ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

Production and Characterization of Bio-Adhesive from Euphorbia Tirucalli Latex

A Thesis Submitted to School of Chemical and Bio-Engineering, Addis Ababa Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Master of Science in Process Engineering

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June 14, 2019
Addis Ababa, Ethiopia

ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAiT)
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DECLARATION

I declare that, this thesis entitled with "Production and characterization of bio-adhesive from euphorbia tirucalli latex*"* for the MSc. Degree at Addis Ababa University, hereby submitted by me, is my original work and has not previously been submitted for the degree at this or any other university, and that all resources of materials used in this thesis have been duly acknowledged.

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Acknowledgment

First and foremost, I would like to thank the almighty GOD for giving me endurance and patience to accomplish this thesis work. I would like to offer my sincere gratitude to my advisor Dr. Sintayehu N. for his valuable support continuous follow up, crucial remarks, priceless suggestion and comments throughout the thesis.

Despite the fact that many people have helped me in so many different ways; it is very difficult to list all. But, it is a must to thank those who have a critical role. Special thanks goes to Mr.Hinta-selassie from chemical Engineering laboratory staff (AAiT) and Ms. Medhanit Mamaye (Ph.D. candidate at AAiT). In addition, I would like to thank Defense Engineering College laboratory technicians for arranging universal tester machine to perform lap shear strength test.

I would like to acknowledge my friends at Addis Ababa institute of technology who have directly or indirectly contributed to my work. Finally, I am very grateful to my family for their encouragement and support.

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List of Acronyms

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BADGE	Bisphenol A Diglycidyl Ether
CAM	Crassulacean Acid Metabolism
DF	Degree of Freedom
ET	Euphorbia Tirucalli
ERCA	Ethiopian Revenues and Customs Authority
FTIR	Fourier Transform Infrared
HMA	Hot Melt Adhesives
IARC	International Agency for Research on Cancer
ISO	International System Organization
LVL	Laminated Veneer Lumber
MDF	Medium Density Fiberboard
MF	Melamine-Formaldehyde
MPa	Mega Pascal
MUF	Melamine-Urea-Formaldehyde
PF	Phenol Formaldehyde
phr	Parts per hundred rubber
PRF	Phenol-Resorcinol-Formaldehyde
PVA	Polyvinyl Acetate
rpm	Revolution per minute
UF	Urea Formaldehyde

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Abstract

Adhesive is bonding material most widely used in manufacturing sectors like shoe, wood, textile, papers, and others. Most of these manufacturing sectors rely on using petroleum-based adhesives such as urea formaldehyde, fevicol, polyvinyl acetate, and phenol formaldehyde resins. As these adhesives are produced from non-renewable resources and they are also carcinogenic to human beings due to formaldehyde emission, it is necessary to prepare adhesives from bio-based sources. In this research bio-based adhesive was produced using Euphorbia tirucalli latex as a renewable feedstock. The process of bio-adhesive production includes extraction of latex from branches of Euphorbia tirucalli using water as a solvent and mixing the extracted latex with silica to formulate the adhesive. 21.6 percentage yield of liquid latex was obtained from the extraction section. Before the preparation of the bio-adhesive the extracted latex was characterized in terms of total solid content, pH, viscosity, density and FTIR. Design Expert® version11.1.0.1 with full factorial was applied to investigate the effect of experimental variables such as latex concentration (30, 40 and 50%), silica load (10, 20 and 30parts per hundred rubber) and mixing time (15, 30, and 45 minutes) on the viscosity and bonding strength of the bio-adhesive. Significances of the experimental variables were analyzed by analysis of variance. Maximum lap shear strength (3.28MPa) with a corresponding viscosity of 567.2mPa.s was obtained when 50% latex concentration was mixed with 20phr silica for 30 minutes and minimum lap shear strength (1.2MPa) with a corresponding viscosity of 398mPa.s was observed when 30% latex concentration mixed with 10phr silica for 15 minutes. Finally, the prepared bio-adhesive was characterized in terms of bonding strength, thermal stability, viscosity, pH, and foam length by taking a sample from the experimental run which gave maximum lap shear strength. The results obtained confirmed that the prepared bio-adhesive is comparable with commercial synthetic adhesives and met the minimum requirements except with limited thermal stability.

Key words: bio-adhesive, viscosity, lap shear strength, and Euphorbia tirucalli

1. Introduction

1.1. Background

An adhesive is any non-metallic material that is capable of joining bodies together by surface adhesion and internal strength without the structure of the bodies undergoing significant changes (Ulmanns, 1985). Adhesives are gluing materials which are directly extracted either from natural sources such as bone, gums and starches or synthetically derived from chemicals like urea-formaldehyde(Packham, 2005). Adhesion is the state in which two surfaces are held together by interfacial forces, which may be valence forces, interlocking action, or both while an adherent is a substrate held to another substrate by an adhesive(Mwambusi, 2016) .

