PROJECT REPORT

On

CASSAVA STARCH MONTMORILLONITE CLAY BIOPLASTICS – DEVELOPMENT, DEGRADATION STUDIES AND POTENTIAL FOR PACKAGING APPLICATIONS

Submitted by

ALEENA MERIN WILSON (AB23CHE015)

In partial fulfillment for the award of the

Bachelor's Degree in Chemistry

DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

ST. TERESA'S COLLEGE (AUTONOMOUS)
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DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

ST. TERESA'S COLLEGE (AUTONOMOUS)

ERNAKULAM

B.Sc. CHEMISTRY PROJECT REPORT

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This is to certify that the project "**CASSAVA STARCH MONTMORILLONITE CLAY BIOPLASTICS – DEVELOPMENT, DEGRADATION STUDIES AND POTENTIAL FOR PACKAGING APPLICATIONS**" is the work done by **ALEENA MERIN WILSON.**

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DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

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CERTIFICATE

This is to certify that the project work entitled "**CASSAVA STARCH MONTMORILLONITE CLAY BIOPLASTICS – DEVELOPMENT, DEGRADATION STUDIES AND POTENTIAL FOR PACKAGING APPLICATIONS**" is the work done by **ALEENA MERIN WILSON,** under my guidance in the partial fulfilment of the award of the Degree of Bachelor of Science in Chemistry at St. Teresa's College (Autonomous), Ernakulam affiliated to Mahatma Gandhi University, Kottayam.

ST. TERESA'S COLLEGE (AUTONOMOUS) ★ ERNAKULAM ★ DEPARTMENT OF CHEMISTRY

Dr. Saritha Chandran A.
Project Guide

DECLARATION

I hereby declare that the project work entitled "**CASSAVA STARCH MONTMORILLONITE CLAY BIOPLASTICS – DEVELOPMENT, DEGRADATION STUDIES AND POTENTIAL FOR PACKAGING APPLICATIONS** submitted to Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous) affiliated to Mahatma Gandhi University, Kottayam, is a record of an original work done by me under the guidance of **Dr. Saritha Chandran A, Professor,** Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous), Ernakulam, Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous), Ernakulam and this project work is submitted in the partial fulfilment of the requirements for the award of the Degree of Bachelor of Science in Chemistry.

ALEENA MERIN WILSON

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I express our sincere gratitude to Almighty God for bestowing us with the strength, guidance, and perseverance to complete this project successfully.

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ALEENA MERIN WILSON

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Chapter 1

Introduction

1.1 PLASTICS

The word plastic was coined from the Greek word ‘Plasticos’, which means to be able to form. Plastic is widely known as a synthetic polymer developed by polymerization of monomers extracted from petrochemials and combined with other chemicals. Monomers are the repeating units of long- chain polymers that are composed of carbon, hydrogen, and oxygen held together by covalent bonds. Ethylene and propylene are common examples of lightweight monomers that are widely used in plastic manufacturing. Plastics have several valuable properties such as being lightweight, toughness, high strength, good stiffness, design capabilities, good insulation, corrosion resistance, and a poor conductor of electricity. Moreover, they are heat- sealable, easy to print on and offer the flexibility of fabricating into various shapes. Unfortunately, conventional plastics have their origin in petrochemical industries making them non-biodegradable and non- renewable. This nature of plastics has been a serious disadvantage to their application leading to huge municipal wastes and environmental degradation (1,2).

1.2 BIOPLASTICS

Bioplastics are biodegradable plastics made wholly or partly from natural polymers derived from sources like sugar cane, potato starch, and cellulose from plants. They break down through microbial activity under suitable conditions to carbon dioxide and water without harming the

environment. Bioplastics reduce carbon footprints, dependence on fossil fuels, and plastic waste issues. They can be fully biodegradable, compostable, or recyclable. Historically, materials like cellulose, rubber, and lignin from plants were used before synthetic polymers like Bakelite emerged in the early 20th century. Modern bioplastics, such as polylactic acid and polyhydroxyalkanoates, are affordable, durable, and mainly used for packaging. Bioplastics decompose easily in aerobic and anaerobic environments through bacteria, algae, and fungi. They offer advantages like biodegradability, flexibility, durability, transparency, and heat resistance, making them an eco-friendly alternative to traditional plastics (3).

1.2.1 ADVANTAGES OF BIOPLASTICS

1. Lower Carbon Emission

Bioplastics are made from renewable natural resources instead of fossil fuels, resulting in significantly fewer greenhouse gas emissions. They can cut carbon emissions by at least 30% and have a 42% smaller carbon footprint than conventional plastics.

2. Enhanced Biodegradability

Many bioplastics break down quickly under suitable conditions (e.g., warmth, moisture, oxygen), often within months, unlike traditional plastics that persist for centuries. Their bio- degradability depends on factors like temperature, moisture, and chemical composition.

3. Improved Sustainability

Bioplastics use renewable resources such as plant oils, sugars, algae, and bacteria, supporting eco-friendly goals and reducing reliance on fossil fuels. They contribute to less waste, pollution, and greenhouse gas

emissions, aiding compliance with environmental regulations.

4. Food Safety

Bioplastics are often non-toxic and safe for food contact, with no impact on taste or smell. They provide good barrier proper- ties to extend shelf life and meet stringent safety standards from agencies like the FDA and EU authorities.

5. Efficient Use of Natural Resources

Bioplastics utilize natural materials, including agricultural waste, reducing landfill waste and dependence on fossil fuels. They support sustainable applications in packaging, automotive parts, medical products, and agriculture, promoting better resource use and environmental protection.

6. Eco-safety

Bioplastics also generates fewer greenhouse gasses and contains no toxins. Bioplastics contribute clearly to the goal of mitigating GHG emissions. By producing 1 kg of bioplastic resin releases only 0.49 kg of CO2 which is about 80% reduction of global warming potential (4).

1.2.2 TYPES OF BIOPLASTIS

Bioplastics can be of various types, which is based on the source that it has been derived from. The most common plastics used presently are:

1. Cellulose – based Bioplastics

Cellulose plastics are derived from cellulose acetate, nitrocellulose and cellulose esters. These kinds of cellulose are present in plant materials like forestry residue and by-products of agricultural production. Researchers and scientists worldwide are currently figuring out how to extract cellulose

efficiently from model feedstock, leaves, stalks, tassels, and husks left after harvesting and then adding inorganic salts to separate the cellulose.

2. Starch-based Bioplastics

Starch plastics are the most common type and widely used bio- plastic, and it constitutes approximately 50% of the bioplastics market. It could also be prepared at home by following processes like 'gelatinizing starch' and 'solution casting'. Pure starch plastics are brittle but it absorbs humidity from the environment. Starch plastics films are also used in the packaging sector for packing consumer goods, bakery items, fruits and vegetables and magazines. These films can also be used as paper. Among the most promising biopolymers for producing edible films, starch is particularly popular because of its affordability.

3. Protein-based Bioplastics

Protein-based plastic is made from various sources of protein like soy, albumin, wheat gluten, etc. Out of the above protein sources, soy protein plastics have been produced for more than 100 years. The best example of the application of soy protein plastic is the body panels used in automobiles. Another usage of protein bioplastics is the films that are used in the packaging industry. However, protein-based plastics are water-sensitive and expensive but the addition of biodegradable polyesters reduces the cost and water sensitivity of these plastics (5).

