PREPARATION AND CHARACTERIZATION OF THERMOSETTING ADHESIVE FROM MODIFIED ENSET STARCH AND *EUPHORBIA TRIGONA MIL* LATEX

BIRHAN WOLDEYOHANNIS DUTEB

A THESIS SUBMITTED TO

THE DEPARTMENT OF CHEMICAL ENGINEERING

SCHOOL OF MECHANICAL, CHEMICAL, MATERIAL ENGINEERING

PRESENTED IN PARTIAL FULFILLMENT OF THE DEGREE OF MASTER'S IN CHEMICAL ENGINEERING

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ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

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APPROVAL PAGE

We, the advisors of the thesis entitled "preparation and characterization of thermosetting adhesive from modified enset starch and *Euphorbia trigona mil* latex**"** and developed by Birhan Woldeyohannis; hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Major Advisor	Signature	Date
Co-advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by Birhan Woldeyohannis have read and evaluated the thesis entitled "preparation and characterization of thermosetting adhesive from modified enset starch and *Euphorbia trigona mil* latex**"** and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical Engineering

Chairperson	Signature	Date
Internal Examiner	Signature	DaDte
Dr Sintayehu Mekuria		*24/11/2021*
External Examiner	Signature	Date

Finally, approval and acceptance of the thesis is contingent upon submission of its final Copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

Department Head	Signature	Date
School Dean	Signature	Date
Office of Postgraduate Studies, Dean	Signature	Date

DECLARATION

I hereby declare that this Master Thesis entitled "preparation and characterization of thermosetting adhesive from modified enset starch and *Euphorbia trigona mil* latex**"** is my original work. That is, it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

Name of the student	Signature	Date

RECOMMENDATION

We, the advisors of this thesis, hereby certify that we have read the revised version of the thesis entitled "preparation and characterization of thermosetting adhesive from modified enset starch and *Euphorbia trigona mil* latex**"** prepared under our guidance by Birhan Woldeyohannis submitted in partial fulfillment of the requirements for the degree of Masters of Science in Chemical Engineering. Therefore, we recommend the submission of the revised version of the thesis to the department following the applicable procedures.

_____	_____	_____
Major advisor	Signature	Date
_____	_____	_____
Co-advisor	Signature	Date

ACKNOWLEDGEMENT

First and foremost, praises and thanks to God, the Almighty, for His showers of blessings throughout my research work to complete the research successfully.

I would like to express my deep and sincere gratitude to my research advisor, Dr. Melaku Tesfaye for providing valuable guidance throughout this research. His dynamism, vision, sincerity, and motivation have deeply inspired me. He has taught me the methodology to carry out the research and to present the research works as clearly as possible. It was a great privilege and honor to work and study under his guidance. I am extremely grateful for what he has offered me. And also I am extending my heartfelt thanks to my co-advisor, Dr. Tatek Temesgen for his, priceless suggestions, comments, and for his constructive criticism throughout the thesis.

I am extremely grateful to my parents for their love, prayers, caring and sacrifices for educating and preparing me for my future. I am very much thankful for my loving and supportive mother, Zewditu Mulugeta for her understanding, prayers, and continuing support to complete this research work.

Finally, my special thanks go to my friends at Adama Science and Technology University for their contribution to my work directly or indirectly.

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LIST OF ACRONYMS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
DMSO	Dimethyl Sulfoxide
ETM	*Euphorbia Trigona Mil*
ETML	*EuphorbiaTrigona mil* Latex
ERCA	Ethiopian Revenues and Customs Authority
FTIR	Fourier Transform Infrared Spectroscopy
LA	Lactic Acid
*m*ETML	Modified *EuphorbiaTrigona mil* Latex
*m*S	Modified Starch
*n*S	Native Starch
OLLA	Lactic Acid Oligomer
RBF	Round Bottom Flask
TGA	Thermogravimetric Analysis
UTM	Universal Testing Machine
VOCs	Volatile Organic Compounds

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ABSTRACT

A substance that is used to join two materials together is called adhesive and most of the adhesives used in many industries are based on non-renewable petro-chemical resources such as phenol/formaldehyde and chemical polyurethane and contain a volatile organic compound (VOCs). As such, this heavy reliance on petroleum and the adverse human health effects of emissions have created an urgent need for renewable resource-based, environmentally-friendly adhesives. In this scenario, an alternative adhesives is produced. Therefore, the focus of this original scientific study is to explore the mechanical properties of adhesive produced with Euphorbia Trigon Mil latex (ETML) and Enset starch as a potential polymeric adhesive. The thermosetting adhesive was prepared from modified enset starch (mS) and modified ETML (mETML) with curing temperature of 90^0C (90-mS-mETML), 100^0C(100-mS-mETML), 110^0C(110-mS-mETML),120^0C (120^0C-mS- mETML), 130^0C(130^0C-mS-mETML), 140^0C(140^0C-mS-mETML) curing time (1,3,6,9,12 hr.) and mixing ratio (100:0,75:25,50:50,25:75,0:100 w/w%) were evaluated. The curing process was carried out in a conventional heating system. In the case of ETML modification, LA (Lactic Acid) was used as a modifier and the process was carried out by using polycondensation reaction. The quality of thermosetting adhesive (mS-mETML) was assessed by determining the mechanical properties. According to mechanical tests, effect of temperature, time, and mixing ratio was studied. The use of excessive-high temperatures can not only increase the curing speed, and also using the higher amount of mETML or ms influences the strength. For this situation, homo-polymerization response beat crosslinking. The mS-mETML cured at 110^0C performed better mechanical properties based on lap shear strength with values of 1.24Mpa for glass and 0.94 for wood respectively. And 110^0C was the maximum crosslinking temperature. The result indicated the potential use of latex from ETM and starch from Enset as an alternative to producing adhesive.

Key points: *Thermosetting adhesive, Alternative binder, Enset starch, Euphorbia trigona Mil*

CHAPTER ONE

1. INTRODUCTION

1.1. Background of the study

Advances in petroleum-based fuels and polymers have benefited mankind in numerous ways. However, petroleum resource is finite, and prices are likely to continue to rise in the future. In addition, global climate change has become an increasingly important problem, and the disposal of items creates an environmental problem. It is necessary to find new ways to secure sustainable world development (Ebnesajjad, 2013). Rapid industrialization has altered the concept of sustainable development among global populations through scientific intervention. With the rapid depletion of essential raw materials, particularly petroleum resources, genuine attempts are being undertaken to produce naturally renewable alternatives with sustainable features. Further, they minimize the risk of adverse effects of non-biodegradability of discarded matter on health and the environment, reduce the scarcity of raw material, and so on (R. Duarah and N. Karak, 2015).

As a consequence of increasing environmental awareness and the growing need to decrease dependence on petroleum resources, great attention has been paid to the possibilities of synthesizing polymeric materials from bio-based, renewable resources. This has sparked increased interest in bio-based binders in adhesive technology. (Heinrich, 2019). Now, most of the adhesives used in many industries are based on the non-renewable petrochemical source this heavy reliance on petroleum and the adverse human health effects of emissions have created an urgent need for a renewable source-based, environmentally-friendly binder (FEICA, 2016). There are a variety of natural adhesives: animal and fish glues, natural gums and resins, and vegetable glues (Gunorubon, 2012). These vegetable glues are made from starches and dextrin and are starch-based (Aliyu & Aliyu, 2014).

Starches are used as components and/or processing aids in the manufacture of products such as food, textile, paper, adhesives, and pharmaceuticals (Gebre-Mariam, Abeba, & Schmidt, 1996; Mohammed, Waghray, Prabhakara, & Rudrayya, 2020). As a raw material in the production of adhesives, it has various advantages, including renewability, biodegradability, availability, low cost, and price stability (Gunorubon, 2012). At present, the starch-based adhesive produced by

existing processes has achieved satisfactory effects in terms of storage stability and dry strength. Even so, most of the starch-based adhesives are thermoplastic adhesives. They are linear polymers in nature, can easily cause excessive expansion during the dehydration process and the adhesive layer deteriorates inside. Consequently, the adhesive layer exhibits poor water resistance and heat resistance. This limits the use of starch adhesives in the field of thermosetting adhesives. To enable the starch adhesive to be used in the field of thermoset, it needs further improvement by modifying the starch adhesive and providing a method for preparing a thermosetting starch adhesive and the water-resistance of the resultant adhesive (Gu et al., 2019). To clear up these and other shortcomings derivatization of starch, such as etherification(Hebeish, Bayazeed, El-Hilw, & Shaarawy, 2021), esterification(Nigussu, Belete, & Gebre-Mariam, 2013; M. V. Tupa, Ramírez, Vázquez, & Foresti, 2015), cross-linking(Zeng et al., 2021), and grafting (Yingmo Hu, 2015) are the modification method (Neelam, Vijay, & Lalit, 2012).

From the different methods, esterification is one of the promising methods of modification of these polymers which has earned significant recognition recently (J. Singh, Kaur, & McCarthy, 2007). which imparts increased hydrophobicity, nature to starch depending on the reagent and conditions used (Jyothi, 2010). Starch is produced from grain or root crops such as sweet potatoes, maize, wheat, rice, yam, or cassava (Gunorubon, 2012), and Enset (Gebre-Mariam et al., 1996). Enset, in comparison to other cultivated Musaceae species, has received comparatively little research attention (Borrell et al., 2019).

Enset (*Ensete ventricosum*) is an important multipurpose indigenous crop for Ethiopia (Yemataw et al., 2018). There are different studies on enset starch that have brought the possibility of using enset starch as pharmaceutical excipients(Getachew, Desta, & Bekele, 2016; Nigussu et al., 2013; Weldegiyorgis, 2006), gelling agent (Ayenew, Mengesha, Tadesse, & GebreMariam, 2021), and nutritional potential (Tesfaye & Girma, 2017) as alternatives to common starches e.g. corn and potato. However, as the far as the author knowledge there is no published paper highlighting the utilization of enset starch for the production of structural adhesive. Moreover, according to the Ethiopian Revenue and customs authority (2020), the country met adhesive demand through importing from abroad. Therefore, this study aims to highlight the utilization of enset starch for the production of adhesive. Using bio-based adhesives definitely presents benefits in terms of environmental and health properties. When thinking of a solution looking for a sustainable

alternative associated with low costs and natural resources is crucial (Nakanishi, Cabral, de Souza Gonçalves, dos Santos, & Junior, 2018). As a result, natural latex could be a viable option. The latex from *Euphorbiaceae* especially ETML got almost no attention in this area.

ETM is a type of Euphorbiaceae plant species (Marathe, Nashikkar, Bundale, & Upadhyay). The latex from ETM is obtained from the trunk of the ETM tree through a systematic" tapping "process. ETML is tacky. This latex is used as adhesive due to its tacky nature. However, it coagulates when left for a period due to its unsaturated backbone. So, it needs some structural modification.

Therefore, this study is the first initiative in scientific studies around the world to explore mechanical properties of adhesive produced with the two approaches listed below

- The first approach developed a matrix by in situ modification of ETML, *n*S, and LA. This approach is not time-consuming and also simple
- The second approach uses a modifier which is AA and LA, to modify nS and ETML respectively to improve the interaction between them.

1.2. Statement of the Problem

Due to the growth of various manufacturing sectors, the demand for adhesives has increased significantly over the years. Most adhesives used in many industries are based on non-renewable petrochemical resources such as phenol/formaldehyde and polyurethane and contain volatile organic compounds (VOCs) as well as residual toxic chemicals such as formaldehyde (Lambuth, 1989).

ETML and Enset starch were selected as potential sources of raw material to prepare thermosetting bio-adhesive in this study. But plant-based adhesives are often weak and prone to environmental conditions that are sensitive to both water and heat (Gan et al., 2019). Even so, most of the starch-based adhesives are thermoplastic adhesives .They are linear polymers in nature, can easily cause excessive expansion during the dehydration process and the adhesive layer deteriorates inside. Consequently, the adhesive layer exhibits poor water resistance and heat resistance. This limits the use of starch adhesives in the field of thermosetting adhesives (Gu et al., 2019). ETML that is used as a binder traditionally is sensitive to water and also it is not stable and coagulates when left for

a period due to its unsaturated backbone chain. Thus, structural modification is required to improve its bonding strength.

To mitigate those problems, these researches focus on the development of a biodegradable and green thermosetting adhesive and also enable the starch-based adhesive to be applied in the field thermoset. That is prepared from the *Enset Ventricosum* starch, LA, and ETML via in-situ modification.

1.3. Research Questions

This research proposed synthesizing thermosetting adhesive from a completely green bio-based material. The thermosetting adhesive was prepared by the reaction between *m*S, and *m*ETML. Therefore, exploring this method to develop bio-based thermosetting adhesive which complement petroleum-based adhesive was done in this study.

To do so, an extensive experimental attempt and characterization were made to answer the following research question.

- **RQ1.** Can it be possible to extract ETML and modify it by using LA?
- **RQ2.** Can it be possible to synthesize or develop a completely green thermosetting adhesive through in-situ modification of LA, Enset starch, and ETML?
- **RQ3.** Can it be possible (applicable) to use the synthesized thermosetting adhesive for substrates like wood and glass?
- **RQ4.** What would be the effect of curing temperature, curing time, and mixing ratio on the lap shear strength of the product?

Based on the above research questions the choices of the systems are framed as follows:

ETML, LA, and Enset starch are selected as the main raw material due to:

- ETML**:** Due to their availabilities, good yield of latex, and also it is simple to grow in various soil types, under differentiated conditions and doesn't need proper administration rehearses.

- ❖ The monomer and pre-polymer (oligomer) produced using LA can be used as a modifier and due to this; it can be used to develop greenly modified polymer.
- ❖ Enset**:** Due to high yielding potential and drought resistance exploring and announcing these indigenous plants starch locally grown by subsistence farmers to the world in the field of development of adhesive.
    - Reducing importation of starch by replacing this indigenous plant starch source.

1.4. Objectives of the Study

1.4.1. General Objectives

The general objective of this research was the preparation and characterization of thermosetting adhesive from *m*S and *m*ETML.

1.4.2. Specific Objectives

- ❖ To extract modify and characterize the ETM tree latex.
- ❖ To synthesize and characterize mS and mETML based thermosetting adhesive.
- ❖ To study the effect of curing temperature, curing time, and mixing ratio on the bond characteristic of the *m*S and *m*ETML based thermosetting adhesive on wood and glass substrate.

1.5. Significance of the study

This research is significant in terms of ensuring the manufacturing of thermoset bio-adhesives from sustainable, green, raw materials. And it will serve as inspiration for other researchers to pursue research in the field of starch-based thermosetting adhesives. Another important aspect of this research is that it aims to rid our country of non-biodegradable petroleum-based adhesives to find more compelement efficient, and safe alternatives to satisfy our green economy.

1.6. Scope of the study

The scopes of the thesis work within the time and resource constraints are as follows:

- ❖ Extracting and Modifying latex from ETM tree.

- ❖ Developing a method for synthesizing starch and ETML based thermosetting adhesive.
- ❖ Characterizing raw materials and synthesized starch and ETML thermosetting adhesive.

1.7. Organization of the Thesis

The thesis' remaining sections are organized as follows:

Chapter 2: Discuss the relevant literature and related works regarding the adhesive and classification of adhesive based on their function, source, and chemical composition and also discuss the related works regarding Enset starch and starch modification. *Euphorbia* and their toxicity are also discussed in this chapter.

Chapter 3: Features the materials and methods for the research, including the collection of ETML and modification of ETML and *n*S; developing a method and developing thermosetting adhesive.

Chapter 4: Explains the results obtained from the desired proposed work, and discusses the characterization of the results that happen in the raw material and thermosetting adhesive formulation using instruments.

Chapter 5: Concludes on each proposed specific objective and recommends different possible directions for further studies.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Biopolymers

Biomaterials are the most favored ones; they are biodegradable, biocompatible, and nontoxic. It can be divided into four significant classes of materials, in particular; polymers, metals, ceramics, and natural materials including those from both plants and animals. Biopolymers are sustainable, harmless to the ecosystem, and biodegradable materials, which can be utilized as an ideal substitute for petrol-based polymers that are manufactured (Oliveira, May, Panzera, Scarpa, & Hiermaier, 2020). The oil emergency during the 1970s, which prompted an improved interest in elective resources, was biomass. Biomass is made out of biopolymers, these biopolymers are multifunctional and their properties can be custom fitted by various systems to produce chemically diverse macromolecules, including, lignin, polyphenols, polysaccharides, particularly starch, and additionally polypeptides (Schnepp, 2013). Among the different biopolymers, starches are the most bountiful class of macromolecules (Hanselmann, Burchard, Ehrat, & Widmer, 1996).

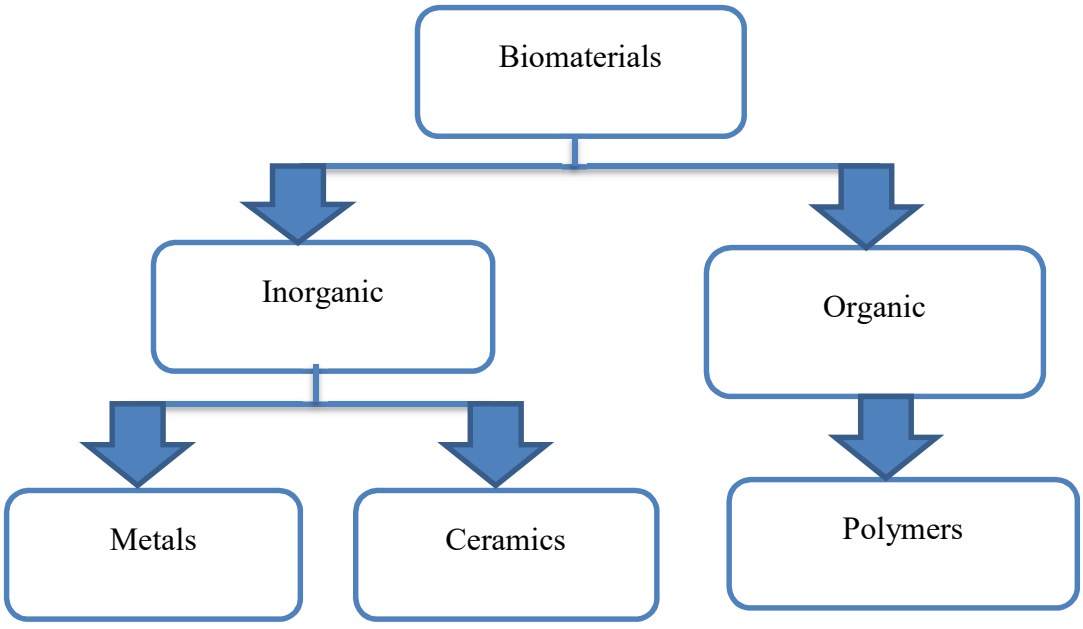

Figure 1: Types of Biomaterials

2.2. Starch

In addition to being a food source, starches have potential application in the development of several products currently supplied by the synthetic polymer industry. Photosynthesis produces starch, uses plants to store chemical energy (Imam, Gordon, Mao, & Chen, 2001). Starch is a low-cost, renewable product derived from abundant plants that is simple to process, the biggest advantage that starches offer compared to petroleum-based polymers is that they can be processed similarly to synthetic polymers, but are biodegradable and produce a smaller greenhouse gas effect. Because of this, there has been an increased interest in using starches from various sources for several novels, non-food applications such as the manufacturing of plastics, coatings, biocomposites, and adhesives (Bressler & Choi, 2015). Starch, in particular, is a very promising biomacromolecule for the development of a wide range of materials with a variety of unique physicochemical features that make them suitable for a variety of applications (Abrham Wondimu, 2014). Therefore, before discussing the use of starch as an industrial resource, first, we have to discuss the structure and fundamental properties of starch.

