DEVELOPMENT AND CHARACTERIZATION OF EHTYLENE-GLYCOL-PLASTICIZED CARBOXYMETHYL CASSAVA STARCH FILMS REINFORCED WITH KAOLIN

BY

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UNIVERSITY OF BENIN

BENIN CITY.

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A RESEARCH WORK WRITTEN IN THE DEPARTMENT OF CHEMISTRY, AND SUBMITTED TO THE COLLEGE OF POST GRADUATE STUDIES IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF MASTERS OF SCIENCE (M.Sc) DEGREE IN INDUSTRIAL CHEMISTRY, UNIVERSITY OF BENIN, BENIN CITY, NIGERIA

DECEMBER, 2025

CERTIFICATION

This is to certify that this project work was carried out by **HARRISON EHIJIE IGBELOKOTOR** with matriculation number **PG/PSC0908438**, under the supervision of **DR. (MRS) IYOBOSA OKUNZUWA** in the Department of Chemistry, University of Benin, Benin City, Edo State.

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HARRISON EHIJIE IGBELOKOTOR	**DATE**
(PROJECT STUDENT)	

DEDICATION

This project is dedicated to God almighty, the father of our Lord Jesus Christ; the only wise God with whom success is sure

ACKNOWLEDGEMENTS

I am deeply indebted to these categories of persons who have made invaluable contributions to the overall success of this work. Special thanks to my project supervisor Dr. (Mrs) Iyobosa Okunzuwa for her kind assistance and supervision, the Head of Department and lecturers of Department of Chemistry, University of Benin for equipping me with the principles of Industrial Chemistry. I wish to thank my project mates who together we all worked as a team. I also want to salute my wonderful irreplaceable wife Mrs. Ada Grace Ehijie for her all-round support. My ultimate appreciation is to God, the father of our Lord Jesus Christ, the source and sustainer of life.

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ABSTRACT

This study focused on the growing environmental concern over conventional petroleum-based plastics by the development and characterization of biodegradable starch-based bioplastic films from carboxymethyl cassava starch. The starch powders were extracted from cassava by cold extraction method which gave a yield percent of 17.3%. The physicochemical properties of the extracted starch resulted in a moisture content 12.3%, pH, 6.0 and gelatinization temperature, 65^{o}C. The cassava starch was modified to carboxymethyl starch (CMS) for improved mechanical properties. The percentage yield of CMS from the native starch was 59%, degree of substitution and gelatinization temperature gave 0.27% and 50^{o}C. The modified CMS was characterized with Fourier Transform Infrared (FT-IR) Spectroscopy. The FT-IR results showed the presence of O-H, C-H, C-O-C stretching and CO-C ring vibration of carbohydrate, and contained a more intense peaks around 1203-1241cm^{-1}, 1417cm^{-1} and 932cm^{-1} which are consistent with the presence of new functional groups which indicates chemical modification of the native cassava starch. The CMS bioplastic films were prepared using casting method by varying ethylene glycol plasticizer (2g, 3g, 4g, 5g) and varying kaolinite filler (0g, 0.5g and 1g) for each weight of the ethylene glycol. The moisture absorption, acid absorption and water absorption showed similar trend of increased absorption as plasticizer levels increases. Films with no filler absorbed more, while filler addition lowered absorption. Solvent solubility showed that bioplastics were soluble in 1M NaOH and showed no significant change (mass and colour) in absolute ethanol. Mechanical testing such as thickness, tensile strength, elongation at break percent and yield percent of prepared bioplastic films were also evaluated. It was discovered that Increasing ethylene glycol improved flexibility but reduces tensile strength, whereas kaolin enhances strength at low plasticizer levels but reduces flexibility. Based on the mechanical testing, the most suitable sample in terms of strength and elongation occurred at 3g plasticizer with 0.5 and 1g filler. Biodegradable ability of

prepared bioplastic films were also investigated using the soil burial method and all the films were found to have totally degraded after three weeks. The decomposition nature of prepared biodegradable CMS films was investigated by TGA/DTA. Analysis indicated thermal stability up to 180 – 200^{o}C with kaolin contributing to improve heat resistance. This study demonstrates that CMS based films reinforced with kaolin and plasticized with ethylene glycol offer an environmental friendly and functional alternative to conventional plastics showing strong potential for sustainable packaging applications.

CHAPTER ONE

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

In recent years, this growing environmental concern over conventional petroleum-based plastics has driven researchers and industry practitioners alike to explore renewable, biodegradable alternatives. Starch-derived materials have emerged as one of the most promising routes, thanks to their renewable origin, inherent biodegradability and cost-effectiveness. Among the many starches available, cassava (*Manihot esculenta*) starch stands out in many tropical regions due to its abundant availability, high amylose content and film-forming capability (Tongdeesoontorn *et al.,* 2011). However, films made solely from native cassava starch often suffer from brittleness, poor mechanical performance and high water sensitivity. Thus, modification through chemical derivation, plasticization and filler incorporation is commonly adopted.

This project explores the production of starch-based biodegradable plastic films using modified carboxymethyl starch (CMS) from native cassava starch as the polymeric matrix, ethylene glycol (EG) as a plasticizer, and kaolin as a mineral filler. The choice of carboxymethylation alters the starch molecular architecture by introducing carboxymethyl groups, thereby enhancing the compatibility, film-forming ability and functional diversity of the starch network. The use of ethylene glycol as plasticizer aims to improve flexibility, reduce brittleness and facilitate processability of the film. Incorporation of kaolin (a naturally occurring clay mineral) serves multiple purposes: (i) it can improve mechanical strength, (ii) it can enhance barrier properties (by reducing free volume and slowing water/vapour diffusion), and (iii) it contributes to dimensional stability and potential cost-effectiveness by utilizing a low-cost mineral filler medium.

Several reported studies support this strategy. For instance, the incorporation of kaolin into cassava starch film blends significantly reduced water vapour permeability and improved tensile strength, when compared to neat starch films (Mohammadi *et al.*, 2021). Another investigation found that clay (kaolin or its thermally-modified form) reinforcement of cassava-starch based bioplastics led to decreased solubility and water diffusion, and in some cases improved biodegradability due to enhanced microbial activity on the modified structure (Montalvo *et al.*, 2023). Meanwhile, the modification of cassava starch by carboxymethylation has been shown to interact favourably with polymer blends and plasticizers to yield films with improved flexibility and mechanical performance (e.g., in cassava starch–PVA blends with carboxymethyl groups).

By combining carboxymethyl cassava starch with ethylene glycol and kaolin filler, this project aims to synthesize, characterize and optimize biodegradable film materials with improved mechanical, barrier and environmental degradation performance, suitable for applications such as packaging films. Ultimately, the goal is to contribute to the body of sustainable materials research, by developing a film that not only utilizes a locally abundant resource (cassava starch) but also incorporates a low-cost filler and processable plasticizer to address the limitations of conventional starch films.

In so doing, the project addresses key challenges: improving the flexibility and mechanical durability of starch-based films, enhancing water and vapour barrier performance via filler reinforcement, achieving satisfactory biodegradability under realistic conditions, and assessing the potential of such films for practical application. In a human sense, the work also aligns with the broader social and environmental imperative: reducing plastic waste, valorizing agricultural resources (in regions such as Nigeria where cassava is plentiful), and moving toward a circular economy model where packaging ceases to be an enduring pollutant and instead becomes a life-cycle-friendly material.

1.1.1 BACKGROUND OF THE STUDY

The global plastic crisis has led to unprecedented pressure on researchers, industries, and governments to pursue environmentally sustainable materials. Plastics remain deeply embedded in modern life, used in packaging, medicine, engineering, consumer products, agriculture, and more. However, the environmental burden of non-biodegradable plastics—manifesting in landfill overflow, microplastic accumulation, and marine pollution—has exposed the fragility of our waste management systems (Reddy *et al.*, 2019).

Consequently, biopolymers derived from natural sources such as cellulose, chitosan, proteins, and starch have gained significant attention. Among these, starch holds a strategic advantage, particularly in regions where agricultural waste and starch-rich crops like cassava, potato, and maize are readily available. Starch-based bioplastics are inherently biodegradable, renewable, and safer for the environment. Yet, their major drawback lies in their physicochemical limitations, which often include high moisture absorption, brittleness, and low mechanical strength (Mali *et al.*, 2020).

Chemical modification addresses these issues by altering the molecular structure of starch. Carboxymethyl starch (CMS) introduces carboxymethyl groups, which increase starch's solubility, reduce crystallinity, and produce more uniform and flexible films. CMS also improves compatibility with plasticizers and fillers, making it an appealing foundation for bioplastic film production (Kittipongpatana & Kittipongpatana, 2019).

However, CMS alone cannot resolve all functional gaps. Plasticizers such as ethylene glycol increase flexibility and reduce brittleness by enhancing polymer chain mobility. Fillers such as kaolin introduce structural reinforcement and moisture resistance. Studies have shown that clay-based fillers can significantly enhance mechanical properties through polymer–filler interactions that restrict matrix mobility while improving structural rigidity (Achor *et al.*, 2021).

This study builds on these insights by exploring how CMS interacts with ethylene glycol and kaolin simultaneously. While each component individually improves certain film properties, their combined influence remains inadequately studied—especially in contexts where locally sourced cassava starch can be used to create sustainable and low-cost bioplastics.

1.1.2 STATEMENT OF THE PROBLEM

Despite the rising interest in biodegradable materials, the global bioplastic industry still struggles with developing materials that match the performance of petroleum-based plastics. Native starch films remain too brittle, weak, and moisture-sensitive to serve in many real-world applications. Even modified starches such as CMS need additional enhancements to achieve adequate tensile strength, flexibility, and dimensional stability.

Plasticizers increase flexibility but often reduce strength; fillers improve strength but may compromise elasticity. Balancing these competing effects requires careful optimization of composition and manufacturing conditions.

Thus, the central problem addressed in this study is the lack of a well-optimized bioplastic film formulation that combines CMS, ethylene glycol, and kaolin to produce a film with desirable mechanical, thermal, and physicochemical properties suitable for practical use.

1.1.3 JUSTIFICATION OF THE STUDY

This research is justified on several grounds:

1. Environmental necessity

Biodegradable films provide a sustainable response to plastic pollution, offering materials that can reintegrate into the environment without causing harm.

2. Local resource utilization

Nigeria is one of the world's leading producers of cassava. Using cassava starch to produce CMS-based films promotes local value addition and encourages industrial growth based on agricultural resources.

3. Advancement of scientific knowledge

The combined effect of CMS, ethylene glycol, and kaolin remains insufficiently explored. This study provides insights that may guide future research and industrial applications.

4. Industrial relevance

Industries such as food packaging require flexible, strong, and environmentally friendly films. CMS-based bioplastics reinforced with kaolin have potential for commercial scalability.

5. Real-world performance (e.g., food packaging trials, shelf life effects, and standardized biodegradation testing) remains underreported for some combinations (Tan *et al.,* 2024; Adamu *et al.,* 2025). These gaps justify a careful experimental study that synthesizes carboxymethyl cassava starch films plasticized with ethylene glycol and reinforced with kaolin, and then characterizes mechanical, barrier and biodegradation endpoints.

1.1.4. COST-EFFECTIVENESS

Cassava starch, ethylene glycol, and kaolin are relatively inexpensive, making the resulting material more accessible for large-scale production.

1.1.5 AIM OF THE STUDY

To produce and comprehensively analyze ethylene glycol plasticized carboxymethyl starch-based bioplastic films reinforced with kaolinite filler, evaluating the biodegradability, thermal, mechanical properties, water absorption, moisture absorption, HCl absorption/solubility, base and ethanol solubility with the goal of optimizing bioplastic film formulation that combines CMS, ethylene glycol, and kaolin to produce a film with desirable properties suitable for practical use.

1.1.6 OBJECTIVES OF THE STUDY

1. To synthesize carboxymethyl starch (CMS) from cassava starch.

2. To formulate bioplastic films using varying proportions of ethylene glycol and kaolin.

3. To analyze structural interactions using FTIR spectroscopy.

4. To evaluate the mechanical properties of the films (tensile strength, elongation at break).

4. To determine the films’ moisture absorption, water solubility, swelling behavior, and biodegradability.

5. To assess thermal characteristics using DTA/TGA.

7. To compare reinforced films against unreinforced CMS films to identify improvements.

1.1.7 SCOPE OF THE STUDY

This study covers:

Extraction and carboxymethylation of cassava starch.

Production of CMS-based bioplastic films with ethylene glycol and kaolin.

Analysis of thermal, mechanical, structural, and physicochemical properties.

It does not involve industrial-scale processing, long-term aging studies, or cost–benefit analysis.

1.2 LITERATURE REVIEW

Plastic pollution and the long persistence of petroleum-derived packaging have driven a strong research push toward biodegradable alternatives derived from renewable biomass (Aashima *et al.*, 2020). Starch–based films are among the most promising solutions because starch is abundant, low-cost and biodegradable, and cassava (Manihot esculenta) is a particularly attractive feedstock in tropical regions due to its large-scale availability and favorable film-forming properties (Tongdeesoontorn *et al.*, 2011; Akmeemana *et al.*, 2023). However, native cassava starch films typically show high brittleness, low flexibility and strong sensitivity to moisture —limitations that must be addressed if such films are to be viable for packaging applications (Tongdeesoontorn *et al.*, 2011; Akmeemana *et al.*, 2023).

1.2.1 STARCH AS A BIOPOLYMER

Starch is a naturally occurring polysaccharide consisting of two major components: amylose, a mostly linear glucose polymer, and amylopectin, a highly branched molecule. Its semi-crystalline structure provides film-forming capability but also introduces challenges such as brittleness, retrogradation, and poor mechanical strength (Jane, 2020).