1.3 STARCH

Starch is one of the major sources in the development of bioplastic. Many previous studies have been conducted by using starch as a natural biopolymer. Starch consists of a long chain of two glucose units joined together, namely branched polymerized amylopectin and amylose, which

gives its granular structure. Due to its large availability, low cost, renewability and biodegradability, starches are commonly used in the production of bio- plastics. Starch can behave like a thermoplastic in the presence of plasticizer, with application of heat and mechanical treatment. As native starch- based films are limited to high water affinity and brittleness, other natural biopolymers are often added as fillers to modify and improve films' properties (6).

1.3.1 TAPIOCA STARCH

Tapioca starch is derived from the cassava root, a tuber native to South America. Cassava root serves as a crucial food source in many countries across Africa, Asia, and South America, largely because it is relatively easy to cultivate. The majority of tapioca's nutrients come from its nearly pure starch content. Tapioca starch is distinguished from other starches by its low residual material content, lower amylose levels compared to other amylose- containing starches, and the high molecular weights of both amylose and amylopectin. The production process involves removing the starchy liquid and allowing the water to evaporate, leaving behind a fine tapioca powder once all moisture is drained. Cassava is an excellent raw material for producing biodegradable plastics, especially in tropical and subtropical regions where it is a major starch source. Due to its lower cost compared to other starches, cassava starch shows great potential for use in bioplastics. However, cassava starch-based bioplastics also have limitations, including low mechanical strength and high water affinity, which are attributed to the intra- and intermolecular interactions within the starch(7).

1.4 CLAY

Clay consists of soil particles smaller than 2 μm, with layers about 1 nm thick and nanoscale dimensions. It is a type of layered silicate mineral made of stacked aluminosilicate layers that have a high aspect ratio and large surface area. Clays are essentially composed of micro-crystalline particles of a small group of minerals, referred to as the clay minerals Clays are widely available, affordable, and commonly used as layered silicates in polymer nanocomposites. Various types of clay differ in properties like exfoliation, swelling, structure, and composition (8,9).

1.4.1 Structure of clay

Clays are layered silicates with thicknesses as thin as 1 nm and lateral sizes between 50 and 1000 nm. They consist of stacked hydrated aluminosilicate sheets, primarily octahedral sheets (with a metal like aluminum sur- rounded by eight oxygen atoms) and tetrahedral sheets (with four oxygen atoms around silicon). These sheets connect through shared oxygen atoms. In 1:1 phyllosilicates like the kaolin group, one octahedral sheet fuses with one tetrahedral sheet, forming layers about 0.7 nm thick. In 2:1 phyllosilicates, a central alumina octahedral sheet is flanked by two silica tetrahedral sheets, with oxygen ions shared between them.

1.4.2 Properties of clay

Clay minerals exhibit several distinctive properties, including:

- A layered structure with dimensions on the nanometer scale.
- Anisotropy with the layers. A thickness of about 0.7 nm for 1:1 (T:O) layers roughly 1 nm for 2:1 (T:O:T) layers.

- Multiple surface types: external basal (planar), peripheral, and internal (interlayer) surface. The surfaces, especially external often internal ones, can be easily modified through adsorption, ion exchange, or grafting.
- Plasticity
- Most of the minerals solidify upon drying or firing, though exceptions exist.

Among clay minerals, smectites are the most commonly used. Their characteristics include colloidal-sized particles, highly disordered layer stacking, high specific surface area, moderate layer charge, high cation exchange capacity, and low environmental pH. They also possess a small anion exchange capacity influenced by pH, and their interlayer spacing changes with ambient humidity. Smectites tend to intercalate foreign substances such as organic compounds and macromolecules. Some types, like those exchanging Li^+ and Na+, can strongly swell in water due to interlayer expansion. Under ideal conditions, these layers can be fully dissolved or exfoliated(8).

1.4.3 Classification of Clay

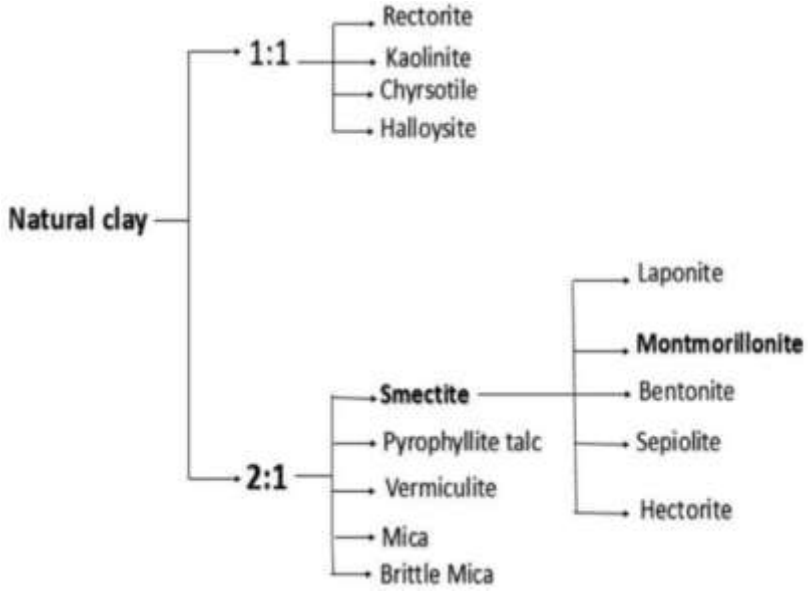


Fig.1.1: Classification of clay materials

1.5 Montmorillonite Clay

Montmorillonite clay, a naturally occurring 2:1 layered silicate, has gained significant attention in recent years due to its exceptional cation exchange capacity, extensive surface area, and tunable porosity. These unique properties make montmorillonite an excellent choice for various applications, including the development of nanocomposite materials and catalysis. Studies have shown that modifying montmorillonite with quaternary ammonium salts enhances its adsorption capabilities for organic pollutants and heavy metals. Additionally, its thermal stability and ease of surface modification further increase its versatility, making it a valuable material in environmental cleanup, drug delivery systems, and polymer reinforcement (10).

1.5.1 Structure of Montmorillonite clay

Structure of MMT Clay is a phyllosilicate mineral with a nanolayered structure composed of stacked layers. The thickness of the layers is about 1 nm. One O-Al(Mg)-O octahedral sheet (approximately 100 nm × 100 nm in width and length) is sandwiched by two O-Si-O tetrahedral sheets in each layer. Since isomorphous substitution generates a net negative charge on the layers, cations are present in the interlayered region of MMT.

The electrostatic and van der Waals forces holding the neighboring layers together contribute to the formation of the initial clay particles. Primary particles combine to form secondary particles that range in size from micrometers to millimeters (10).

