PROJECT REPORT

On

CASSAVA STARCH MONTMORILLONITE CLAY BIOPLASTICS- DEVELOPMENT, DEGRADATION STUDIES AND SUITABILITY FOR FOOD PACKAGING APPLICATIONS

Submitted by

VOLGA K. (AM23CHE015)

In partial fulfillment for the award of the
Post graduate Degree in Chemistry

DEPARTMENT OF CHEMISTRY
AND
CENTRE FOR RESEARCH

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This is to certify that the project work titled "**CASSAVA STARCH MONTMORILLONITE CLAY BIOPLASTICS- DEVELOPMENT, DEGRADATION STUDIES AND SUITABILITY FOR FOOD PACKAGING APPLICATIONS**" is the work done by **VOLGA K.** under the guidance of **Dr.Saritha Chandran A., Assistant Professor,** Department of Chemistry and Centre for Research, St.Teresa's College, Ernakulam in partial fulfillment of the award of the Degree of Master of Science in Chemistry at St. Teresa's College, Ernakulam affiliated to Mahatma Gandhi University, Kottayam.

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DECLARATION

I hereby declare that the project work entitled "**CASSAVA STARCH MONTMORILLONITE CLAY BIOPLASTICS- DEVELOPMENT, DEGRADATION STUDIES AND SUITABILITY FOR FOOD PACKAGING APPLICATIONS**" submitted to the Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous), affiliated to Mahatma Gandhi University, Kottayam, Kerala is a record of an original work done by me under the guidance of **DR. SARITHA CHANDRAN A.**, Assistant Professor, Department of Chemistry and Centre for Research, St.Teresa's College (Autonomous), Ernakulam. This project work is submitted in the partial fulfillment of the requirements for the award of the Degree of Master of Science in Chemistry.

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Chapter 1

Introduction

1.1 PLASTICS

A family of materials known as plastics can be molded while still flexible and then hardened to keep the desired shape. These substances may be created artificially or naturally. Plastics are made of polymers. A polymer is a material that has multiple repeating units in it. The word "polymer" comes from the Greek words poly, which means many, and meros, which means parts or components. The chain is made up of at least 1,000 polymerized links that are linked together. Plastics are utilized all throughout the world because of their many benefits, including affordability, flexibility, durability, and light weight. A few examples of materials are tar, shellac, tortoise shell, animal horn, cellulose, amber, and tree sap latex (1)(2).

1.2 BIO PLASTICS

Natural resources are the source of bioplastics, also known as biodegradable plastics. They can lessen pollution and show promise as a substitute for non-biodegradable polymers derived from petroleum. Bio- based and biodegradable polymers hold great potential as environmentally benign products that can help restore biodiversity and create a sustainable future. Because at least one stage in the degradation process was caused by the metabolism of naturally occurring microbes in the environment, biopolymers are considered biodegradable materials. It is possible to create biodegradable polymers from both natural and biological sources, including proteins, lipids, carbohydrates, and cellulose (3).

1.2.1 Advantages of Bioplastics

1. Reduction of Carbon Emissions

The low amount of carbon released into the atmosphere during the production process is one benefit of using bioplastics. Compared to the four tonnes of carbon emissions created by the production of traditional plastics, which contributes to the greenhouse effect and global warming, bioplastics only generate roughly 0.8 tonnes.

2. Uses less energy

Bioplastics can be produced with less energy and don't require the recycling of fossil fuels. Conventional plastics, on the other hand, require burning fossil fuels and require more energy to produce. More bioplastics can be manufactured with less of an impact on the environment because less energy is required.

3. Reducing the Need for Landfill Space

To get rid of them, non-biodegradable plastics are transported to landfills. As a result, landfills are created on property that could have been utilized for residential, commercial, or agricultural purposes. Since bioplastics can be absorbed by the soil and turned into compost or humus, using them eliminates the need to build more landfills.

4. Reusable

In contrast to other plastics that can release harmful compounds, particularly when burned, biodegradable plastics are non-toxic and recyclable.

5. Biodegradability

Many bioplastics are biodegradable or compostable, which can help reduce the accumulation of plastic waste in the environment.

6. Lower Toxicity

Bioplastics often lack harmful additives like bisphenol A (BPA) found in some petroleum-based plastics, making them safer for use in food packaging and medical applications (4).

1.2.2 Types of Bioplastics

Plastics can be of various types, 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.

2. Starch-based Bioplastics

Starch-based plastics are the most common type and widely used bioplastic 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.

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

The Starch Growing environmental consciousness has sparked interest in the creation of bioplastics derived from renewable resources. Both natural and biological resources can be used to create biodegradable polymers. Because of its alluring availability, affordability, and performance, starch has been regarded as one of the most promising natural polymers. A polymeric carbohydrate called starch or amylum is made up of many glucose units connected by glycosidic linkages. The majority of green plants synthesize this polymer in order to store energy. It is the most prevalent carbohydrate in the human diet worldwide and can be found in significant quantities in staple foods such cassava, rice, wheat, potatoes, and maize (corn). From its Germanic origin, the word "starch" means "strong, stiff, strengthen, stiffen." It is a white, odourless, and tasteless powder that is insoluble in cold water. By weight, starch typically comprises 20–25% amylose and 75–80% amylopectin, depending on the plant. In the food sector, starch processing yields a large amount of the sugars utilized in processed meals. The majority of starches can be combined with warm water to create pastes. Wheat paste is one type of paste that can be used as a glue, stiffener, or thickener. Starch is mostly used in the non-food industrial sector as an adhesive in the paper-making process. Prior to ironing, some textile materials can be made stiffer by applying a starch solution. Because it is cheap, widely available, and renewable, starch is the best option for natural polymer resources when it comes to making bioplastics. Since the amylose content of the starch affects the processes of gelatinization, which are essential for the creation of films (6) (7).

1.3.1 Tapioca Starch

Cassava root, a tuber that is indigenous to South America, is used to make tapioca, a starch. Many nations in Africa, Asia, and South America depend heavily cassava root as a food source, and it is comparatively simple to farm. The majority of the nutrients in tapioca are found in its nearly pure starch. The low amount of residual materials, lower amylose content compared to other amylose-containing starches, and high molecular weights of amylose and amylopectin in tapioca starch set it apart from other starches. After the starchy liquid is gone, the water is then allowed to evaporate. After all the water has drained, we are left with fine tapioca powder. Cassava is a viable raw material for the creation of biodegradable plastics since it is a significant supplier of starch in tropical and subtropical climates. Cassava starch has a higher potential for usage in bioplastic because it is less expensive than other starches. By studying more about the starch-based kind of cassava, Indonesia, the world's third- largest producer, has enormous potential to develop bioplastic as a material substitute for synthetic plastic. In addition to its advantages, the cassava starch-based bioplastic has low mechanical characteristics, a high water affinity, and other disadvantages due to the intra- and intermolecular interactions in the starch (8).

1.4 CLAY

Clay is a portion of the soil fraction that contains particles smaller than 2 μm. The clay layers are around 1 nm thick and have nanoscale dimensions. Clay belongs to the class of natural or manmade minerals known as layered silicates, which are composed of regular stacks of aluminosilicate layers with a high aspect ratio and large surface area. Layered silicates are commonly available and reasonably priced. At the moment, clays are the most commonly used layered silicates in the production of polymer nanocomposites. There are many different kinds of clay, each with its own special properties including exfoliation and swelling, as well as variations in structure and composition (9).

1.4.1 Structure of Clay

With a minimum thickness of 1 nm and lateral dimensions ranging from 50 to 1000 nm, clays are layered silicates composed of stacks of hydrated aluminosilicates. Their basic building blocks are octahedral sheets with eight oxygen atoms around a metal, like aluminium, and surrounding silicon. The tetrahedral and octahedral sheets are connected by the exchange of oxygen atoms. The hydroxyl form has unshared oxygen atoms. Tetrahedral and octahedral sheets usually stack in a specific mode and ratio to form 1:1 layered silicates, which are also called phyllosilicates. Clay layers made of octahedral sheets with eight oxygen atoms surrounding a metal, such as magnesium aluminium, and tetrahedral sheets with four oxygen atoms are an example of phyllosilicates. The kaolin group is one such combination. Here, the kaolin group is made up of one octahedral and one tetrahedral fused together (1:1). An octahedral sheet and a tetrahedral sheet fuse together to form the 1:1 layered structure known as the kaolin group. The layers are 0.7 nm thick and are composed of common oxygen atoms and Al:Si2O(OH)s. On the other hand, a central alumina octahedral sheet is fused by the tip to two external silica tetrahedra in the 2:1 layered silicate crystal lattice, also referred to as 2:1 Phyllosilicate. This means that the oxygen ions in the octahedral sheet are also a part of the tetrahedral sheets.