Starch's advantages for bioplastic production include:

- Renewable origin
- Low cost
- Biodegradability
- Ease of modification
- Excellent film-forming behavior

However, native starch films absorb moisture readily due to the abundance of hydroxyl groups, leading to swelling, reduced strength, and poor stability (Mali *et al.,* 2020). These limitations necessitate chemical or physical modification for practical application.

1.2.1 CHEMICAL MODIFICATION: CARBOXYMETHYLATION

Chemical modification of starch is a common strategy to improve functional properties. Carboxymethylation introduces carboxymethyl groups onto the starch backbone, increasing hydrophilicity in a controlled way while improving inter-polymer interactions and compatibility with other film components (Tongdeesoontorn *et al.,* 2011; Lin *et al.,* 2022).

Carboxymethyl starch (CMS) is produced by etherification of starch with monochloroacetic acid in the presence of alkali. This reaction introduces carboxymethyl groups, resulting in:

- Increased water solubility
- Reduced retrogradation
- Decreased crystallinity
- Enhanced thermal stability
- Improved flexibility in films

(Kittipongpatana & Kittipongpatana, 2019; Surojanametakul *et al.,* 2021).

The Degree of Substitution (DS) significantly influences CMS functionality. CMS with DS values ranging from 0.2 to 0.6 is commonly employed for bioplastic applications due to its improved mechanical and swelling behavior.

CMS also exhibits better compatibility with plasticizers and fillers than native starch, making it an excellent candidate for biocomposite film production.

Studies also show that blending cassava starch with carboxymethyl cellulose (CMC) or using carboxymethylated starch derivatives report improved tensile strength, altered water uptake and modified barrier behaviour compared with films from native starch alone (Tongdeesoontorn *et al.*, 2011; Lin *et al.*, 2022). These effects are attributed to new hydrogen-bonding patterns and electrostatic interactions introduced by the carboxylate functionalities, which can increase cohesive energy density of the film matrix and help tailor its hydric behaviour.

1.2.2 PLASTICIZERS — role and choice of ethylene glycol

Plasticizers are essential for converting brittle thermoplastic starch into flexible films. Glycerol is the most widely used plasticizer in the literature, producing highly flexible but often overly hygroscopic films (Mbey *et al.*, 2012; Abera *et al.*, 2020).

Plasticizers reduce stiffness and improve elasticity by inserting themselves between polymer chains. Commonly used starch plasticizers other than glycerol include sorbitol, urea, and polyols. Ethylene glycol is particularly attractive due to its small molecular size and strong hydrogen-bonding capability, promoting enhanced chain mobility and film flexibility (López *et al.*, 2019).

Ethylene glycol (EG) is less commonly used than glycerol or sorbitol, but mechanistic studies show that small polyol plasticizers —including EG—can interact strongly with both amylose and amylopectin chains, lowering glass transition temperature and promoting chain mobility (Smits *et al.*, 2003).

Studies by Sharma *et al.*, 2022; Martins *et al.*, 2020 also reveals that ethylene glycol:

- Increases elongation at break
- Reduces glass transition temperature (tg)
- Decreases tensile strength at high concentrations
- Reduces surface cracking and brittleness

- Enhances molecular dispersion

Recent experimental work has directly tested ethylene glycol as a plasticizer in non-conventional starch films and reported improvements in flexibility and homogeneity at certain concentrations, although the balance between tensile strength, elongation and water sensitivity must be optimized (Lubis, 2018; Arroyo-Esquivel *et al.,* 2025). EG's lower molecular weight relative to glycerol means it may produce different plasticizing behaviour (more mobility but potentially higher volatility or migration), so its concentration and processing conditions need careful control.

1.2.3 MINERAL FILLERS: kaolin and clay minerals

Inorganic fillers such as clays and kaolin are commonly added to biopolymer films to improve mechanical strength, thermal stability and barrier properties (Mbey *et al.,* 2012; Méité *et al.,* 2022). Kaolin (kaolinite) is a 1:1 layered aluminosilicate that is abundant and inexpensive; its plate-like particles can act as physical barriers to mass transfer and as stress-bearing inclusions within the polymer matrix. Classical work on cassava starch–kaolinite composites demonstrates that kaolinite reduces water vapour permeability and can increase tensile strength when well dispersed, but the effects depend strongly on filler loading, particle dispersion and interfacial adhesion (Mbey *et al.,* 2012; 2014). When poorly dispersed or present at high loadings, kaolin may act as stress concentrators and reduce elongation at break. Recent studies using metakaolin or thermally modified kaolin report similar trends: improved mechanical and barrier responses at optimized filler contents but with trade-offs in flexibility (Méité *et al.,* 2022).

1.2.4 COMBINED STRATEGIES: modified starch + plasticizer + filler

A convergent theme in the literature is that the best film performance may arises when chemical modification, plasticization and filler reinforcement are combined in a coordinated way.

Carboxymethylated starch improves polymer–filler compatibility in many blends (Lin *et al.,* 2022; Tavares *et al.,* 2019), while an appropriately chosen plasticizer (glycerol, sorbitol or EG) tunes ductility and processability (Abera *et al.,* 2020; Lubis, 2018). Clay/kaolin fillers can offset the strength losses that occur with higher plasticizer loadings and simultaneously improve barrier performance (Mbey *et al.,* 2012; Méité *et al.,* 2022). Several studies on cassava-based films reinforced with clay minerals or kaolinite report a synergistic effect: moderate kaolin content plus suitable plasticizer concentration and surface interactions produce films with both higher tensile strength and acceptable elongation (Mbey *et al.,* 2012; Gunathilake *et al.,* 2024).

1.2.5 BIODEGRADABILITY AND APPLICATION PERFORMANCE

Biodegradability remains a central endpoint: cassava-derived films biodegrade relatively quickly under composting or soil conditions owing to their hydrophilic nature and enzymatic accessibility (Akmeemana *et al.,* 2023; Maitha *et al.,* 2024). Importantly, filler addition (kaolin) may slow water ingress slightly and alter degradation kinetics, but does not generally prevent biodegradation when filler content is moderate (Mbey *et al.,* 2012; Méité *et al.,* 2022). For packaging applications, the interplay between mechanical strength, barrier performance, processing costs and biodegradation profile will dictate practical viability; several recent pilot studies demonstrate that cassava-starch films with mineral fillers can protect food while degrading in realistic environments (Tan *et al.,* 2024; Gunathilake *et al.,* 2024).

The literature supports the promise of cassava starch as a sustainable film matrix, shows that carboxymethylation improves film interactions and mechanical cohesion, and indicates that mineral fillers like kaolin can boost strength and barriers — but it also shows that the plasticizer choice (and its concentration) and filler dispersion are make-or-break factors. This project sits squarely at this intersection: by systematically testing carboxymethyl cassava starch + ethylene glycol + kaolin which gave a useful niche of knowledge and produce results that are both scientifically meaningful and practically relevant to reducing plastic waste where cassava is available. that’s research that matters — to soils, to consumers, and to communities that grow cassava.

CHAPTER 2

MATERIALS AND METHODS

2.1 MATERIALS

Analytical weighing balance

Magnetic stirrer with hot plate

Water bath (set at 80°C for gelatinization)

Thermometer (for temperature monitoring)

Mold (for film casting)

Spatula

Oven

Desiccator (for moisture prevention and sample preservation)

Drying trays

Airtight storage container

Cassava root

Mesh sieve (chiffon fabrics)

2.2 REAGENTS

Concentrated sodium hydroxide

Hydrochloric acid

Acetic anhydride

Ethylene glycol

Kaolinite

Ethanol

Distilled water

Phenolphthalein

Isopropyl alcohol

2.3 METHODOLOGY

2.3.1 Sample Collections and Preparation

Cassava Starch Preparation

The cassava tubers were manually peeled and cleaned with portable water before being mechanically grated. Three times as much water as the shredded cassava was added to the mixture. The mixture was sieved using a coarse sieve and filtered with a filter cloth. The filtrate was then allowed to settle for six hours. Afterward, the starch was mixed with water again and left to settle for a full day, followed by manual decantation. The dewatered wet starch was oven-dried at a low temperature for four hours to ensure that the starch had the lowest possible moisture content.

2.3.2 Starch Yield

The starch yield from the extraction process was calculated using the Equation below.

$$\text{Starch yield (\%)} = \frac{\text{weight of extracted starch (g)}}{\text{weight of cassava tubers}} \times 100$$

2.3.3 Determination of Gelatinization Temperature, pH, and Moisture content of extracted starch:

1 g of dried extracted starch was placed in a beaker filled with 10 ml of distilled water and subjected to heat treatments using a hot plate. While stirring and noting the temperature at which gel formed. The

gelatinization temperature was recorded using a thermometer. The starch pH was recorded using a calibrated pH meter.

The moisture content was determined using the methodology proposed by Alobi *et al.*, (2017). A weighed quantity of the starch was dried in an oven at 105^{o}C for 24 h. The dried sample was weighed, and the percentage moisture content was calculated using the Equation

$$\text{Moisture content (\%)} = \frac{\text{initial} - \text{final weight}}{\text{initial weight}} \text{ x } 100$$

2.3.4 Preparation of Carboxymethyl Starch

Organic slurry method of modification was used as described by Lawal, *et al.*, (2007). 10.0 g of the native cassava starch was suspended in 2-propanol (200 ml). 10 ml 3% (w/v) of aqueous sodium hydroxide solution was added. The mixture was stirred at controlled temperature (40 °C) for 10 min. 80 ml Sodium monochloroacetate of 2.0 M concentration was added and stirring was continued for 10mim. The pH of mixture was adjusted to about 5.0 by addition 3% hydrochloric acid. The carboxymethyl starch was filtered and washed with 80 % aqueous ethanol until the pH of liquid becomes neutral (7.0). The modified starch was dried at 50 °C for 6 hrs. The dried carboxymethyl starch was passed through a 100-mesh sieve.

$$\text{yield (\%)} = \frac{\text{weight of modified starch (g)}}{\text{weight of native starch (g)}} \text{ x } 100$$

2.3.5 Determination of Degree of Substitution of Carboxymethyl starch:

$$\text{\%COOH} = \frac{\text{Volume of NaOH x Normality of NaOH x 45 x 100}}{\text{Weight of dry CMS sample x 1000}}$$

$$\text{DS} = \frac{162 \text{ x \%COOH}}{4500 - (58 \text{ x \%COOH})}$$

2.3.6 Fourier Transform Infrared (FT-IR) spectroscopy determination of native starch and modified starch

The FT-IR analysis of both the native and modified starch were carried out on a Perkin Elmer FT-IR spectrophotometer (Perkin Elmer, Inc., MA, USA) using a potassium bromide (KBr) disc. The spectra was able to recorded (16 scans) in the transparent mode from 4000 to 400 cm-1 (Bernardino-Nicanor *et al*., 2017)

2.3.7 Preparation of Biodegradable Plastic Film and Casting of films

The preparation was done following a refined modification of the method proposed by Nwaka *et al* (2025). 10 g of carboxymethyl starch (CMS) was weighed in a beaker to which 100 mL of distilled water was added. It was stirred at 350 rpm for 10 min on a magnetic stirrer. Kaolinite powder was then added at different weight, 0g : 0% (w/w), 0.5g :5% (w/w), 1g: 10% (w/w) and stirred. Ethylene glycol was also added at different weight (2g, 3g, 4g, 5g) and stirred at 350 rpm for 15 min. The solution was heated at about 80 ^{o}C to form gel with continuous stirring. The slurry was then poured onto a tin-can mould, dried in a hot air oven at 50 ^{o}C and stored at room temperature.

2.3.8 Experimental Design for Biodegradable plastic Film Formulation

TABLE: 2.1 Bioplastic film Formulation

	ETHYLENE GLYCOL (plasticizer)	FILLER(kaolinite)
	2g	0g
		0.5g
		1.0g

Carboxymethyl Starch (CMS)	3g	0g
		0.5g
		1.0g
	4g	0g
		0.5g
		1.0g
	5g	0g
		0.5g
		1.0g

2.4 Physicochemical properties and Characteristics of bioplastic Film

Chemical Properties of Biodegradable Film; all carried out using the method proposed by Nwaka *et al*., (2025) with slight modifications.

Water Absorption Resistance: The water absorption resistance of the prepared bioplastic films was evaluated by soaking them in water at room temperature for 24 hours, drying them with cotton pieces, and weighing them. The percentage of water absorption was calculated

$$\text{Water absorption (\%)} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100$$

Acid Absorption Resistance: For acid absorption resistance, 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

Acid Absorption (%) = $\frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}}$ x 100

Base Absorption Resistance: the base absorption resistance was tested by soaking the films in 1M sodium hydroxide solution and weighing them at regular intervals. The percentage of base absorption was calculated

Base Absorption (%) = $\frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}}$ x 100

Moisture Absorption Resistance: Moisture absorption resistance was determined by drying the bioplastic films in a desiccator until a constant weight (W1) was achieved, then placing them in a normal atmosphere for 24 hours, and weighing them again (W2). The percentage of moisture absorption was calculated

Moisture Absorption (%) = $\frac{W2 - w1}{w2}$ x 100

Solvent Solubility Test: The solubility test involved placing the bioplastic film pieces in test tubes containing ethanol and observing solubility at 28-30 °C

Biodegradability Test: The biodegradability property was tested using the soil burial method. Bioplastic films (2 inches by 2 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

(%) Weight loss = $\frac{W1 - W2}{W1}$ x 100

2.5 Mechanical Properties

Thickness of the Film

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

Mechanical Properties: 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 10kN**, the percentage elongation was also calculated,

$\%Elongation = (L-Lo)/Lo \times 100$, where L is the final length and Lo is the initial length. Tensile Strength, Elongation at Break, Ultimate Elongation, Toughness, Yield Point, is obtained from the stress – strain curve.