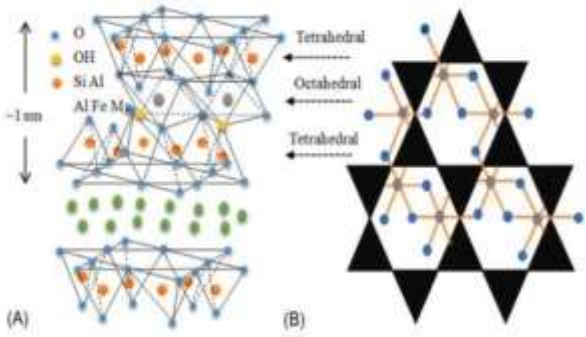


Fig 1.2 Structure of MMT Clay

1.5.2 Modified Montmorillonite Clay

Modified montmorillonite (MMT) clay, through changes to its surface properties, enhances the performance of bioplastics by increasing compatibility with polymer matrices, thereby extending their shelf life. MMT clay can be rendered more hydrophobic via physical or chemical methods such as organophilization, which boosts its interaction and dispersion within biopolymers. This results in nanocomposites with superior barrier properties, significantly reducing moisture and gas

permeability. The presence of modified MMT makes it harder for molecules like water vapor and oxygen to penetrate the bioplastic. In addition to improving barrier effectiveness, modified MMT also enhances the mechanical strength and thermal stability of bioplastics, reinforcing their resistance to environmental degradation, heat, and pressure (11).

1.5.3 Importance of MMT Clay in Extending Shelf life of Bioplastics

MMT clay plays a crucial role in extending the shelf life of bioplastics, which serve as eco-friendly alternatives to traditional plastics. By enhancing the barrier properties of bioplastics and reducing the transmission of oxygen and moisture, this modified clay helps prolong their durability. Additionally, MMT clay's antibacterial properties inhibit microbial growth, improving food safety and maintaining packaging integrity. Its thermal stability ensures consistent performance across various temperatures. Combining bioplastics with MMT clay enables manufacturers to create high-performance, sustainable packaging solutions for food, cosmetics, and pharmaceuticals This synergy supports the preservation of product freshness and quality while minimizing environmental impact, meeting the growing demand for environmentally responsible packaging options. However, in the present work, the focus is limited to mechanical strengthening and biodegradation behavior.(12)

In view of the limitations of native starch-based bioplastics and the promising reinforcing potential of modified montmorillonite clay, the present work aims to develop and evaluate starch–MMT nanocomposite bioplastics for improved mechanical strength and environmental performance.

1.6 OBJECTIVES OF OUR WORK

- To develop starch-based biodegradable bioplastic films using cassava starch.
- To chemically modify montmorillonite (MMT) clay to improve compatibility with the starch matrix.
- To confirm clay modification using XRD and FT-IR analysis.
- To evaluate the effect of incorporating modified MMT on mechanical properties.
- To study the thermal stability of the developed bioplastics using TGA.
- To investigate biodegradation behaviour under soil, water, air, and bacterial exposure conditions.
- To assess the potential suitability of the developed material for eco-friendly packing applications.

Chapter 2

Materials and Methods

2.1 MATERIALS

- Cassava powder
- Acetic acid
- Plasticizer (Glycerol)
- Distilled water

2.2 MODIFICATION OF MONTMORILLONITE CLAY

Here, the adduct was made by combining cetyltrimethylammonium bromide (CTAB) (1.4616g) with an organic acid known as cinnamic acid (0.592g) at 100 ml of purified water and 4g of MMT clay were mixed together in a 1000 ml beaker. The necessary amounts of cinnamic acid and CTAB were mixed with 100 milliliters of distilled water in a 200 milliliters beaker. The two suspensions described above were combined separately for half an hour using a magnetic stirrer. The synthesized adduct was add- ed to this clay suspension along with 600 milliliters of distilled water. It was covered and constantly swirled with a magnetic stirrer for 48 hours. Centrifugation was used to separate the changed clays. Finally, the chemically modified clay was dried in a hot air oven set to 80°C. These were pulverized with a mortar and pestle to produce finely powdered modified clay (13).

Fig 2.1: Modification of Montmorillonite clay

2.3 PREPARATION OF VIRGIN BIOPLASTICS

Table 1: The weight ratios of the components of the V1 sample

Sample name	Tapioca powder (g)	Acetic acid (ml)	Distilled Water (ml)	Plasticizer (ml)	Tapioca powder: Plasticizer ratio
V1	10	10	60	0.5	1:0.05

The above ratio was used for this study and this will be mentioned as "Virgin" sample here on. Cassava powder, glycerol, acetic acid, and distilled water were combined thoroughly. After ensuring a smooth consistency with no lumps, the mixture was found to be somewhat thin and runny. The mixture thickened and grew more translucent as the

temperature increased. When the mixture was thick and clear, it was taken off the heat source. To prevent lump formation, care was taken to prevent the mixture from becoming overheated. After that, the mixture was poured on a ceramic tile and allowed to cool and dry and was flaked off the tile (14).

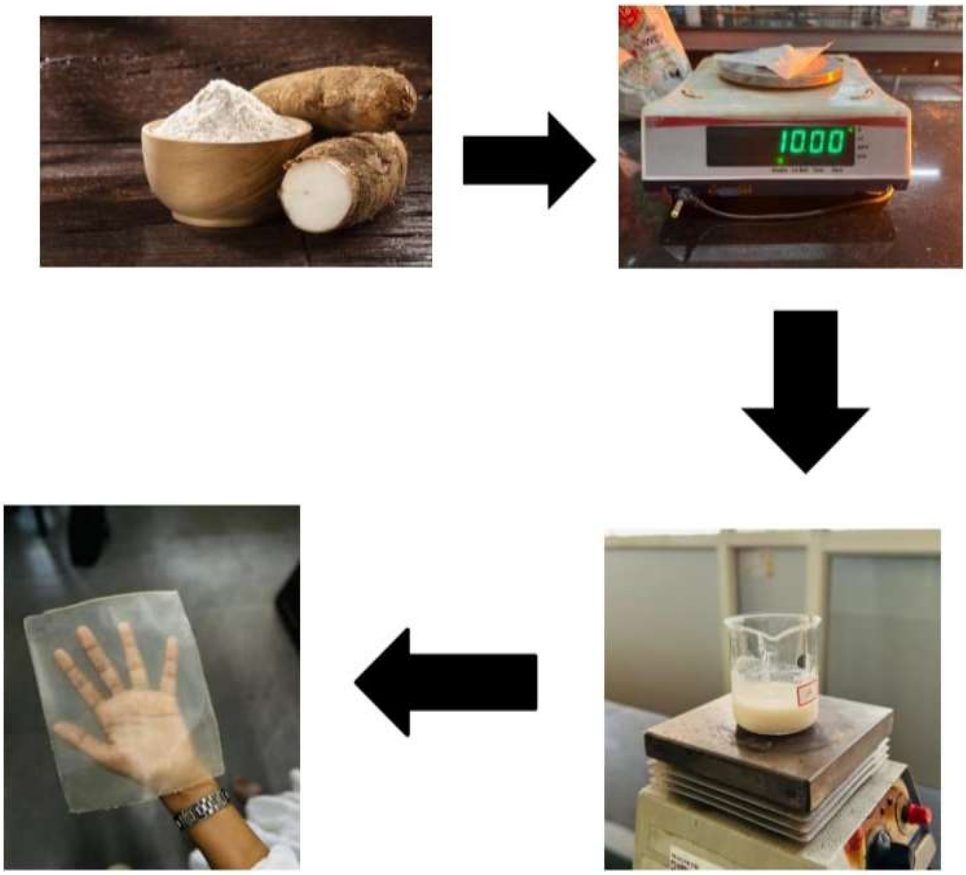


Fig 2.2: Preparation stages of Virgin Bioplastic

2.4 PREPARATION OF MONTMORILLONITE CLAY INCORPORATED BIOPLASTICS

Modified clay incorporated bioplastics were prepared by mixing modified clay with cassava powder, acetic acid and glycerol as given in the table 2.