1.4.2 Properties of Clay

Clay minerals are characterized by certain properties, they include:

- Layered structure with dimensions in nanometer range
- The anisotropy of the layers
- The 1: 1 (T:O) layer thickness is approximately 0.7 nm, 2: 1 (T:O:T) layer thickness is approximately 1 nm
- The presence of several types of surfaces: external basal (planar) and peripheral surfaces as well as internal (interlayer) surfaces
- The ease with which external, and often internal, surfaces can be modified (by adsorption, ion exchange, or grafting)
- Plasticity
- Solidification upon drying or firing; this is true for most (but not all) clay minerals

Mostly used clay minerals are smectites. Smectites have the following properties: Colloidal-sized particles, highly disordered layer stacking, high specific surface area, moderate layer charge, high cation exchange capacity, and low environmental pH. Also, a small anion exchange capacity that is dependent on pH, interlayer separation that varies depending on ambient humidity, a propensity for intercalation of foreign substances including organic compounds and macromolecules, and the ability of some members (e.g., Li^+ and Na^+ exchange types) to exhibit strong swelling of the interlayer in water. Under optimal conditions, the layers can be completely dissolved (exfoliated) (10).

1.4.3 Classification of Clay

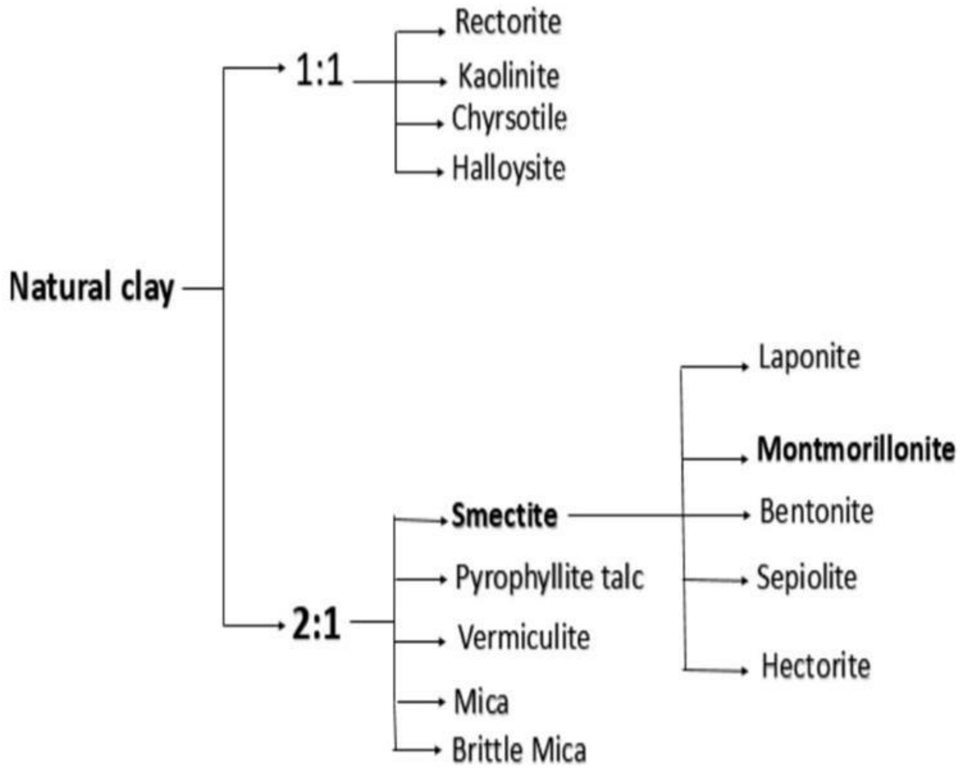


Fig.1.1: Classification of clay materials

1.5 MONTMORILLONITE CLAY

Recent years have seen a notable increase in interest in montmorillonite clay, a naturally occurring 2:1 layered silicate, because of its remarkable cation exchange capacity, large surface area, and adjustable porosity. Because of these special qualities, montmorillonite is a great option for a number of uses, such as the creation of nanocomposite materials and catalysis. It has been demonstrated that the organomodification of montmorillonite with quaternary ammonium salts improves its adsorptive properties against organic contaminants and heavy metals. Furthermore, its thermal stability and ease of surface modification enhance its versatility, making it a valuable material in environmental remediation, drug delivery systems, and polymer reinforcement (11).

1.5.1 Structure of Montmorillonite Clay

The nanolayered structure of MMT, a phyllosilicate mineral, is made up of stacked layers. The layers are roughly 1 nm thick. Two O-Si-O tetrahedral sheets are positioned between one O-Al(Mg)-O octahedral sheet (about 100 nm × 100 nm in width and length) in each layer. Cations exist in the interlayered region of MMT because the isomorphous replacement has made the layer positively charged. The original clay particles were formed by the electrostatic and van der Waals interactions holding adjacent layers together. Primary particles aggregate to create secondary micrometer-scale to millimeter-scale particles (11).

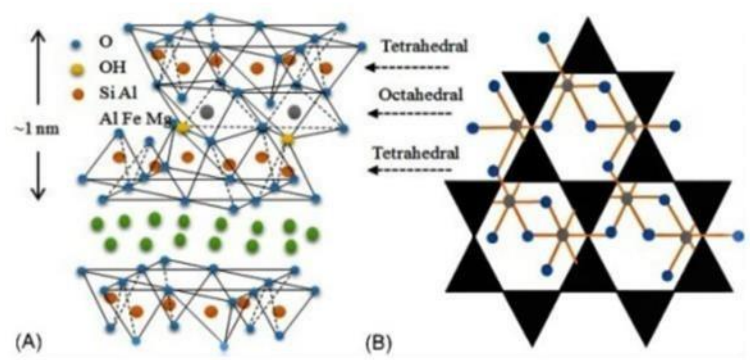


Fig 1.2 Structure of MMT Clay

1.5.2 Modified Montmorillonite Clay

Through surface property modification, modified montmorillonite (MMT) clay provides improved performance in prolonging the shelf life of bioplastics by improving compatibility with polymer matrices. MMT clay can be made more hydrophobic by physical or chemical processes including organophilization, which improves its interaction and dispersion with biopolymers. As a result, nanocomposites with improved barrier qualities are created, considerably lowering the permeability to moisture and gases. Because of the modified MMT, molecules have an even more difficult time passing through the bioplastic, making it more difficult for water vapor and oxygen to do so. Modified MMT improves bioplastics' mechanical strength and thermal stability in addition to their barrier qualities, strengthening their resistance to environmental deterioration, heat, and pressure (12).

1.5.3 Importance of MMT Clay in Extending Shelf life of Bioplastics

MMT clay is a valuable addition to bioplastics, an environmentally friendly substitute for conventional plastics. By improving the bioplastic's barrier qualities and lowering the transfer of oxygen and moisture, this modified clay increases its shelf life. Furthermore, the antibacterial qualities of MMT clay prevent the formation of microorganisms, enhancing food safety and package integrity. Additionally, the bioplastic performs consistently at different temperatures, thanks to its thermal stability. Manufacturers may build high-performing, environmentally friendly packaging solutions for food, cosmetics, and pharmaceutical applications by mixing bioplastics with MMT clay. This allows for the preservation of product freshness and quality while minimizing the impact on the environment. This collaboration makes it possible to create cutting- edge, environmentally beneficial products that meet the rising need for packaging options that are friendly to the environment (13).

1.6 OBJECTIVES OF OUR WORK

- To develop biodegradable bioplastics using cassava starch as the primary base material.
- To modify montmorillonite clay using acid-amine adducts to improve compatibility with the biopolymer matrix.
- To characterize the montmorillonite clay using using X-ray Diffraction (XRD) and Fourier-Transform Infrared Spectroscopy (FT-IR).
- To compare the effects of unmodified and modified montmorillonite clay on the mechanical properties of the bioplastics.
- To optimize the concentration of modified montmorillonite clay for achieving the best mechanical and thermal properties.
- To investigate the thermal stability of bioplastics using thermogravimetric analysis.

- To evaluate the biodegradability of the developed bioplastics under different environmental conditions, including soil, air, water, and bacterial exposure.
- To assess the migration behavior of bioplastics in various food simulants to determine their safety for packaging applications.
- To analyze the structural changes in the bioplasticsusing X-ray Diffraction (XRD)
- To explore the potential of these enhanced bioplastics as sustainable alternatives to conventional petroleum-based plastics.

Chapter 2

Literature Survey

Noorul Hidayah binti Yusoff and colleagues have addressed the pollution caused by synthetic plastics by investigating cassava starch-based bioplastics reinforced with nanoclay. Their research demonstrated that the material completely degrades within six days and its tensile strength improves from 5.2 MPa to 6.3 MPa, suggesting a promising environmentally friendly alternative. In a related study, they examined the incorporation of tapioca starch (TS) as a filler in poly lactic acid (PLA) bioplastics. Their findings indicated that adding TS increased tensile strength to 9.7 MPa at 30 wt% loading; however, performance declined at higher loadings. Although the inclusion of TS reduced impact resistance, it enhanced the tensile modulus, rendering the composite suitable for specific applications (14).