2.6 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.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 RESULTS

Table 3.1 Percentage Starch Yield, gelatinization temperature, pH and moisture content of extracted starch from cassava

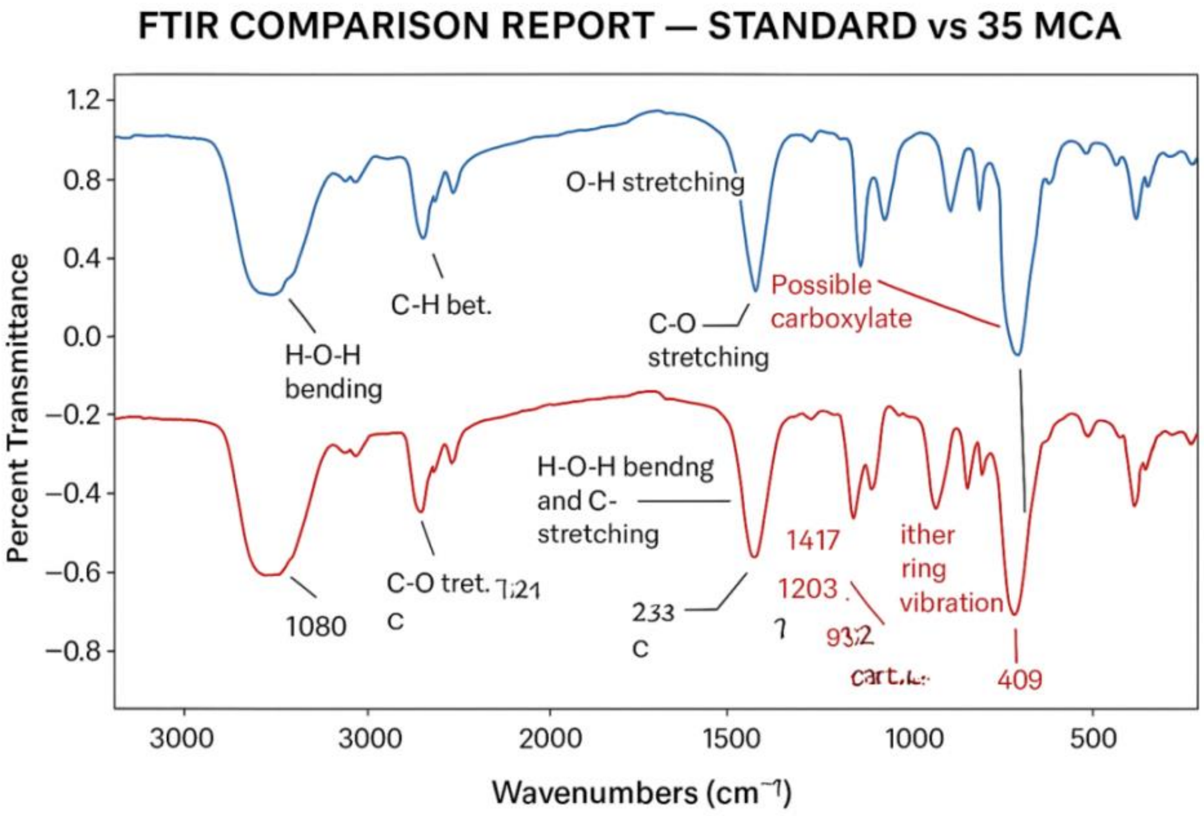
% Starch yield	Gelatinization temperature	pH	Moisture content
17.3%	65^oC	6.0	12.3%

Table 3.2 Degree of substitution [DOS], percentage yield and gelatinization temperature of modified starch

Sample	Percentage yield	DOS	Gelatinization temp.
Carboxymethyl starch	59%	0.27	50^oC

3.1.1 Fourier Transform Infrared (FT-IR) spectroscopy determination of native starch and modified starch

FT-IR In simple terms, both the native (standard) and CMS (known as MCA) samples exhibit characteristic fingerprints of starch-based materials showing strong O-H stretching around 3400cm^{-1}, C-H stretching at about 2030cm^{-1}, H-O-H bending near 1638cm-1, and carbohydrate related C-O/C-O-C vibrations in the 1150-1000cm^{-1} region. The modified CMS (MCA) sample contains additional and more intense peaks around 1203-1241cm^{-1},˜ 1417cm^{-1} and 932cm^{-1}. These are consistent with the presence of new functional groups such as carboxylates, ethers or esters, indicating chemical modification. This suggests successful chemical modification which introduces a new functional group to improve solubility and film properties. The comparison between native (standard) and CMS (MCA) is shown in Figure 1 below.



3.2 Physicochemical properties of bioplastic film

Table 3.3: Percentage water absorption, acid absorption and moisture

Samples	**Water absorption (%)**	**Acid absorption (%)**	**Moisture (%)**

CMS 2g-0g	73.9	25.2	5.90
CMS 2g-0.5g	70.0	22.4	5.40
CMS 2g-1g	67.2	19.0	4.92
CMS 3g-0g	77.7	36.5	7.20
CMS 3g-0.5g	72.1	30.2	6.48
CMS 3g-1g	65.0	26.6	5.9
CMS 4g-0g	88.0	40.6	8.40
CMS 4g-0.5g	74.8	35.1	7.56
CMS 4g-1g	66.1	31.2	6.89
CMS 5g-0g	105	45.5	9.80
CMS 5g-0.5g	90.4	40.7	8.64
CMS 5g-1g	88.4	37.0	7.87

Moisture absorption

Results shows that moisture absorption increased steadily with higher ethylene glycol levels, indicating enhanced hydrophilicity as plasticizer concentration increased. Films without filler consistently showed the highest moisture uptake, while kaolin, especially at 1g slightly reduced absorption by improving structural compactness, however this reduction was limited, and the plasticizer remained the dominant factor. The interaction between both EG and kaolin was evident, which shows that moisture behavior is dependent on their combined influence.

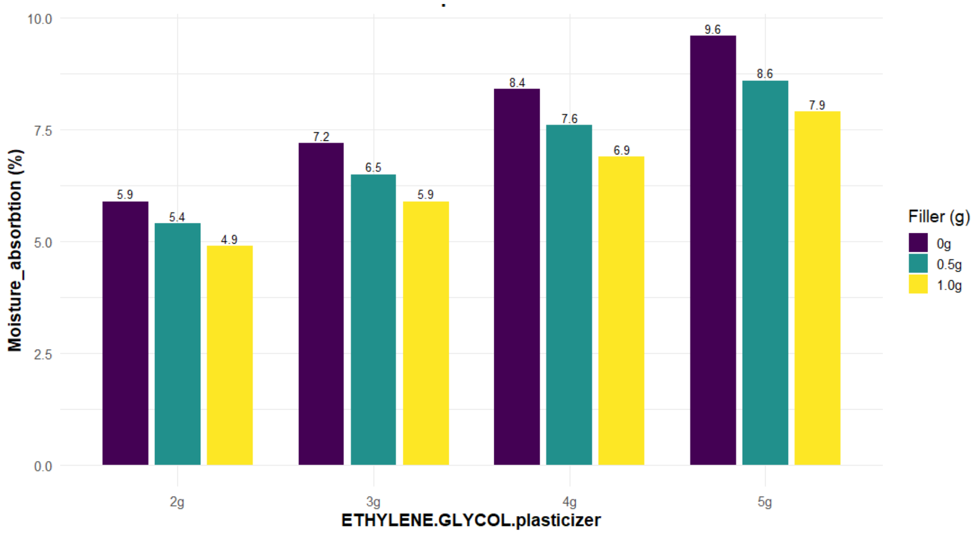


Fig 2: Moisture absorption test on bioplastic films

Water absorption

Water followed the same trend as moisture absorption, rising progressively with increased plasticizer levels. Films with no filler absorbed more water while filler addition helped lower water uptake to some extent. The strongest reduction occurred at 1g filler, though higher plasticizer weakened this effect. This shows that plasticizer had a stronger impact on water absorption than filler

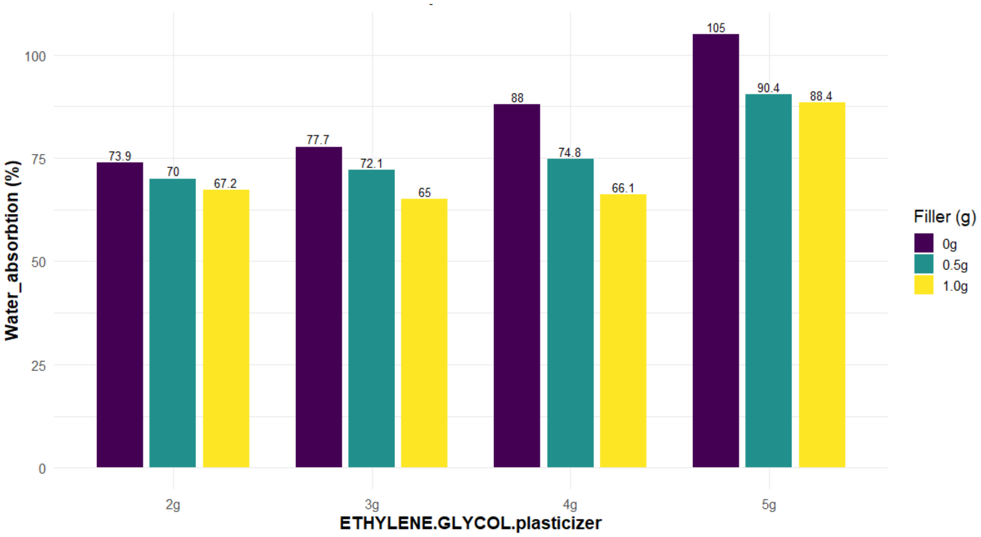


Fig 3: Water absorption test on bioplastic films

Acid absorption

According to the results obtained, the acid absorption of bioplastic shows a clear relationship between plasticizer effect and that of filler (kaolin) on the bioplastic film. There was an increase in acid uptake as the ethylene glycol content increases but a significant decrease as the kaolinite filler increases. This indicate that kaolinite acts as strong barrier which aligns with reports that clay materials reduces acid diffusion by creating a tortuous path within polymer matrices (Mohammadi *et al.*, 2021; Kizil *et al.*, 2021).

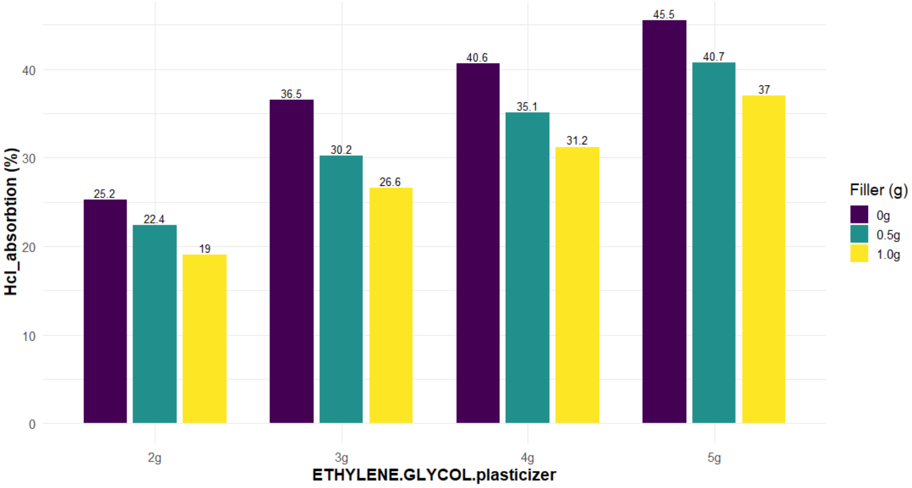


Fig 4: Acid absorption test on bioplastic films

Table 3.4: Chemical resistance test of bioplastic

Chemical name	**properties**
1. 1M NaOH	bioplastics fully dissolved
2. Ethanol (absolute)	bioplastics showed no colour change and no significant change in mass

3.3 Physicomechanical properties of bioplastic film

Plasticizer/Filler	Yield Point (Strain, Stress)	Elongation at Break (Strain)	Thickness (mm)	Tensile Strength (MPa)
2g-0g	1.99%, 0.95 MPa	5.03%	0.29	11.975 MPa
2g-0.5g	1.15%, 0.86 MPa	2.80%	0.30	6.676 MPa
2g-1g	1.15%, 2.15 MPa	2.80%	0.34	5.028 MPa
3g-0g	1.17%, 0.86 MPa	7.85%	0.21	17.5 MPa
3g-0.5g	1.18%, 1.10 MPa	6.10%	0.26	14.68 MPa
3g-1g	1.45%, 2.25 MPa	18.50%	0.19	21.98 MPa
4g-0g	1.10%, 1.12 MPa	5.10%	0.37	13.02 MPa
4g-0.5g	1.19%, 2.10 MPa	7.50%	0.37	15.68 MPa
4g-1g	1.12%, 2.30 MPa	7.00%	0.21	14.88 MPa
5g-0g	1.25%, 2.50 MPa	18.10%	0.30	19.99 MPa
5g-0.5g	1.32%, 1.75 MPa	9.10%	0.21	17.50 MPa
5g-1g	1.12%, 2.30 MPa	6.40%	0.51	12.34 MPa

Elongation at Break:

Flexibility increased sharply at 5g plasticizer, particularly in the 0 g filler group (~18%). The 1g filler group displayed its highest elongation at 3g plasticizer (~19%), followed by a decline at higher plasticizer levels. The results confirm that plasticizer and filler interact in determining the mechanical balance between strength and flexibility. Increasing plasticizer boosts elongation but may reduce tensile strength, while adding filler enhances strength at low plasticizer levels but reduces flexibility. The most favourable mechanical balance appears around 3g plasticizer with 0.5–1g filler.