Table 2: Compositions of modified incorporated bioplastics

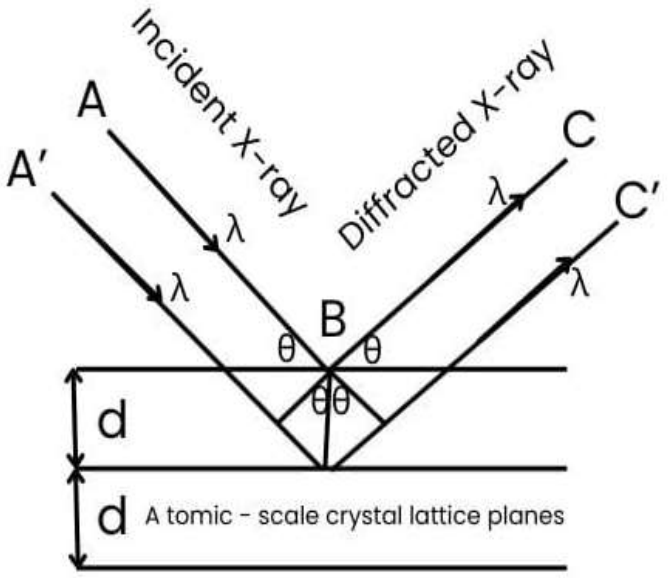
Sample name	Tapioca powder (g)	Acetic acid (ml)	Distilled water (ml)	Plasticizer (ml)	Modified MMT Clay (g)
MMMT1	10	10	60	0.5	0.5

2.5 CHARACTERIZATION TECHNIQUES

The practice of examining a material's inherent structure and characteristics using techniques from outside the substance is known as characterization in material science. Characterization can be done through tests or analyses on real materials. To see the internal structure of the specimen, analysis techniques are used to simplify and enlarge it and gain a better understanding of the distribution of the specimen's basic pieces and their interactions.

2.5.1 X-Ray Diffraction Studies of Montmorillonite Clay

One accurate and widely used method for figuring out the crystal structure of thin films is the X-ray diffraction technique. The crystal structure, orientation, lattice constants, crystalline size, flaws, and stress in the thin film are all fully revealed by it. The unit cell characteristics and micro structural parameters (grain size, micro strain, etc.) can be inferred from the lines, position and shape, respectively.



X-rays are wave-like and are therefore diffracted by the crystal's lattice to produce a distinctive pattern of peaks of reflections at various angles and intensities. Bragg's relationship provides the condition that atoms on successive planes must be in phase for the diffracted beam from them to cancel.

$$\mathbf{n\lambda = 2dsin\theta}$$

Here, λ is the incident beam's wavelength, n is the order of diffraction, d is the inter-spacing, and θ is the angle of diffraction. XRD is the most effective technique for characterizing homogeneous and inhomogeneous stress- es because it can precisely measure the position of the diffraction peak. XRD analysis was performed to determine basal spacing changes in the layers of clay.

2.5.2 FT-IR of Montmorillonite Clay

The FT-IR analysis were conducted to investigate the modified clay's absorption capabilities across various wavelengths, providing valuable insights into its molecular structure and vibrational properties. Infrared spectroscopy is a powerful method for monitoring and analyzing clay–fluid interactions. FT-IR spectra were used to evaluate the specimen of adduct modified clay made with cinnamic acid-CTAB adduct modified clay. Using KBr pellets, the spectra was captured in the 4000–400 cm^{-1} range. A plot of transmittance percentage against wavenumber is produced. Whatever their makeup, various groups in the molecules produce characteristic absorption bands with wavenumbers that fall within a given range. The wavenumber values at which absorption is detected can be used to identify the presence of functional groups. The intercalation of the modifiers in the clay was confirmed in the current study using infrared data(15,16).

2.5.3 Mechanical Strength

Mechanical strength is a critical parameter for evaluating the applicability of bioplastics in packaging and structural applications. Tensile strength and percentage elongation at break were measured using Shimadzu Autograph Series Universal Testing Machine (AGSX5KN) The samples, were cut to 8 cm length and 1 cm breadth for testing. The clay incorporated bioplastic which exhibited maximum tensile strength was used for degradation studies.

2.5.4 Thermogravimetric Analysis

At temperatures between 0-750°C, thermogravimetric examination of the clay incorporated sample was carried out using a Hitachi-STA 7300 TGA equipment.

2.5.5 Biodegradation Studies

The natural components used to make bioplastics allow for their natural destruction and decomposition. We conducted the following biodegradation investigations to see if the produced bioplastics could break down in the natural environment.

- Soil Degradation
- Air Degradation
- Water Degradation
- Bacterial Degradation

Soil Degradation

One way to investigate the biodegradation of polymers is to evaluate weight loss. A previously weighed tiny portion of the samples- virgin and clay incorporated samples was removed, weighed, and then buried five centimeters deep in the soil. On the 31st day, the sample's final weight was noted.

Air Degradation- Shelf-life testing

A previously weighed tiny piece was removed, weighed, and stored at room temperature. On the 31st day, the final weight was recorded. The percentage of biodegradation was computed. The fungal attack on the sample was also checked every day.

Water Degradation

A previously weighed tiny piece was removed, weighed, and submerged in 100 milliliters of water. On the 31st day, the final weight was recorded, and the amount of biodegradation was computed.

Bacterial Degradation

Four distinct bacterial species were used in our bacterial degradation investigations of the produced bioplastic film. From the sample with the highest tensile strength, a tiny piece was removed, weighed, and placed into each test tube that included the cultivated bacteria. The final weight was measured and the changes were recorded. Within 5 days, practically all bioplastics were broken down. Degradation percentage was calculated.

Chapter 3

Results and discussion

3.1 X-RAY DIFFRACTION STUDIES

X-ray diffraction analysis was carried out to evaluate the structural modification of montmorillonite (MMT) clay after treatment with the cinnamic acid–CTAB adduct. The basal spacing (d-spacing) of layered silicate clays is highly sensitive to intercalation of organic molecules, and therefore XRD serves as an effective tool to confirm modification.

3.1.1 XRD Pattern of Unmodified Clay

The XRD pattern of unmodified MMT clay (fig. 3.1) shows a characteristic basal reflection at $2\theta = 7.081°$, corresponding to a d-spacing of 12.47 Å. This peak represents the natural interlayer distance of the clay sheets.