2.2.1. Structure of Starch

The features of starch, like poly-usefulness (numerous hydroxyl gatherings) and non-toxicity, are what make it a particularly pursued polymer for different applications. It's additionally a somewhat cheap polymer with a variety of alternatives to modify it for explicit necessities (Imam et al., 2001). Starch contains carbon, hydrogen, and oxygen in a 6:10:5 proportion. Amylose and amylopectin, two somewhat various polymers, make up starch. Starch is a combination of two polysaccharide parts: amylose and amylopectin, the two of which are comprised of various sizes and forms of glucose (Tester, Karkalas, & Qi, 2004). The proportion of amylose to amylopectin changes relying upon the botanical origin of the starch (Norström, Demircan, Fogelström, Khabbaz, & Malmström, 2018). A few characteristics of starch, like its insolubility in cold water, low shear resistance, low thermal resistance, low flexibility, and restricted elastic property are for the most part factors that limit the number of uses (J. Singh et al., 2007).

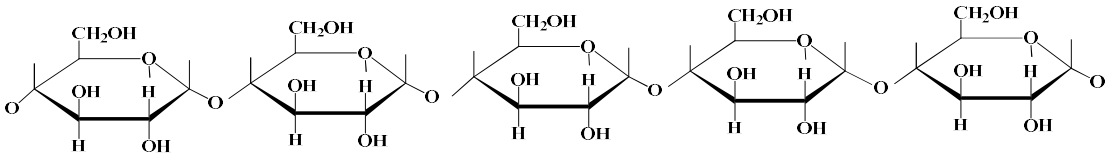

Figure 2: The linear polymer, Amylose (Adapted from (Bauer et al., 2014))

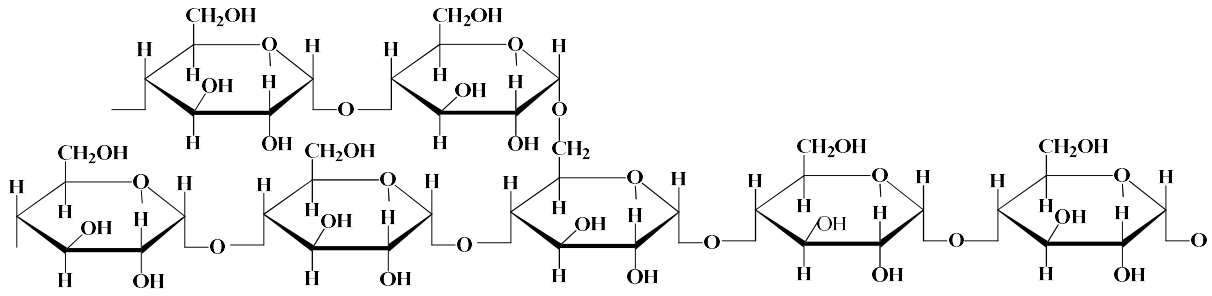

Figure 3: The branched polymer, Amylopectin (Adapted from (Baumann & Conner, 1994))

To solve these and other shortcomings the modification of starch, physically and chemically, has been extensively studied. Derivatization of starch, such as etherification, esterification, cross-linking, and grafting; decomposition (acid or enzymatic hydrolysis and oxidation of starch); or physical treatment of starch, such as heat or moisture, are the most common methods of starch modification (Neelam et al., 2012).

Table 1: Some types and properties of modified starches

Types	**Properties**	**Some related works**
Pre-gelatinization	Coldwater dispensability	(Ulfa, Putri, Fibrianto, & Widjanarko, 2021; F. Xu et al., 2021)
Etherification	Improved clarity of starch paste, greater viscosity	(Hebeish et al., 2021)
Dual modification	Stability against acid, thermal and mechanical degradation	(Hazarika & Sit, 2016; R. Wang et al., 2021)
Esterification	Lower gelatinization temperature and retrogradation higher swelling power	(Shah, Masoodi, Gani, & Ashwar, 2017; N. Singh, Chawla, & Singh, 2004)

Acetylation, which is esterification one of the chemical modifications of starch, can be influenced by acetic anhydride or vinyl acetate when an alkaline catalyst is present to esterify a fraction of OH groups with acetyl groups (Nigussu et al., 2013; J. Xu & Shi, 2019). The DS of hydroxyl moieties varies depending on the reaction circumstances, with a theoretical maximum DS of 3 (Nigussu et al., 2013).

Table 2: Related works on acetylation of starch

Title	**Materials used**	**Degree of Substitution**	**Reference**
Effect of acetylation on the properties of corn starch	Corn starch, acetic anhydride, and acetic acid	0.85-2.89	(Chi et al., 2008)
Organo-catalytic acetylation of starch: Effect of reaction conditions on DS and characterization of esterified granules	Acetic anhydride, corn starch, and a-hydroxy-carboxylic acid	0.03–2.93	(M. V. Tupa et al., 2015)
Acetylation and characterization of Enset starch and evaluation of its direct compression and a drug release sustaining properties.	Enset starch acetic anhydride, and NaOH	0.672- 2.142	(Nigussu et al., 2013)
Effects of acetic acid/acetic anhydride ratios on the properties of corn starch acetates	Corn starch was pre-treated with acetic acid and acetic anhydride	2.93	(Cherif Ibrahima Khalil Diop a, 2011)
Effect of Acetylation on Some Properties of Rice Starch	Acetic anhydride, rice starch	0.03	(Gonzalez & Pérez, 2002)

2.2.2. Function of Starch as a Renewable Resource

Several characteristics of starch, such as its insolubility in cold water, loss of viscosity, and thickening power after cooking, limit the number of industrial applications. Poor stability and processing tolerance, low shear resistance, low thermal resistance, low flexibility of starch-based films, and limited tensile property retention in watery environments are all factors that limit the number of industrial applications (J. Singh et al., 2007). However, Starch is used for a variety of purposes, including thickening, stabilizing, texturizing, gelling, film formation, encapsulation, water retention, shelf life extension, coating, and sizing (Ulfa et al., 2021).

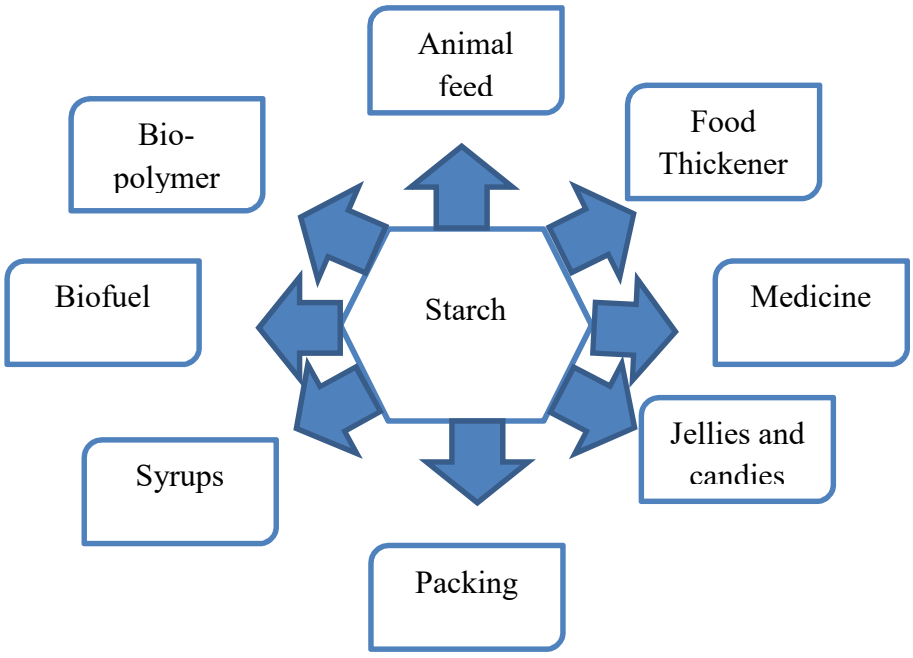

Figure 4: Uses of starch (https://www.researchgate.net/figure/Non-food-uses-of-starch)

Starch as Thickener and Stabilizer

Stabilizers are significant fixings in fabricated dairy items as a result of their capacity to further develop thickness and sensory properties. Stabilizers, Some are synthetic, and many of them have a plant origin, which is considered the least expensive and incorporates the most generally utilized ones (Altemimi, 2018). (Rengsutthi & Charoenrein, 2011) examined corn starch as a thickener and stabilizer in stew sauce.

Film Formation of Starch

Starch films have benefits like low thickness, flexibility, and transparency through their abundance in nature is of significant importance. Accordingly utilizing starch films and expands resistance against humidity. A few strategies can be utilized; including the starch adjusting procedures, for example, crosslinking of starch (Sharma, Kaur, Sandhu, Nain, & Janghu, 2021).

Starch as a Gelling Agent

Gelling agents are the gel-shaping or forming agents when dissolved in a fluid stage as a colloidal combination frames a feebly strong inside structure (Ayenew et al., 2021). There are different reports on the gelling qualities of various starches (Brunnschweiler et al., 2005; Javanmard, Chin, Yusof, & Endan, 2012).

Starch as a Renewable Resource for Bio-Adhesive

Starch has benefits as a raw material in the production of adhesives, including renewability, biodegradability, and inexpensiveness. Starch is delivered from grain or root yields like yams, maize, wheat, rice, sweet potato, or cassava (Gunorubon, 2012) and enset (Gebre-Mariam et al., 1996). In contrast to the other cultivated starch source plant, enset has received relatively little research attention (Borrell et al., 2019).

2.3. Overview of Enset plant and its starch *(Ensete ventricosum, Musaceae)*

The genus Ensete (*Ensete ventricosum (Welw) Cheeseman*) belongs to the Musaceae family. (Zeleke et al., 2019). Enset is a multipurpose crop providing a range of functions such as food, medicinal, ritual, and soil preservation (Borrell et al., 2019; Yemataw et al., 2018). The existence of various enset varieties is credited with various uses (Tsehaye & Kebebew, 2006). Enset can be found in the wild across much of Africa's central, eastern, and southern regions. However, it is known to have been domesticated and cultivated in Ethiopia, where the farming system was established (Dr Admassu Tsegaye (Chairman), 2016). It's called "false banana" because it looks a lot like the banana plant (Musa acuminate, Musaceae)(Abrham Wondimu, 2014; Mohammed et al., 2020). It takes about 4 to 5 years for a corm to mature, after which a single corm can produce 40 kg of food (Weldegiyorgis, 2006). (Dr Admassu Tsegaye (Chairman), 2016) estimates that

about one-fifth of Ethiopia's population (20 million) is dependent on this crop, which is grown primarily in the southern region and surrounding areas of Oromia.

The two main food items are kocho and bulla, which are both indigenous to the area. The pseudo-stem and corms are cut and crushed, and the exuding liquid containing starch is collected in the manufacturing of these two products majorities of the water are allowed to drain away, and the wet starch is collected, leaving behind the fibrous material known as kocho. Bulla is used to make porridge and "atmit," a hot syrup-like preparation and kocho are used to make various bread (Gebre-Mariam et al., 1996). Enset Starch is made up of two D-glucose polymers: amylose, which is a fundamentally unbranched [1-4] linked glucan, and amylopectin, which is made up of chains of α [1→ 4] linked glucose organized in a highly branched structure with α [1→ 6] branching links (Abrham Wondimu, 2014).

Figure 5: Enset plant and its parts in the garden. (Adapted from (Gebre-Mariam et al., 1996))

Table 3: Proximate composition of Enset starch

Proximate Composition	**Amount (%)**	**Reference**
Moisture Content	14%	(Awol, 2020; Gebre-Mariam et al., 1996)
Ash Content	16%	(Awol, 2020; Gebre-Mariam et al., 1996)

Amylose Content	29.0	(Awol, 2020; Gebre-Mariam et al., 1996)
Amylopectin Content	71.0	(Awol, 2020; Gebre-Mariam et al., 1996)

As a result, the amylose content of enset starch was determined to be 29.0%, and the particle size distribution was normal, similar to that of potato starch. Enset starch had a granule size of 37.7 µm, which was equivalent to potato starch (38.2 µm). The powder diffractograms of enset and potato starch using X-rays (B pattern) (Gebre-Mariam et al., 1996).

So far, (廣瀬理恵子 et al., 2010) studied Enset starch for food and industrial uses and found characteristics of high gelatinization properties whereas (Gebre-Mariam et al., 1996) obtained its use as a binder and disintegrant for tablets. (Tesfaye & Girma, 2017) investigated nutraceutical applications Enset starch, unfortunately, there is no work done for the potential of this crop as an alternative adhesive production.

2.4. Overview of Adhesive

An adhesive is a substance that is applied to the surfaces of objects to permanently connect them through an adhesive bonding technique (Andrew, 2008). The adhesive must have surface adherence and cohesion to facilitate bonding (Gadhave, Mahanwar, & Gadekar, 2017). And also through a process called adhesion, makes things adhere or stick together without deformation or failure (Mwambusi, 2016; Q. Xu, Wen, & Wang, 2016).

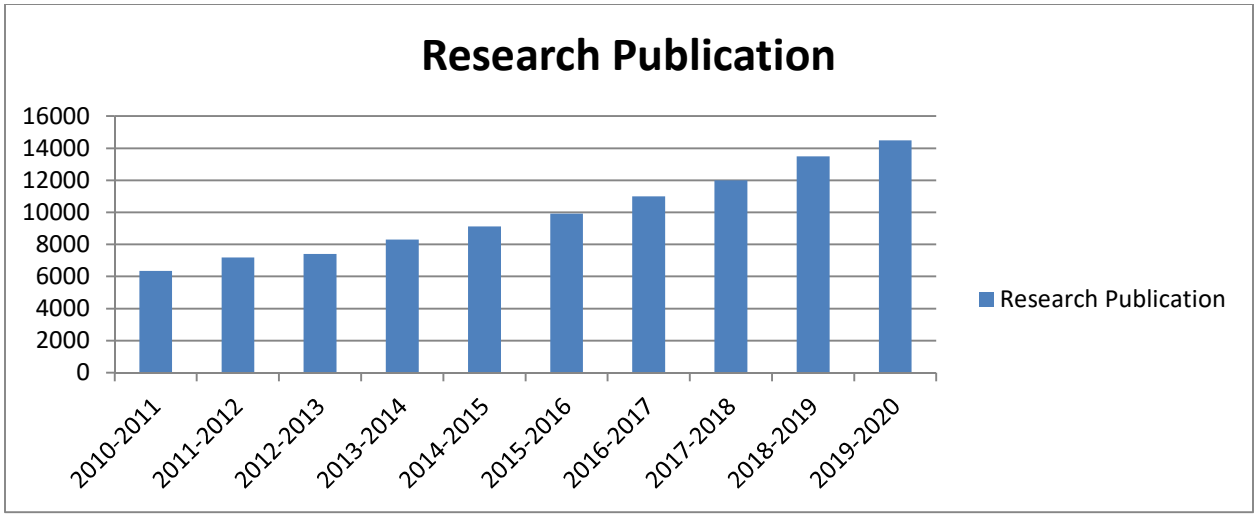

Figure 6: Research publication on bio-adhesive (Source: Google Scholar)

2.4.1. Adhesion Theory

An adhesive is a substance that is used to join two materials together. (Ebnesajjad, 2010). Adhesion is the property of an adhesive that allows a load to be transferred from the adherend to the adhesive joint (A.V. Pocius, 1997). This means that the adhesive must be able to generate adhesion to the substrate and have the required bond strength after setting (cohesion). As a result, the adhesive's interaction with the substrate must be excellent (Alphonsus V. Pocius, 2012).

High internal strength is also required for optimal adherence (cohesion). The internal strength of the adhesive is determined by the type of bonding that happens between the adhesive and the substrate. The strength of covalent bonds, polar bonds, hydrogen bonds, or London interactions determines cohesion (Glavas, 2011). Adsorption, simple mechanical interlocking, diffusion, electrostatic contact, and weak-boundary layer are the most popular theories of adhesion (Alphonsus V. Pocius, 2012).

2.4.2. Profiles on the Consumption of Adhesives

Table 4: Global adhesive market size

Year	Global Adhesives Market Size US$(in billion)
1975	2.2
1987	5.5
2009	20.6
2010	41
2017	51.7
2019	53

By 1987, it had risen to 83%. Synthetic adhesives have improved adhesion to a variety of substrates, can be applied at higher speeds, have superior properties, and have helped to create new, difficult items (Brief, 1990). In 2009, the Asia-Pacific region was the largest consumer of formulated adhesives, with China being the region's largest consumer (Nugusse, 2019b). Between

2020 and 2030, the global adhesives market is expected to grow at a CAGR of 4.5 percent, from US$ 53 billion in 2019 to US$ 85.7 billion by 2030 (H.B. Fuller Company).

Ethiopian Consumption of Adhesives

There is a high demand for adhesive in Ethiopia due to the growth of various sectors, particularly current housing construction activities, woodworking, textile industries, and shoe industries. An industrial adhesive is imported to meet the country's needs. ERCA reported that adhesive that is imported has continuous increment from period to period to fulfill the demand. In the figure below the consumption of adhesive is increasing dramatically except for the years 2012. In these years there was a slight decline compared to the others.