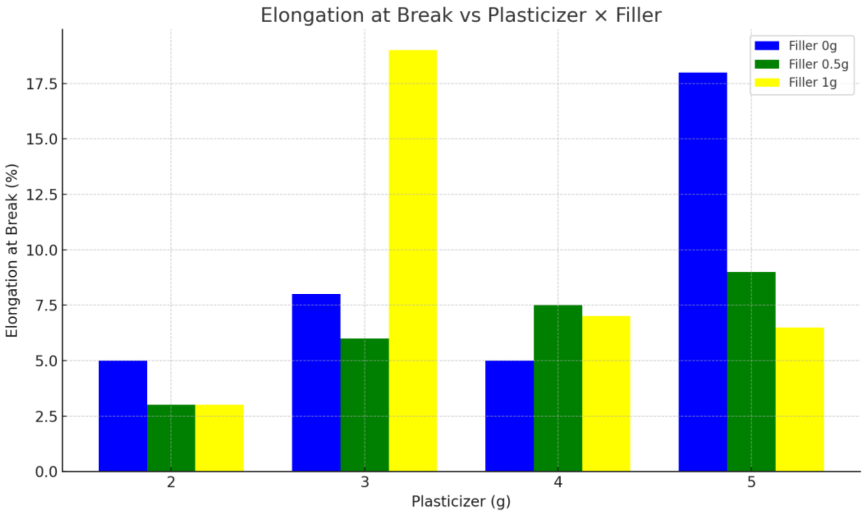


Fig 5: Elongation at break of CMS bioplastic film, using EG plasticizer and Kaolinite filler

Tensile Strength:

Tensile strength increased with plasticizer addition up to 3 g, after which the response varied depending on filler concentration. The 1 g filler group produced the highest tensile strength at 3g plasticizer (~22.5 MPa), while higher plasticizer levels reduced strength for this same filler amount. Films containing 0 g and 0.5 g filler showed gradual increases in strength up to 5 g plasticizer.

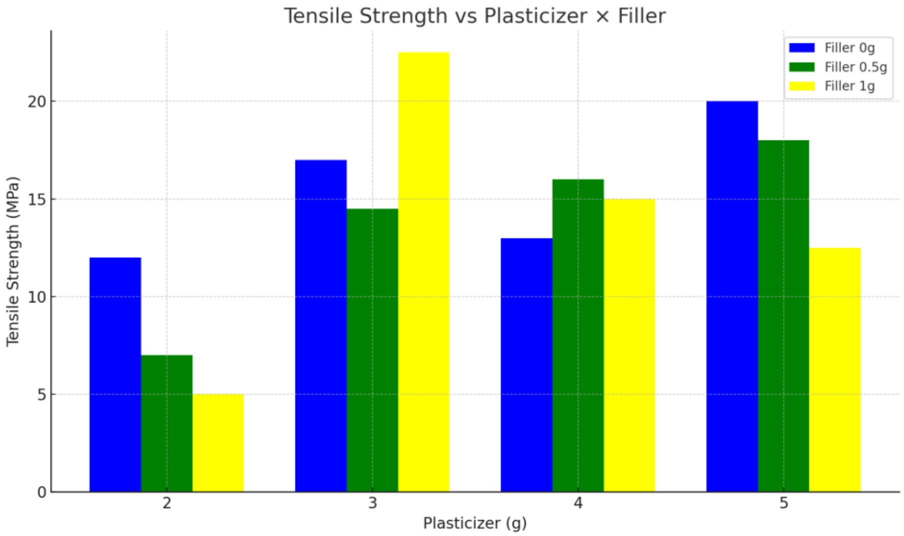


Fig. 6: Tensile strength of CMS bioplastic film, using EG plasticizer and Kaolinite filler

Thickness:

The thickness of a polymer film is a crucial structural attribute because it influences not only the film's mechanical integrity but also its optical clarity, diffusion behaviour, and biodegradation characteristics (Müller *et al.*, 2020). In the present study, the thickness of the carboxymethyl starch-based bioplastic films ranged between 0.19 mm and 0.51 mm, demonstrating measurable sensitivity to variations in plasticizer–filler composition.

- **General Behaviour of Film Thickness**

Across all twelve formulations, thickness did not follow a linear trend but instead reflected the complex interactions between starch chains, ethylene glycol, and kaolin particles. Films containing 1 g of kaolin filler exhibited the greatest variability, spanning from 0.19 mm to 0.51 mm, whereas films containing 0 g and 0.5 g kaolin displayed a more constrained and stable range (0.21–0.37 mm).

This pattern aligns with observations by Méité *et al.* (2022), who noted that higher mineral filler loading can disturb the homogeneity of starch-based matrices during film casting.

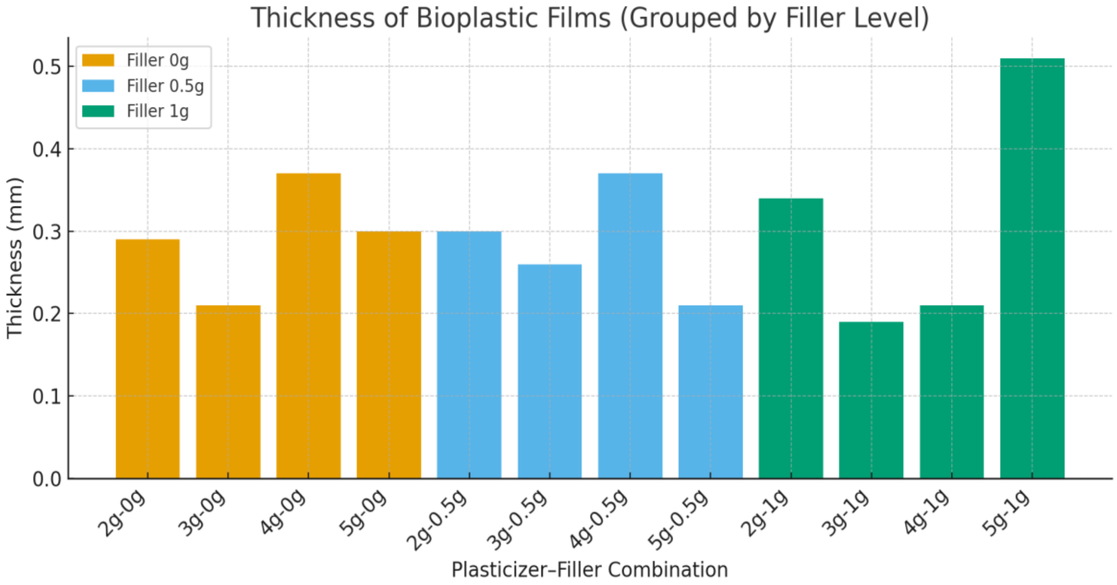


Fig 7: Thickness of CMS bioplastic films

- **Influence of Ethylene Glycol (Plasticizer)**

Although plasticizers typically enhance polymer mobility and promote smoother film formation (Arroyo-Esquivel *et al.*, 2025), increasing ethylene glycol levels from 2 g to 5 g did not produce a uniform directional change in thickness.

However:

At 0 g filler, thickness oscillated slightly around 0.21–0.37 mm.

At 0.5 g filler, thickness was relatively consistent.

At 1 g filler, fluctuations increased dramatically.

This suggests that once filler content crosses a threshold, plasticizer influence is overshadowed by the disruptive effects of solid particles on the polymer matrix.

- **Role of Kaolin Concentration**

The filler effect was the most pronounced structural determinant. Kaolin, being an inorganic particulate, can either reinforce the polymer matrix or induce discontinuities depending on its loading and dispersion (Lin *et al.*, 2022).

The thickness behaviour in this study supports this dual-role model:

- 0g kaolin: Produced films with moderate and predictable thickness, reflecting unobstructed polymer–plasticizer interactions.
- 0.5 g kaolin: Offered the most uniform range, suggesting an optimal zone where filler enhances film structuring without overwhelming the matrix.
- 1 g kaolin: Introduced significant heterogeneity in thickness, likely due to particle agglomeration, uneven sedimentation, or reduced matrix continuity—phenomena also reported by Tavares *et al.* (2019) in starch–clay systems.

- Structural Interpretation

At higher kaolin loading (1g), the filler likely interferes with starch chain entanglement, casting flow, and water evaporation dynamics. Such interference can create thin zones where the film stretches excessively and thick zones where particulates accumulate. Similar irregularities have been documented in starch-based films reinforced with metakaolin and other silicate minerals (Meité *et al.*, 2022).

This explains the presence of both:

The thin-film extreme at 0.19 mm, and

The maximum recorded thickness of 0.51 mm,

within the same 1g filler category.

- Overall Interpretation

The data demonstrate that kaolin content is the dominant factor governing thickness uniformity, whereas ethylene glycol exerts a more moderate influence. At lower filler concentrations (0–0.5 g), the biopolymer network remains relatively stable and continuous. However, at 1 g, the structural equilibrium becomes disrupted, generating pronounced thickness variability. This indicates that while mineral fillers can enhance material properties, their loading must be carefully optimized to prevent detrimental microstructural inconsistencies.

Biodegradability

The biodegradability profiles presented in the charts illustrate a clear and progressive increase in degradation across all formulations as incubation time advances from Week 0 to Week 3. As expected, all samples begin at 0% degradability, but the rate and extent of degradation vary subtly depending on the ethylene-glycol plasticizer concentration and the kaolin filler content.

Across the different formulations, films containing higher ethylene glycol levels generally exhibit slightly faster degradation, particularly noticeable in the 5g EG series. This behaviour aligns with the role of plasticizers in reducing polymer crystallinity and enhancing molecular mobility, thereby making the matrix more accessible to microbial activity. Similarly, the inclusion of kaolin modifies the degradation pattern, although its effect is more nuanced. At lower filler contents (0.5 g), the films tend to show marginally enhanced degradability, likely due to the disruption of the starch network, which creates more pathways for water and microorganisms. However, at 1g kaolin, the trend stabilizes, suggesting that excess filler may contribute to a more compact matrix, slightly moderating the degradation rate.

By Week 3, all samples reach approximately 100% degradability, demonstrating that the carboxymethyl starch–based films, irrespective of formulation, retain strong biodegradation potential. The difference lies primarily in the rate at which each composition progresses towards complete breakdown. Notably, combinations such as 3g EG + 0.5 g kaolin and 4 g EG + 0.5 g kaolin show comparatively steeper increases between Weeks 1 and 2, indicating accelerated breakdown within this interval.

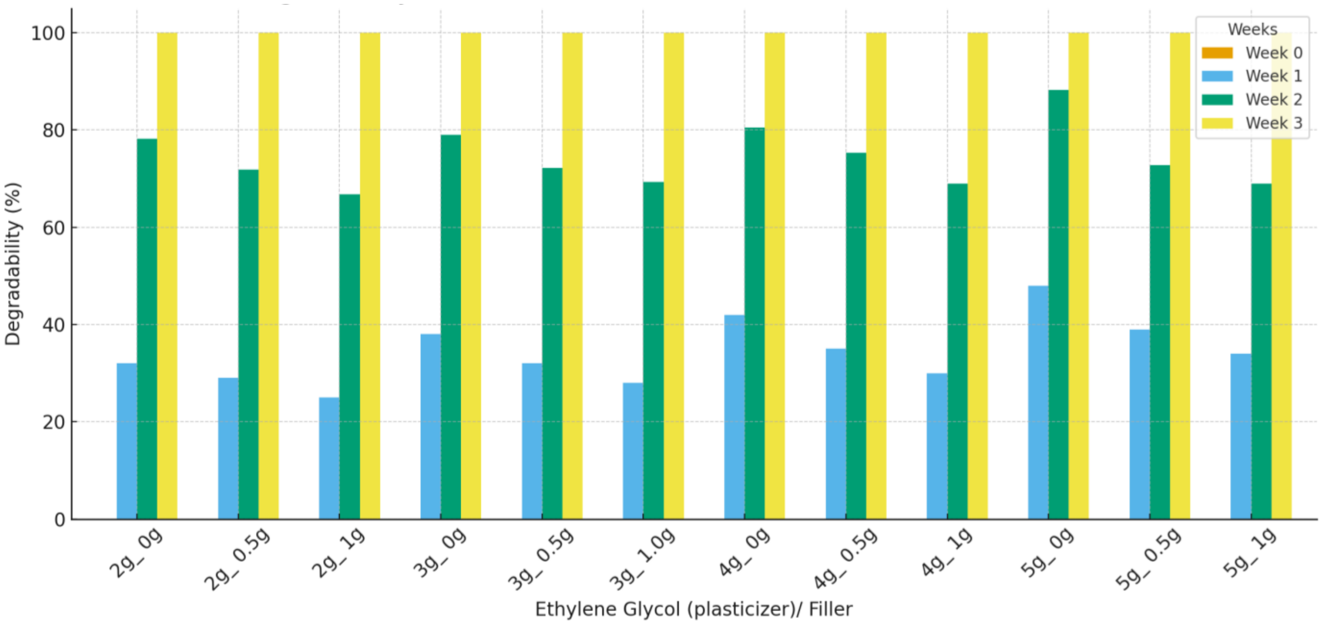


Fig. 8: Biodegradability over time for varying plasticizer and filler combinations

Overall, the biodegradability behaviour confirms that the incorporation of ethylene glycol and kaolin does not inhibit the environmental degradability of the films. Instead, these additives influence the kinetics of degradation in predictable and manageable ways, offering valuable insights for tailoring film properties to specific application requirements.

