and microbial accessibility. The best compromise between degradation rate and structural stability was achieved with 4 g glycerol and 0.5 g kaolinite**,** which showed balanced biodegradability (72%) and adequate mechanical integrity.

Thermal analysis (TGA/DTA) revealed a characteristic three-stage decomposition pattern, with major polymer degradation occurring between 170 °C and 225 °C. Glycerol lowered thermal stability, reducing onset degradation temperatures to as low as 55°C high plasticizer concentrations. At the same time, kaolinite enhanced heat resistance, shifting the onset temperatures upward to 70–75 °C and increasing the residual mass. Glass transition temperatures (Tg) ranged from 55 to 90 °C, decreasing with glycerol and slightly increasing with higher kaolinite loading. These findings suggest that the films can be engineered for various temperature-sensitive applications by adjusting the composition of plasticizers and fillers.

Overall, the dual-modified cassava starch films exhibited a favourable combination of complete biodegradability, tunable flexibility, and moderate to high thermal stability**.** The synergistic effects of acetylation, carboxymethylation, glycerol plasticization, and kaolinite reinforcement provide a reliable pathway for tailoring properties to meet various packaging requirements. This work highlights the strong potential of chemically modified cassava starch as a sustainable alternative to petroleum-based plastics, providing a foundation for future optimization in industrial bioplastic development.

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