Nurul Aina Ismail investigated the synthesis and characterization of biodegradable starch-based bioplastics using potato and yam starch as raw materials. The chemical, mechanical, and thermal properties were analyzed through FTIR, TGA, and tensile strength testing. FTIR analysis identified O-H, C-H, C=O, and C-O peaks, confirming successful bioplastic formation. The tensile strength of the potato-based bioplastic was 0.6 MPa, while the yam-based bioplastic achieved 1.9 MPa. TGA revealed 50% weight loss at 250°C for potato starch and 310°C for yam starch. Soil burial tests demonstrated biodegradation rates of 43% for potato-based bioplastics and 26% for yam-based bioplastics within a week. These bioplastics were identified as promising alternatives to conventional plastics due to their favorable mechanical, thermal, and biodegradable properties (15).

Arifa Shafqat conducted research using wood dust and potato peel as fillers to investigate the environmentally friendly synthesis of bioplastics from banana peel starch (BPP) and a composite of banana peel, maize, and rice starch (COM). A total of 24 bioplastic samples were produced by testing various combinations of glycerol and sorbitol as plasticizers. The physical and chemical characteristics of the bioplastics, including moisture content, solubility in water and alcohol, biodegradability, tensile strength, and FT-IR analysis, were examined. The results demonstrated their potential for diverse applications and highlighted their biodegradability, reinforcing their feasibility as eco-friendly alternatives to conventional plastics (16).

Nanoparticles, particularly layered silicates such as clay, have gained significant attention for enhancing material performance due to their environmental benefits, natural abundance, and ability to improve properties. In the 1980s, Toyota pioneered the use of clay-based nanocomposites in automobiles, which spurred ongoing interest in nanoparticle-reinforced materials. Recent efforts have focused on developing nanocomposite-reinforced bioplastics as sustainable alternatives to traditional plastics. Despite advancements, challenges related to design, manufacturing, and large-scale application remain. This paper reviews progress in the use of nanoparticle additives to enhance starch-based bioplastics and proposes future research directions for improving their performance and practical implementation (17).

Amun Amri and his colleagues investigated the use of graphene oxide (GO) as a filler to enhance the properties of bioplastics made from cassava starch. The composite was prepared using glycerol as a plasticizer with varying GO contents (5–15% v/v) and different mixing durations (30 and 60 minutes). The results showed that mechanical properties improved with higher GO content and longer mixing durations. At 15% GO and 60 minutes of mixing, the bioplastic achieved a tensile strength of 3.92 MPa, an elongation of 13.22%, and a Young's modulus of 29.66 MPa. While longer mixing times reduced water absorption and biodegradation rates, increasing GO content enhanced both. These findings demonstrate that GO has significant potential as a filler for improving the performance of cassava starch-based bioplastics (18).

Biqiong chen and his coworkers addressed the difficulties in comprehending the physical structures of nanocomposites and how their properties differ from those of conventional composites due to the growing attention being paid to them. Important problems include figuring out the volume fractions of reinforcement, evaluating the contents of clay galleries, figuring out the ratios of intercalate to exfoliation, measuring polymerization inside clay galleries, and comprehending how semi-crystalline polymers affect crystallinity. Furthermore elements like the elastic modulus of clay platelets, the limits of X-ray diffraction, the thermodynamic forces underlying intercalation and exfoliation, and molecular and clay platelet mobility are examined. Although computer models are advancing quickly, they still rely on approximations that could be confusing to non-specialists (19).

B.K.G. Theng examined the impact of both modified and unmodified clay as reinforcements in polymer matrices, focusing on the development and applications of polymer/clay nanocomposites. Theng's work outlines the classification of natural clays, various types of nanocomposites, and synthesis techniques. The study also provides an in-depth analysis of clay modification methods and characterization techniques that emphasize the relationship between structure and properties. Furthermore, Theng highlights the influence of processing methods on achieving the desired material characteristics (20).

Syed Abusale Mhamad Nabirqudri investigated the effect of modified montmorillonite (MMT) clay doping on the electrical and mechanical properties of poly(methyl methacrylate) (PMMA) composites. Using the solvent casting method, they fabricated composites with different weight percentages of MMT clay and characterized them using FTIR, SEM, and DC conductivity studies. The results revealed that the 30 wt% composite exhibited the highest conductivity of 1.59×10^{-3} S/cm due to polymer chain elongation, which enhanced charge transport. Dielectric measurements indicated a low dielectric constant (2.5) and dielectric loss (3.3), leading to an improved conductivity of 5×10^{-3} S/cm. Cole–Cole plots confirmed a reduction in electrical resistance, while mechanical tests demonstrated a tensile strength of 55 MPa and 8% strain, making the material suitable for encapsulation in sensor and solar applications (21).

S.J. Eichhorn addresses the complexities inherent in understanding the structure and characteristics of nanocomposites, especially when compared to traditional composites. The authors delve into critical aspects such as calculating reinforcement volume fractions, assessing impacts on polymer crystallinity, determining intercalation ratios, and estimating clay gallery contents. They also explore the thermodynamics of intercalation and exfoliation, the mobility of clay platelets, and the role of X-ray diffraction in characterizing these materials. While computational models offer insights into polymer-clay systems, the authors acknowledge that these models often rely on approximations that may be challenging for non-specialists to grasp. By drawing parallels between nanocomposites and conventional composite theory, this review provides a nuanced understanding of these issues, facilitating a deeper comprehension for both newcomers and seasoned researchers in the field (22).

Namory Méité examined the water adsorption and microbiological properties of bioplastics made from cassava starch and reinforced with crude kaolin or metakaolin a kaolinitic clay processed at 700 °C. Bioplastics without reinforcement (BP) and those containing 5 wt% of either metakaolin (BPMKB) or crude kaolin (BPKB) were produced using the casting/evaporation method. The results indicated that clay-reinforced bioplastics were less soluble and exhibited reduced water diffusion and permeability compared to non-reinforced bioplastics. This improvement in hydric characteristics was attributed to a decrease in free volume between starch macromolecules caused by interactions with clay platelets. These interactions are believed to promote a more uniform and compact microstructure (23).

Montmorillonite (MMT) and modified MMT (DA-M, ODA-M, ALA-M, LEA-M, and HEA-M) were used in the melt intercalation process to create biodegradable poly(butylene succinate) (PBS) nanocomposites. For DA-M, ODA-M, and LEA-M, transmission electron microscopy revealed uniform dispersion, whereas particle clusters were seen for ALA-M, HEA-M, and MMT. Improved clay dispersion, higher tensile modulus, and lower tensile strength at 3 weight percent inorganic material were all correlated, according to X-ray diffraction. PBS/LEA-M composites with

3–10 weight percent inorganic material had higher storage modulus and glass transition temperature, according to dynamic viscoelastic study (24).

To address the environmental problems caused by synthetic plastics, Nanang Eko Wahyuningtiyas and Heru Suryanto focused on developing bioplastics made from cassava starch reinforced with nanoclay. The bioplastic, produced using cassava starch, glycerol (as a plasticiser), and nanoclay, was evaluated through various tests, including XRD, tensile strength, moisture absorption, and biodegradability. The results indicated that the bioplastic's tensile strength increased from 5.2 MPa to 6.3 MPa with the addition of nanoclay. Furthermore, the study showed that the nanoclay-reinforced bioplastic could completely degrade by the sixth week (25).

Chapter 3

Materials and Methods

3.1 MATERIALS

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

3.2 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 millilitres of distilled water in a 200 millilitre beaker. The two suspensions described above were combined separately for half an hour using a magnetic stirrer. The synthesised adduct was added to this clay suspension along with 600 millilitres 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 pulverised with a mortar and pestle to produce finely powdered modified clay. (26)

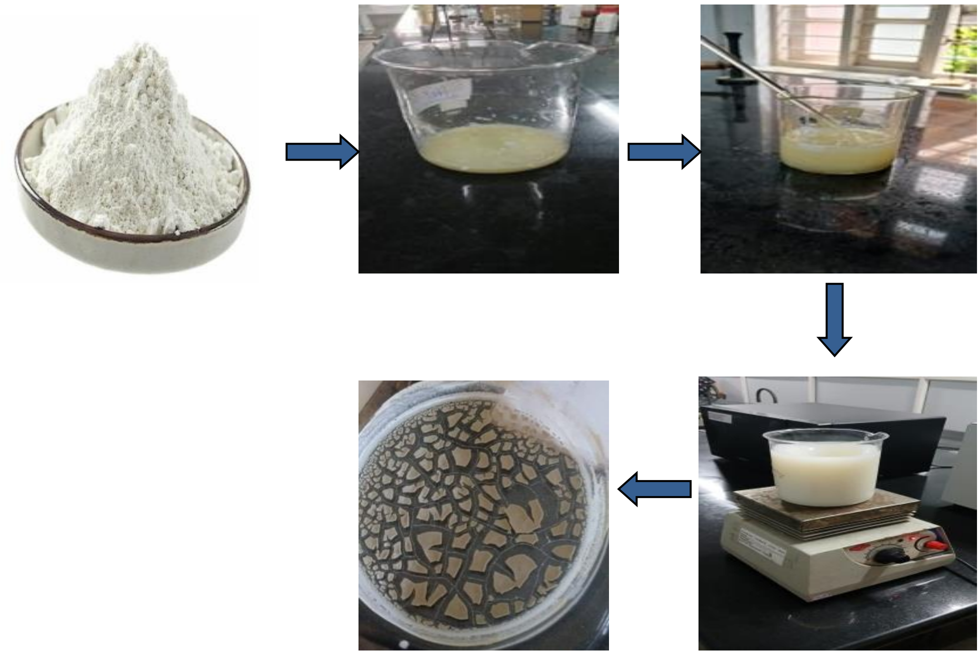


Fig 3.1: Modification of Montmorillonite clay

3.3 PREPARATION OF VIRGIN BIOPLASTICS

The preparation of bioplastics is already reported by our group earlier (27). The mechanical properties of the samples were tested and we have reported the following weight ratio of the components of the virign sample which gave highest tensile strength.