TGA/DTA results for the bioplastic films

CMS 2.0 – 0g

TGA analysis: the results show that the bioplastic film maintains thermal stability up to 200ºC, after which major degradation begins. The incorporation of ethylene glycol slightly lowered the degradation onset temperature but enhanced the flexibility and ductility of the film (Shogren, 2019). DTA analysis: An endothermic peak below 120ºC corresponded to moisture evaporation. A second weak endothermic transition between 150-210ºC was associated with the volatilization of ethylene glycol. A strong exothermic peak observed between 240-320ºC confirmed the decomposition of the starch polymer matrix consistent with the major mass loss observed in TGA

CMS 2.0-0.5g

Showed three main weight loss stages. An initial 10% loss below 180ºC was due to moisture and volatile plasticizer evaporation. Major degradation occurred between 180-340ºC (=33% loss) from starch and plasticizer breakdown, while a stable residue of about 40% remained beyond 340ºC, mainly from kaolin. DTA peak near 310ºC confirmed the main decomposition point. Overall, the film is stable below 200ºC, with kaolin improving thermal stability and ethylene glycol enhancing flexibility (Sanyang *et al.,* 2016; Gonzalez-Gutierrez *et al.,* 2010).

CMS 2.0 – 1g

The major degradation occurred between 200ºC and 340ºC, representing the breakdown of starch matrix and volatilization of organic components. The result indicate good thermal stability below 200ºC, making the film suitable for moderate-temperature applications. Kaolin improves heat resistance, while EG contributed to flexibility. DTA: DTA peaks confirms that its structural degradation is centered in the typical range reported for starch-based bioplastics (Sanyang *et al.,* 2016; Gonzalez-Gutierrez *et al.*, 2010)

CMS 3.0g – 0g

The main decomposition occurred between 200 – 330^{o}C, representing the breakdown of starch matrix ad volatilization of organic components. With no kaolin filler, the film left only a very small final residue indicating almost complete thermal degradation of the organic material. DTA peaks around mid-200 to 300^{o}C confirmed this major decomposition phase. Overall the film is stable below 200^{o}C but becomes more thermally sensitive at higher temperatures due to the absence of kaolin. Increased EG enhances flexibility for but also increases low-temperature volatility. (Sanyang *et al.,* 2016; Gonzalez-Gutierrez *et al.,* 2010)

CMS 3.0 – 0.5g

The bioplastic showed an initial weight loss between 120oC due to moisture, followed by major decomposition between 200 – 350^{o}C and a peak degradation around 350 – 380^{o}C. A residue of about 12% remained at high temperature, attributed to kaolin and char. The results indicate that ethylene glycol slightly reduced early stability while kaolin improved thermal resistance and residue formation. DTA pattern shows a strong endothermic transition between 200 - 350^{o}C linked to polymer degradation. The pattern confirms the materials stability up to about 200^{o}C before significant thermal breakdown begins

CMS 3.0 – 1.0g

TGA: The major degradation peak around 320 – 350^{o}C indicating the breakdown of starch matrix and plasticizer. About 20% residue remained at high temperature due to kaolin inorganic content. The higher filler load improved thermal resistance compare to lower kaolin suggesting enhanced stability and char formation. DTA: shows a small endothermic peak at 30 – 60^{o}C from moisture loss. A broader transition at 150ºC – 250ºC marks the start of starch matrix degradation and breakdown of plasticizer interactions (Liu *et al.,* 2019). This region is more gradual compared to films without fillers, indicating that kaolin improves thermal resistance by slowing decomposition.

CMS 4.0 – 0g

With 4.0g of ethylene glycol, the film becomes more flexible due to strong plasticizing effect. TGA: a more noticeable initial weight loss occurs below 100ºC, and the main degradation begins around 150ºC – 200ºC, showing the higher plasticizer content further reduces thermal stability (Liu *et al.,* 2019). DTA: the endothermic peak appears near 50-60ºC, indicating a lowered Tg and increased softness (Bhoopathi *et al.,* 2020). A clear exothermic peak around 200 – 230ºC marks the rapid breakdown of the CMS matrix during heating (Zhong *et al.,* 2021).

CMS 4-0 – 0.5g

TGA shows a small moisture/volatile loss below 120ºC, and large mass (73%) between 200 – 350ºC (main polymer plasticizer decomposition) and a final inorganic rich residue (11 – 12%) from kaolin. DTA confirms with a major endothermic/degradation peak near 360 - 380ºC, indicating the temperature of fastest breakdown - so the film is safe for low-temperature use (<200ºC) but undergoes significant chemical degradation above 200ºC

CMS 4.0 – 1g

TGA: the film shows only a small weight loss at low temperature (moisture/volatile loss), then a major decomposition centered around 341ºC where the sample falls rapidly 18% mass by 351ºC - indicating polymer/backbone degradation - and finally levels off to a char/residue 0f 8.5% at the highest temperatures. DTA curve shows a mild endothermic event around 30 – 60ºC linked to moisture loss followed by a broader endothermic drop indicating polymer softening and final degradation of the CMS-EG-kaolin structure (Bhoopathi *et al.,* 2020).

CMS 5.0 – 0g

From TGA/DTA analysis, the bioplastic remained stable up to 200°C, after which it showed a major thermal breakdown around 360 – 370°C. Residual mass was low (8%) indicating massive decomposition after the main peak. Overall the fill is suitable for low-temperature application but degrades rapidly above 300°C.

CMS 5.0 – 0.5

TGA: the film shows 8% early weight loss below 150°C from moisture and ethylene glycol with major degradation at 320-335°C, leaving 12 – 13% residue at 850°C due to kaolin and char formation. DTA displays an endothermic transition around 220 – 240°C and a stronger peak near 320 – 335°C linked to polymer breakdown, followed by minor high temperature events from char-mineral interactions

CMS 5.0 – 1g

TGA: the film show weight loss of about 3% below 150oC from moisture, followed by major degradation between 250 – 350°C as the CMS polymer breaks down. A final residue of about 19 – 20% remains at 850°C, reflecting the contribution of kaolin and char formation. The higher ethylene glycol content slightly lowers the onset of degradation but improves flexibility.

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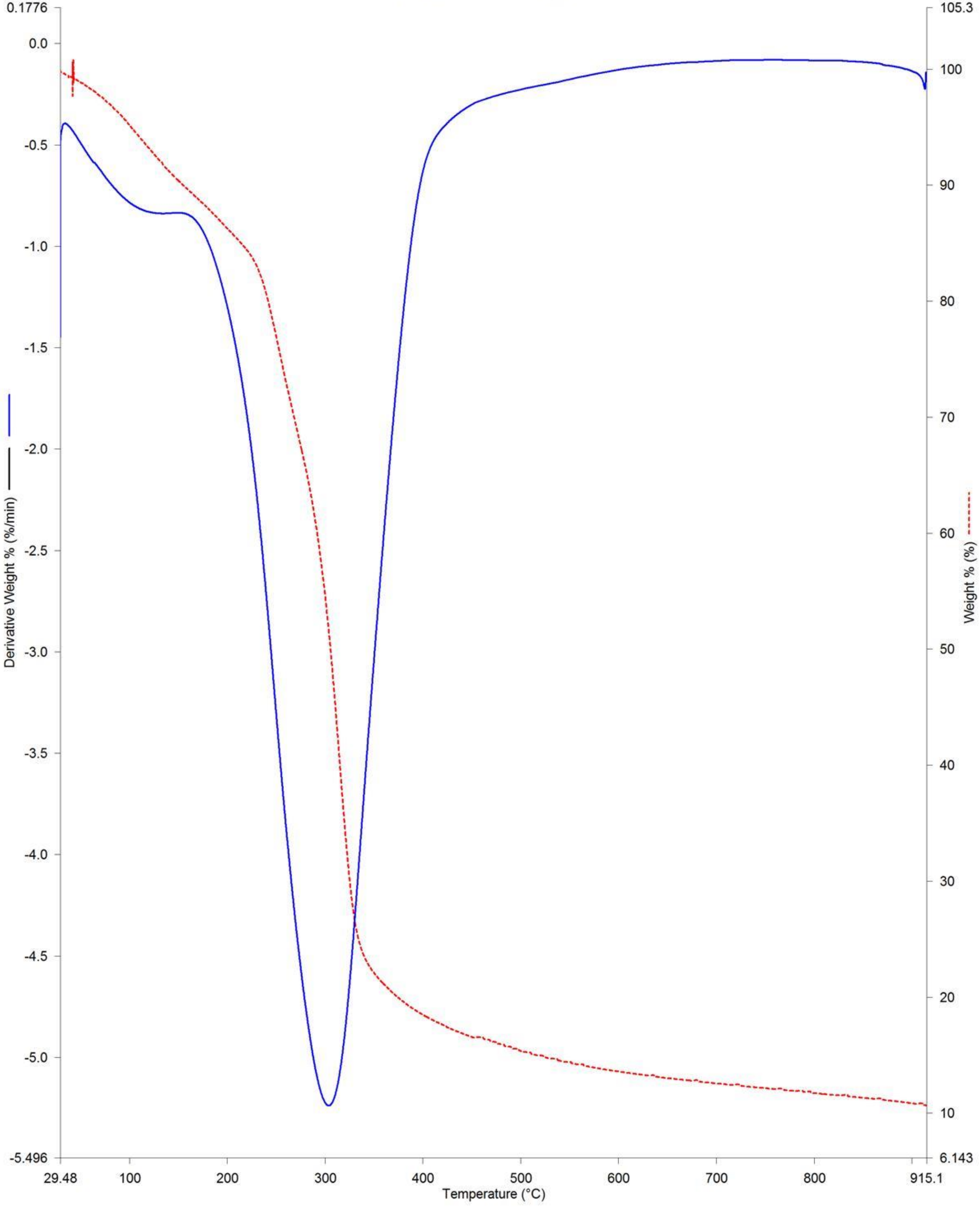
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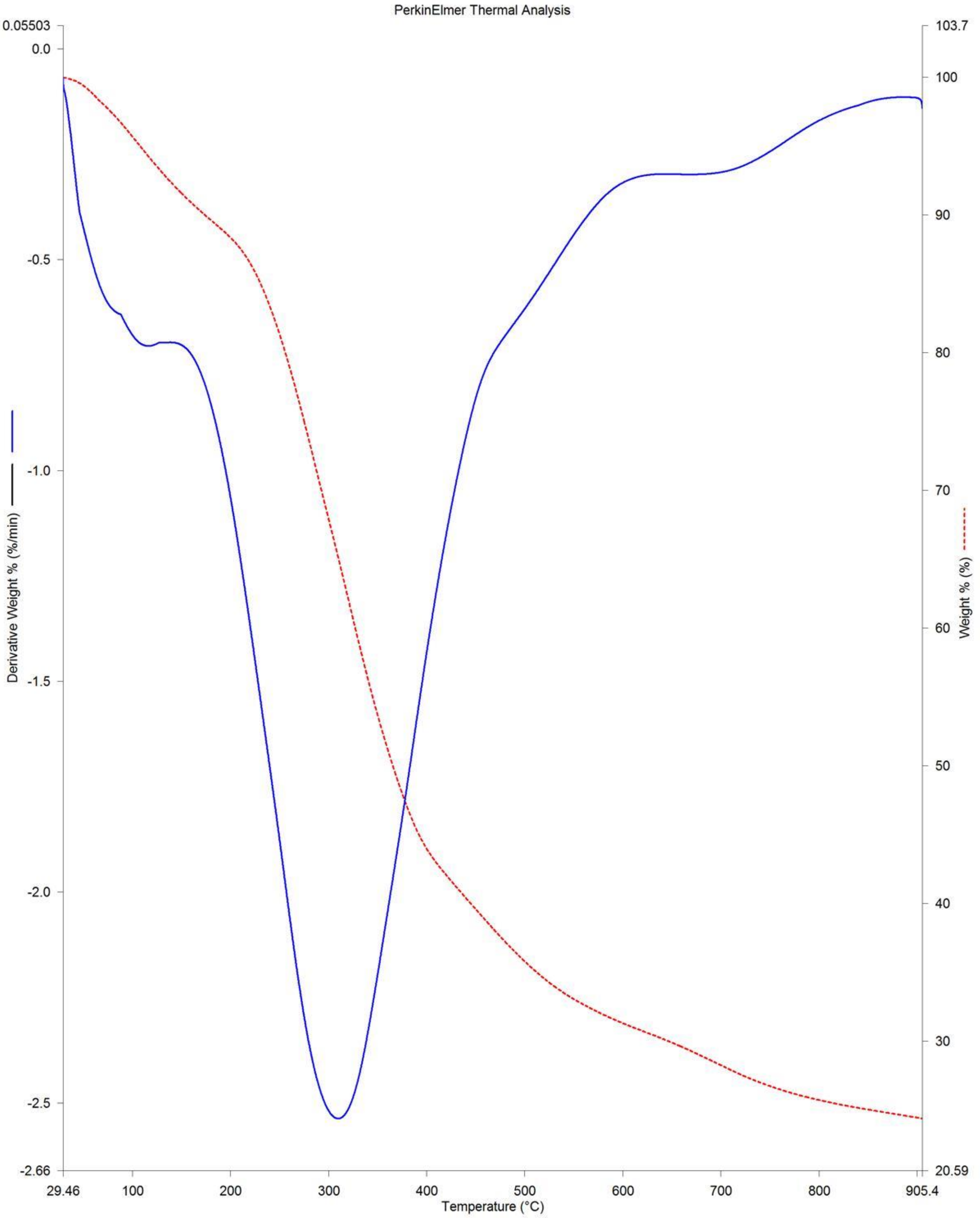