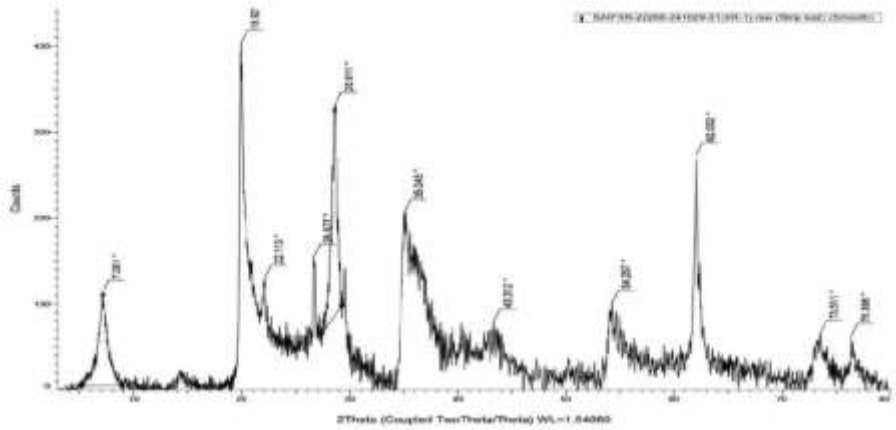


Fig 3.1: XRD Pattern of Unmodified clay

3.1.2 XRD Pattern of Modified Clay

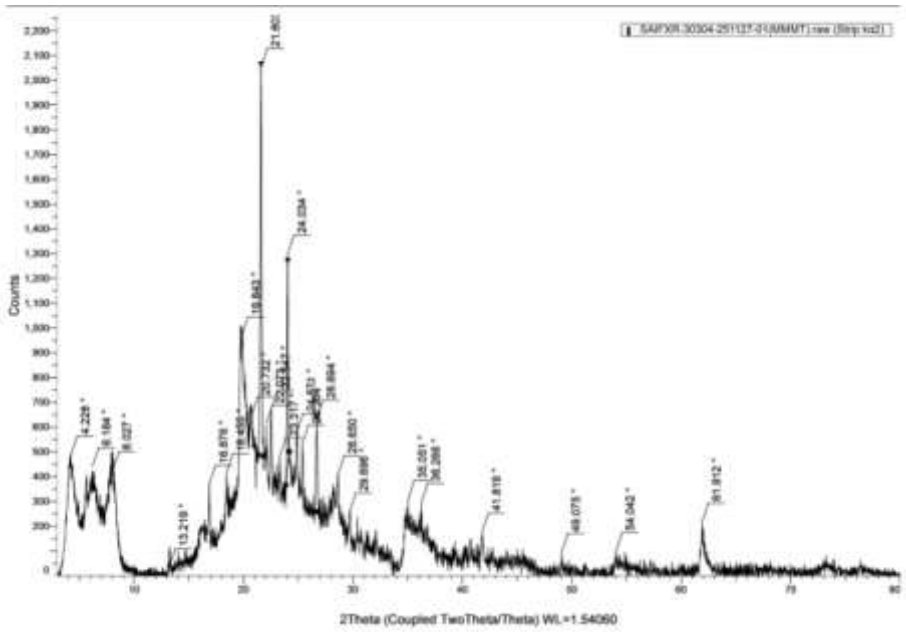


Fig 3.2: XRD pattern of Modified clay

Table 3: d-spacing values

Sample	Angle 2θ (degree)	d-spacing (Å)
Unmodified clay	7.081	12.47
Modified clay	4.228	20.88

The XRD of modified MMT clay is given in fig. 3.2. After modification with CTAB and cinnamic acid, the XRD peak shifted significantly to 2θ = 4.228°, corresponding to a d-spacing of 20.88 Å. This increase in d-spacing clearly indicates the successful intercalation of organic modifier molecules into the interlayer region of the clay. The expansion of the interlayer spacing suggests that the hydrophobic alkyl chains of CTAB were inserted between the silicate layers, resulting in increased gallery

spacing. The shift in peak position confirms that the modification process was successful and that the clay structure was altered to improve compatibility with the starch matrix.

3.2 FT-IR SPECTROSCOPY ANALYSIS

FT-IR spectroscopy was performed to identify functional groups present in both unmodified and modified MMT clay and to confirm successful chemical modification.

3.2.1 FT-IR Spectrum Analysis of Unmodified MMT Clay

The FTIR spectrum of the unmodified montmorillonite clay is shown in fig: In pure MMT clay, a broad band at 3455.11 cm^{-1} indicates the –OH stretching of water molecule in the interlayer of the clay. The band at 3629.21 cm^{-1} represents the – OH stretching of Al-OH bond. The band observed at 1637.36 cm^{-1} corresponds to –OH bending vibration of water molecule in the interlayer of the clay. The band identified at 1046.16 cm^{-1} represents the Si-O-Si stretching vibration and the bands at 524.22 cm^{-1} and 463.92 cm^{-1} are identified as the Al-O-Si and Si-O-Si bending vibrations respectively. The band observed at 916.01 cm^{-1} belongs to the bending vibration of Al-OH. These peaks confirm the typical structural features of montmorillonite clay.

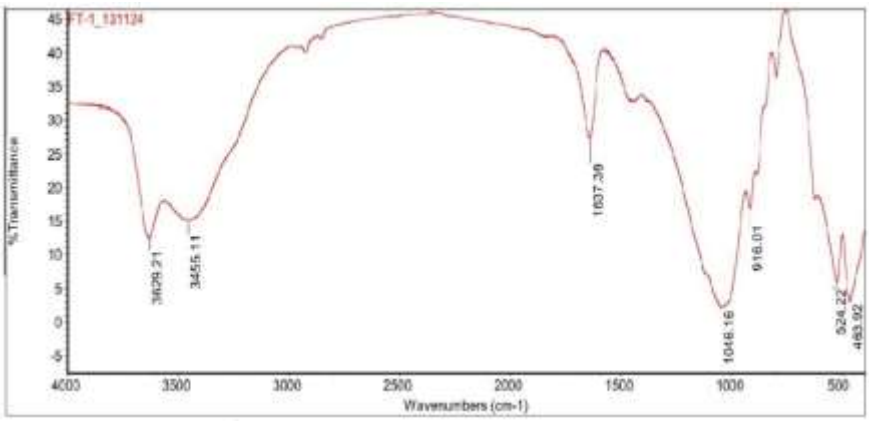


Fig 3.3: FT-IR spectrum of Unmodified clay

The vibrational frequencies of the peaks are listed in the given table 4.

Table 4: Vibrational frequencies of unmodified clay

Wavenumber (cm^{-1})	**Vibration**
3629.21	-OH stretching of Al-OH
3455.11	-OH stretching of water
1637.36	-OH bending of water
1046.16	Si-O-Si stretching
916.01	Al-OH bending
524.22	Al-O-Si bending
463.92	Si-O-Si bending

3.2.2 FT-IR Spectrum Analysis of Modified MMT Clay

The absorption at 3627.36 cm^{-1} is associated with the acid groups -OH stretching vibration. The stretching for $-CH_2$ and $-CH_3$ of CTAB is represented by the extra bands that were discovered at 2851.07 cm^{-1} and 2920.08 cm^{-1}, respectively. The intercalation of CTAB's alkyl group into the clay's interlayer is supported by these bands. The absorption bands at 1635.68 cm^{-1} correspond to the C=C stretching vibration of alkene, whereas the band at 1705.84 cm^{-1} is caused by the C=O stretching of cinnamic acid. The appearance of alkyl and carbonyl stretching vibrations confirms the successful incorporation of organic modifiers into the clay structure. These modifications increase hydrophobicity and improve compatibility with the starch matrix.