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 mentioed 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.

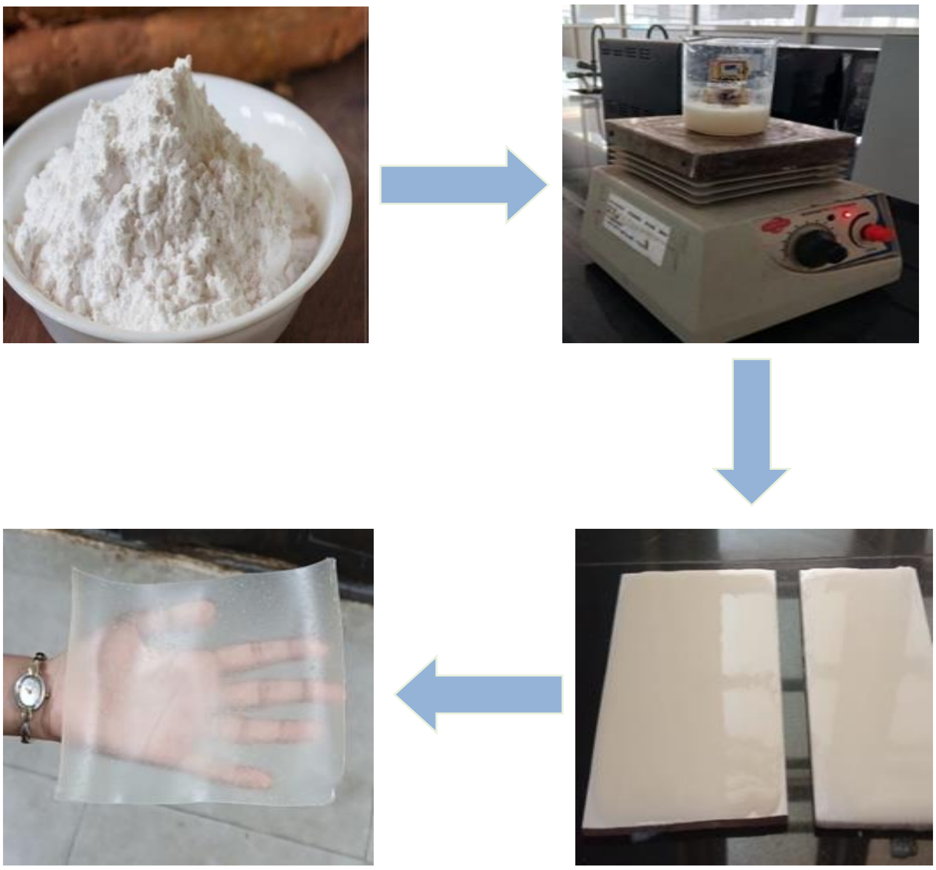


Fig 3.2: Preparation stages of Virgin Bioplastic

3.4 PREPARATION OF MONTMORILLONITE CLAY INCORPORATED BIOPLASTICS

Ummodified clay incorporated bioplastics were prepared by mixing unmodified clay with cassava powder, acetic acid and glycerol as given in the table. Similarly, modifed clay incorporated bioplastics were also prepared. The preparation process is identical to that outlined earlier.

Table 2: Compositions of unmodified and modified incorporated bioplastics

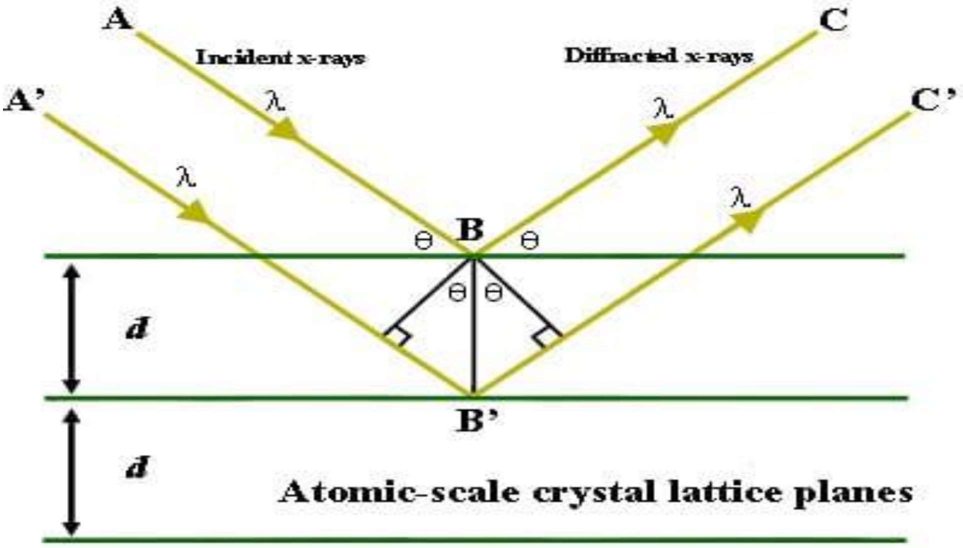
Sample name	% of unmodified clay (Amount of unmodified MMT clay added are 0.5g, 1g)	Sample name	% of modified clay (Amount of modified MMT clay added are0.5g, 1g)
UM1	4.76%	MM1	4.76%
UM2	9.09%	MM2	9.09%

3.5 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.

3.5.1 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.

$$n\lambda = 2d\sin\theta$$

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 stresses because it can precisely measure the position of the diffraction peak. The Debye Scherrer formula can be used to calculate the crystallite size.

$$D = \frac{K\mu}{\beta\cos\theta}$$

where D represents the wavelength of the X-ray, θ is the diffraction angle, the Scherrer constant is K, and the full width at maximum height of a diffraction peak is β. The extensive use of the XRD method in materials characterization can be somewhat explained by the fact that it is a non-destructive approach that doesn't require complex sample preparation. Furthermore, X-ray diffraction typically requires a small amount of powder and only offers the aggregate information about the particle sizes. It should be mentioned that this technique is highly helpful in characterizing nanoparticles because the estimation would only work for very small particles.(28)

3.5.2 FT-IR of Montmorillonite Clay

The FT-IR analysis was conducted to investigate the modified clay's absorption capabilities across various wavelengths, providing valuable insights into its molecular structure and vibrational properties.

FT-IR imaging was 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 (29).

3.5.3 Mechanical Strength

The Shimadzu Autograph Series Universal Testing Machine (AGSX5KN) was used to test the samples, which were cut to 8 cm length and 1 cm breadth. The clay incorporated bioplastic which gave maximum tensile strength was used for degradation studies.

3.5.4 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.

3.5.5 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 centimetres deep in the soil. On the 31st day, the sample's final weight was noted.

Air Degradation

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 millilitres of water. On the 31stday, 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.

3.6 MIGRATION STUDIES

The Overall Migration Limit (OML) is the maximum amount of non-volatile substances that can migrate from a food packaging material or container into food. The overall migration is determined by exposing the item to a chemical food simulant for a specified and appropriate length of time, after which the extracted residue is dried and weighed. To analyze and quantify the transfer of nanoparticles to food products and simplify their subsequent detection, food simulants are used instead of real food. The food simulants vary in terms of their chemical properties, thus representing several different food types: hydrophilic (water based), lipophilic (fatty foods) or amphiphilic (foods with watery and fatty properties). It measures the inertness of a food packaging material or article. The overall limit is considered as 60mg/kg of the packaging material(30)(31)(32).

The possible overall migration rate of the bioplastic samples was evaluated by the total immersion of the biofilms in two different food simulant media- Distilled water, and 3% v/v acetic acid. The bioplastic films were cut in to dimensions of 2.5 × 2.5 cm and put into test tubes containing 13 mL of the corresponding food simulant. And it was observed for about 7 days. After that, the films were removed and the simulants were placed in petridishes and dried in Hot air oven (KEMI) MODEL No-KOS-5. The dried plates were then weighed using an Analytical balance (Radwag) (33). European Union Legislation governing plastics materials and articles intended for food contact requires migration testing to demonstrate compliance (Schaefer 2007; Veraart and Coulier 2007). The legislation specifies a limit on the total mass of substance permitted to migrate. This is called the overall migration limit (OML). The OML applies to all plastics and is 60 mg/kg of food or food simulant or 10 mg/dm^2 expressed on a contact area basis. The OML was established to ensure the inertness of plastics and prevent unacceptable adulteration of the food (34).

Chapter 4

Results and Discussion

4.1 X-RAY DIFFRACTION STUDIES

By examining the location, form, and intensity of the XRD peak for modified clay, one can ascertain the extent of intercalation or exfoliation.