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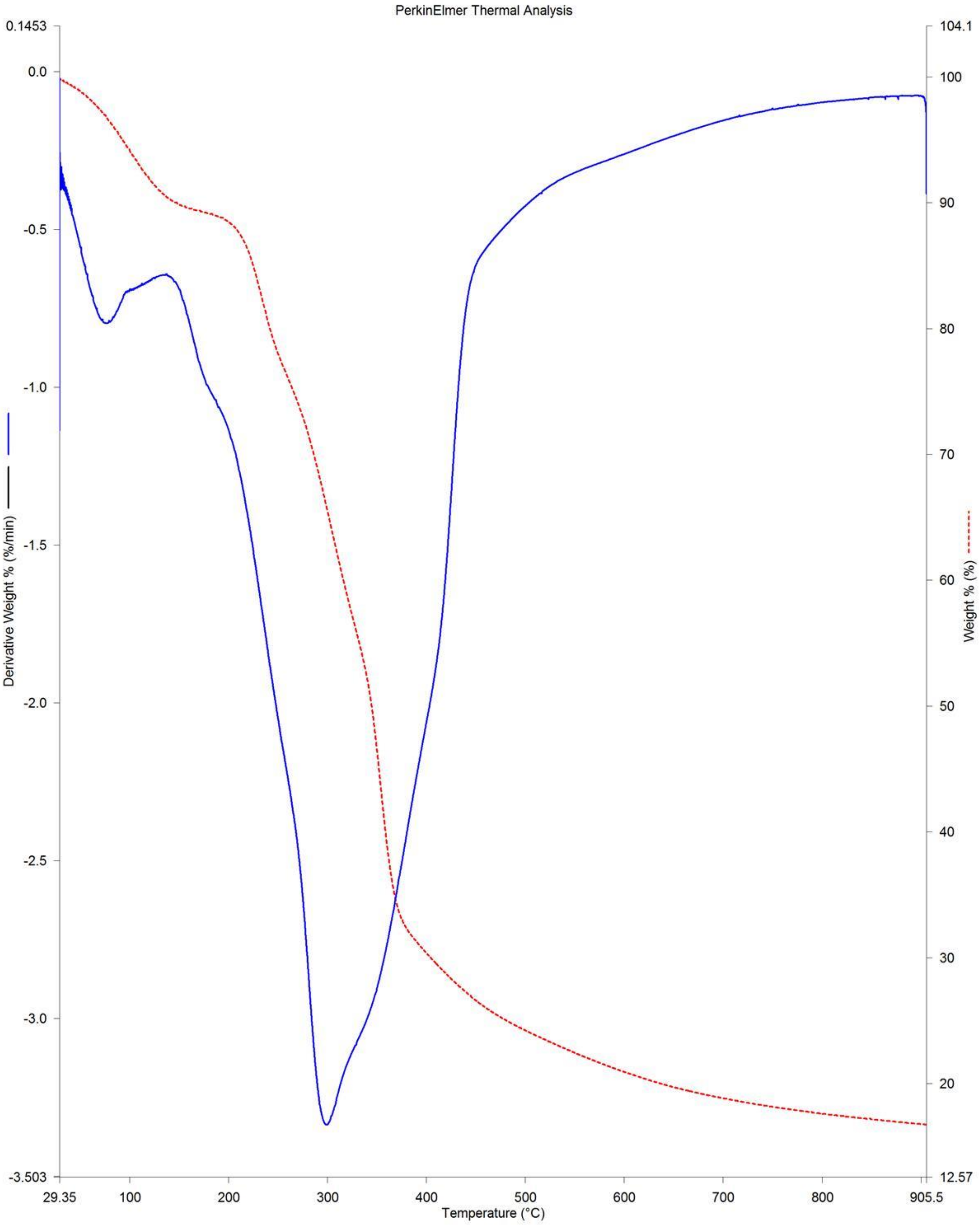

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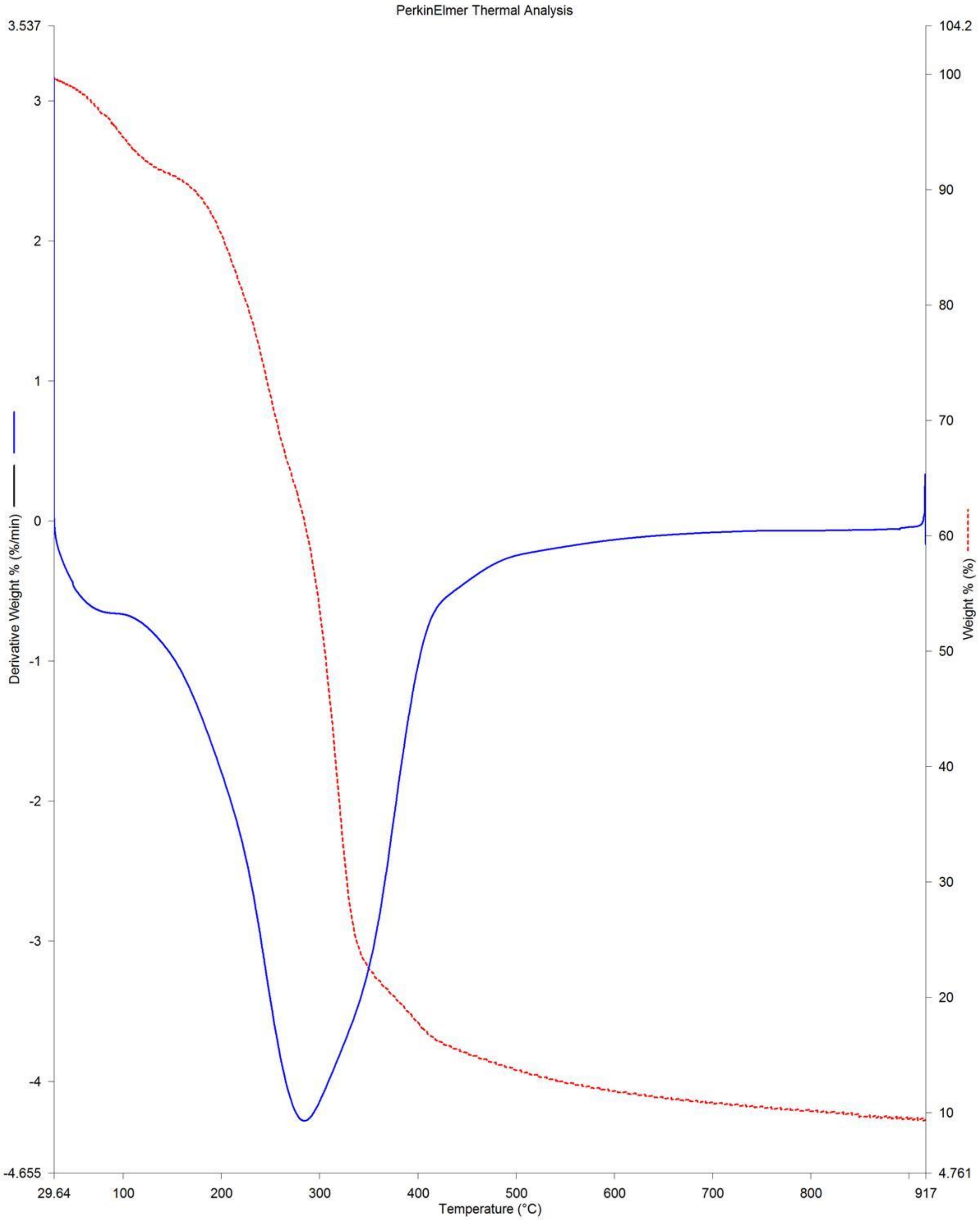

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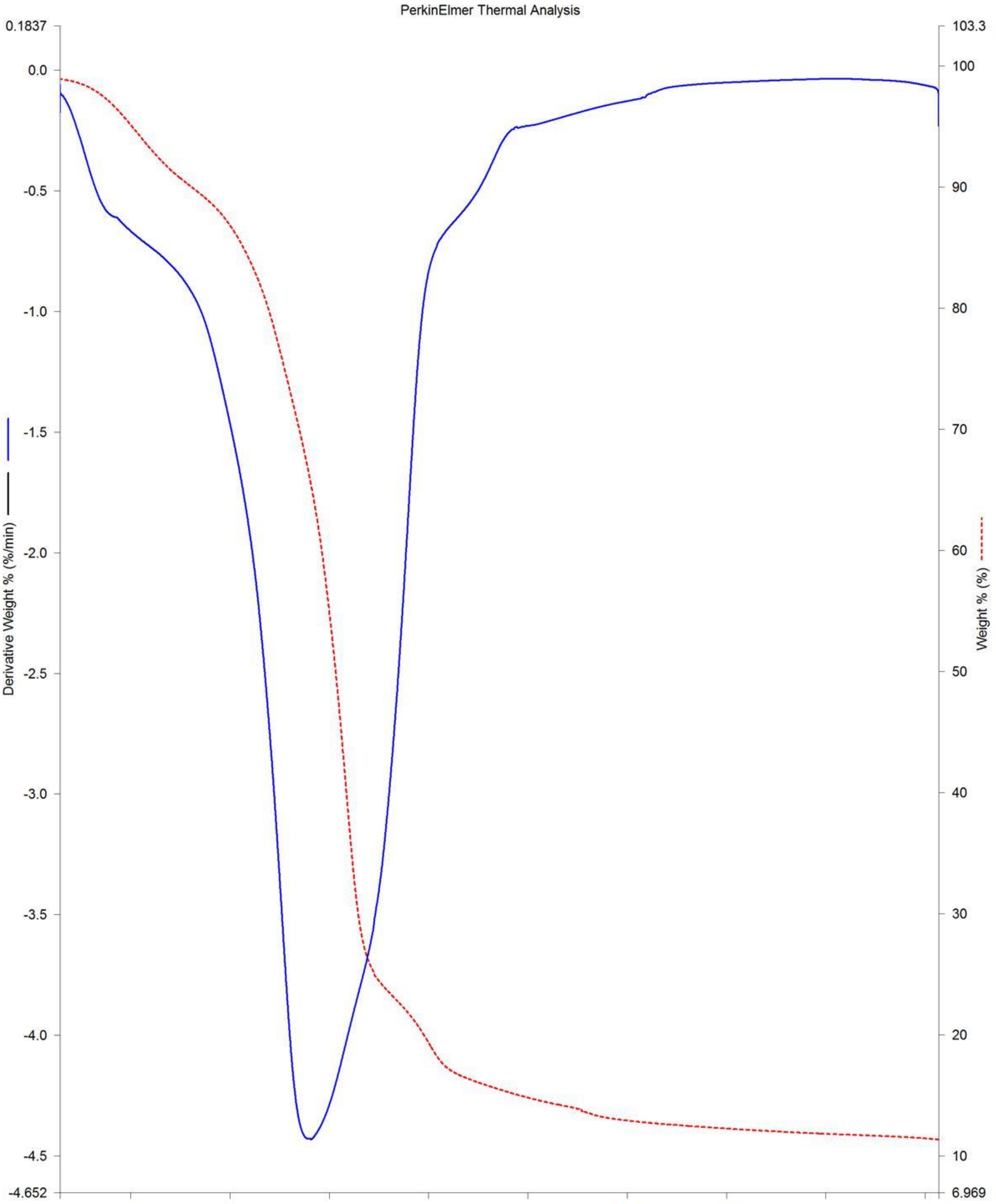