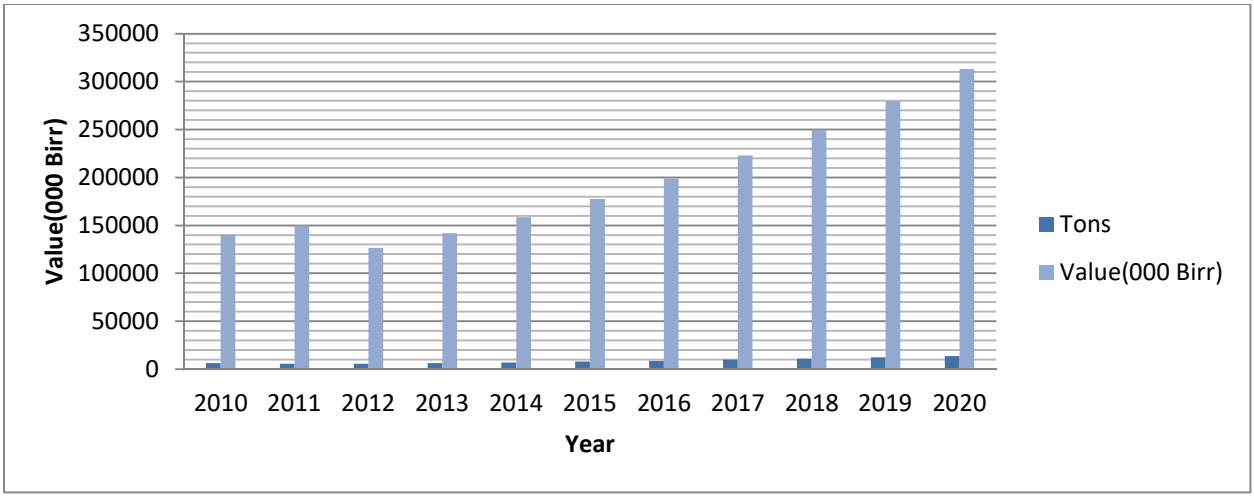

Figure 7: Amount of adhesive consumption in Ethiopia (Source: ERCA)

2.5. Classification of Adhesives

This section discusses adhesive categories from a variety of perspectives, including source, function, physical form, application manner, and context (Andrew, 2008).

2.5.1. Classification of Adhesives by Sources

Adhesives are divided into two categories: natural and synthetic. The synthetic category is further subdivided into two categories: industrial compounds and special chemicals (Andrew, 2008).

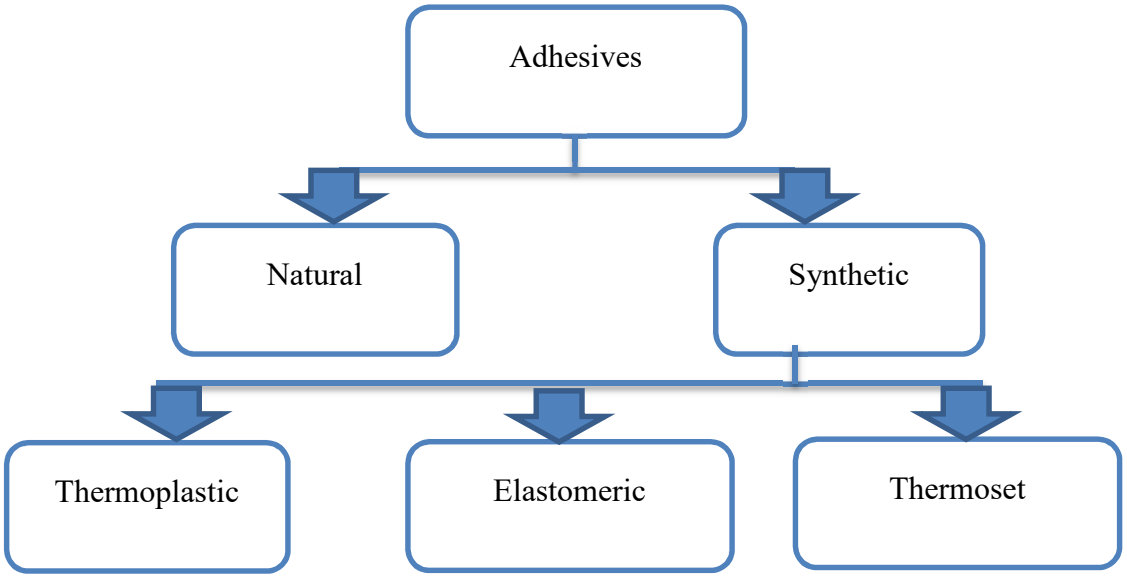

Figure 8: A Simple Classification of Adhesive Source

Natural Adhesives

Natural adhesives are classified according to whether they come from vegetable or animal and natural gums sources. Proteins including soybean, wheat gluten, and whey as well as carbs like starch, are found in vegetables. Blood, fish skin extracts, casein (milk), and collagen extracts from animal bones or hides are examples of animal sources (Hamarneh, 2010).

These include Protein-Based Wood Adhesives (Animal-Based Wood Adhesives (Abadi Hadush*, 2018; Hamarneh, 2010). Casein-based Adhesives (Schwarzenbrunner, Barbu, Petutschnigg, & Tudor, 2020; Skeist & Miron, 1990) Blood-based Adhesives(Jang, 2011), Starch-Based Vegetable Adhesives (Petar A., 2020; Zhang, Ding, Gu, Tan, & Zhu, 2015).

Synthetic Adhesives

Synthetic adhesives are classified as thermosetting, thermoplastic, elastomeric, or mixtures of these categories based on their chemical composition (alloys) (Andrew, 2008).

2.5.2. Classification by Chemical Composition

Thermosetting, thermoplastic, elastomeric, or a mixture of these types are the different types of synthetic adhesives (alloys) (Ebnesajjad, 2010; Petrie, 2007).

Thermosetting Adhesives

After the initial cure, these materials cannot be heated or melted. Depending on the type of adhesive, curing is accomplished through a chemical reaction that occurs at room temperature or a higher temperature. Some thermosetting adhesives necessitate a lot of pressure, whereas others merely need contact pressure (Petrie, 2007). One disadvantage is that they require precise measuring and mixing to ensure that the specified proportions are blended and the final mixture is uniform. The adhesive's usable life is limited once it's been combined (Andrew, 2008; Petrie, 2007).

Because thermosetting adhesives are highly cross-linked after curing, they have good heat and solvent resistance. Bonds can tolerate temperatures ranging from 93 to 260 degrees Celsius and their strip strength is sufficient. The main application is for strained joints that are exposed to moderately high temperatures (Ebnesajjad, 2010). Thermosets play a key role in the industry because of their high modulus, which allows them to modify desired final qualities. High cross-linking density provides strength, durability, and thermal and chemical resistance (Raquez, Deléglise, Lacrampe, & Krawczak, 2010). Most materials can be bonded with thermosetting adhesives, but structural applications are the focus (Andrew, 2008).

Thermoplastic Adhesives

These materials do not crosslink during curing and can be melted without affecting their characteristics significantly (Ebnesajjad, 2010). These adhesives are not normally suggested for usage over 66 degrees Celsius; however, they can be used up to 90 degrees Celsius in some applications. Non-metallic materials, such as wood, leather, plastics, and paper, are the most typically bonded (Petrie, 2007). Thermoplastic adhesives are not commonly utilized for structural applications, except for some hot-melt adhesives (Andrew, 2008).

Elastomeric Adhesives

These materials are made up of polymers that are either synthetic or naturally occurring. They have a higher hardness and elongation than other materials. Latex, dispersions, pressure-sensitive tapes, and single-or-multiple-part solvent-free liquids or pastes are all examples of elastomeric adhesives. These adhesives can be made for a wide range of applications, but they're most

commonly used because of their high flexibility and peel strength (Petrie, 2007). It's possible to work in temperatures ranging from 66 to 204 degrees Celsius. Elastomeric adhesives are never totally melted. Bond strengths are low, but flexibility is high (Ebnesajjad, 2010).

2.5.3. Classification of adhesive by Function

Structural Adhesives

These are high-strength, high-performance materials. Their primary function other than binding is to keep structures and withstand heavy loads (Andrew, 2008).

Non-structural Adhesives

These adhesives are only meant to hold materials in place, not to withstand heavy loads. This category is also known as "holding adhesives" these adhesives are designed to fill gaps are used to adhere paper to paper in office applications (Andrew, 2008).

2.6. Bio-based Adhesives

Renewable materials have been used as adhesives for longer than synthetic polymers, although they have been phased out in many applications due to the lower cost of manufacture or superior properties of synthetic Proteins, natural rubber, and polysaccharides, particularly starch, natural gums, and cellulose, are some examples of renewable polymers that have previously been used as binders (Sweatt, 1946).

Table 5: Related work on Bio-based Adhesives

Title	Method	Reference	Shear Strength (MPa)
The preparation and performance of a novel lignin-based adhesive without formaldehyde	Mixing	(Gong et al., 2020)	1.70
Soy protein-based adhesive with superior bonding strength and water resistance by designing densely crosslinking networks	One-pot strategy (No catalyst) (No solvent)	(Zeng et al., 2021)	1.11-2.79

Preparation, characterization, and properties of starch-based adhesive for wood-based panels	Grafting polymerization	(Gu et al., 2019)	1
A starch-based sustainable tough hyperbranched epoxy thermoset	one-pot synthesis	(Qiao et al., 2013)	62

Their advantage over synthetic adhesives, in this case, is that they are non-toxic, green and also reduce the use of formaldehyde, but the reduction of the formaldehyde. The physical and mechanical qualities of the finished products are greatly influenced by the binder. When thinking of a solution to all the above-mentioned issues, looking for a sustainable alternative associated with low costs and natural resources is crucial (Nakanishi et al., 2018). Therefore, an alternative could be the use of natural latex.

2.7. Natural Latex

Latex, a sticky secretion that pours from some plants when they are wounded, is present in about 20000 species belonging to 40 families (Bauer et al., 2014). Plants use latex as a natural defense against natural enemies (Lewinsohn, 1991). It's also used in a variety of other applications where significant strength is required. Latex gloves, condoms, catheters, balloons, swim caps/fins, foam goods, and a wide range of product components remain important application markets (Beswick, December 2002). Spurge/castor family (*Euphorbiaceae*), milkweed family (*Asclepiadaceae*), mulberry family (*Moraceae*), and dogbane family (*Apocynaceae)* were all assessed as potential renewable latex sources (Mishra & Parida). Natural latex is colloidal polymer dispersion in water. The polymer's fundamental unit is cis 1, 4-polyisoprene.

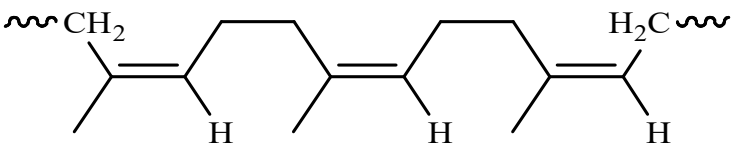

Figure 9: Chemical Structure of 1, 4-polyisoprene.

Euphorbiaceae species mainly used latex is from *Hevea brasiliensis* and it was obtained by tapping (Jacob, d'Auzac, & Prevot, 1993), which is farmed in tropical areas, particularly in Southeast Asia (Bauer et al., 2014). Other latex-producing plants have been studied primarily for their potential to replace *Hevea brasiliensis* as a natural latex source or to exploit new latex sources in areas where *Hevea brasiliensis* cannot be grown [1]. Plant latex has been extensively investigated, but little is known about the biochemical characteristics of latex from the huge genus Euphorbia, despite the efforts of various authors to address this gap. (Spanò et al., 2012).

2.7.1. Introduction Euphorbia Trigona mil

Plant Description

Euphorbia trigona is a type of *Euphorbiaceae* plant variety. Euphorbias are named after Euphorbus, a Greek surgeon (Bigoniya, Shukla, & Singh, 2010). Euphorbia is the biggest genus in the Spurge family, with over 6974 genres (Hong-Bing Wang 2011). It has an upright stem and several upward-growing branches. Two or three sides might be found on a stem or branch. The stem is dark green with bright green V-shaped designs on it. On the stem's ridges, the 5 mm (1 /4 in) thorns grow in pairs. The plant has never been known to flower (Cullen, Knees, Cubey, & Shaw, 2011), and it may be a hybrid. Euphorbia trigona is somewhat simple to grow in various soil types, under differentiated conditions, and doesn't need uncommon administration rehearses. (Rizk, 1987) looked into the chemical elements of *Euphorbiaceae* plants as well as their economic importance. In nature, the family is also known for producing useful secondary metabolites like alkaloids and flavonoids (Rani, Murthy, Goud, & Pullaiah, 2003).

Ethiopia has high resources of Euphorbia trigona. For instance, it is found in Wello, Gojam, Gondar, Shoa, Tigray, Harerge, Sidamo, Gamogofa, Ilubabor, and Bale (Nugusse, 2019a).

Figure 10: Euphorbia Trigona Mil plant

Latex and Its Chemical Composition

Sterols, terpenoids, vitamins, insecticides, and anti-cancer medicines are all major components of Euphorbia latex (Bauer et al., 2014). Terpenes including diterpenes and triterpenes, steroids, glycerol, phenolic, and flavonoids have been frequently found in Euphorbia species (Shi, Su, & Kiyota, 2008). The latex from the Euphorbia species is poisonous and can cause skin irritations (Bigoniya et al., 2010) and poisonous milky sap (white latex). The milky sap is notably corrosive, on contact with skin may cause temporary burning pain or no light insight. Swallowing of the sap is potentially fatal causing severe inflammation of the walls of the stomach and intestine with perforation in some cases (Hohmann & Molnár, 2004). The compounds most relevant to the toxicity and considerable biological activities in Euphorbias are diterpenes, especially those with tigliane, and ingenane skeletons (Hong-Bing Wang 2011; Jakupovic, Morgenstern, Bittner, & Silva, 1998). Diterpenes are chemical compounds that are made up of four isoprene units and have the molecular formula $C_{20}H_{32}$. They have antibacterial and anti-inflammatory properties (Davis & Croteau, 2000). For what it's worth under tension, it runs out from the smallest injury and hardens or coagulates inside a couple of moments on contact with the air. The presence of polycyclic diterpene esters in Euphorbia plants sap makes it profoundly aggravation, which is a hindrance to bugs and herbivores (Webster, 1986).

Medicinal, phytochemical, and antibacterial research of Euphorbia trucalli L. was investigated by (Upadhyay, Singh, & Kumar, 2010). (Van Deenen, Prüfer, & Gronover, 2011) reported that the

Euphorbia trigona latex is a potent inhibitor of fungal growth. (Nugusse, 2019a) investigated from the species of Euphorbia which is Euphorbia trucalli latex investigated the most prevalent polymer found in plant latex is cis-1,4 polyisoprene (rubber), which has a sticky character. Amine carboxyl, $-CH_2$, and ester were also found to have latex-specific bands. The presence of proteins in the latex was confirmed by functional groups of amines. Proteins also play a role in the latex's tackiness (Nugusse, 2019a). The phorbols and their derivatives are effective tumor promoters. The phorbols do not cause cancers directly, but they do stimulate tumor growth after exposure to a sub-carcinogenic dose of a carcinogen. As a result, they can be classified as co-carcinogens (Nugusse, 2019a).

In general, even at extremely low concentrations, these reactions cause a great range of additional biological effects. Because they stimulate PKC, which is involved in signal transduction and developmental processes in most cells and tissues, they are responsible for skin irritation and tumor promotion in a variety of life forms (Silinsky & Searl, 2003).

Table 6: Related works on Euphorbia

Title	**Method for leaf extraction**	**Findings**	**Reference**
Thermal behavior of chitosan/natural rubber latex blends	Tapping	Antibacterial and anti-inflammatory properties	(Davis & Croteau, 2000)
Phytochemical and Antimicrobial Studies of Euphorbia tirucalli	Soxhlet Extraction	Medicinal, phytochemical, and antibacterial effect	(Upadhyay et al., 2010)
Potent inhibitor of fungal growth	Wounding	The anti-microbial activity of plant latex proteins was conducted	(Van Deenen et al., 2011)

Phytochemical Profiles of Euphorbia and Antioxidant Activities of Leaf Extracts of Euphorbia Species	Soaking	Quantify total phenolic content, total flavonoids, and total radical scavenging activities belonging to the Euphorbiaceae family	(Gapuz & Besagas, 2018)

Table 7: Phytochemical constituents of leaf extracts of selected Euphorbia Trigona

Phytochemicals	**ETM Extract**
Alkaloids	++
Anthraquinone	_
Carbohydrates	+
Flavonoids	+
Glycosides	_
Saponins	++
Steroids	_
Tannins	+++

+++ implies heavy color appearance, ++ is for definite appearance, + is slight appearance and is the absence of color appearance.

The latex from ETM shows less viscous white liquid (Nugusse, 2019b). ETML is a renewable resource used in the formulation of adhesive traditionally but often the adhesive formulated using ETML is not stable and coagulate when left for a while due to its unsaturated backbone. Thus, structural modification is required to improve its nature. The processing of the natural latex, like modification, is used to achieve different properties for the production of materials such as healthcare gloves latex films and as an ingredient for the development of adhesive. Therefore, this study is the first initiative in scientific studies around the world to explore the mechanical properties of adhesive produced with LA-based modified latex as a potential polymeric adhesive. For this study green modifier was selected. And also this green modifier is a cost-effective, easily available, nontoxic, and potentially biodegradable modifier, which is called LA.

Table 8: Related works on natural latex-based materials

Author	Types of material	Ingredients	Method	Title	Finding
Zhi-Fen Wang , Z.P.b., Si-Dong Li , ,(Zhi-Fen Wang a, 2009)	Composite	Starch and Natural rubber	Blending	The impact of esterification on the properties of starch/natural rubber composite	Enhanced thermal stability and mechanical properties of composite
Sweeta Akbari, A.G., Tanveer Ahmed Khan, (Sweeta Akbari, 2014)	Adhesive	Starch and Natural rubber	Mixing	Synthesis and characterization of medium-density fiberboard by using a mixture of natural rubber latex and starch as an adhesive	Increasing the mechanical and physical properties of medium fiberboard
Nakanishi, E.Y., *et al.* (Nakanishi et al., 2018)	Polymeric binder	Natural rubber latex, ammonia	Mixing	Formaldehyde-free particleboards using natural latex as the polymeric binder	They showed attractive performance towards thermal stability.
You-Ping	Composite	Starch, styrene-	In situ modification	A strategy to prepare high-performance	Demonstrated better interfacial

Wu., *et al..,* (You-Ping Wu a, 2006)		butadiene rubber,		starch/rubber composites: In situ modification during the latex compounding process	adhesion is achieved by the modification.
Nuttakun Kanjanathaworn, D.P., *et al.* (Nuttakun Kanjanathaworn 2013)	Film.	Chitosan Poly(methyl methacrylate),	emulsion polymerization process	Emulsion polymerization	The deposition of PMMA-CS particles caused an increase in surface roughness, effectively reducing the in vitro cytotoxicity.

2.8. Lactic Acid

Lactic acid (IUPAC systematic name: 2-hydroxy-propanoic acid), an organic acid obtained by fermenting glucose or maltose or taken from milk), is a viable alternative to petroleum raw materials (Komesu et al., 2017). Optimally preferably pure lactic acid is now created by the batch fermentation process of maize and other carbohydrates (Martinez et al., 2013). On the synthesis of lactic acid-based adhesives, there are very few papers accessible.