4.1.1. XRD Pattern of Unmodified Clay

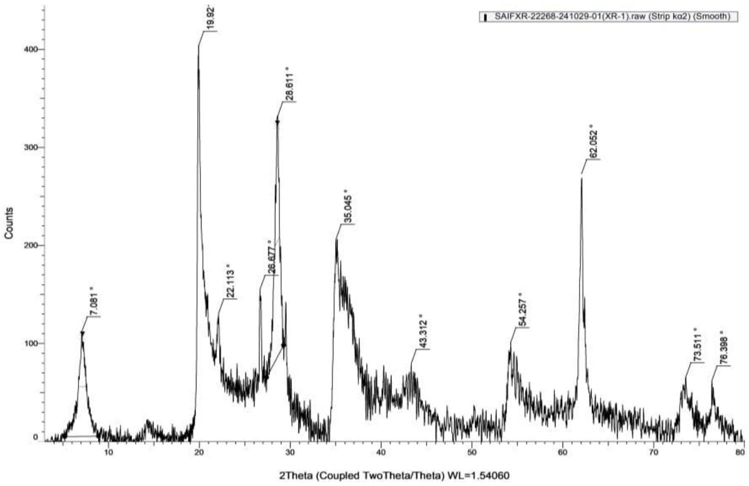


Fig 4.1: XRD Pattern of Unmodified clay

4.1.2 XRD pattern of Modified Clay

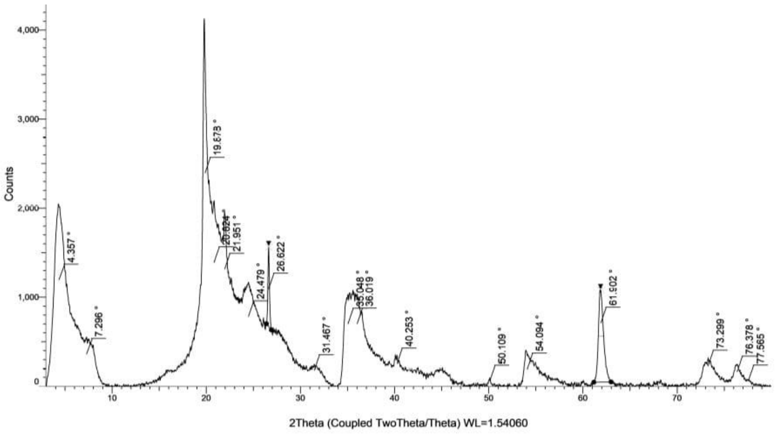


Fig 4.2: XRD pattern of Modified clay

Table 3:d-spacing of Modified and Unmodified Montmorillonite Clay

Sample	**Angle 2θ (degree)**	**d-spacing (Å)**
Unmodified clay	7.081	12.47
Modified clay	4.357	20.6

The unmodified Montmorillonite clay has a peak at 2θ=7.081°, corresponding to a d-spacing of 12.47Å. The modified Montmorillonite clay shows a shift in the peaks, suggesting an increase in the interlayer spacing. This indicates successful intercalation of CTAB (Cetyltrimethylammonium Bromide) and cinnamic acid into the clay layers.

4.2 FT-IR SPECTROSCOPY ANALYSIS

The FT-IR spectra of the modified clay at concentrations are displayed in figures. By examining the distinctive bands, the FT-IR absorption bands were verified(35) .

4.2.1 FT-IR Spectrum Analysis of Unmodified MMT Clay

The FTIR spectrum of the montmorillonite clay is shown in fig: 4.3. For pure MMT clay, a broad band at 3448.68 cm^{-1} indicates the -OH stretching of water molecule in the interlayer of the clay. The band at 3633.47cm^{-1} represents the -OH stretching of Al-OH bond. The band observed at 1641.04 cm^{-1} corresponds to -OH bending vibration of water molecule in the interlayer of the clay. The band identified at 1046.40 cm^{-1} represents the Si-O-Si stretching vibration and the bands at 521.90 cm^{-1} & 467.67 cm^{-1} were identified as the Al-O-Si and Si-O-Si bending vibrations respectively. The band observed at 915.76cm^{-1} which belongs to the bending vibration of Al-OH.

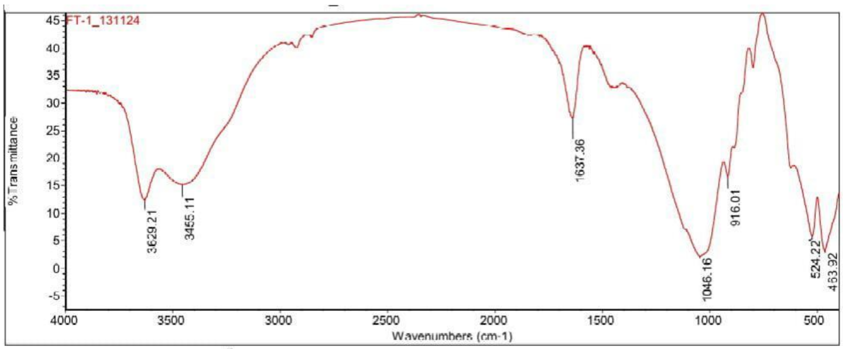


Fig 4.3: FT-IR spectrum of Unmodified clay

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

Table 4: Vibrational frequencies of unmodified clay

Wavenumber (cm^{-1})	Vibration
3633.47	-OH stretching of Al-OH
3448.68	-OH stretching of water
1641.04	-OH bending of water
1046.40	Si-O-Si stretching
915.76	Al-OH bending
521.90	Al-O-Si bending
467.67	Si-O-Si bending

4.2.2 FT-IR Spectrum Analysis of Modified Montmorillonite Clay

The absorption at 3431.87 cm^{-1} is associated with the acid group's -OH stretching vibration. The stretching for $-CH_2$ and $-CH_3$ of CTAB is represented by the extra bands that were discovered at 2852.17 cm^{-1} and 2925.30 cm^{-1}, respectively. The intercalation of CTAB's alkyl group into the clay's interlayer is supported by these bands. The absorption bands at 1639.74 cm^{-1} and 1488.88 cm^{-1} correspond to the C=C stretching vibration of alkene and arene, whereas the band at 1706.24 cm^{-1} is caused by the C=O stretching of cinnamic acid.

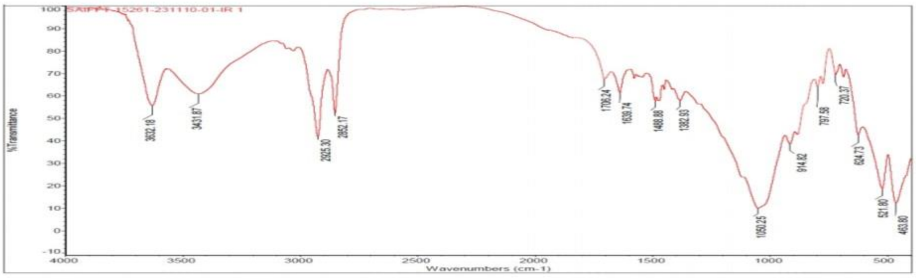


Fig 4.4: FT-IR spectrum of modified clay

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

Table 5:Vibrational frequencies of Modified clay

Wavenumber (cm^{-1})	Vibration
3632.18	-OH stretching of Al-OH
3431.87	-OH stretching of acid
2852.17	$-CH_2$ stretching
2925.30	$-CH_3$ stretching
1706.24	C=O stretching
1639.74	C=C stretching of alkene
1488.88	C=C stretching of arene
1050.25	Si-O-Si stretching
914.82	Al-OH bending
521.80	Al-O-Si bending
463.80	Si-O-Si bending

4.3 XRD OF BIOPLASTICS

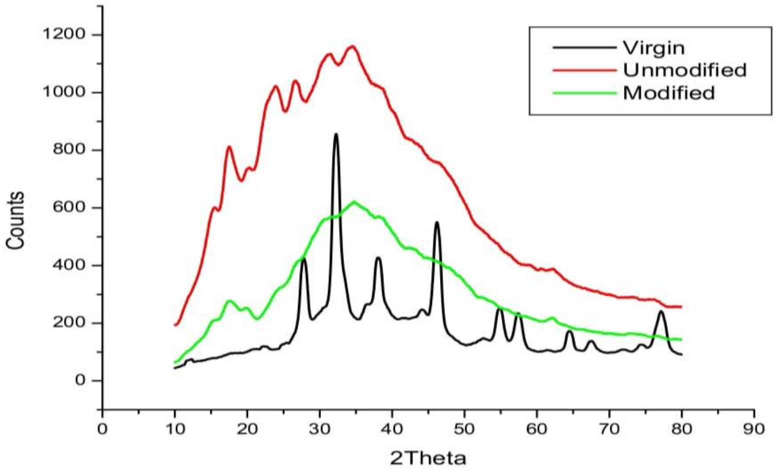


Fig:4.5 XRD graph of V1,UM2,MM1

The peak position analysis shows that V1 represents the natural crystallinity of the bioplastic matrix without clay. In UM2 (unmodified MMT), minor peak shifts indicate limited interaction with the polymer due to poor compatibility, leading to poor dispersion. However, MM1 (modified MMT) shows greater peak shifts, suggesting improved intercalation and exfoliation due to chemical modification, which enhances clay-polymer interaction.