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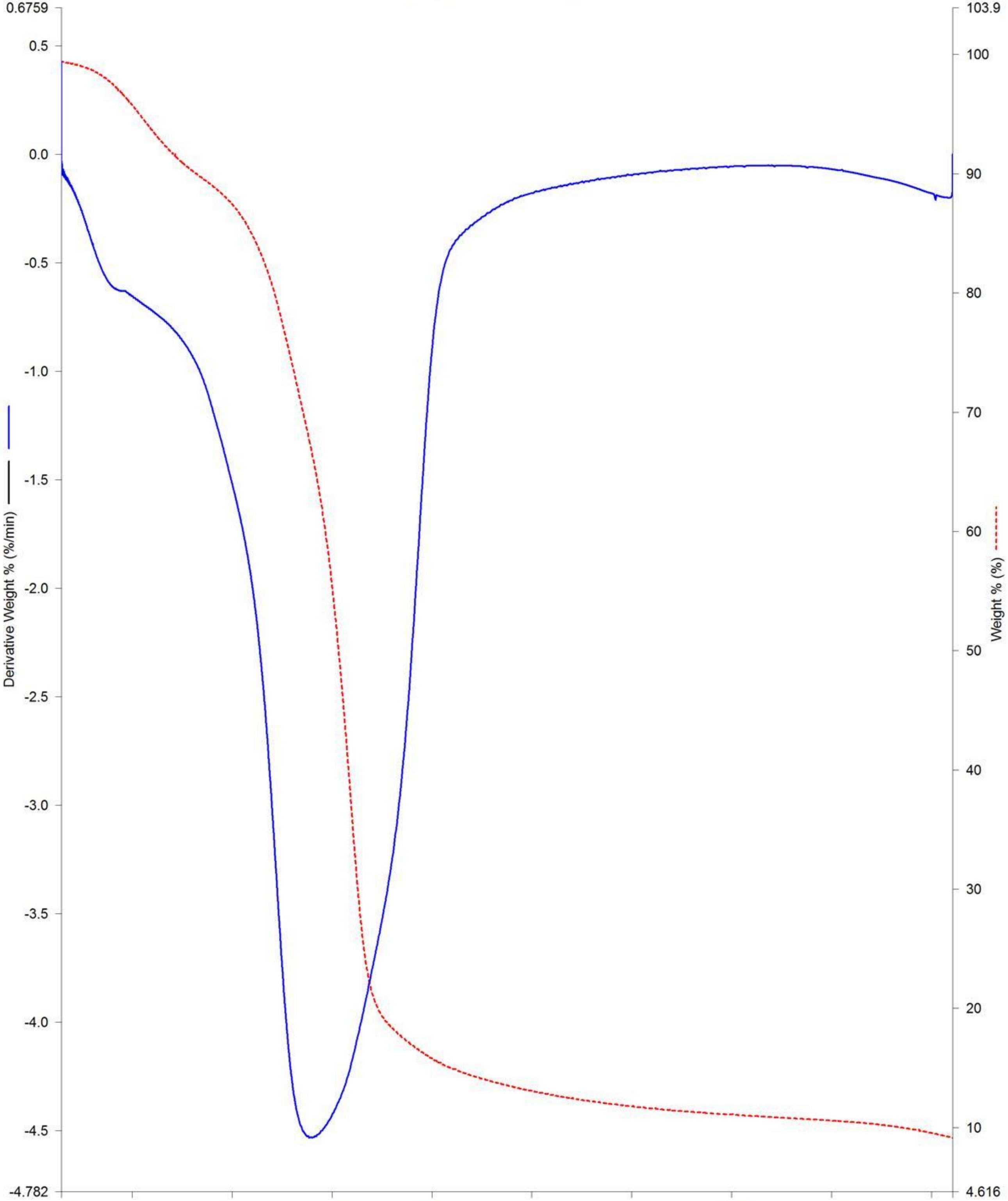
PerkinElmer Thermal Analysis



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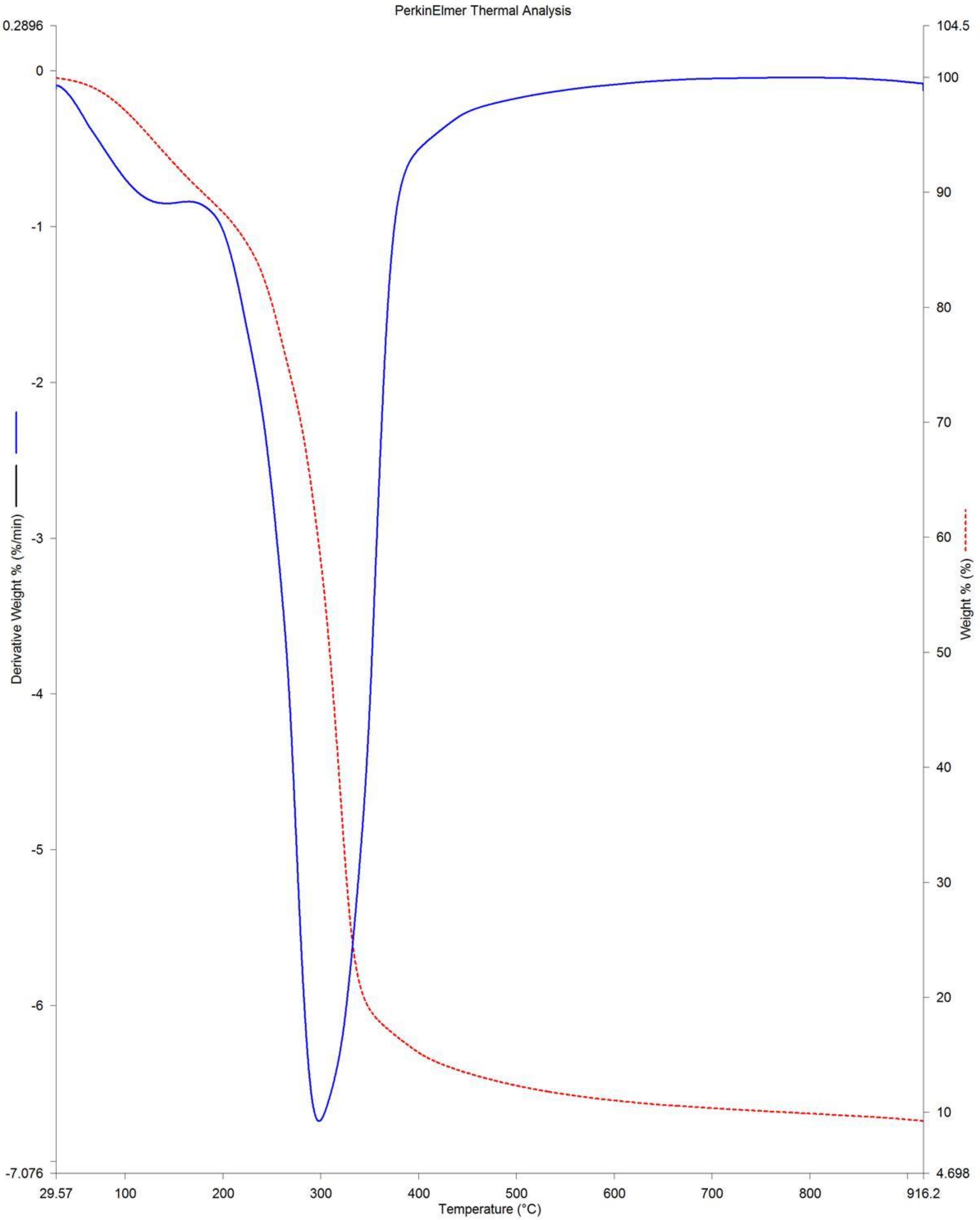

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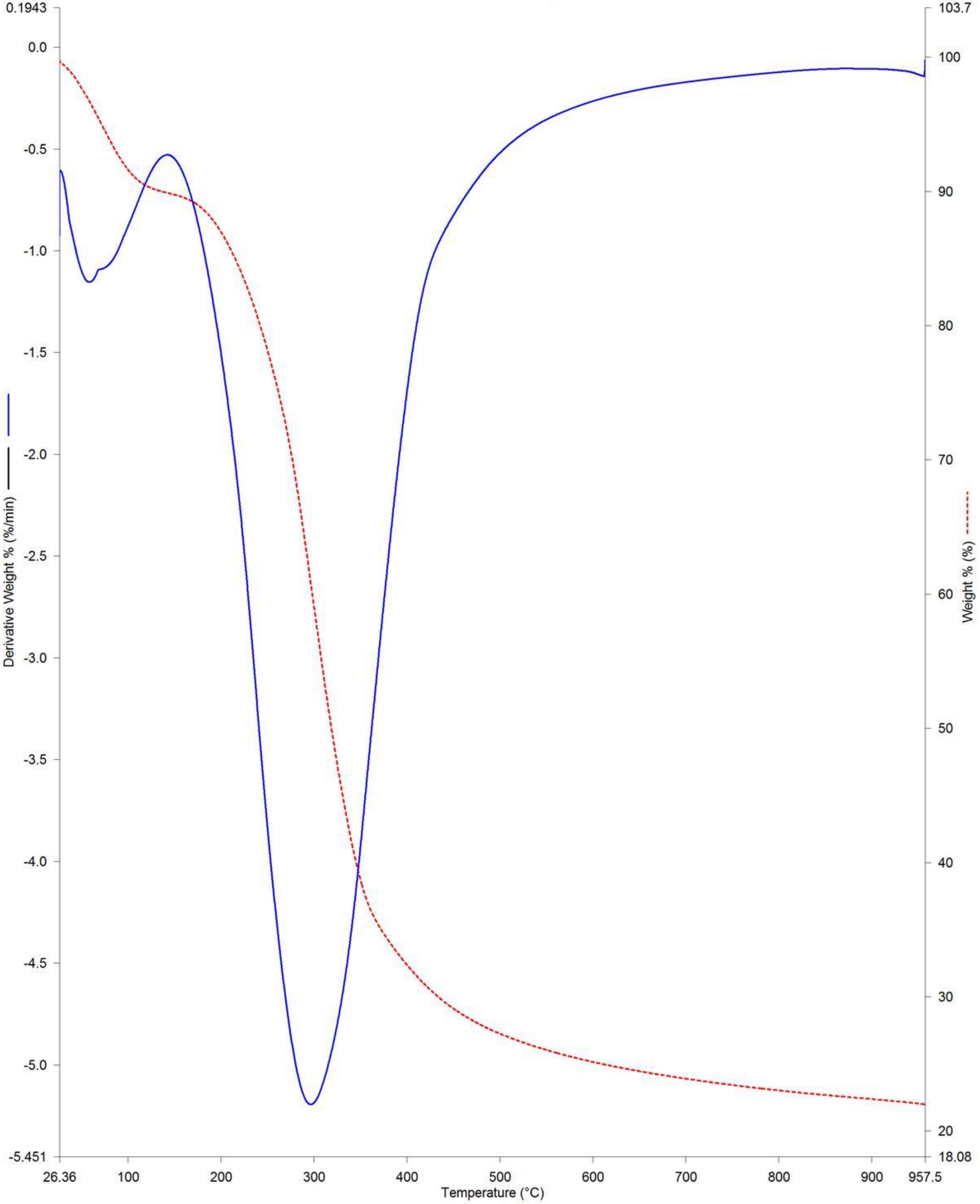
PerkinElmer Thermal Analysis



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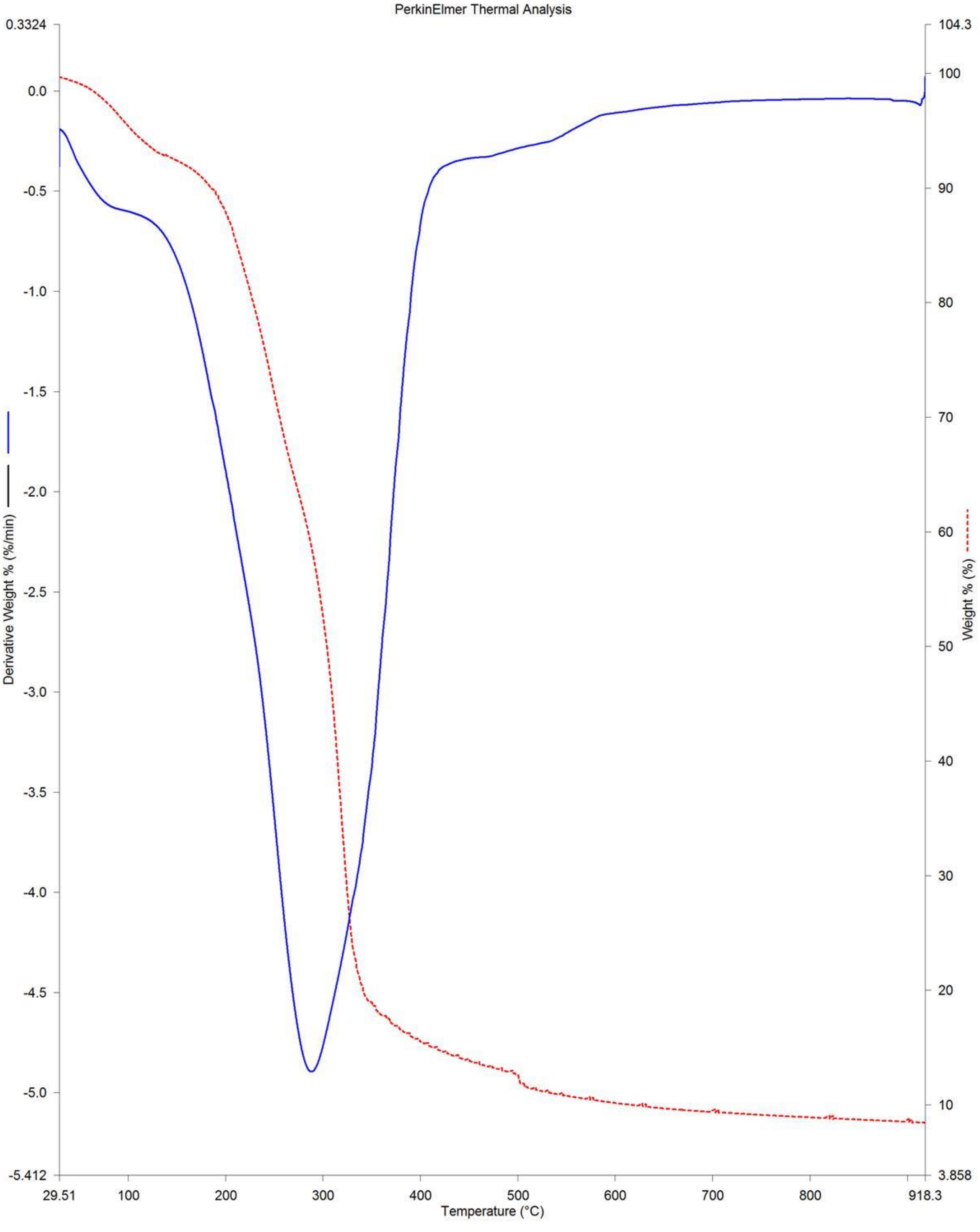