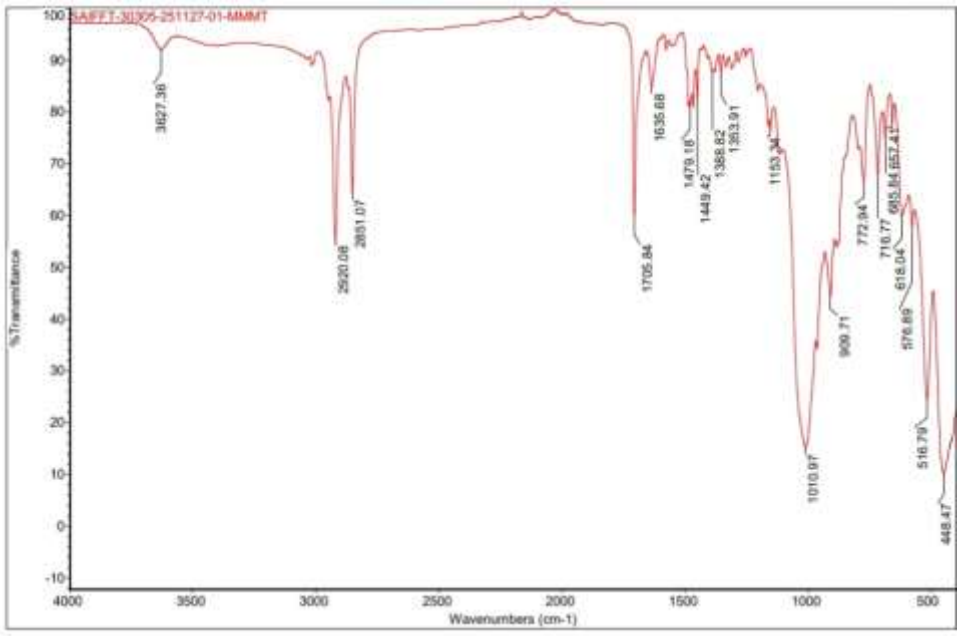


Fig 3.4: FT-IR spectrum of modified clay

The vibrational frequencies of the peaks are listed in table 5.

Table 5: Vibrational frequencies of Modified clay

Wavenumber (cm^{-1})	Vibration
3627.36	-OH stretching of Al-OH
2851.07	-CH2 stretching
2920.08	-CH3 stretching
1705.84	C=O stretching
1635.68	C=C stretching of alkene
1010.97	Si-O-Si stretching
448.47	Si-O-Si bending

3.3 MECHANICAL STRENGTH

Tensile strength and elongation at break were analyzed. Tensile strength refers to the maximum load or stress a material can endure before it stretches or breaks. On the other hand, elongation at break measures the extent to which a material can elongate, relative to its original length, while still maintaining its tensile strength. The virgin bioplastic with cassava starch: plasticizer ratio of 1:0.05 shows a tensile strength of 3.49 N/mm^2.

$$\frac{4.87 - 3.49}{3.49} \times 100 = 39.54\%$$

An approximately 39.5% increase in tensile strength was observed. The results of mechanical strength testing of the virgin and modified clay incorporated Bioplastic is shown in the following table(17).

Table 6: Mechanical properties of V1 and MM1

Bioplastic	Tensile Strength (N/mm^2)	Percentage Elongation (%)
V1	3.49	0.744
MM1	4.87	5.01

The improvement in tensile strength can be attributed to:

- Better interfacial interaction between modified clay and starch matrix
- Improved dispersion of clay layers
- Enhanced stress transfer between filler and polymer

The increase in elongation suggests that the modified clay acted as an effective reinforcing agent while maintaining flexibility.

The enhanced mechanical properties demonstrate that chemical modification of MMT improved compatibility with the hydrophilic starch matrix.

3.4 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis was used to examine the bioplastic sample's thermal stability. The definition of bioplastic's thermal stability is the material's capacity to withstand heat and preserve its qualities, including strength, toughness, and elasticity, at a specific temperature. Therefore, the sample's thermal stability aids in determining the temperature at which sample degradation occurs. Using peaks from DTG analysis, the DTG graph provides a clear picture of how bioplastic breaks down at a given temperature(18–20).

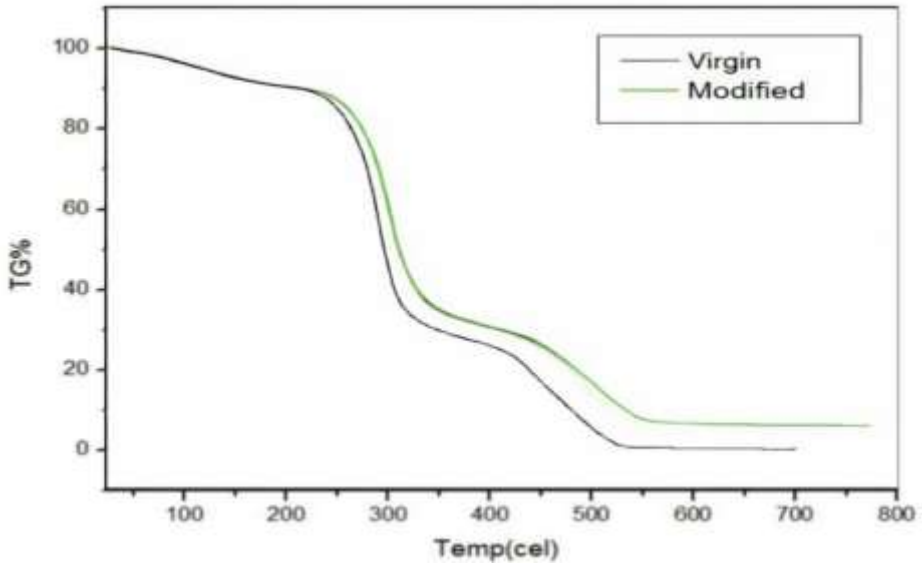


Fig 3.5 TGA graph of V1 and MM1

Table 7: Thermal degradation characteristics of bioplastics

Feature	V1	MM1
Onset Degradation Temperature (°C)	266.6	275.4
Peak Degradation Temperature (°C)	294.4	301.3
Weight remaining at peak degradation temperature (%)	55.49	53.4
Weight loss (%) at peak degradation temperature	44.51	46.6
Weight remaining at 500°C (%)	6.08	16.23
Temperature at 50% weight loss	300.7	311.74

Thermograms demonstrate that the polymer's thermal stability was marginally enhanced by the addition of Montmorillonite clay. The TGA data indicates the thermal stability of two different materials (V1, MM1).