Figure 11: Chemical structure of L-(+)-Lactic acid and D-(-)-lactic acid

In the food, pharmaceutical, cosmetics, and chemical industries, it is currently the most extensively used organic acid (Champomier-Vergès, Maguin, Mistou, Anglade, & Chich, 2002). It can be used as neutralizers, solvents, and cleaning agents employed to make biodegradable polymers with medicinal applications (Komesu et al., 2017).

$C_3H_6O_3$ is the chemical formula for this carboxylic acid. It's an alpha hydroxy acid since it has a hydroxyl group next to the carboxyl group (AHA). It can lose a proton from the acidic group in the solution, resulting in the lactate ion (CH_3CH (OH) COO^-) [96]. Two optical isomers of lactic acid exist L-(+)-lactic acid, also known as (S)-lactic acid, is one, while D-(-)-lactic acid, also known as (R)-lactic acid, is the other. The biologically relevant isomer is L- (+)-lactic acid. The chiral carbon atom has a hydroxyl group connected to it, whereas one of the terminal carbon atoms belongs to the carboxylic group and the other to the methyl group. As a result, lactic acid exists in two optically active isomeric forms (Martinez et al., 2013).

Table 9: Physiochemical properties of lactic acid (Source (Ameen & Caruso, 2017))

Properties	**Value**
Empirical Formula	$C_3H_60_3$
Chemical Name	2-hydroxypropanoic acid
Compound name	Lactic Acid
Taste	Mild Acid Taste
Dissociation Constant	1.37×10-4
Molecular Point	90.08 g/mol
Boiling Point	122^0C
Melting Temperature	L: 53 °C
Color	Colorless

Table 10: Related work on Lactic acid-based Adhesive

Author	**Types of Adhesives**	**Ingredients**	**Method**	**Title**

Tripathi, N. and V. Katiyar, (Tripathi & Katiyar, 2018)	Structural (Glass, Ceramic)	LA, Gum Arabic	Graft co-polymerization	L-LA (88% aqueous solution) and Gum Acacia (gum Arabic)
Moini, N., et al.,(Moini et al., 2019)	Structural (Steel)	LA, amidosulfunic acid and methyl methacrylate	Insitu Polycondensation Reaction	Engineered Green Adhesives Based on Demands: Star-Shaped Glycerol – LA Oligomers
Sweah, Z.J. and A.J. Mohammed (Sweah & Mohammed, 2021)	Structural (wood)	PVA , aloe Vera gel, lactic acid	Mixing	Study of mechanical properties behavior of biodegradable blends based on wood adhesive, LA, PVA alcohol, and aloe Vera

CHAPTER THREE

3. MATERIALS AND METHODS

Chapter Overview

This chapter aims to present the materials required, sample collection, preparation and treatment method, and proper characterization techniques that need to be followed for various experiments which were performed in this research work. For simplicity, the required materials, experimental protocols, and characterization techniques were categorized into three sections. The first section described the collection and modification of ETML; the second section described the pre-treatment and modification of *n*S; the third section described the synthesis protocol and characterization techniques followed for the development of thermosetting adhesive. Afterward, the synthesized thermosetting adhesive had been evaluated using, lap shear strength, migration test, contact angle, Fourier transforms infrared (FTIR), and Thermal gravimetric analysis (TGA).

3.1. Materials and Consumable

In carrying out experiments for the extraction and modification of the latex from the ETM tree, pretreatment and modification of raw starch, and synthesizing of thermosetting adhesive by the materials and equipment listed below were used.

ETML was collected from Adama city in front of medhanialem church and bulla was purchased from Adama city, Franco market.

3.1.1. Beneficiation Equipment/Chemicals

The equipment, materials, and chemicals used for the thesis are listed in Table 11.

Table 11: List of materials/equipment and chemicals used during the development of thermosetting adhesive.

	Chemicals	Equipment/Materials
Collection of latex from ETM tree	-	Cutting knife, collecting cup
Modification of ETML	Lactic Acid (88% aqueous solution)	Temperature controlled reactor, Horizontal condenser, RBF, Petri dish, Cylinder, Chiller.
Pre-treatment of Starch	Sodium Metabisulphite	Distilled water, Fine muslin cloth, Ball mill, Sieve, Oven
Modification of Starch	Acetic anhydride, Sodium Hydroxide,	PH meter, Hot plate, Oven, mixer Temperature controlled reactor
Development of Thermosetting Adhesive	-	Oven, Petri dish, Spatula

3.2. Methods for the Preparation of Thermosetting Adhesive

The methods for the preparation of thermosetting adhesives were discussed in the following subheadings. The work was focused on studying the effect of three factors (curing temperature, curing time, and mixing ratio) on the mechanical strength of the adhesive. The responses to be studied were bonding strength.

3.2.1. Collection of Latex from ETM Tree

Latex extraction was simply carried out by taping according to the method listed in (Silpi et al., 2007). The latex was obtained by cutting the tree's bark with a knife 30° angle from the horizontal cut was used to expose the most latex vessels per length of the incision. As a result, latex flowed

immediately into the cup attached to the tree. Because severed vessels became clogged by latex coagulum, the flow gradually decreased and was eventually plugged after 1–5 minutes.

Figure 12: Collection of Latex from ETM Tree

3.2.2. Isolation and Pretreatment of Starch

Starch isolation was carried out according to the method listed in (Gebre-Mariam et al., 1996). The enset starch, also known as a bulla, was prepared by suspending it in large quantities of distilled water with 0.075% sodium metabisulphite by weight. The supernatant was decanted after allowing the particles to settle. The sedimented starch was treated with sodium metabisulphite solution until the suspension became transparent. After that, the sample was run through fine muslin to eliminate any remaining cell debris. And the translucent suspension was collected and filtered and was allowed to settle. The starch that was sedimented was washed several times with distilled water and followed by sieving after each washing until the wash water was clear and free of suspended impurities. Finally, the resulting starch was dried at room temperature, milled to a fine powder in a ball mill, sieved using a sieve with 0.5mm sieve size, and stored in a plastic bag until final usage.

Figure 13: Pretreatment of Enset Starch

3.3. Preparation of Acetylated Starch

Enset starch acetylation was conducted by a modification procedure adapted from (Mark & Mehltretter, 1972) with some modifications. Before acetylating, the enset starch was dried in an oven for 24 hr. at 50 °C to minimize the interference of moisture on the chemical reaction. Dried starch (15 g) was mixed with acetic anhydride at weight ratios of 1:3 and 1:4 in a beaker. After stirring for 5 min, a 50 % aqueous NaOH solution was added. The temperatures of 90,100,110,120, 130, and 140°C were used and held at this temperature for the designated times of 60, 120, 180, 240, and 300 min. The NaOH was added at levels of 0.3 g/g, of starch. To stop the reaction and cleanse the reaction products excess distilled cold water was poured into the

reactor. 50°C was used to dry the acetylated starch. Before testing, the dried starch acetate was grounded.

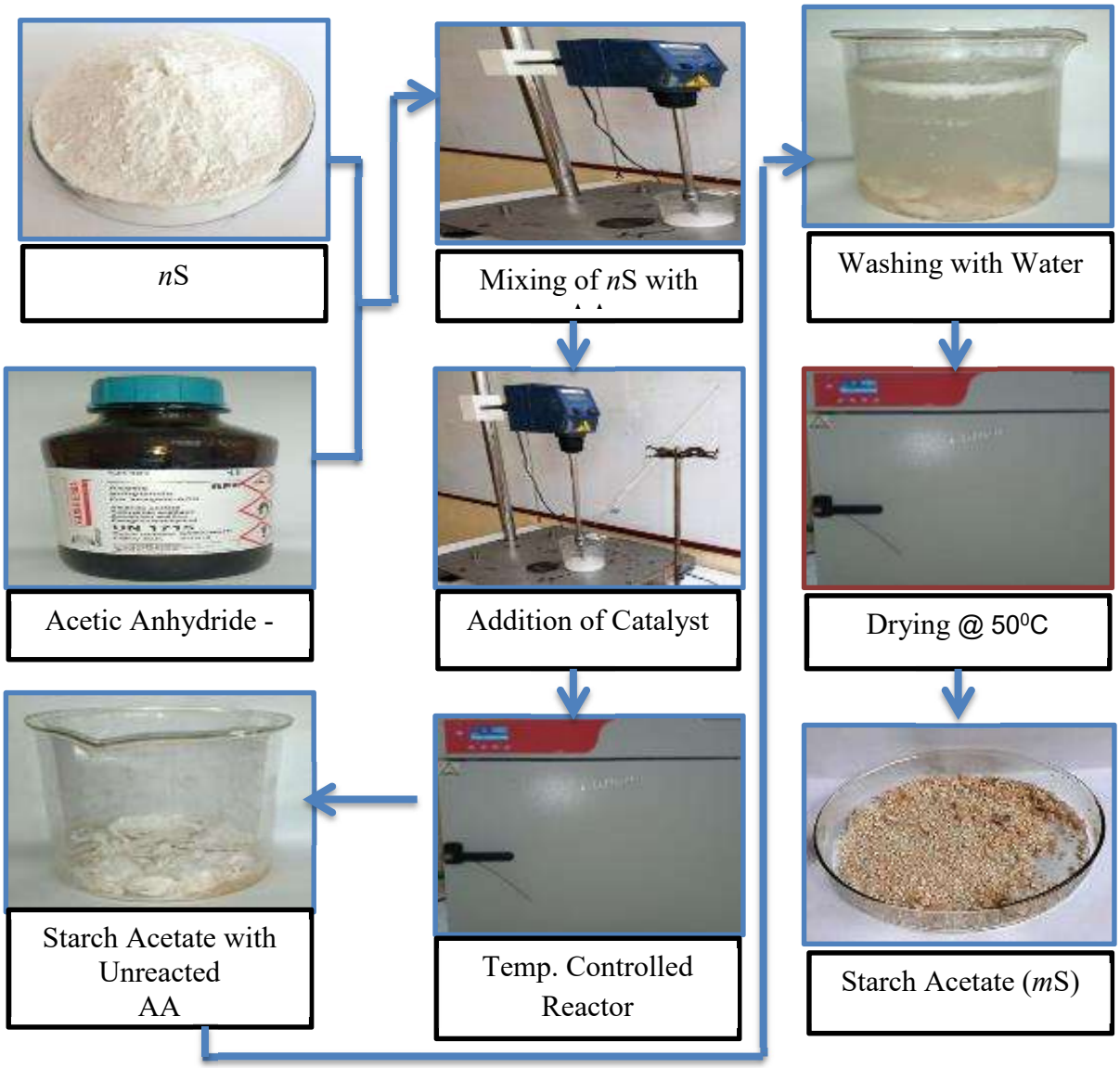

Figure 14: Modification of Enset Starch

3.3.1. Determination of the Degree of Substitution (DS)

The starch acetate degree of substitution was determined by back titration using the method of (Miladinov & Hanna, 2000). In a 250 mL vessel, 0.5 g of acetylated starch was combined with 50 mL of distilled water, and the pH was adjusted to 7 with 0.02 N HCl. Then 25 mL of 0.5 N NaOH was added and vigorously stirred on a hot plate until a clear solution was formed. With HCl 0.02

N, the excess NaOH was titrated back to pH 7. The DS was calculated as (Y. Xu, Miladinov, & Hanna, 2004).

$$\text{Degree of Substitution} = \frac{162 \times (N_{NaOH} \times V_{NaOH} - N_{HCl} \times V_{HCl})}{1000 \times W - 42\,(N_{NaOH} \times V_{NaOH} - N_{HCl} \times V_{HCl})} \quad \text{.....Equation1}$$

Where NNaOH was the normality of NaOH, VNaOH was the volume of NaOH, NHCl was the normality of HCl used to back titrate, VHCl was the volume of HCl used to back titrate, and W was the sample weight (g).

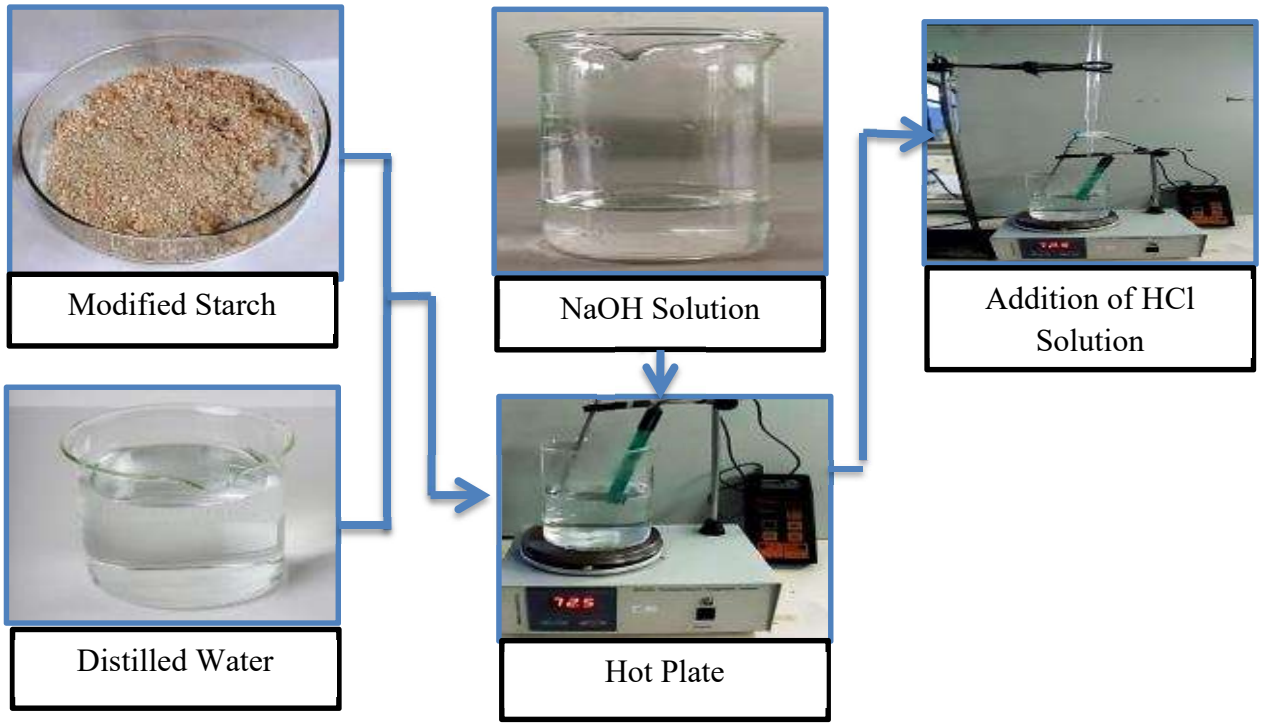

Figure 15: Determination of Degree of Substitution

3.4. Preparation of Thermosetting of Adhesives

3.4.1. Method one: In Situ Modification of LA, ETML, and *n*S Polycondensation Reaction Using Conventional Heating System

Desired amount aqueous LA, ETML and *n*S powder loading (0, 25, 50, 75, 100 wt%/v). Experimental runs are tabulated in the table below with different ratios and this ratio is determined by doing a preliminary experiment.

Summarily *n*S, ETML, and LA were initially taken in RBF in various proportions and were mixed vigorously using a spatula. The mixture was placed in the oven and the poly-condensation reaction was performed with a set temperature of 150 °C for 3hr. the system and the outlet of the RBF were connected to the condenser inlet from which the byproducts were continuously passed. Then water started to come out and the condensation reaction was accelerated and collected in the byproduct receiver. The sample was collected and kept in sealed vials for further analysis.

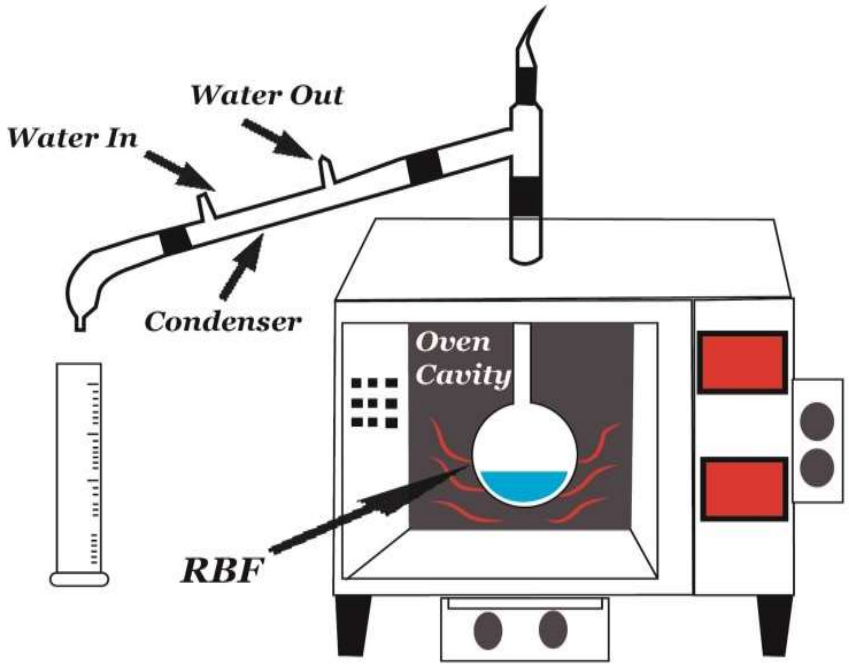

Figure 16: Schematic Diagram of polycondensation reaction of In situ modification of LA, ETML, and *n*S

Table 12: In Situ modification of LA, ETM-latex, and *n*S experimental protocol

Reacting Component Weight to volume Ratio (wt% / V(ml))	**Reaction Time (h)**	**Run**	**Starch (%)**	**Latex (%)**
100	3	1	0	100
		2	25	75
		3	50	50
		4	75	25
		5	100	0
75	3	6	0	100
		7	25	75
		8	50	50
		9	75	25
		10	100	0
50	3	11	0	100
		12	25	75
		13	50	50
		14	75	25
		15	100	0
25	3	16	0	100
		17	25	75
		18	50	50
		19	75	25
		20	100	0
0		21	0	0

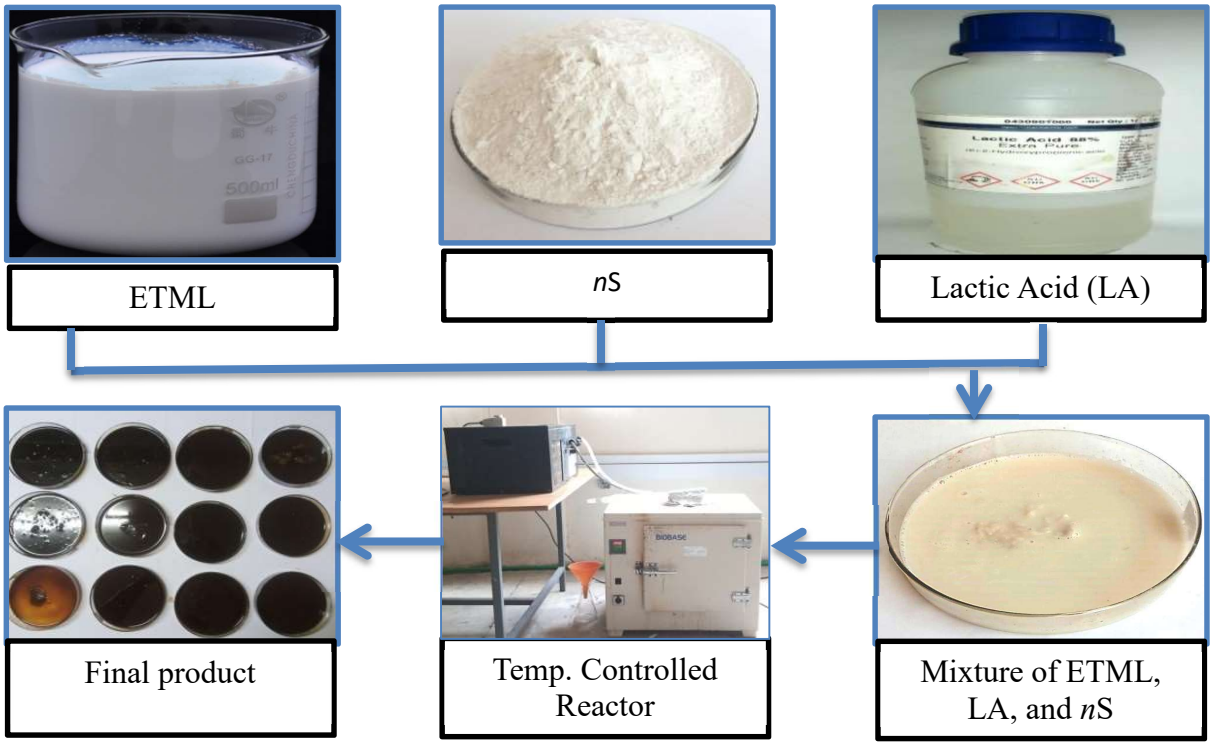

Figure 17: In Situ modification of LA, ETM-Latex, and *n*S

Synthesis of Lactic Acid Oligomers

Oligomers of lactic acid (OLLA) were synthesized by a polycondensation reaction. Oligomerization of lactic acid through polycondensation was performed using a conventional heating system in the absence of any catalyst simply by distilling out water from 88wt% aqueous solution of LA at temperatures of 150 ºC.