Regarding intensity and peak broadening, higher intensity indicates greater crystallinity, with V1 likely having the sharpest peaks. UM2 may have slightly reduced crystallinity due to minor clay disruption, while MM1 likely has broader and less intense peaks, indicating better dispersion and increased amorphous content.

In terms of crystallinity and amorphous content, V1 has the highest crystallinity as it is pure bioplastic. UM2 shows slightly reduced crystallinity since unmodified MMT remains aggregated, whereas MM1 has the lowest crystallinity due to better dispersion of modified MMT, which disrupts the crystalline structure.

The effect of modification is evident in peak shifts and broadening. UM2 has peaks similar to V1, confirming poor dispersion and phase separation. In contrast, MM1 shows broader peaks and larger shifts, indicating better exfoliation and stronger interfacial interaction with the polymer, improving structural and barrier properties.

Overall, modification significantly enhances the dispersion of MMT in the polymer matrix, reducing crystallinity and improving material properties, whereas unmodified MMT (UM2) remains poorly dispersed and has minimal impact.

4.4 MECHANICAL STRENGTH

The mechanical properties of bioplastics are the most important among their physical characteristics, particularly in terms of their practical applications. As discussed in Chapter 3, key mechanical properties such as 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. From previous studies, the virgin bioplastic with cassava starch:plastisizer ratio of 1:0.05 shows a tensile strength of 5.8197N/mm^2. The results of mechanical strength testing of the virgin, unmodified and modified clay incorporated Bioplastic is shown in the following table.

Table 6:Mechanical properties of V1,UM2,MM1

Bioplastic	**Tensile Strength (N/M^2)**	**Percentage Elongation (%)**
V1	5.8197	1.2327
UM1	2.8308	1.3894
UM2	3.4809	1.7496
MM1	6.7766	2.4724
MM2	4.5014	2.0247

From this it is clear that 0.5 g of modified clay incorporated Bioplastic shows maximum tensile strength of 6.7766 N/mm^2(36)(37).

4.5 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.

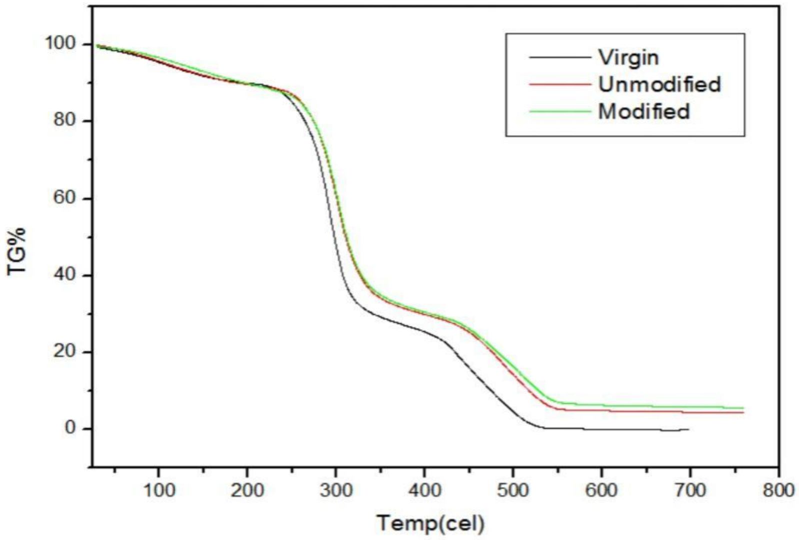


Fig:4.6 TGA graph of V1,UM2,MM1

Table 7:Thermal degradation characteristics of biooplastics

Feature	V1	UM2	MM1
Onset Degradation Temperature (℃)	266.6	250.0	275.4
Peak Degradation Temperature (℃)	294.4	300.6	301.3
Weight remaining at peak degradation temperature (%)	55.49	55.0	53.4
Weight loss (%) at peak degradation temperature	44.51	45.0	46.6
Weight remaining at 500℃ (%)	6.08	18.57	16.23
Temperature at 50% weight loss	300.7	311.07	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 three different materials (V1, UM2, MM1). MM1 has the highest onset and peak degradation temperatures - 275.4°C, 301.3°C, respectively, suggesting better thermal stability than V1 and UM2. UM2 retains the most weight at 500°C (18.57%), indicating higher resistance to high-temperature decomposition.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%), meaning it undergoes more complete decomposition. UM2 and MM1 have slightly better temperature resistance at 50% weight loss (~311°C) than V1 (300.7°C). MM1 and UM2 have enhanced thermal stability compared to V1 (38)(39)(40)(41).

4.6 BIODEGRADATION STUDIES

4.6.1 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 30.30%.

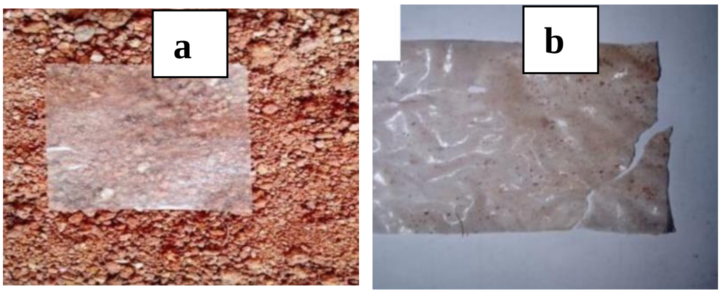


Fig 4.7: Soil degradation of V1 a) Day 1 b) Day 31

Air Degradation

The photographs of the samples taken on day 1 and day 31 are shown in fig. 4.8. Fungal attack was observed on the 31stday. Hence the sample had a minimum shelf life of 31 days and the percentage degradation on the 31stday was 6.92%.

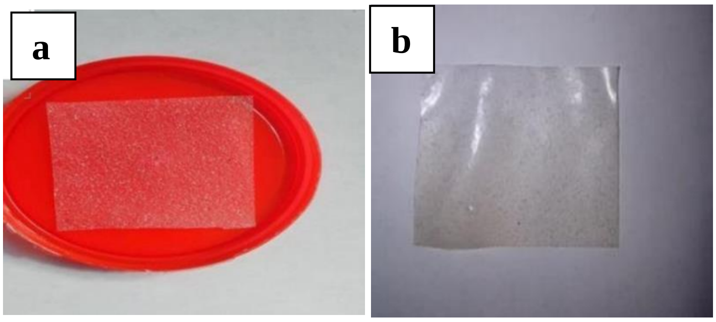


Fig 4.8: Air degradation of V1 a) Day 1 b) Day 31

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 figure 4.9. 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 80.12%.

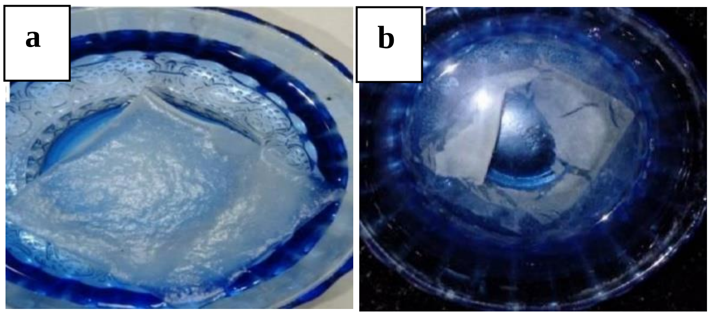


Fig 4.9: Water degradation of V1 a) Day 1 b) Day 31

4.6.2 Biodegradation Studies of Unmodified Montmorillonite Clay incorporated Bioplastic

Biodegradation studies were carried out on unmodified clay-incorporated bioplastics, focusing on the variant with the highest tensile strength, UM2.

Soil Degradation

Figure 4.10 represents photographs of unmodified clay-incorporated bioplastic taken on Day 31. The percentage degradation observed was 57% .

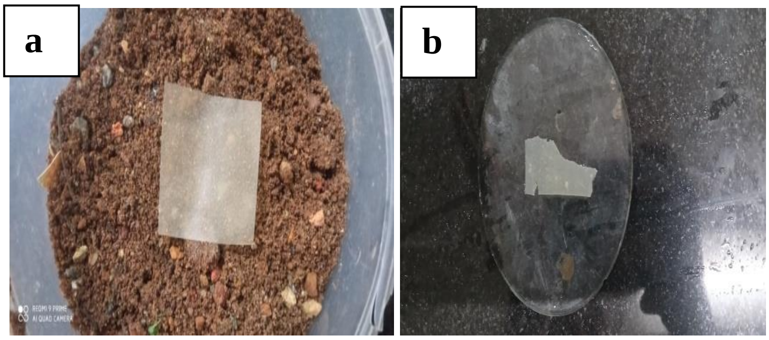


Fig 4.10:Soil degradation of UM2 a) Day 1 b) Day 31

Air Degradation

A piece of bioplastic from UM2 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 the figure 4.11. Fungal growth was observed by Day 14 indicating a minimum shelf life of 14 during which the sample exhibited a 18% degradation on the 31stday.