MM1 has the highest onset and peak degradation temperatures - 275.4°C, 301.3°C, respectively, suggesting better thermal stability than V1. V1 degrades at a lower temperature and retains the least weight at 500°C (6.08%), showing the lowest thermal stability. MM1 has the highest weight loss at peak degradation (46.6%); light variation in weight loss may be attributed to organic modifier decomposition. MM1 has slightly better temperature resistance at 50% weight loss (~311°C) than V1 (300.7°C). MM1 has enhanced thermal stability compared to V1.

3.5 BIODEGRADATION STUDIES

Biodegradation studies were conducted under soil, air, and water conditions over a period of 31 days to evaluate environmental stability.

3.5.1 Biodegradation Studies of Virgin Bioplastic

Soil Degradation

Photographs of virgin bioplastic (V1) captured on Day 1 and Day 31 during soil degradation studies reveal that by Day 31, the material had degraded by 6.67%.

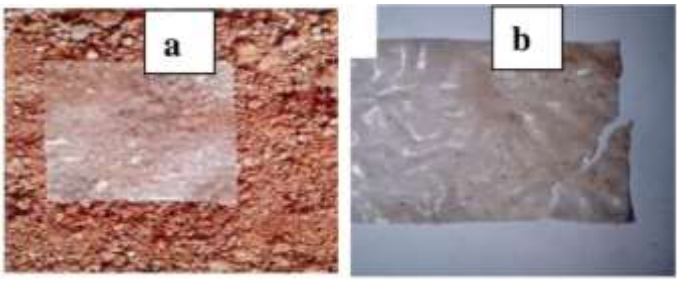


Fig 3.6: Soil degradation of V1 a) Day 1 b) Day 31

Air Degradation

The photographs of the samples taken on Day 1 and Day 31 are shown in fig. 3.7. Fungal attack was observed on Day 19 and the percentage degradation of the sample on the 31st day was 14.12%.

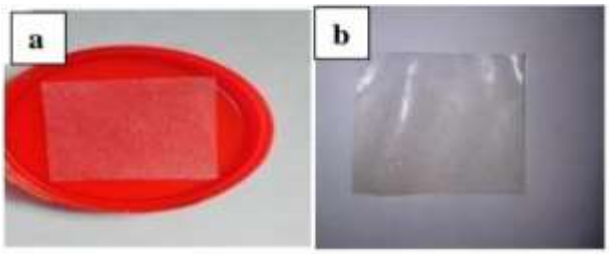


Fig 3.7: Air degradation of V1 a) Day 1 b) Day 31

Water Degradation

The sample V1 was immersed in water as outlined in Chapter 2. Photographs of the sample taken on Day 1 and Day 31 are presented in the fig. 3.8. Biodegradation occurs in the presence of water and bacteria, and as expected, the sample exhibited gradual dissolution. On the 31st day, the percentage degradation was found to be 87.84%.

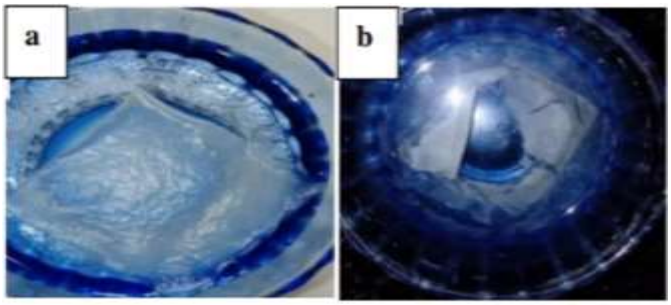


Fig 3.8: Water degradation of V1 a) Day 1 b) Day 31

3.5.2 Biodegradation Studies of Modified Montmorillonite Clay Incorporated Bioplastic

Biodegradation studies were carried out on modified clay-incorporated bioplastics, focusing on the variant with the highest tensile strength, MM1.

Soil Degradation

Fig.3.9 presents photographs of modified clay-incorporated bioplastic taken on Day 1 and Day 31 during soil degradation studies. The

percentage degradation observed on the 31st day was 16%. Modified clay increased soil degradation from 6.67% to 16%.

The modified clay-incorporated bioplastic showed higher degradation in soil compared to the virgin sample. This may be due to increased surface heterogeneity and microbial interaction at the polymer–clay interface. Both samples confirmed biodegradable behavior.

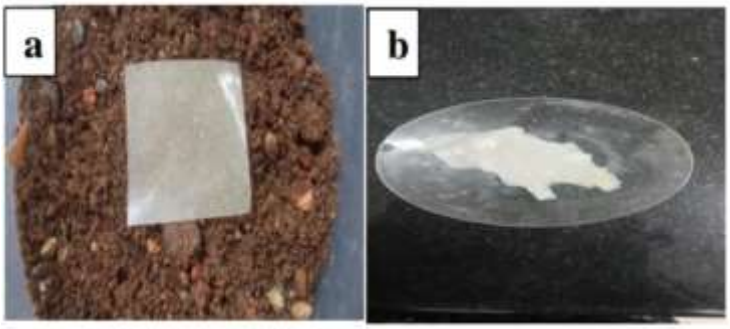


Fig 3.9: Soil degradation of MM1 a) Day 1 b) Day 31

Air Degradation

A piece of bioplastic from MM1 was stored in air at room temperature for 31 days to evaluate its shelf life, with photographs taken on Day 1 and Day 31 displayed in fig 3.10. Fungal growth was observed on Day 29 indicating a minimum shelf life during which the sample exhibited a 4.38% degradation by the 31st day.

Virgin sample showed 14.12% degradation after 31 days. Modified sample exhibited comparatively lower degradation under ambient conditions. This suggests that clay reinforcement enhances environmental stability during usage.

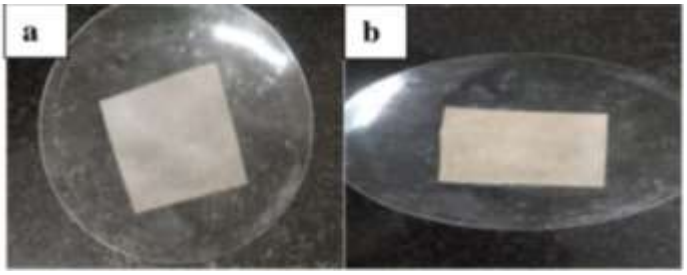


Fig 3.10: Air degradation of MM1 a) Day 1 b) Day 31

Water Degradation

A piece of bioplastic was submerged in 100 ml of water and monitored for 31 days, with photographs taken on Day 1 and Day 31 displayed in the figure. 3.11. By the 31st day, the percentage degradation was found to be 51.25%.

The virgin sample showed very high degradation in water due to the hydrophilic nature of starch.

The reduced degradation in the modified sample indicates:

- Improved moisture resistance
- Reduced water penetration
- Enhanced structural integrity due to clay reinforcement

This balance between durability and biodegradability is desirable for packaging applications.