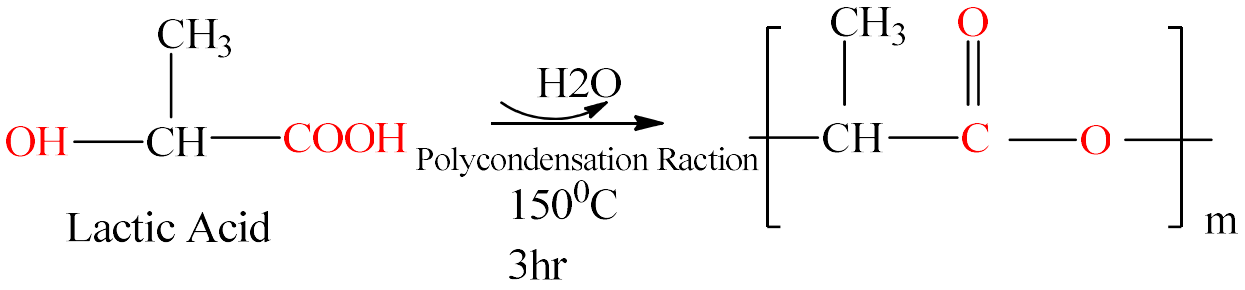

Figure 18: Production scheme of OLLA

3.4.2. Method Two and Three: Reaction between *m*S and LA-based *m*ETML

ETML and LA were initially taken in the round bottom flask with a 1: 1 ratio and were mixed vigorously using a spatula. The mixture was added to RBF and placed in the oven and the modification reaction occurred through the poly-condensation reaction and it was performed with the system with a set temperature of 150 °C for 3h. After 3h of modification, the precipitate and filtrate part was seen. The *m*ETML that forms precipitate was separated from the filtrate part. The *m*ETML that was separated from the filtrate had high flexibility and elasticity. But its binding strength for substrate was not good enough. To enhance its binding strength, the *m*ETML was blended with the mS at room temperature. Then the mixture was placed into the temperature-controlled reactor by using a Petri dish and the reaction was performed with the system with a set temperature of 100 °C for 3h. After 3h of reaction, it was unable to detach or remove the sample from the petri dish. This scenario gives a clue for the sample became an adhesive for glass substrate and the process flow diagram is seen below in figure 19.

The third method was developed by using the information that was gained from methods one and two. The *m*ETML that was blended with the *m*S at room temperature in method two was cast on the substrate using Spatula and inserted into a temperature-controlled reactor with different highly elevated curing temperatures (90, 100, 110, 120, 130, and 140 ºC), curing time (1, 3, 6, 9, and12 hr.), mixing ratio (100:0, 75:25, 50:50, 25:75, 0:100 w/w%) to cure. Then the synthesized material was kept in a sealed container for further analysis. And the process flow diagram is seen below in figure 20.

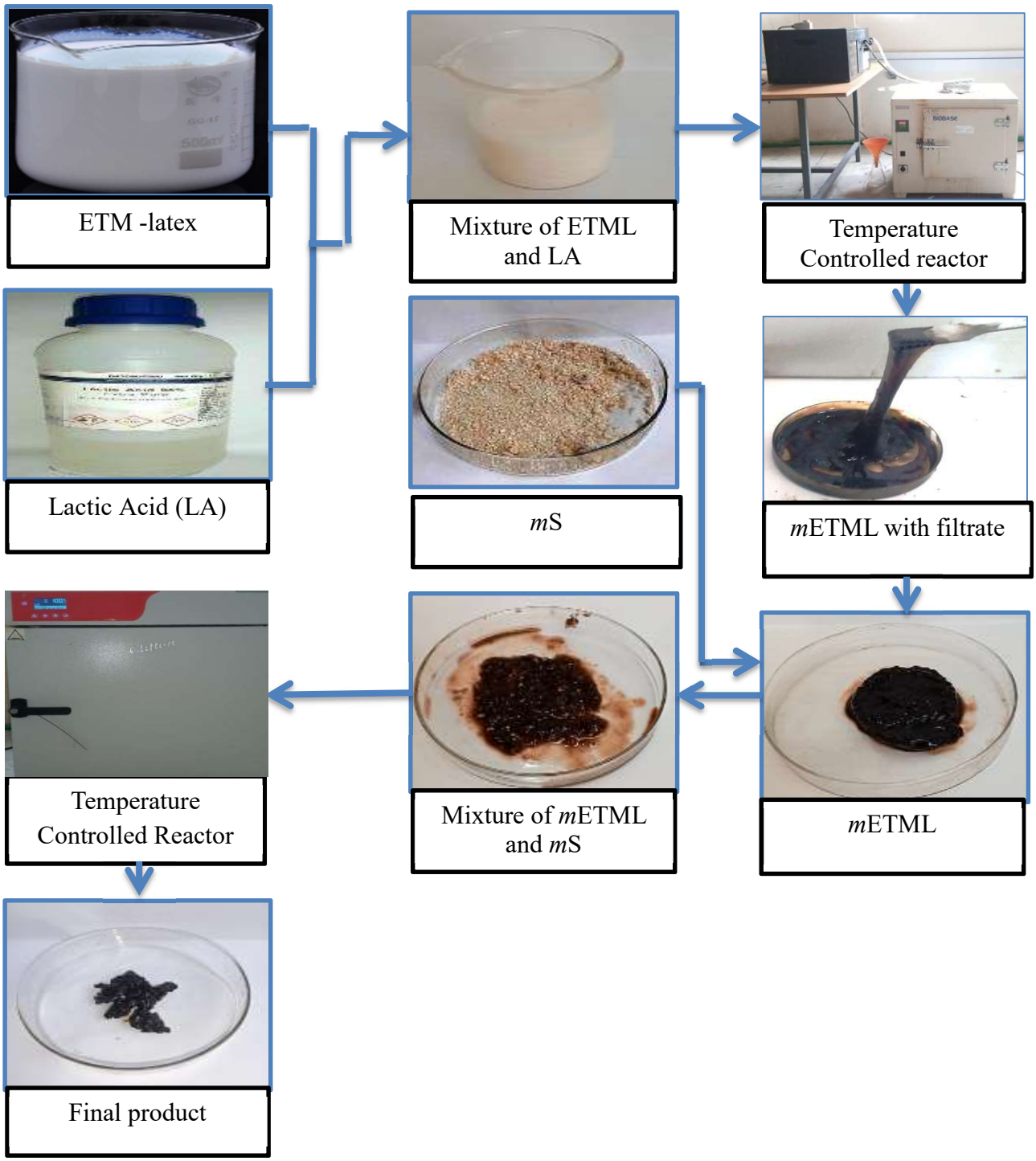

Figure 19: In situ Modification of LA-based modified ETML and mS

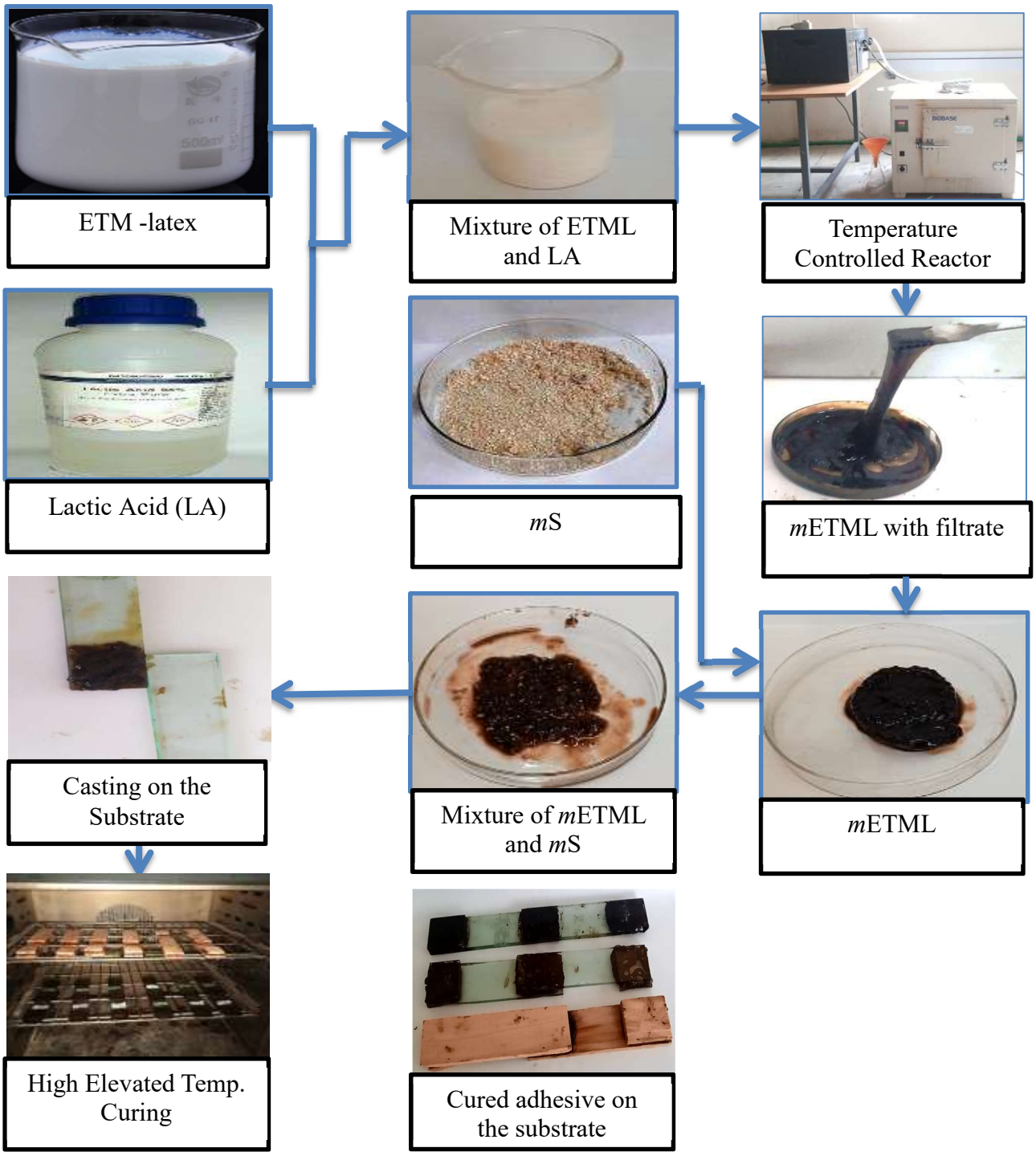

Figure 20: In situ Modification of LA-based modified ETM-Latex and Acetylated Enset Starch Curing on the Substrate by using Conventional Heating System

Table 13: Experimental design for studying the effect of Curing Temperature, Time and Reacting Component Mixing Ratio

Run	Curing Temperature(°C)	Curing Time (hr.)	*m*S: *m*ETML ratio(w/w)
1	90	1	1:0
2	100	3	1:1
3	110	6	1:2
4	120	9	2:1
5	130	12	0:1
6	140		

3.5. Experimental Protocol for Characterization

Experimental protocols for the characterization of extracted raw and *m*ETML, isolated and pretreated *n*S, and the synthesized thermosetting adhesive were discussed in the following.

3.5.1. Important Physical Parameter Analysis for Raw Material

Moisture content determination: The moisture content of starch was determined according to the method described by (Getachew et al., 2016). Summarily, 5 g of enset starch was weighed into a previously washed, dried, and weighed petri dish and was heated in an oven at a temperature of 105℃ ± 5 for 4 hours. The samples were then placed back into an oven and dried until constant weight (± 0.1% change in the weight percentage solids upon one hour of re-heating the sample. The moisture content was determined by the weighted sample from the result of triplicate measurements using equation (1).

$$\textbf{Moisture Content (\%)} = \frac{Wo - Wf}{Wo} * 100 \quad \text{.....Equation 2}$$

Where Wo and Wf are the weights of starch samples before and after drying, respectively.

pH measurement: A solution of 10% *n*S and *m*S was prepared using distilled water. Then it was stirred for 30 min using a magnetic stirrer. Afterward, the pH of the supernatant was measured using a calibrated pH meter.

3.6. Characterization of Thermosetting Adhesive

3.6.1. Lap Shear Test Analysis

The adhesive strength was determined by using UTM.

Preparation of specimens: A Test specimen was constructed under the procedure of the ASTM standard method. The specimens was prepared from wood and glass using ASTM standards (ASTM D1002).

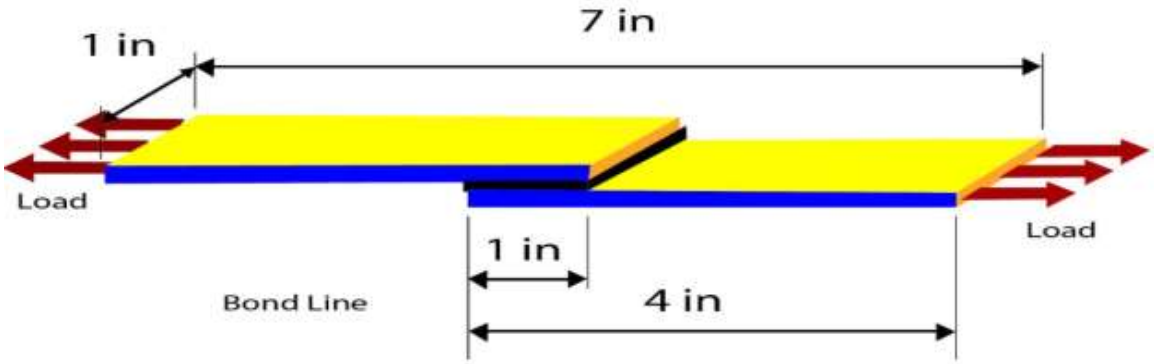

Figure 21: Geometry of Specimen Preparation

3.6.2. Migration Test

The rectangular samples (25* 30 mm^2) that were attached by the adhesive that was cured at a temperature and time of 110^0C and 12hr immersed in water with different times 1, 3, 6, 9, 12, 24, 36,48,60,72 hr. After immersion, it was inserted into ovens at 105°C± 5 to test the migration rates of the adhesive. The samples were taken out at regular intervals and then weighed on an analytical balance.

The migration rates (ώ) were calculated by the following equation:

$$\bar{W} = \frac{m1-m2}{m1} * 100\% \quad \text{..... Equation 3}$$

Where, m_1 and m_2 are the mass of the sample before and after they were put into the vacuum oven, respectively.

3.6.3. Contact Angle Measurement

Contact angle measurement was simply carried out by adapting the method listed in (Le & Nguyen, 2020). A 5% (w/w) solution of *m*S in DMSO was prepared by heating 2 ml of DMSO with 0.12 g

of *m*S at 75 ºC for 1 hr. This mixture was sprayed on dry, clean glass slides (2.5* 10 cm). The glass sheet was dried at 70 ºC for 2 hr. and weighed again at which point the weight remains constant. Then a drop of water (20µL) was dropped on it, and the contact angle of the water drop was measured. The same procedure was followed for both *n*S.

3.6.4. Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectra of the synthesized bio-adhesive will be recorded by using an FTIR spectrophotometer (model IS50-ABX) in the range of between 400 and 4000 cm^{-1}.

3.6.5. Thermal Gravimetric Analysis

The thermal stability of the synthesized bio-adhesive will be determined by thermogravimetric analysis. The analysis was performed in the range from 25 ºC to 800 ºC at a rate of 10 ºC/min heating range under a controlled inert atmosphere by measuring their mass as a function of temperature. The behavior of Wight mass loss and decomposition temperature was observed from the TGA thermograph.

CHAPTER FOUR

4. RESULT AND DISCUSSION

Given the vast hydroxyl structure of the *n*S is hydrophilic and has low shear and thermal resistance and therefore cannot be used as adhesive without modification. Consequently, the water resistance and heat resistance of starch adhesives must be improved. And also, the nature of ETML without modification is not good enough, exposure to air makes it cure so fast. In this study, AA and LA were used to modify the *n*S and ETML respectively to develop a thermosetting starch-based adhesive. The thermosetting adhesive was prepared after the modification of *n*S and ETML, and then the effects of the curing temperature, curing time, and the mixing ratio of the *m*S and *m*ETML on the lap shear of adhesive strength were investigated in detail.