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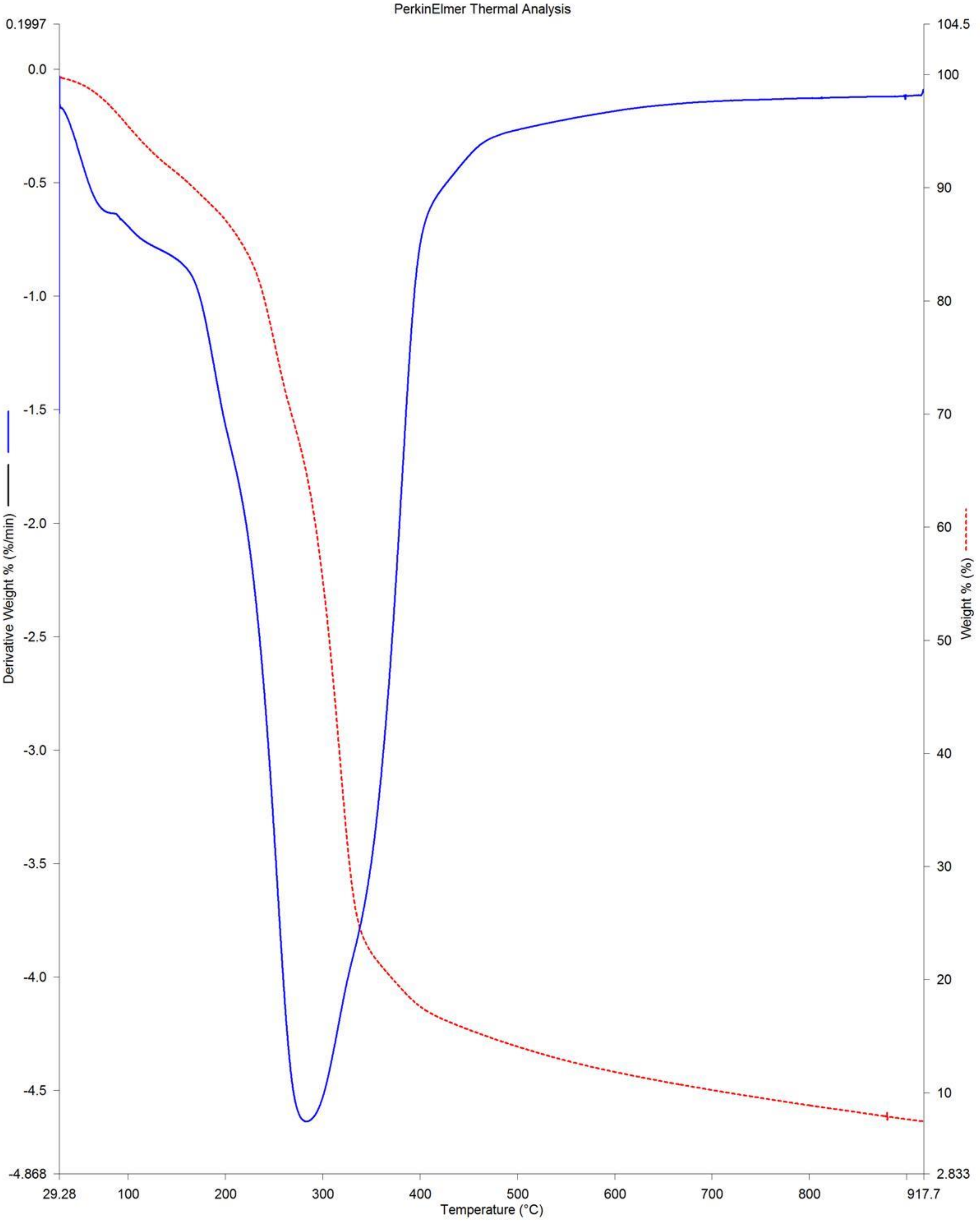

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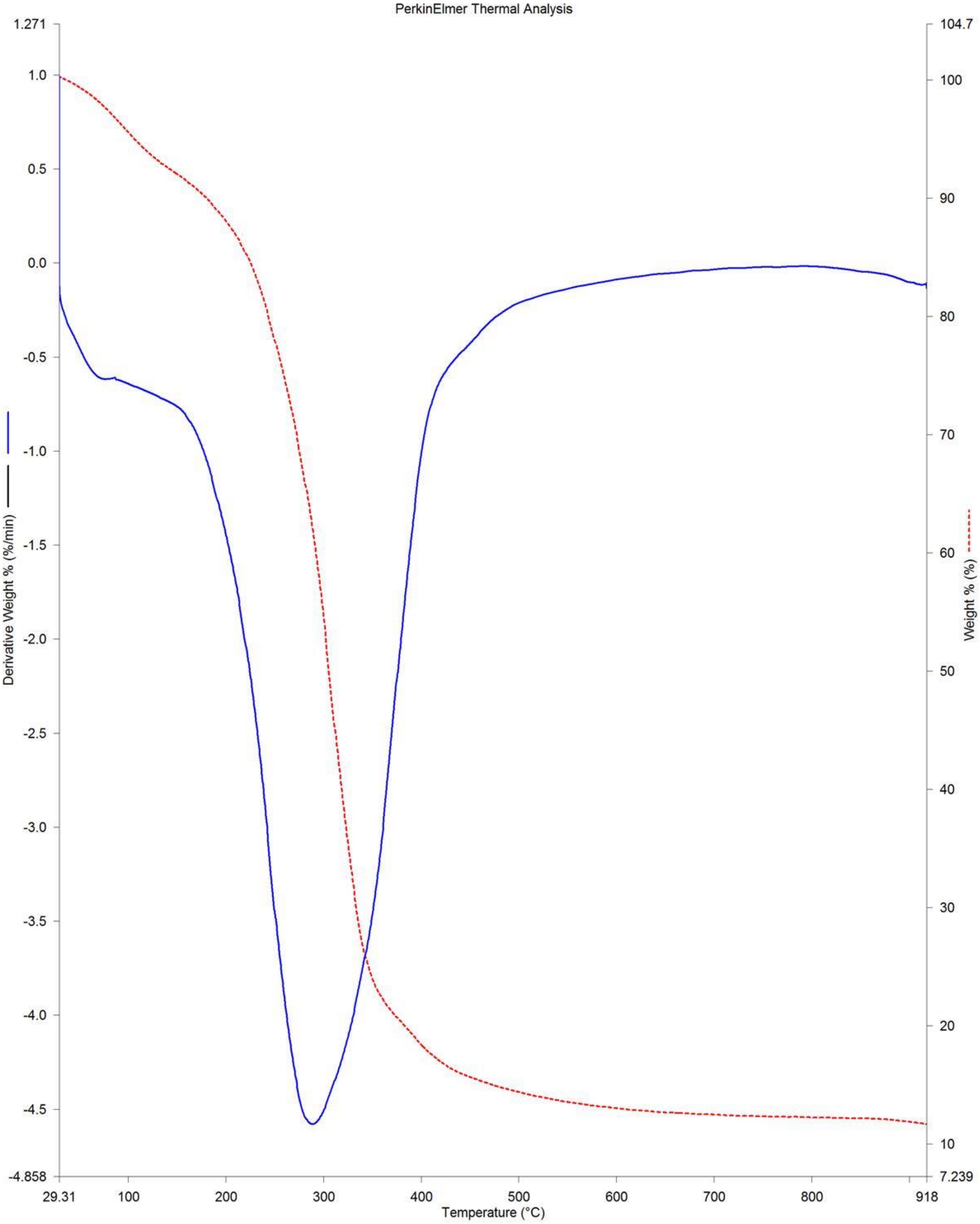

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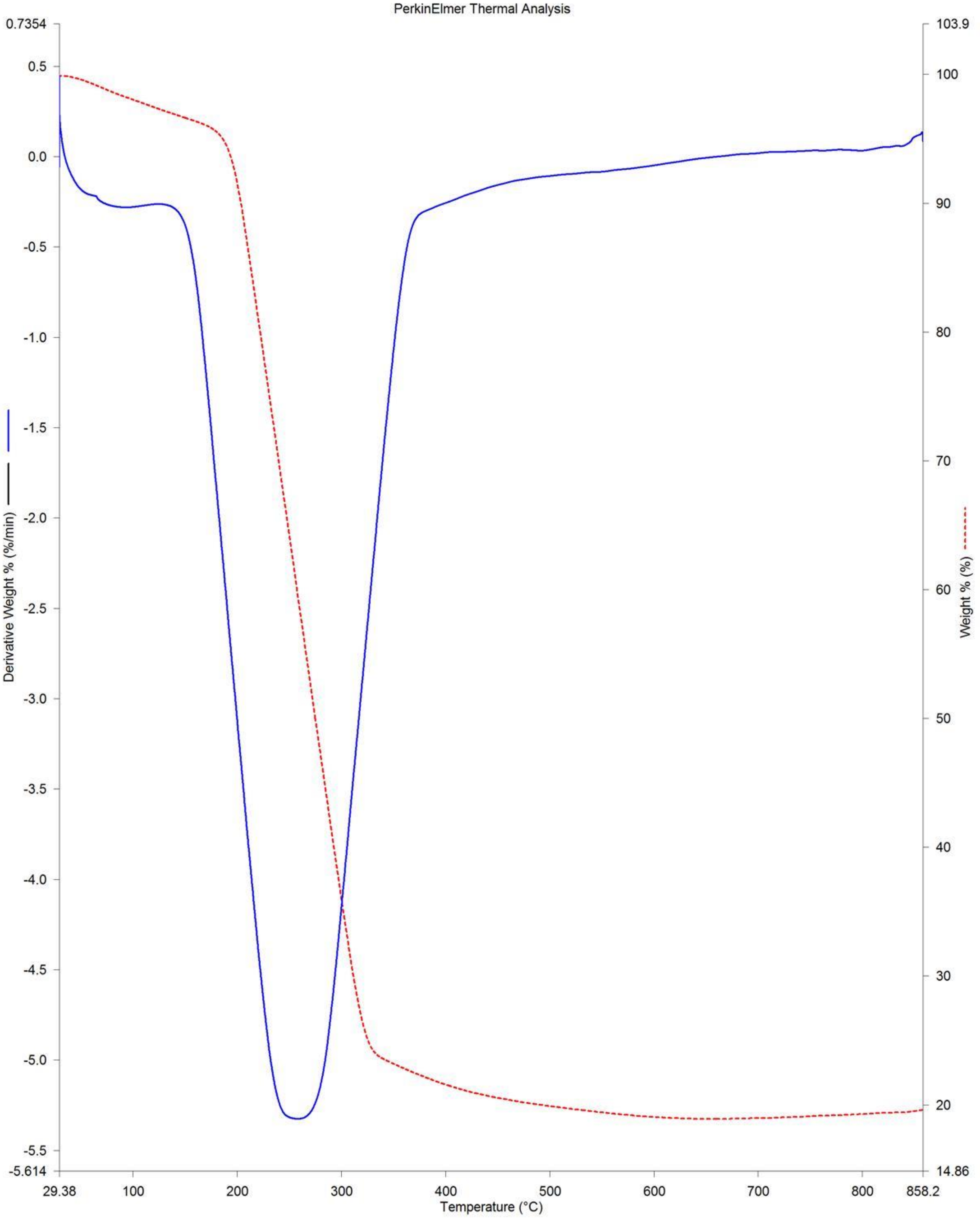

30/10/2025 13:58:23

1) Heat from 30.00°C to 900.00°C at 10.00°C/min

3.4 Conclusion

This project set out to develop and comprehensively assess carboxymethyl starch (CMS)-based bioplastic films plasticized with ethylene glycol and reinforced with kaolin. The central objective was to enhance the mechanical strength, thermal stability, moisture behaviour, and biodegradation profile of starch-derived films to make them more suitable for modern packaging and environmental applications. The extraction and modification process of starch produced a yield of 59.0%, a reduced gelatinization temperature and an acceptable moisture content.

The findings demonstrate that CMS remains a highly promising and adaptable biopolymer. Ethylene glycol proved effective in improving flexibility, reducing brittleness, and creating a more homogeneous polymer network by lowering intermolecular forces. Kaolin, on the other hand, contributed structural reinforcement, enhanced thermal resistance, and reduced moisture sensitivity—addressing some of the most persistent limitations of starch-based films. The combined use of these additives created a synergistic effect. Films exhibited improved mechanical balance, and enhanced performance in moisture related parameters such as water uptake and moisture content. Films with no filler showed higher moisture and water absorption than those with kaolin fillers. Films were soluble in alkaline medium and showed no significant change in mass and colour in absolute ethanol. TGA/DTA analysis further confirmed higher onset degradation temperatures and stability up to 180 – 200^{o}C, indicating better endurance during processing and storage. Biodegradation studies showed that although kaolin slightly slowed degradation, all films remained fully biodegradable, preserving their environmental advantage as alternatives to petroleum-based plastic films.

All results confirm that the integration of ethylene glycol and kaolin meaningfully enhances the functionality of CMS based bioplastics without undermining their sustainability. These results provide a strong foundation for future material optimization and support the potential for large scale applications in packaging, agriculture, and single use consumer products. Further research may explore advanced fillers, polymer blends, nanostructured reinforcements, or bioactive additives to extend the performance and broaden the industrial relevance of CMS based films.

Recommendations

- Ethylene glycol should be kept at the effective concentration to balance flexibility with reduced moisture sensitivity.
- Using finer kaolin can further enhance mechanical strength and barrier properties.
- Future studies should include water vapour transmission rate (WVTR), tensile cycling and shelf life stability to better understand real-world behavior.
- Exploring other natural additives like blending CMS with biodegradable polymers (e.g PVA or PLA) or adding nano-clays could boost barrier and mechanical performance.
- Pilot-scale casting or extrusion trials are recommended to assess the commercial feasibility of the most promising formulations.

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