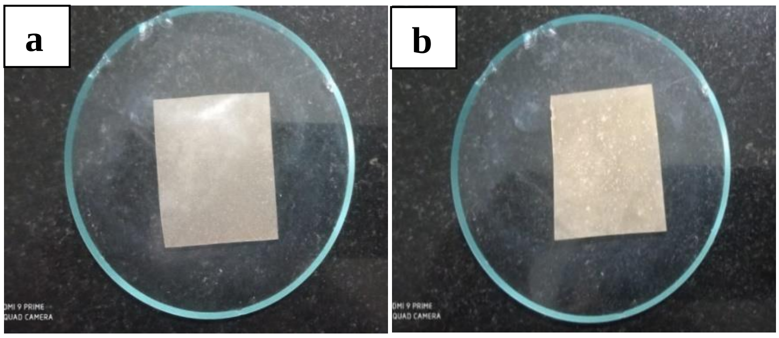


Fig 4.11:Air degradation of UM2 a) Day 1 b) Day 31

Water Degradation

Photographs were taken on Day 1 and Day 31which is given in figure 4.12. By the 31stday, the percentage degradation was found to be 15%.

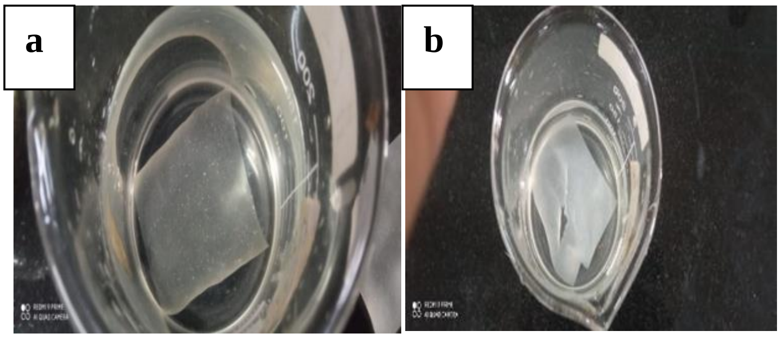


Fig 4.12:Water degradation of UM2 a) Day 1 b) Day 31

4.6.3 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

Figure 4.13 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 67.64 % .

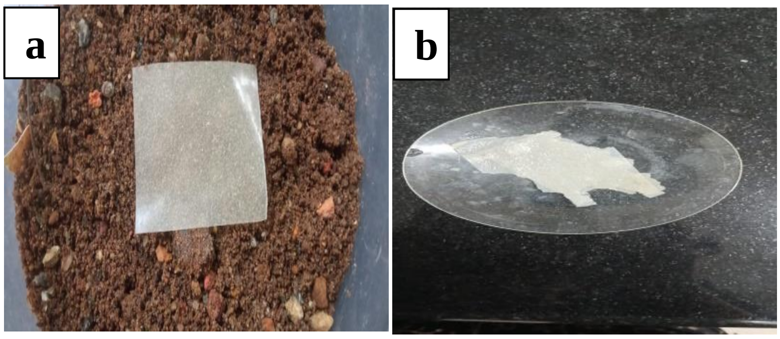


Fig 4.13:Soil degradation of MM1 a) Day 1 b) Day 31

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 figure 4.14. Fungal growth was observed on Day 14 indicating a minimum shelf life during which the sample exhibited a 10% degradation by the 31stday.

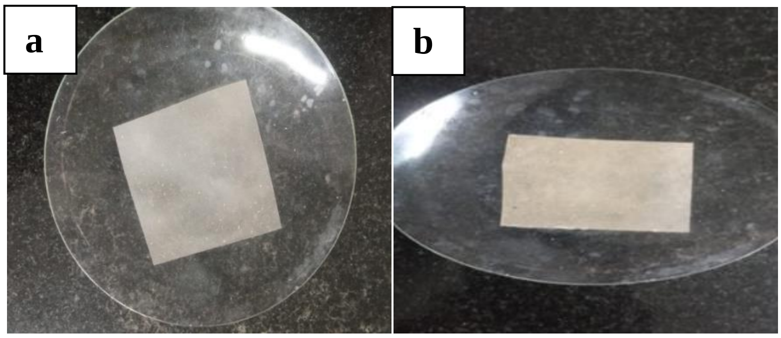


Fig 4.14:Air degradation of MM1 a) Day 1 b) Day 31

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 4.15. By the 31st day, the percentage degradation was found to be 41.12%.

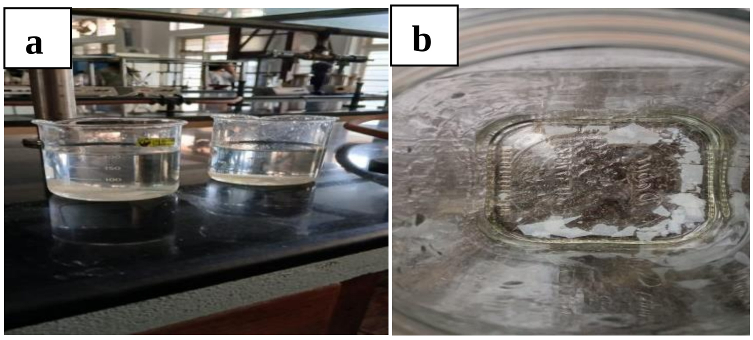


Fig 4.15:Water degradation of MM1 a) Day 1 b) Day 31

4.6.4 Bacterial Degradation

The degradation of Virgin (V1), unmodified (UM2) 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 cm² 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.

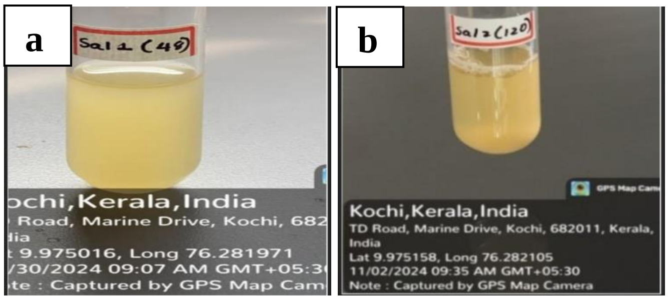


Fig 4.16: Degradation of V1 against Salmonella typhimurium

a)partial degradation b)complete degradation

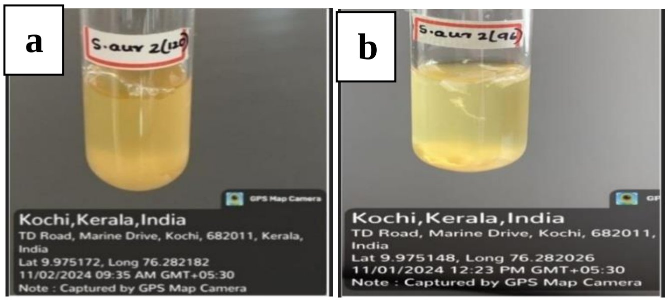


Fig 4.17: Degradation of UM2 against Staphylococcus aureus

a)partial degradation b)complete degradation

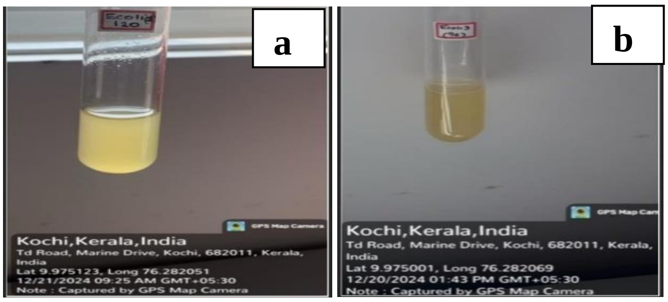


Fig 4.18: Degradation of MM1 against Escherichia coli

a)partial degradation b)complete degradation

4. 7 MIGRATION STUDIES

4.7.1 Bioplastics in Distilled water

Table 8: Migration studies of bioplastics in distilled water

Time duration	**Migration rate**		
	V1	**UM2**	**MM1**
2 hours	Not measurable	0.20	0.08
4 hours	Not measurable	0.21	0.47
8 hours	3.0	0.35	0.56
1 day	8.0	23.0	28.0
3 days	13.844	87.0	135.0
5 days	18.404	103.0	364.0
7 days	23.240	305.0	678.0

Table 8 represents the migration studies of the bioplastics in distilled water. Virgin bioplastic shows the lowest migration rate. Unmodified clay-incorporated bioplastic (UM2) shows higher migration. Modified clay-incorporated bioplastic (MM1) exhibits the highest migration over time.

4.7.2 Bioplastics in 3%v/v Glacial Acetic acid

The migration rates of the bioplastics in 3 % v/v glacial acetic acid is given in table 9.