4.1. Important Physical Parameter Analysis for Raw Material

Table 14: Important Physical Parameter of *n*S, *m*S and ETML

Physical Parameter Analysis	**Native Starch (*n*S)**	**Acetylated Starch (*m*S)**	**ETML**
Moisture Content (%)	11.8	10.0	23
pH	5.61	4.41	4.2

4.1.1. Moisture Content (%)

The important physical parameters *n*S and *m*S are presented in Table 14. The moisture content of the *n*S in the present study was 11.80%. A similar result was also reported by (Nigussu et al., 2013). However, (Gebre-Mariam et al., 1996) and (Awol, 2020) reported that the moisture content was 14.17% and 14.53% respectively. The moisture content of the acetylated Starch of the present study was 10.0% and a similar result also was reported by (Nigussu et al., 2013). And the moisture content of ETML was 23%. If the moisture content is high, always there is the chance of microbial spoilage, which results in microbiological damage, this not only affects the physical characteristics but also affects the functional properties (Awol, 2020).

4.1.2. pH

The pH of the *n*S and mS starch suspension in this study was found to be 5.61 and 4.41% respectively. pH can also affect starch properties. The permitted pH level for starch is between 4

and 7. Lower levels of native starch pH indicate contamination by low molecular weight organic acids probably formed by microbial actions on starch (Mohammed et al., 2020). And the pH level of ETML in this study was 4.2. This implies that the latex from ETM is somehow acidic.

4.2. Degree of Substitution

Among the various trials during preliminary studies, the highest DS of Starch acetate obtained was 2.53. During the preliminary studies, different reaction conditions were employed to synthesize Starch acetate with high DS.

Table 15: Reaction Conditions for the Synthesis of Starch Acetate

Reaction condition	Starch/Acetic Anhydride Ratio	NaOH (50% w/w) Per g of starch	Reaction Temperature(°C)	Reaction Time (hr)	Degree of Substitution
1	1:3	0.3	140	3	2.53
2	1:3	0.3	120	3	1.4
3	1:3	0.3	100	3	0.7

4.3. Characterization of Raw Materials

4.3.1. FTIR Analysis of *n*S and *m*S

The FTIR spectra of *n*S and *m*S with DS 2.53 are presented in Figure 22. The infrared spectrum of *n*S is also included for comparison. The OH moieties of monomers in starch are replaced with acetyl moieties during the acetylation reaction. *n*S show characteristic bands of the polysaccharide at 3590 cm^{-1}assigned to the stretching of hydrogen-bonded O-H groups and a similar result was also reported by (M. V. Tupa et al., 2015). C–H stretching modes of polysaccharides are seen at 2920cm^{-1}. A similar result was also reported by (Ali, Ahmad, & Ganat, 2021; M. V. Tupa et al., 2015). FTIR spectra of *m*S showed bands characteristic of the chemical structure of the polysaccharide, i.e. stretching of hydrogen-bonded O–H groups at (3639–3374 cm^{-1}) and the result was confirmed by (M. Tupa, Maldonado, Vázquez, & Foresti, 2013). The peak intensity attributed to O-H stretching at *m*S was decreased, following the esterification reaction, possible because some quantity of unreacted hydroxyl groups was still present. When *m*S was compared to *n*S, *m*S had a new absorption band at 1745 cm^{-1} and 1047 cm^{-1} which is assigned to the stretching of the

ester carbonyl C=O, and C–O band stretching was seen at indicating the acetylation of *n*S. A similar result was also reported by (Nigussu et al., 2013; M. V. Tupa et al., 2015) and (M. V. Tupa et al., 2015) respectively. The band assigned to the stretching of hydroxyl groups of starch gradually diminished as a result of the rising number of hydroxyls that were replaced by ester groups, whereas the band assigned to the ester bands grew with the acetylation level.

Additional characteristic absorption bands appeared at 995,587, and 554 cm^{-1} due to the entire anhydroglucose ring stretching vibrations. And the similar result was also reported by (Chi et al., 2008).

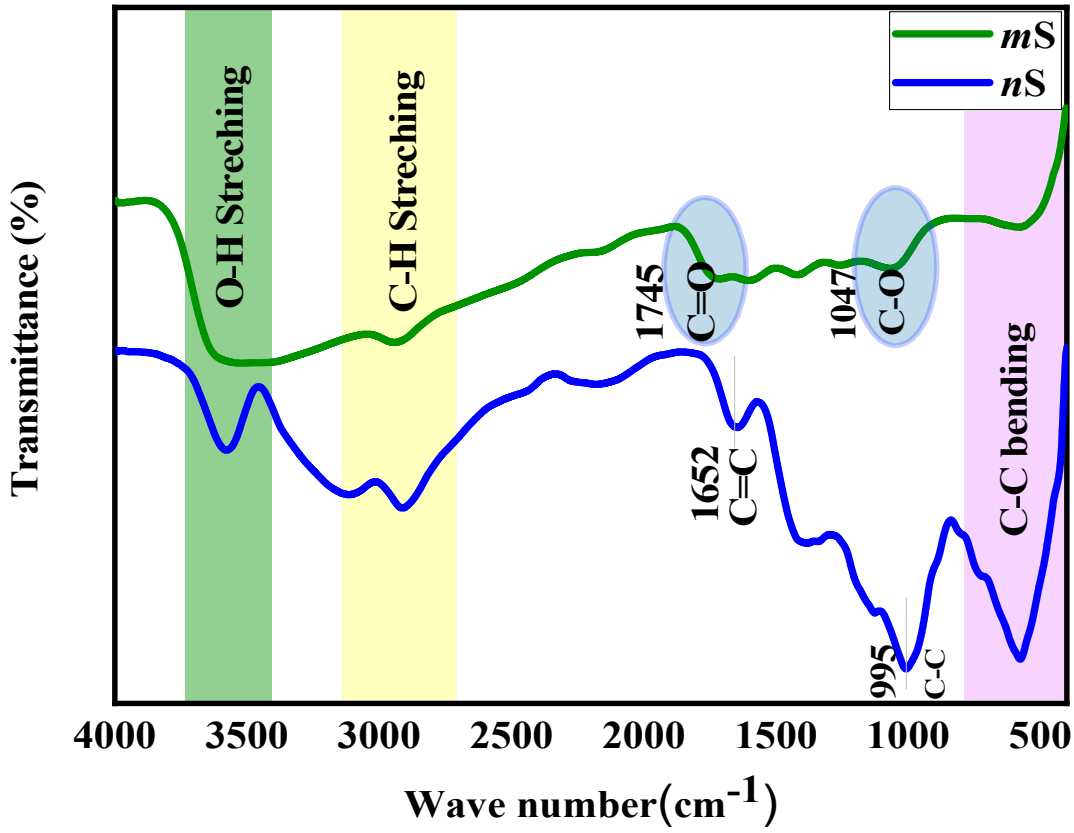

Figure 22: FTIR analysis of *n*S and *m*S

4.3.2. Thermal Stability Analysis of *n*S and *m*S

The thermal gravimetric analysis of *n*S and *m*S is shown in Figure 23 with decomposition peaks as a function of temperature. Based on the TGA result *n*S and *m*S show major degradation peaks

in four and two mass loss steps respectively. These decomposition peaks are seen in the DTG curve.

For the *n*S, the first decomposition peak which occurs at a temperature of about 85℃ shows a 16% weight loss. The first decomposition is attributed to the release of physically adsorbed and hydrogen-bonded water that remained in starch even after preconditioning. The result was confirmed by (Ali et al., 2021). The second and extra high-temperature decomposition peak shows 70% weight loss in the temperature range of about 199-435 ℃ intervals. This weight loss was assigned to starch decomposition. The decomposition of starch occurs as a result of inter and intramolecular dehydration reactions of starch molecules. A similar result was also reported by (Ali et al., 2021; M. V. Tupa et al., 2015). The third and fourth decomposition peak shows 12% and 2 % weight loss in the temperature of 452-576 and 591-651 ℃. Moreover, the decomposition temperature when weight loss at T_{10}, T_{50}, $T_{max,}$ and T_{90} are, 113 ℃, 336 ℃, 339 ℃, and 486 ℃ respectively.

The *m*S samples with DS in the 2.53 showed two mass losses. The first decomposition peak shows a 13% weight loss in the temperature range of 113-202 ℃. This decomposition is attributed to starch dehydration, the one attributed to the condensation of remaining hydroxyl molecules with water as a main product of decomposition. A similar report was also reported by (Ali et al., 2021). The second and the major peak has a weight loss of 70%, which is in the temperature of 206-417℃. This high weight loss has previously been attributed to evolving of acetic anhydride from acetates decomposition. A similar result was also reported by (M. V. Tupa et al., 2015). Moreover, the decomposition temperature when weight loss at T_{10}, T_{50}, T_{max}, and T_{90} are, 146 ℃, 307 ℃, 314 ℃, and 429 ℃ respectively. This analysis is used to define a suitable temperature for using this *n*S and *m*S for other applications. The peak attributed to the decomposition of the acetate groups introduced was centered at 314 ℃, a temperature value almost 22 ℃ less than the temperature at which the maximum weight loss occurred for native starch (i.e., 336℃). The fact that starch's crystal structure was disrupted as a result of the alteration may have contributed to the lower initial degradation temperature (Ojogbo, Blanchard, & Mekonnen, 2018). And also the increase in thermal stability of *nS* than *m*S has been mainly attributed to the impurities (Ali et al., 2021) due to unreacted acetic anhydride, which was not washed out from the system, leading to the decomposition faster.

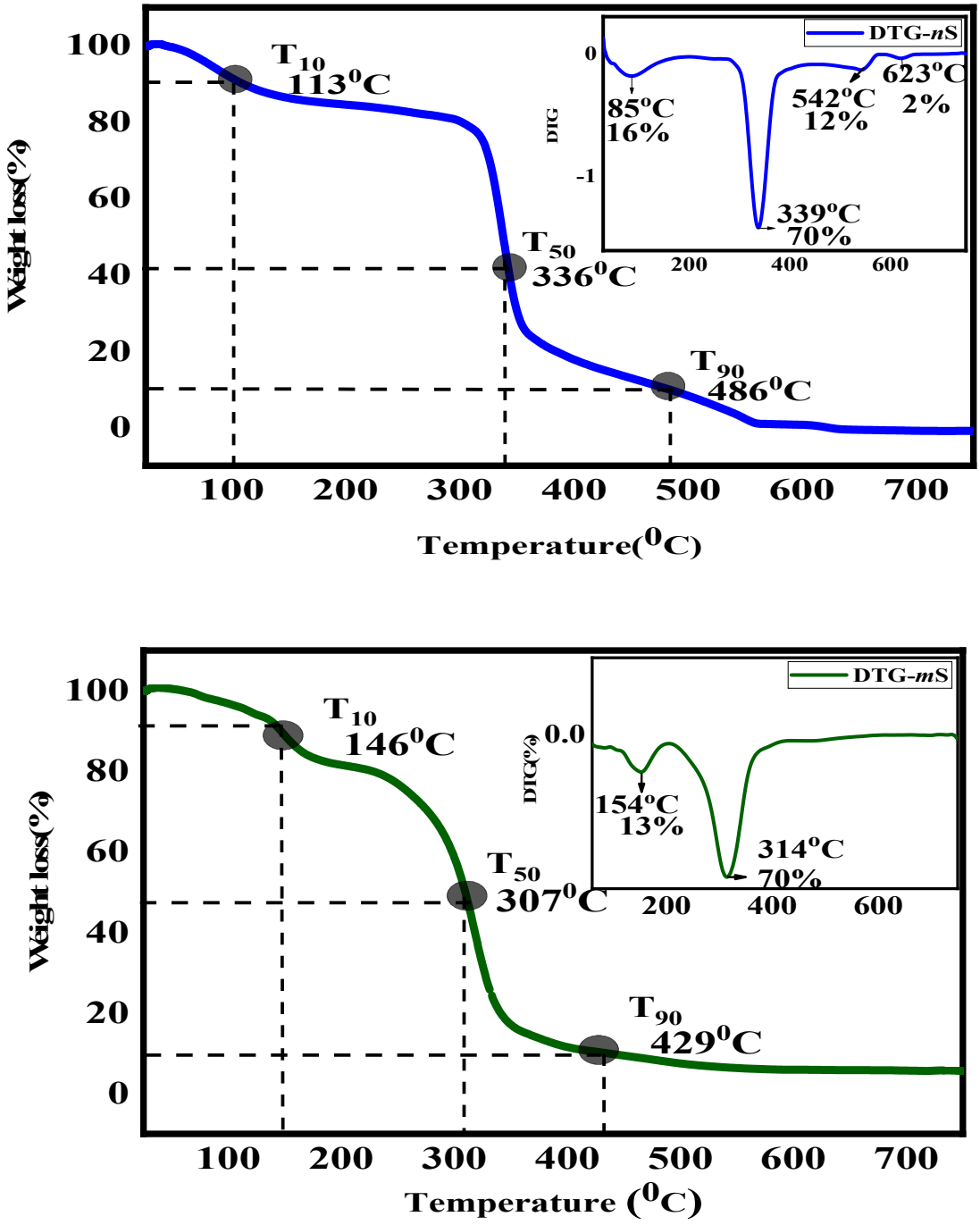

Figure 23: Thermal stability analysis of *n*S and *m*S

Table 16: Degradation temperature for *n*S and *m*S

	T_{10}	T_{50}	T_{max}	T_{90}
***n*S**	113	336	339	486
***m*S**	146	307	314	429

4.3.3. FTIR Spectral Features of the Raw and *m*ETML

The FTIR spectra of raw and *m*ETML were obtained. The latex from ETM shows a band characteristic of the broad peak at 3600-3199cm^{-1}, which is attributed to O–H stretching, confirming the presence of the hydroxyl group in the ETML. A similar result was reported by (Bautista-Hernández, Aranda-Ledesma, Rojas, Tafolla-Arellano, & Martínez-Ávila, 2021; H.-B. Wang, Wang, Liu, Qin, & Kang, 2015). And at the peak of 2952 cm^{-1} the presence of C–H is observed due to the elongation of the methyl and methylene groups (Bautista-Hernández et al., 2021) and peaks at 1638cm^{-1} are due to C=C stretching of cis-1,4-polyisoprene. A similar result was also reported from the latex of *Hevea brasiliensis and E. Haracias* by (Kangwansupamonkon, Gilbert, & Kiatkamjornwong, 2005; Mooibroek & Cornish, 2000) and (Spanò et al., 2012). cis-1,4 polyisoprene is the most common polymer available in plants latex which has tacky nature (Mooibroek & Cornish, 2000). In the case of *m*ETML, the band assigned to the stretching of hydroxyl groups of latex become narrowed as a consequence of the increasing number of hydroxyls which were replaced by ester groups at 1735cm^{-1} which is C=O stretching confirmed by (Mahmoud, Fadl, Mohamed, & Ibrahim, 2021) and C-O stretching at (1210cm^{-}1) both confirm the formation of a new peak during modification. This is due to the reaction between the lactic acid oligomer C=O and the O-H group on the raw latex.

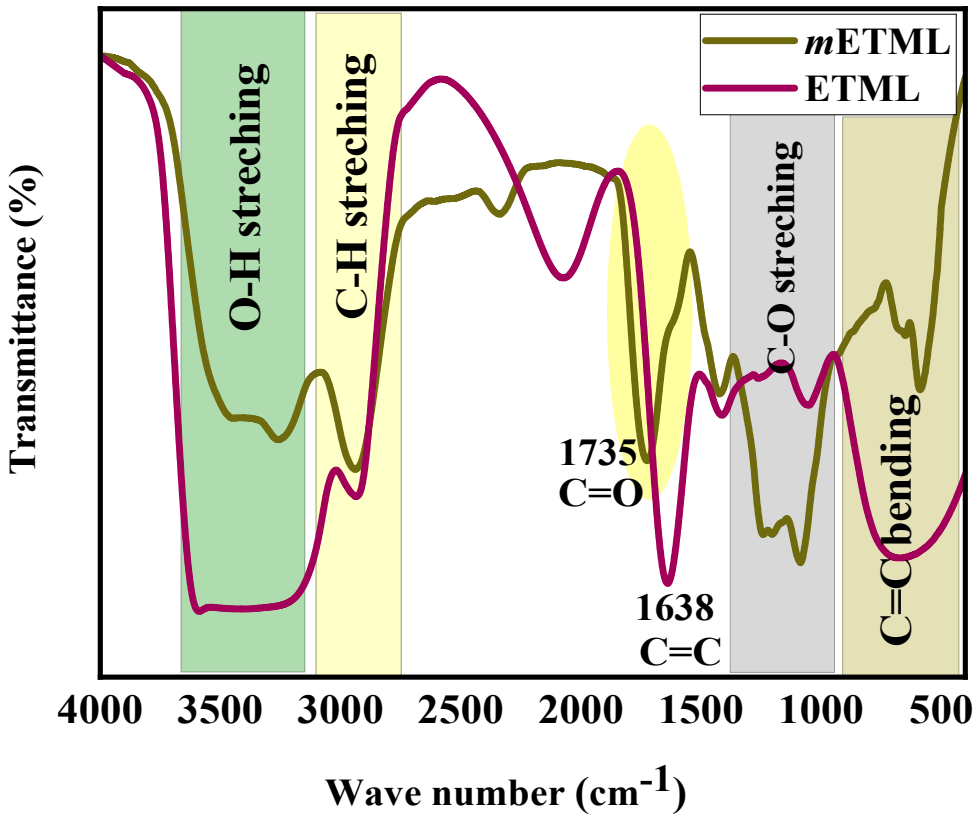

Figure 24: FTIR Spectral Features of the Raw and *m*ETML

4.3.4. Thermal Stability Analysis of the Raw and *m*ETML

The thermal gravimetric analysis of Raw and *m*ETML is shown in Figure 25 below with decomposition peaks as a function of temperature.

Based on the TGA result, the ETML shows degradation in three mass loss steps with two major degradation peaks, the first and major decomposition steps show 52% weight loss in the temperature range of about 0-215 ℃. This decomposition is attributed to the release of moisture content and condensation of remaining hydroxyl molecules with water as a main product of decomposition. The second decomposition peak with the temperature range of 215- 447 ℃ has a weight loss of 33%.. A similar result was reported from the latex of natural rubber by (Rao & Johns, 2008). The third decomposition steps show 4% weight loss in the temperature range of about 455-593 ℃. And this decomposition is expected to be the degradation of some macromolecules. Moreover, the decomposition temperature when weight losses are at T_{10}, T_{50},

$T_{max,}$ and $T_{90,}$ are 78 ℃, 110 ℃, 96 ℃, and 374 ℃ respectively. From DTG curve, it can be observed that the maximum ETML decomposition or weight loss, which occurs in the temperature range of 0-215℃.