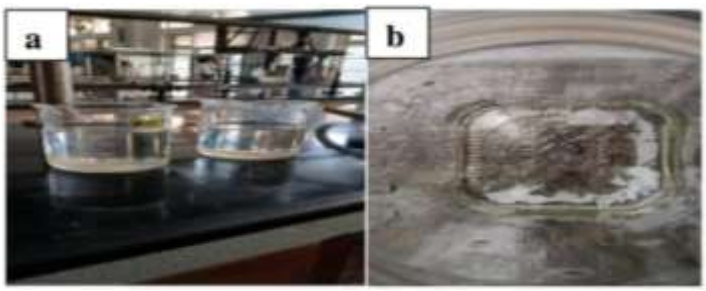


Fig 3.11: Water degradation of MM1 a) Day 1 b) Day 31

Table 8: Percentage degradation of V1 and MM1 in different environments

Degradation	Sample	Initial Weight(g)	Final Weight (g)	Percentage Degradation (%)
Soil	V1	0.150	0.140	6.67
	MM1	0.160	0.145	16
Air	V1	0.170	0.146	14.12
	MM1	0.160	0.153	4.38
Water	V1	0.140	0.018	87.84
	MM1	0.160	0.078	51.25

3.5.3 BACTERIAL DEGRADATION

The degradation of Virgin (V1) and Modified bioplastic (MM1) in presence of 4 different types of bacteria were monitored. The photographs of the samples in the culture media are given below. This study investigates the degradation of modified bioplastics against four bacterial strains: *Escherichia coli*, *Staphylococcus aureus, Bacillus cereus,* and *Salmonella typhimurium*. The nutrient broth was sterilized and inoculated with bacteria, and 1 cm^2 bioplastic samples were added for incubation over 24-120 hours, with weight loss recorded as a measure of degradation. The degradation observations revealed that E. coli caused degradation from day 1, progressing to partial degradation by3-4 days and complete degradation by day 5.

Staphylococcus aureus showed weight loss on the first two days, with partial degradation on days 3-4, leading to complete degradation by day 5.

Salmonella typhimurium exhibited weight loss on day 1, with partial degradation following over days 2-4, and complete degradation by day 5. *Bacillus cereus* also caused weight loss from day 1, with partial degradation on days 3-4, and complete degradation by day 5. Virgin unmodified clay incorporated bioplastics demonstrated similar degradation trends, indicating high biodegradability, while modified bioplastics degraded more slowly, suggesting increased microbial resistance, potentially beneficial for long- lasting applications.

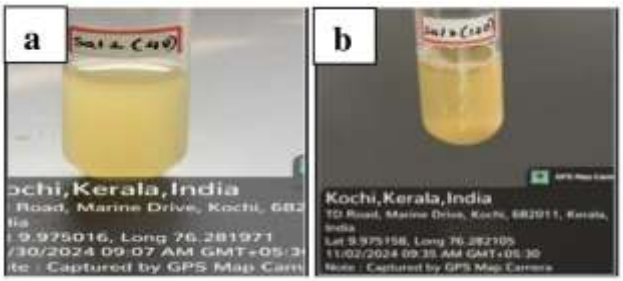


Fig 3.12: Degradation of V1 against Salmonella typhimurium
a) partial degradation b) complete degradation

Fig 3.13: Degradation of MM1 against Escherichia coli
a) partial degradation b) complete degradation

Overall, the experimental findings consistently demonstrate the effectiveness of chemically modified montmorillonite (MMT) clay as a reinforcing agent in starch-based bioplastics. The significant shift in the XRD basal reflection and the corresponding increase in d-spacing confirm

successful intercalation of organic modifiers into the clay interlayer, indicating structural modification of MMT. FT-IR spectroscopy further validated this modification through the appearance of characteristic alkyl and carbonyl functional group vibrations associated with CTAB and cinnamic acid. Mechanical testing revealed a substantial improvement in tensile strength, with an approximate 39% increase observed upon incorporation of 0.5 g of modified clay, along with enhanced elongation at break. This improvement can be attributed to better interfacial adhesion and stress transfer between the starch matrix and the dispersed clay layers. Biodegradation studies showed that the modified bioplastic retained its biodegradable nature while exhibiting improved stability under water and air exposure conditions, indicating enhanced resistance to premature environmental degradation during usage. Collectively, these results establish that chemical modification of montmorillonite clay significantly enhances the structural and functional performance of starch-based bioplastics while maintaining their environmental compatibility.

Chapter 4

Conclusions

The present study focused on the development of biodegradable starch-based bioplastics reinforced with chemically modified montmorillonite (MMT) clay. The work was undertaken in response to the environmental concerns associated with conventional petroleum-based plastics, which are non-biodegradable and contribute significantly to pollution and waste accumulation.

Cassava (tapioca) starch was selected as the base material due to its abundance, renewability, low cost, and good film-forming ability. However, native starch-based bioplastics generally exhibit poor mechanical strength and high water sensitivity. To address these limitations, montmorillonite clay was chemically modified using a cinnamic acid–cetyltrimethylammonium bromide (CTAB) acid–amine adduct in order to improve its compatibility with the hydrophilic starch matrix.

X-ray Diffraction (XRD) analysis confirmed an increase in basal spacing of montmorillonite after modification, indicating successful intercalation of organic modifiers into the clay interlayer. Fourier Transform Infrared (FT-IR) spectroscopy further verified the presence of functional groups associated with CTAB and cinnamic acid in the modified clay. These results confirmed the effectiveness of the clay modification process.

Bioplastic films were prepared using starch, glycerol as plasticizer, and acetic acid. The effect of incorporating 0.5 g of modified montmorillonite clay on the mechanical properties was evaluated. Tensile testing revealed that the tensile strength increased from 3.49 N/mm^2 for the virgin sample (V1) to 4.87 N/mm^2 for the modified clay-incorporated sample (MM1), representing an approximate 39% improvement. The percentage elongation at break also increased significantly. This enhancement can be attributed to improved interfacial interaction and better stress transfer between the starch matrix and the dispersed modified clay layers.

Thermogravimetric analysis revealed that the inclusion of montmorillonite clay enhanced the thermal stability of the bioplastics. The modified clay incorporated bioplastics showed the highest onset and peak degradation temperatures (275.4℃ and 301.3℃) respectively, indicating superior thermal resistance compared to the virgin samples. This improved thermal stability can be attributed to the barrier effect of the well-dispersed modified clay layers, which restricted the diffusion of volatile degradation products and heat transfer within the polymer matrix.

Biodegradation studies were conducted under soil, air, and water conditions over a period of 31 days. The virgin bioplastic exhibited measurable degradation in all environments, confirming its biodegradable nature. In soil, degradation increased from 6.67% (V1) to 16% (MM1), indicating that clay incorporation did not hinder soil biodegradation. In water, the virgin sample showed high degradation (87.84%), while the modified sample exhibited lower degradation (51.25%), suggesting improved structural integrity and reduced water sensitivity due to clay reinforcement. In air exposure studies, the modified bioplastic showed

comparatively lower degradation, indicating enhanced stability and shelf life under ambient conditions.

The bacterial degradation tests further confirmed that the modified bioplastics exhibited increased resistance to microbial activity, which shows potential for use in eco-friendly packaging applications.

Overall, the incorporation of chemically modified montmorillonite clay improved the mechanical strength and environmental stability of starch-based bioplastics while retaining their biodegradable character. The study demonstrates that clay reinforcement is an effective strategy to enhance the performance of starch bioplastics. Although further studies such as long-term durability assessment and large-scale processing would be required for commercial applications, the developed materials show promising potential as eco-friendly alternatives to conventional plastics.

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