Table 8: Migration studies of bioplastics in 3%v/v glacial acetic acid

Time duration	**Migration rate**		
	V1	**UM2**	**MM1**
2 hours	3.0	0.10	0.10
4 hours	3.2	0.22	0.22
8 hours	7.0	0.32	0.32
1 day	9.076	28.0	28.0
3 days	20.66	93.0	143.7
5 days	190.192	113.0	428.9
7 days	235.194	500.0	876.6

Migration in acetic acid is generally higher than in distilled water. Virgin bioplastic has moderate migration, but spikes on day 5. Unmodified clay bioplastic (UM2) has higher migration than virgin but lower than modified clay bioplastics. Modified clay-incorporated bioplastic (MM1) shows the highest migration, reaching 876.6 mg/kg in 7 days.

The migration study of virgin (V1), unmodified clay-incorporated bioplastic (UM2), and modified clay-incorporated bioplastic (MM1) in distilled water and 3% v/v glacial acetic acid reveals that virgin bioplastic exhibited the lowest migration rate, indicating better stability and lower release of non-volatile substances over time. However, a significant increase in migration was observed in acetic acid after prolonged exposure (Day 5). Unmodified Clay bioplastic had a higher migration rate than virgin bioplastic, suggesting that the presence of unmodified clay increased the release of substances from the material. The migration was significantly higher in acetic acid compared to distilled water. Modified Clay bioplastic showed the highest migration rate among all samples, with migration levels exceeding 678 mg/kg in distilled water and 876.6 mg/kg in acetic acid after 7 days. This suggests that modification of the clay structure may have altered the bioplastic's barrier properties, leading to increased solubility or interaction with the food simulants.

Distilled water resulted in lower migration rates compared to acetic acid, demonstrating that acidic environments enhance the leaching of substances from the bioplastics. The modification of clay did not enhance stability but rather increased migration, which might indicate poor compatibility or dispersion within the bioplastic matrix. The results suggest that virgin bioplastic is the most stable option for packaging applications, while the incorporation of modified clay needs further optimization to reduce migration and improve the material's suitability for food contact applications (42).

Fig 4.19: Migration study of V1distilled water and 3% v/v glacial acetic acid

Fig 4.20: Migration study of UM2 in distilled water

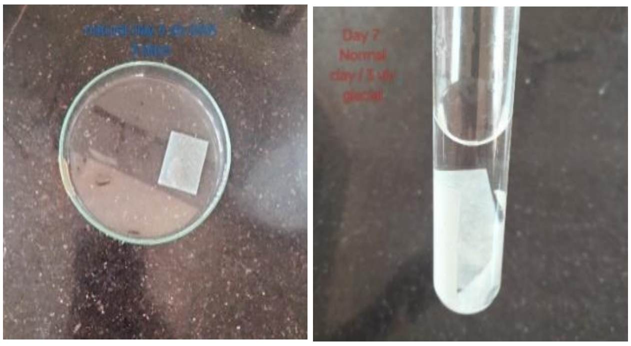


Fig 4.21: Migration study of UM2 in 3% v/v glacial acetic acid

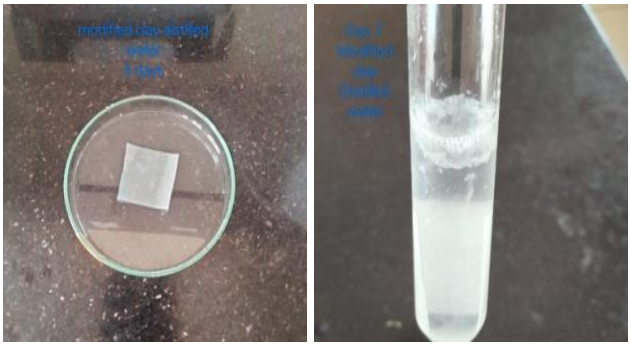


Fig 4.22: Migration study of MM1 in distilled water

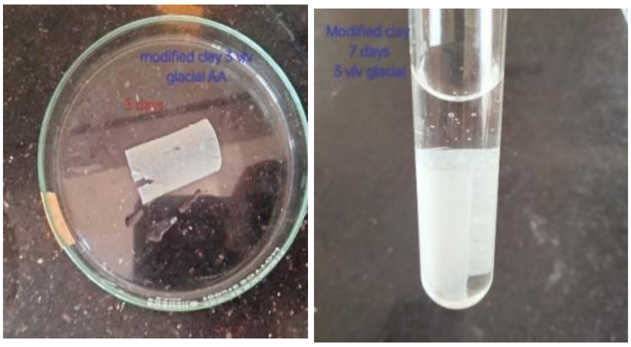


Fig 4.23: Migration study of MM1in 3% v/v glacial acetic acid

Chapter 5

Conclusions

This research focused on developing and optimizing starch-based bioplastics reinforced with montmorillonite clay to provide an environmentally friendly alternative to conventional plastics. Plastics, derived from non-renewable petroleum resources, are known for their durability and versatility but are also a significant environmental hazard due to their non-biodegradable nature. In response to this challenge, bioplastics have emerged as a promising alternative. They are made from renewable resources and are biodegradable, thus reducing environmental pollution. In this study, cassava starch was used as the base material due to its abundance, cost-effectiveness, and favorable film-forming properties. To enhance the mechanical and thermal stability of these bioplastics, montmorillonite clay, both in its unmodified and modified forms, was incorporated into the polymer matrix.

The research adopted a systematic approach to developing bioplastics by first synthesizing modified montmorillonite clay using an acid-amine adduct method. Cetyltrimethylammonium bromide (CTAB) and cinnamic acid were used as modifying agents. FT-IR analysis confirmed the successful intercalation of these adducts into the MMT interlayer, leading to the formation of modified clay with enhanced hydrophobicity and better compatibility with the biopolymer matrix. This modification aimed to overcome the inherent hydrophilicity and poor mechanical properties of tapioca starch-based bioplastics.

X-ray Diffraction (XRD) and Fourier-Transform Infrared Spectroscopy (FT-IR) analyses were employed to investigate the structural changes in the bioplastics. XRD patterns confirmed the intercalation and exfoliation of clay layers within the polymer matrix, which contributed to enhanced mechanical and thermal stability. FT-IR spectra revealed the successful incorporation of organic modifiers in the modified clay, confirming the effectiveness of the acid-amine adduct method for clay modification. The structural analysis validated the compatibility and dispersion of modified clay within the biopolymer matrix, which was crucial for achieving the desired material properties. The study successfully achieved the objectives of developing and optimizing starch-based bioplastics with enhanced mechanical and thermal properties while maintaining biodegradability

Different concentrations of unmodified and modified montmorillonite clay were incorporated into the bioplastics to evaluate their impact on the material's mechanical, thermal, and biodegradability properties. The mechanical tests showed a significant improvement in tensile strength and elongation at break with the addition of 0.5% modified clay, which exhibited the highest tensile strength of 6.7766 N/mm^2. This enhancement can be attributed to the uniform dispersion of modified clay in the polymer matrix, which facilitated better stress transfer and interaction between the starch molecules and the clay layers. In contrast, unmodified clay demonstrated relatively lower mechanical strength due to poor dispersion and weak interfacial adhesion with the hydrophilic starch matrix.

Thermogravimetric analysis revealed that the inclusion of montmorillonite clay enhanced the thermal stability of the bioplastics. The modified clay-incorporated bioplastic showed the highest onset and peak degradation temperatures (275.4°C and 301.3°C, respectively), indicating superior thermal resistance compared to the unmodified and 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.

The biodegradation studies were conducted in four different environments: soil, air, water, and bacterial exposure. In soil degradation tests, virgin bioplastics exhibited 30.3% degradation on the 31st day, confirming their high biodegradability. However, the incorporation of 0.5% modified clay increased the degradation rate to 67.64 %, indicating higher degradation. In air, the virgin bioplastics showed a degradation of 6.92 %, while that of modified clay incorporated samples showed 10 % degradation on 31st day. Fungal attack on the sample was observed on 31st day for the virgin bioplastic, but on the modified clay incorporated sample, it was observed on 14th day itself. This indicates lesser shelf- life of the modified clay incorporated bioplastics. In water, the virgin sample showed a degradation of 80.12 %, while that of modifed sample had a lesser degradation of 41.12 %. This reduction can be attributed to the enhanced structural integrity and water resistance provided by the modified clay layers. Thus incorporation of modified clay to bioplastics increased the degradation rate in soil and air and lesser degradation rate in water. The modified clay incorporated bioplastics can be used until 14 days without any fungal attack and after use, it will degrade in soil and water.

The bacterial degradation tests further confirmed that the modified bioplastics exhibited increased resistance to microbial activity, which could be beneficial for applications including food packaging.

Migration studies were conducted using distilled water and 3% v/v acetic acid as food simulants to evaluate the safety of these bioplastics for food packaging applications. The results showed that virgin bioplastics exhibited the lowest migration rates, whereas modified clay-incorporated bioplastics demonstrated the highest migration levels. This increased migration rate was attributed to the possible leaching of unreacted modifiers and the altered barrier properties of the bioplastics due to clay modification. Although modified clay incorporation enhanced mechanical and thermal properties, its impact on migration behavior necessitates further optimization to ensure food safety compliance.

The research demonstrated that the modification of montmorillonite clay improved the tensile strength, thermal stability, and durability of bioplastics. However, it also highlighted the need to optimize migration behavior for food packaging applications.

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