The TGA analysis of the *m*ETML shows degradation in two mass loss steps with one major degradation peak, the first and major decomposition steps show 91% weight loss in the temperature range of 0-474 ℃ with major degradation temperature of 380 ℃ This may be attributed to the decomposition of the modified cis-1, 4-polyisoprene group. The second weight loss is 7% which is at a temperature of 470-584 ℃. This is attributed to the decomposition of macromolecules formed during the modification reaction. Moreover, the decomposition temperature when weight loss is at T_{10}, T_{50}, T_{max} and $T_{90,}$ are 189℃, 352℃, 380 ℃ and 435℃ respectively. This analysis is used to define a suitable temperature for using ETML and *m*ETML individually or together for many purposes like the preparation of thermosetting adhesive. From TGA results, it can be observed that the maximum *m*ETML decomposition or weight loss, which occurs in the temperature of 380 ℃, which is more stable than raw ETML. Therefore, for both raw ETML and *m*ETML chemical reactions to take place, they should be below the maximum degradation.

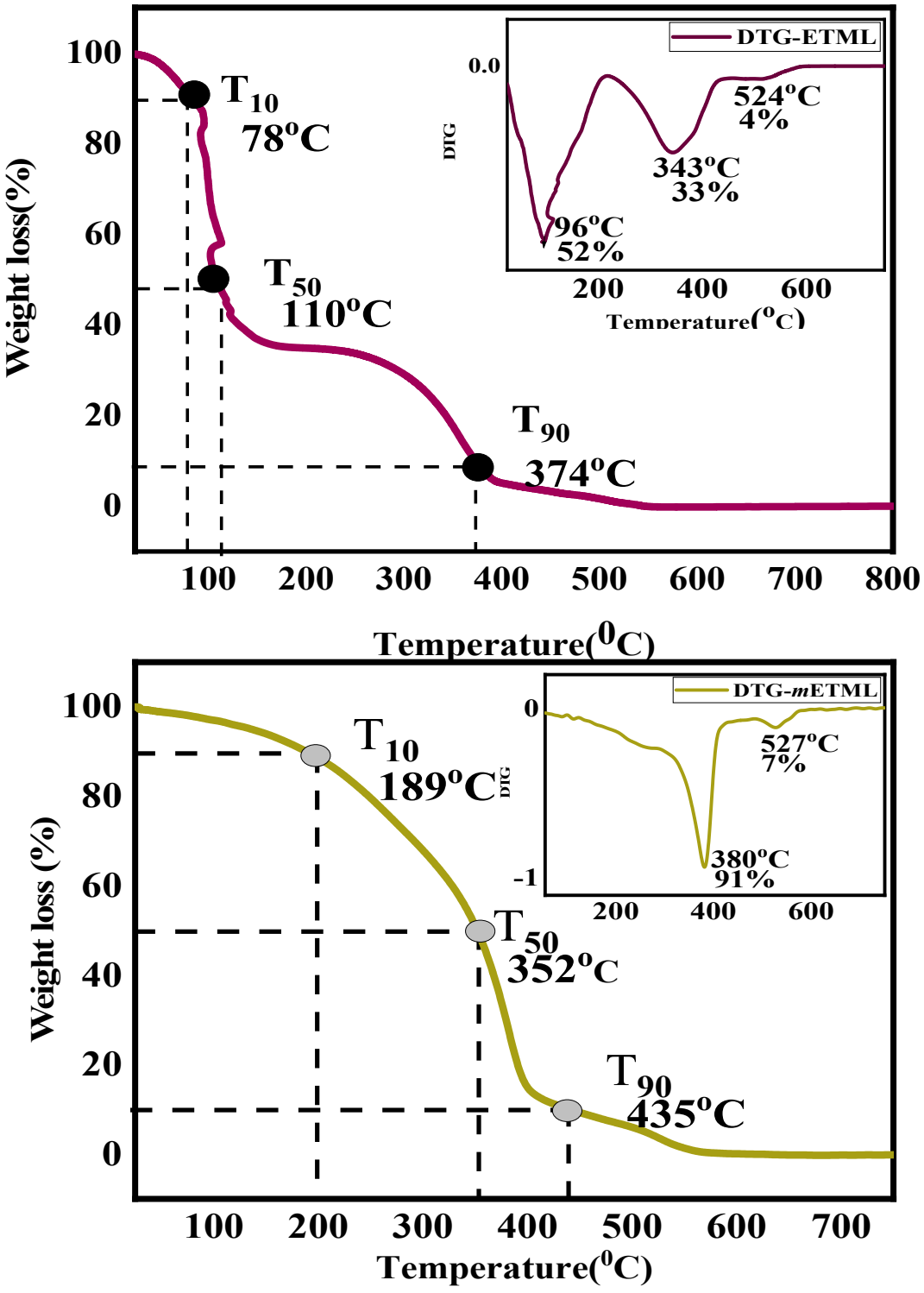

Figure 25: TGA and DTG curve of Raw and Modified ETM-latex

Table 17: Degradation temperature for ETML and mETML

	T_{10}	T_{50}	T_{max}	T_{90}
ETML	78	110	96	374
mETML	189	352	380	435

4.4. Characterization of Thermosetting Adhesive

4.4.1. Lap Shear Joint Adhesive Strength Test

The sample was applied on the surface of the substrates at room temperature and cured at high elevated temperatures. The specimens were adjusted under their corresponding standard system. For each specimen, the ultimate load at failure was measured. The temperature was kept at 25 °C after the preparation. The Adhesive strength was tested on glass and wood substrates.

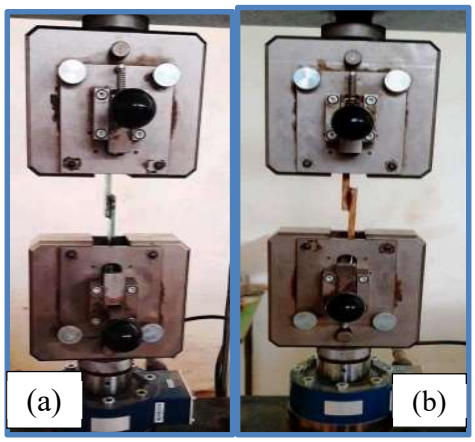

Figure 26: Lap Shear Strength Test Setup (a) Glass, (b) Wood

Tensile lap shear force was applied during measuring the adhesive bonding strength. The maximum lap shear strength was found 1.24 and 0.94 MPa for glass and wood substrate respectively.

Lap Shear Joint Adhesive Strength Test for Method One: In situ Modification of LA, ETML, and *n*S

The mechanical properties of the in situ modified components, *n*S, LA, and ETML are dominated by many factors, such as the dispersing ability, and the interfacial combination. In this case, the bond strength that occurs between the three was not applicable for mechanical testing. This is due to the strong interaction between hydroxy groups; the starch particles have a strong self-aggregation nature and therefore exhibit poor dispersion within the ETML matrix. And also the surface of the starch without modifiers is relatively smooth which strongly suggests that the interfacial combination is weak. A similar result was reported by (You-Ping Wu a, 2006; Zhi-Fen Wang a, 2009).

Table 18: Lap Shear Joint Adhesive Strength Test for In situ Modification of LA, ETML, and *nS*

Mixing Ratio (wt%/v(ml)	Reaction Time (h)	Run	Starch (%)	Latex (%)	Result–Mechanical Testing
100	3	1	0	100	Not applicable
		2	25	75	>>
		3	50	50	>>
		4	75	25	>>
		5	100	0	>>
75	3	6	0	100	>>
		7	25	75	>>
		8	50	50	>>
		9	75	25	>>
		10	100	0	>>
50	3	11	0	100	>>
		12	25	75	>>
		13	50	50	>>
		14	75	25	>>
		15	100	0	>>
25	3	16	0	100	>>

	17	25	75	>>
	18	50	50	>>
	19	75	25	>>
	20	100	0	>>
0	21	0	0	>>

Lap Shear Joint Adhesive Strength Test for Method Two and Three: Reaction between LA-based Modified ETML, and *m*S

4.4.2. Determination of the Effect of Curing Temperature, Time and Mixing Ratio on the Bond Characteristic of the Thermosetting Adhesive

Table 19: Effect of curing Temperature on the Bond Characteristic of the *m*ETML and *m*S Based Thermosetting Adhesive

(a) On glass substrate

Temperature (ºC)	mS: mETML ratio(w/w)	Time	Force (KN)	Failure	Tensile (MPa)
90	50:50	12hr	0.40	Adhesive	0.50
100			0.84	Adhesive	1.06
110			0.93	Substrate	1.24
120			0.70	Adhesive	0.93
130			0.60	Adhesive	0.80
140			0.57	Adhesive	0.76

(b) On wood substrate

Temperature (ºC)	*m*S: *m*ETML ratio(w/w)	Time	Force (KN)	Failure	Tensile(MPa)
90	50:50	12hr	0.16	Adhesive	0.22
100			0.26	Adhesive	0.35
110			0.36	Adhesive	0.48
120			0.24	Adhesive	0.32

130	-	-	-
140	-	-	-

It was observed in the table above that increasing the temperature accelerated the curing reaction of the acetylated starch-based adhesive. The lap shear strength of the adhesive was increased with curing temperatures of 90 to 110 °C. Because the adhesive reaction was thermally accelerated, this was expected. Extending cross-linking process of the polymer chains during curing was linked to the formation of a stronger polymer network but dramatically the lap shear strength of adhesive was diminished in the temperature range between 110 °C to 140 °C and found that the adhesion strength decreased sharply from 1.24 to 0.76 and 0.48 to 0 Mpa for glass and wood respectively with the increase of exposure temperature. However, increasing the curing temperature generally yields cross-linking density increases, an opposite effect can be attained at excessively high temperatures. As a result, as previously stated, excessively high temperatures can improve curing speed while simultaneously limiting molecular diffusion during the synthesis of this thermosetting adhesive, resulting in cross-linked structures with lower mechanical performance.

Table 20: Effect of curing time on the bond characteristic of the *m*ETML and *m*S Based Thermosetting Adhesive

(a) On glass substrate

Time(h)	***m*S: *m*ETML ratio(w/w)**	**Temperature(ºC)**	**Force (KN)**	**Failure**	**Tensile (MPa)**
1	50:50	110	0.58	Adhesive	0.77
3			0.63	Adhesive	0.84
6			0.64	Substrate	0.85
9			0.65	Adhesive	0.86
12			0.93	Substrate	1.24

(b) On wood substrate

Time(hr.)	mS: mETML ratio(w/w)	Temperature(ºC)	Force (KN)	Failure	Tensile(MPa)
1	50:50	110	-	-	0
3			-	-	0
6			-	-	0
9			0.06	Adhesive	0.08
12			0.36	Adhesive	0.48

Curing time increment influences the crosslinking reaction rate and lap shear strength positively. Additionally, the adhesive lap shear strength showed dependence on curing time this is due to the crosslinking reaction being dependent on curing time. In the table above the adhesive lap shear strength shows incremental change (0.77 to 1.24Mpa) and (0 to 0.48 MPa) for glass and wood adhesive with increasing curing time due to getting enough time for reaction (1-12hr). The maximum adhesive strength was achieved at 12hr. The curing temperatures of 110 ºC were selected as the optimum temperature from the above experiment and the curing time was 1, 3, 6 9, and 12hr. In this case12hr was found as the local optimum curing time.

Generally, the adhesive lap shear strength increased with increasing curing time, because the molecules got sufficient time for crosslinking reaction.

Table 21: Effect of *m*S: *m*ETML Ratio on the Bond Characteristic of the Acetylated Starch-based Adhesive

(a) On glass substrate

mS: mETML ratio(w/w)	Time(hr.)	Temperature(ºC)	Force (KN)	Failure	Tensile (MPa)
100:0	12	110	0.05	Adhesive	0.06
75:25			0.71	Adhesive	0.94
50:50			0.93	Substrate	1.24
25:75			0.66	Adhesive	0.88
0:100			0.40	Substrate	0.53

(b) On wood substrate

mS: mETML (w/w)	Time(hr.)	Temperature(ºC)	Force (KN)	Failure	Tensile(MPa)
100:0	12	110	-	-	0
75:25			0.35	Adhesive	0.46
50:50			0.71	Adhesive	0.94
25:75			0.01	Adhesive	0.01
0:100			-	-	0

From the result, that the cross-linking reaction was mixing ratio-dependent. The shear adhesive strength shows continuous increment from 1:0 (w/w) to its optimum point. The lap shear strength of the adhesive reached its maximum at the optimal *m*S: *m*ETML ratio of 1:1 (w/w). Further increasing either the *m*ETML ratio of starch decreases the lap shear strength because homo-polymerization reaction prevailed over crosslinking. Therefore, the *m*S: *m*ETML ratio of 1:1 is considered optimal. With this feeding ratio, the starch-based adhesive exhibited the optimal lap shear adhesive strengths of 1.24 MPa and 0.94 MPa for glass and wood respectively. The crosslinking reaction among *m*S and *m*ETML was proved to form a complex network to improve the performance of the starch-based adhesive.

4.4.3. Migration Test Result

The rate of adhesive migration in the water as a function of time has been shown in figure 27. The migration or leaching property of adhesive is highly dependent on the number of unreacted components in the sample. The Migration rate of adhesive was increased slowly with time. This implies that the curing reaction that takes place was not 100%. The water that the bonded substrate was immersed in was penetrated the adhesive layer and washed out the unreacted component and created void space. This facilitates an increase in water percolation into the remaining part of the adhesive. And consequently, an increase in swelling capacity leads to softening of the adhesive and The structural disintegration probably weakens and enhances the leaching of the sample (Easteal, 2001). The adhesive at 72hr had a higher migration rate than the other for the same adhesive loading (50:50wt/wt.) in which some structural disintegrity was observed. The migration

rate in mass percent when immersion time at 1, 3, 6, 9, 12, 36, 48, 60 and 72hr, were 99.69 %, 99.38 %, 99.23 %, 99.22%, 99.20%, 99.19%, 96.58% ,94.40% and 90.46 % respectively.

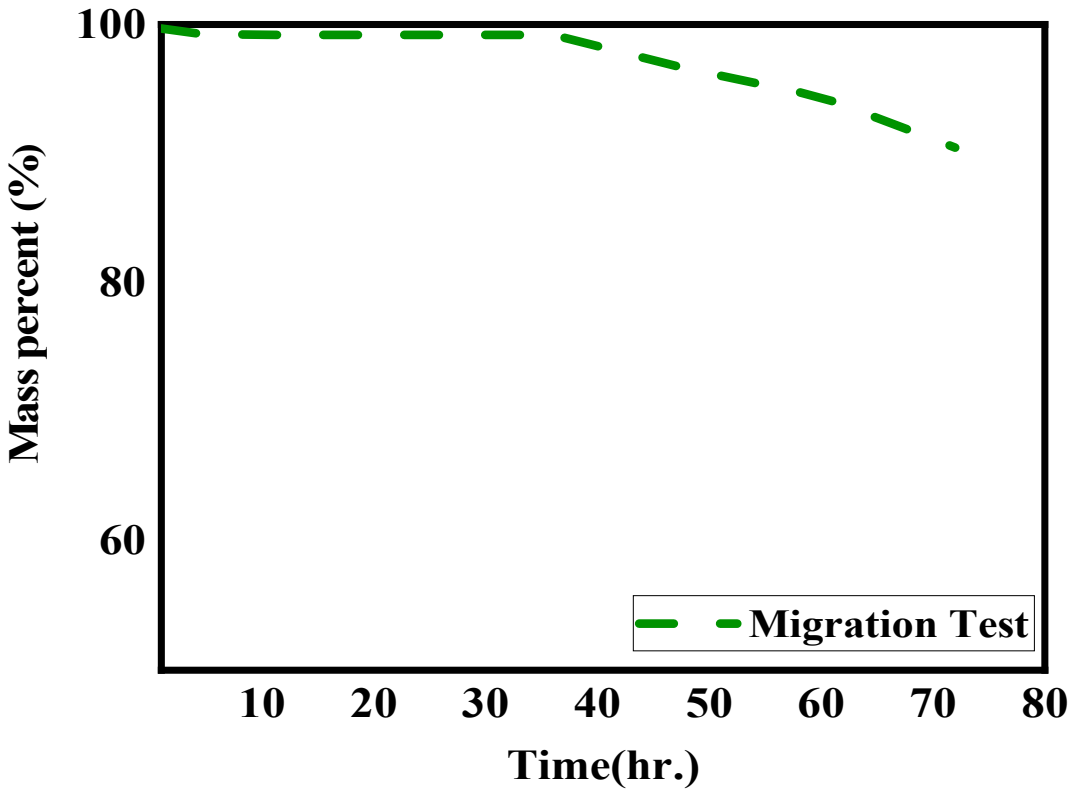

Figure 27: Migration rate test of 110-ms-mETML (a) (0-72hr) (b) (50-72hr)

4.4.4. Contact Angle

Contact angle measurements have long been used to investigate surface wettability. The contact angle produced between the solvent droplet and the polymer that comes into contact is typically used to explain the surface wettability behavior of adhesive. The water wettability of native and modified starch films and thermosetting adhesive was investigated using distilled water as the solvent. The increased hydrophobicity of the esterified starches after esterification was the most noticeable aspect and determined by contact angle measurement. When adding a drop of distilled water, it was spread on the starch film surface and gave the lowest contact angle value than the *m*S and this is due to many OH groups on the surface of the *n*S macromolecule. The reduced

hydrophilicity in *m*S was attributed to the replacement of hydrophilic hydroxyls by the relatively hydrophobic ester groups. The contact angle for *m*S was larger than for the native one after acetylation, demonstrating that modification changed the surface polarity of starch dramatically. Compared with native and DS 2.53 acetylated starch, the contact angle was increased from 58 to 71 ºC. An almost similar result was reported by (Guo et al., 2020; Poddar, 2014). The *m*S has improved the hydrophobicity performance of starch materials. And also, the thermosetting adhesive which cross-linked *m*S with *m*ETML exhibited hydrophobicity with contact angles of 87 º. The increase in contact angle resulted from the replacement of some of the remaining hydrophilic hydroxyl groups by the reaction between the *m*S and *m*ETML.

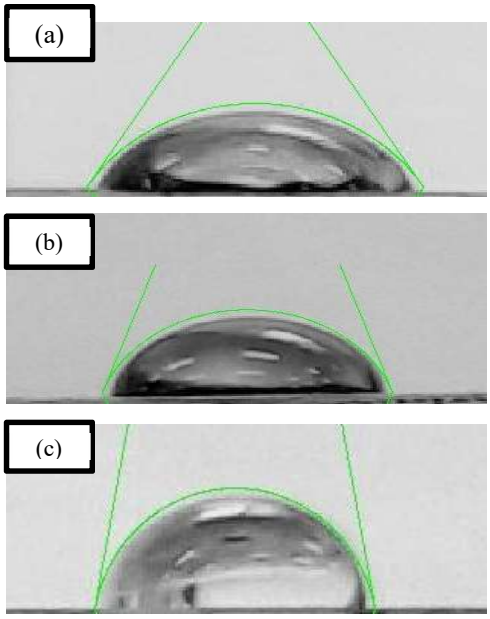

Figure 28: Contact angle of (a) *n*S (b) *m*S (c) *m*S-*m*ETML

4.4.5. FTIR Spectral Features of the Synthesized Thermosetting Adhesive

The hyperbranched thermosetting adhesive was then obtained by the reaction between the *m*ETML and *m*S. the mechanical strength of the adhesive increases with the reaction time and the reaction was carried out for 12 h at 110 °C.

To confirm the different chemical functionalities present in the structure of the thermosetting adhesive, FTIR spectroscopy was used, as shown in Fig. 29. Compared to the IR spectrum of *m*ETML and *m*S, thermosetting adhesive showed an absorption band in the region of 3147 $cm^{-}1$ attributed to the stretching vibration of OH, in which its intensity is increased and which shows

some slight shifting. The bands at 2949 cm⁻1 are assigned to the vibrational absorptions of the C-H bond, in which the peak intensity is also increased. The absorption band at 1740 cm ⁻1 is assigned to the C=O bond which confirmed the formation of the ester group is shifted to 1643 cm ⁻1 and its peak intensity was increased. The peak at 1235 cm ⁻1 in *m*ETML is shifted to higher in the formation of crosslinking reaction in the thermosetting adhesive. The intensity of the O-H bending area is reduced and the intensity of the C-O is increased.

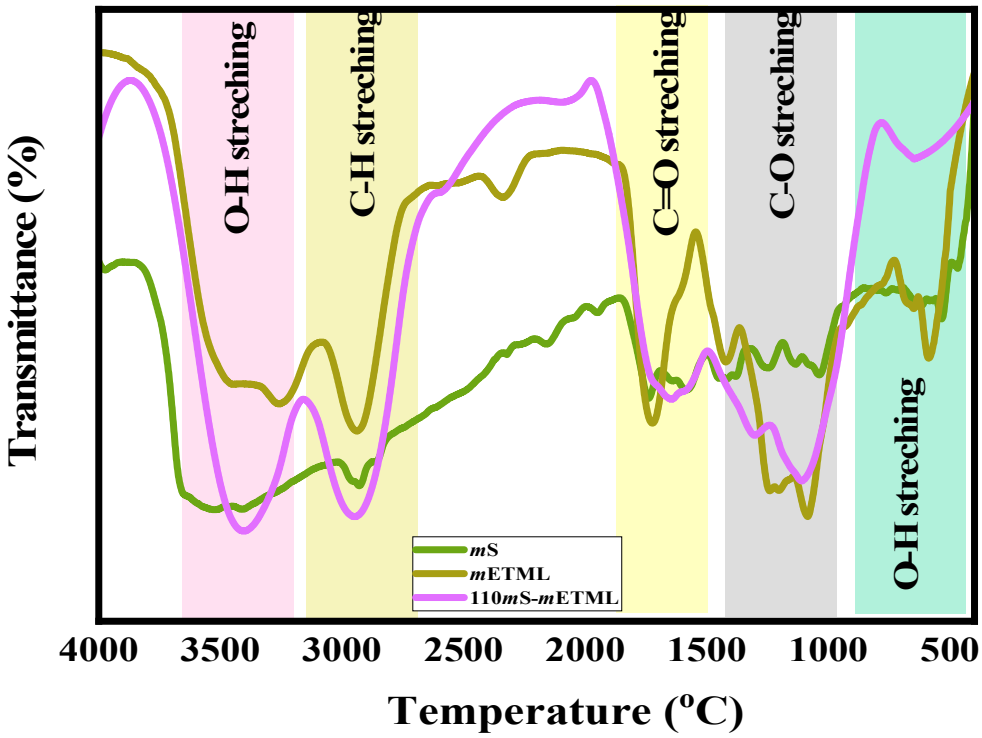

Figure 29: FTIR Spectral Features of the Synthesized Thermosetting Adhesive

4.4.6. Thermal Stability Analysis of Synthesized Thermosetting Adhesive

Thermal analysis of thermosetting adhesive is compared with the *m*S and *m*ETML, from the DTG curve it is shown that there is the formation of huge hump having thermal stability compared to the *m*S. *m*S and *m*ETML have major two degradation steps for each. In these steps, there was a different component that was degraded within different stages which was discussed in the *m*S and *m*ETML thermal Stability analysis section. The major or maximum degradation of *m*S and

*m*ETML was above 314 ℃ and 380 ℃. Using below this temperature for reaction mechanism may be used for saving half of the material from degradation.

Thermogravimetric analysis data of synthesized adhesive showed a three-stage weight loss. The first one took place from room temperature to 125 ºC, and it is assigned to dehydration Water molecules that have been physically adsorbed and connected by hydrogen bonds can be lost at this stage. The major peaks from *m*S and *m*ETML in the DTG curve are changed in the synthesized adhesive to a major peak which is in the temperature range 224-390 ℃ with a weight loss of 63%. This thermal decomposition is a result of the structural decomposition of the synthesized adhesive molecules. The third one took place in the temperature range of 663-776 ºC, and it is assigned to the degradation of macromolecule formed during the crosslinking reaction. Both *m*S and *m*ETML above 442 and 543 ℃ respectively show zero thermal property but due to cross-linking reaction increased their thermal property to a higher temperature. But the thermosetting adhesive some thermally stable macromolecules ner to 776 ºC.

90-140 ºC was a selected temperature from a preliminary investigation for the reaction of thermosetting adhesive.

Table 22: TGA analysis for selected weight loss and maximum degradation

	T_{10}	T_{50}	T_{90}	T_{max}
*m*S	129^0C	310^0C	427^0C	314^0C
*m*ETML	189^0C	352^0C	435^0C	380^0C
110-*m*S-*m*ETML	177^0C	324^0C	726^0C	318^0 C

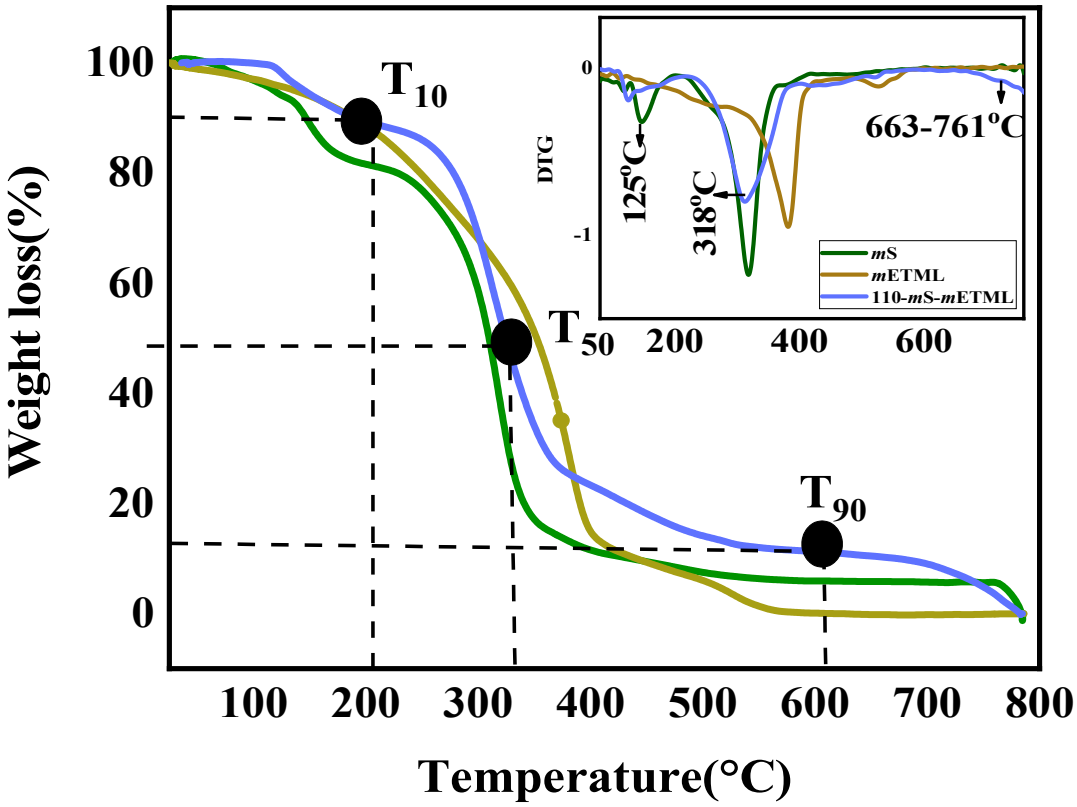

Figure 30: TGA and DTG curve of synthesized Thermoset Adhesive

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

This research work discussed the preparation and characterizing of *m*S and *m*ETML based thermosetting adhesive.

Due to the hydroxyl group making it hydrophilic, and its low shear and thermal resistance both ETML and *n*S need modification. LA and AA were selected as a modifier for ETML and *n*S respectively. The modifications occur at the hydroxyl group on both the ETML and *n*S, and this is proved by FTIR analysis. The FTIR analysis had absorption bands at 1745 cm^{-1} which is attributed to the stretching of the ester carbonyl C=O indicating the acetylation of starch. And also, absorption bands at 1735cm^{-1} which is C=O stretching both confirm the formation of the ester group during modification ETML. This is can be related to the interaction of the hydroxyl group of ETML with C=O of an OLLA. And also in the case of starch When *m*S was compared to *n*S, *m*S had a new absorption band at 1745 cm^{-1} and 1047 cm^{-1} which is assigned to the stretching of the ester carbonyl C=O, and C–O band stretching was seen at indicating the acetylation of *n*S. these peaks are also is confirmed by FTIR analysis.

The effect of the curing temperature, curing time, and reacting component mixing ratio on the bond strength of adhesive was studied. The temperature that was used in the research study was selected by doing preliminary investigations. The lap shear strength of adhesive was increased and decreased with curing temperatures from 90 °C to 110 °C and 120 °C to 140 °C respectively. The use of excessive-high temperatures can not only increase the curing speed but also limits molecular diffusion. And 110 °C was selected as the optimum crosslinking temperature. The adhesive lap shear strength increases with the increase of curing time because the adhesive got sufficient time for crosslinking reaction. And also the cross-linking reaction was dependent on the mixing ratio. The lap shear strength of the adhesive reached its maximum at the optimal *m*S: *m*ETML ratio of 1:1 (w/w). Further increasing either the ETML ratio of starch decreased the lap shear strength because homo-polymerization reaction prevailed over crosslinking. The bonding strength of the thermosetting adhesive was determined using UTM and the best yield strength was found 1.24 MPa for glass substrate and 0.94 MPa for the wood substrate. The contact angle value of *m*S shows

improvement when compared to *n*S, and this is due to the replacement of hydrophilic hydroxyls by the relatively hydrophobic ester groups. The increase in contact angle was observed in thermosetting adhesive resulting from the replacement of some of the remaining hydrophilic hydroxyl groups by the reaction between the *m*S and *m*ETML.

Thus, it can be finally concluded that the thermosetting adhesives which are biodegradable matrix prepared from *m*ETML and *m*S based copolymers would turn out to be the best option as a biodegradable adhesive for glass substrates.

5.2. Recommendation

The thermosetting adhesive prepared from *n*S and ETML showed good quality, which is comparable with other starch-based thermosetting adhesives in terms of bonding. However, there is still more work to be done in the following areas:

- Since the strength of the prepared thermosetting adhesive was only tasted on glass and wood specimens. Therefore, check its applicability on other materials.
- Since the effect of curing time on the bond characteristic of the thermosetting adhesive was investigated until 12 hr. We recommended that further investigation above 12 hr. and see the effect of time increment on bond strength.
- In this study, the functional groups that were found in the thermosetting adhesive are investigated through FTIR, but for further structural investigation NMR has to be done
- Since this research is new further works should be done on selection and considering of other green modifiers and checking the strength of adhesive by using other than LA.
- Assessment of the costs and feasibility of latex extraction and adhesive preparation
- In the modification reaction of ETML by using LA The grafting efficiency was not calculated. We recommended that to do the grafting efficiency by changing the ratio of both ETML and LA.
- Moreover, People who work with *Euphorbia* plants should wear eye protection as well as gloves to protect themselves from the plant's toxicity.

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Appendix 1: Picture of some laboratory works

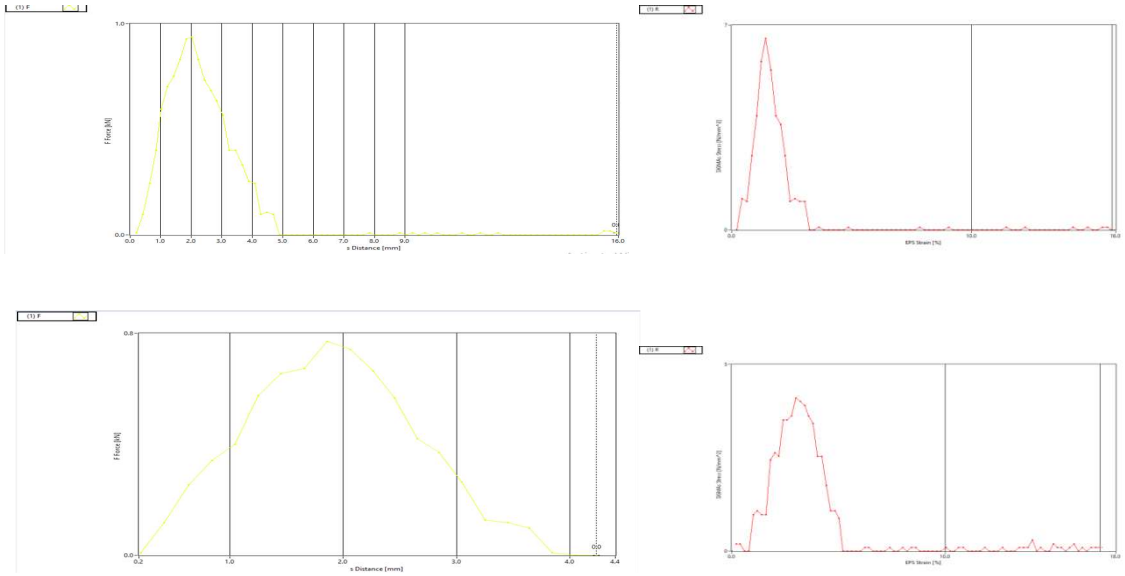
Appendix 2: Some Chemicals used in the laboratory

Appendix 3: Lap Shear Strength data of some synthesized Adhesives

mm	kN	%	N/mm^2	mm	kN	%	N/mm^2
0.1875	0.0000	0.1875	0.0000	0.2031	0.0000	0.2031	0.0000
0.3906	0.0000	0.3906	0.0000	0.4219	0.1074	0.4219	1.0742
0.5781	0.0000	0.5781	0.0000	0.6250	0.0977	0.6250	0.9766
0.7812	0.0000	0.7812	0.0000	0.8281	0.2539	0.8281	2.5391
0.9844	0.0977	0.9844	0.9766	1.0312	0.3906	1.0312	3.9062
1.1875	0.0977	1.1875	0.9766	1.2187	0.5762	1.2187	5.7617
1.3906	0.0879	1.3906	0.8789	1.4062	0.6543	1.4062	6.5430
1.5937	0.0977	1.5937	0.9766	1.6250	0.5469	1.6250	5.4687
1.7969	0.1074	1.7969	1.0742	1.8281	0.3906	1.8281	3.9062
1.9687	0.0977	1.9687	0.9766	2.0312	0.3613	2.0312	3.6133
2.1719	0.0977	2.1719	0.9766	2.2344	0.2539	2.2344	2.5391
2.3594	0.0000	2.3594	0.0000	2.4375	0.0977	2.4375	0.9766
2.5625	0.0000	2.5625	0.0000	2.6406	0.1074	2.6406	1.0742
2.7656	0.0000	2.7656	0.0000	2.8437	0.0977	2.8437	0.9766
2.9531	0.0000	2.9531	0.0000	3.0469	0.0977	3.0469	0.9766
3.1562	0.0000	3.1562	0.0000	3.2500	0.0000	3.2500	0.0000
3.3594	0.0000	3.3594	0.0000	3.4375	0.0000	3.4375	0.0000
3.5625	0.0000	3.5625	0.0000	3.6250	0.0098	3.6250	0.0977
3.7656	0.0000	3.7656	0.0000	3.8281	0.0000	3.8281	0.0000
3.9687	0.0000	3.9687	0.0000	4.0312	0.0000	4.0312	0.0000
4.1719	0.0000	4.1719	0.0000	4.2500	0.0000	4.2500	0.0000
4.3594	0.0000	4.3594	0.0000	4.4531	0.0000	4.4531	0.0000
4.5312	0.0000	4.5312	0.0000	4.6719	0.0000	4.6719	0.0000
4.7344	0.0098	4.7344	0.0977	4.8594	0.0098	4.8594	0.0977
4.9375	0.0000	4.9375	0.0000	5.0469	0.0000	5.0469	0.0000
5.1250	0.0000	5.1250	0.0000	5.2500	0.0000	5.2500	0.0000
5.3281	0.0000	5.3281	0.0000	5.4531	0.0000	5.4531	0.0000
5.5312	0.0000	5.5312	0.0000	5.6562	0.0000	5.6562	0.0000
5.7344	0.0000	5.7344	0.0000	5.8594	0.0000	5.8594	0.0000
5.9219	0.0000	5.9219	0.0000	6.0625	0.0000	6.0625	0.0000

6.1250 0.0000 6.1250 0.0000	6.2656 0.0000 6.2656 0.0000
6.3281 0.0000 6.3281 0.0000	6.4531 0.0000 6.4531 0.0000
6.5469 0.0000 6.5469 0.0000	6.6562 0.0000 6.6562 0.0000
6.7500 0.0195 6.7500 0.1953	6.8594 0.0000 6.8594 0.0000
6.9531 0.0000 6.9531 0.0000	7.0469 0.0000 7.0469 0.0000
7.1562 0.0000 7.1562 0.0000	7.2500 0.0000 7.2500 0.0000
7.3437 0.0000 7.3437 0.0000	7.4531 0.0000 7.4531 0.0000
7.5469 0.0000 7.5469 0.0000	7.6406 0.0000 7.6406 0.0000
7.7500 0.0000 7.7500 0.0000	7.8437 0.0098 7.8437 0.0977
7.9375 0.0000 7.9375 0.0000	8.0312 0.0000 8.0312 0.0000
8.1250 0.0000 8.1250 0.0000	8.2344 0.0000 8.2344 0.0000
8.3281 0.0000 8.3281 0.0000	8.4375 0.0000 8.4375 0.0000
8.5312 0.0000 8.5312 0.0000	8.6250 0.0000 8.6250 0.0000
8.7344 0.0098 8.7344 0.0977	8.8281 0.0000 8.8281 0.0000
8.9219 0.0000 8.9219 0.0000	9.0312 0.0098 9.0312 0.0977
Data End	Data End

Appendix 4: Graph from Lap Shear Strength Test



Appendix 5: contact angle image of native, modified starch and thermosetting adhesive