The technology of adhesives and their uses dates back several millennia. Nowadays, a number of industries such as leather, wood working industry, shoes industry, which use adhesive, are increasing in number every year. Global formulated adhesive consumption in 2017 was 16 million metric tons worth USD 51.7 billion(Growney, 2018). In our country Ethiopia due to the growth of different manufacturing and construction sector, particularly the present housing construction activities, wood working and furniture sectors highly demand for adhesives. The total consumption of adhesives in Ethiopia reached 7000 ton in 2015 with the average growth rate of 17% over the last fifteen years. This figure shows that there is an increasing demand for adhesive. In Ethiopia, adhesive is produced from natural blood in Addis Ababa Abattoir which produces a modest quantity of adhesive for domestic consumption(Gebremedhin, 2017).

Adhesives can be classified into two categories which are adhesives from petrochemical and natural material(Huang, 2007). Synthetic adhesives are typically derived from petrochemicals. Adhesives such as urea formaldehyde, phenol formaldehyde, fevicol, and poly vinyl are synthetic adhesives usually used in commercial manufacturing sectors since they adhere well and can form strong bond. However, they are restricted because of their non-renewability and toxicity as well as their high cost (Lei, 2009). Therefore, to solve such problems bio-based adhesive being of industrial interest lately. This is because bio based adhesives are environmentally friend and renewable materials. Bio-based (natural)adhesives are produced from natural origin such as animal, vegetable, casein, and blood(Eckelman, 1977). Bio-based adhesives definitely present benefits in terms of environmental and health properties.

In this study Euphorbia tirucalli tree is selected as a source of raw material for synthesis of bio-adhesive. *Euphorbia tirucalli* is a type of Euphorbiaceae plant species(Gupta et al., 2013). *Euphorbia tirucalli* is relatively easy to grow in different soil types, under diversified conditions, and does not require special management practices. Ethiopia has high resources of *Euphorbia tirucalli*. For instance, it is found in Wello, Gojam, Gonder, Shoa, Tigray, Harerge, Sidamo, Gamogofa, Ilubabor and Bale. In Ethiopia, Euphorbia tirucalli is used as a live fence, fire wood and in hedge rows but not used for other purposes(Abay et al., 2017).

Euphorbia tirucalli contains white milky latex in any part of the shoot. Latex is a colloid system having the rubber particles dispersed in water. Latex (white fluid) is tacky in nature. The synthetic latex is prepared from raw materials based on petroleum and/or coal which are non-renewable and, therefore, must be used with economy(Juliet et al., 2018). Natural latex which is a renewable resource can be used as adhesive due to its tacky nature. However, due its low viscosity and poor bonding strength relative to synthetic adhesives, it cannot be used directly as an adhesive. In addition, plant-based adhesives are brittle and vulnerable to environmental conditions(Wadley et al., 2009). Thus, it is necessary to improve its properties. In this study silica was selected as reinforcement agent to prepare the bio-adhesive.

This research work is aimed at studying the replacement of synthetic adhesives by bio-based adhesive from *Euphorbia tirucalli* latex and evaluating its performance.

1.2. Problem Statement

In our country Ethiopia due to the growth of different manufacturing sectors specifically textile, shoe, woodworks, packaging industries and bookbinding, the demand for adhesives has increased significantly over the years. The country`s requirement of adhesive is met through import which leads to additional foreign currency demand**.**

Furthermore, most of the current produced adhesives are basically made from petroleum derived chemicals which are non-renewable and environmentally unfriend. Adhesives like urea formaldehyde, phenol formaldehyde, fevicol, and poly vinyl acetate are the most commonly used petroleum based products in many manufacturing sectors. However, the increasing cost of petrochemical-based products ,depletion of petroleum and growing perception of environmental protection have encouraged the development of bio-based adhesives from cheap and renewable resources. In addition , these types of adhesives are highly volatile and are also classified as gaseous contaminant as well as carcinogenic substance(Thuraisingam et al., 2016). As a solution to the problems, it is inevitable to replace petroleum based adhesives by bio-based adhesives. Beside the mentioned problems, the raw materials required to produce synthetic adhesives are also not available in Ethiopia. Therefore, it is necessary to consider how to use locally available natural resources. In this study *Euphorbia tirucalli* tree is opted as a potential source of raw material to prepare bio-adhesive because it contains a natural white liquid (latex), which has a tacky nature. In Ethiopia, it is found in Wello, Gojam, Gonder, Shoa, Tigray, Harerge, Sidamo, Gamogofa, Ilubabor and Bale. Natural latex which is a renewable resource can be used as adhesive due to its tacky nature. However, due its low viscosity and poor bonding strength relative to synthetic adhesives, it cannot be used directly as an adhesive. Thus, it is necessary to improve its properties. In this study silica was selected as reinforcement agent to prepare the bio-adhesive. Due to its availability, easiness to cultivate and being non–edible plant, *Euphorbia tirucalli* tree can be a good candidate source of raw material for preparation of adhesive.

1.3. Objectives

1.3.1. General objective

The general objective of this thesis work is to investigate bio-adhesive production from *Euphorbia tirucalli* tree latex

1.3.2 Specific objectives

The specific objectives of this thesis work are:

- To extract latex from *Euphorbia tirucalli* tree branches using water as a solvent
- To study the characteristics of the extracted latex in terms of total solid content, pH, viscosity, density, and functional groups
- To investigate preparation of bio-adhesive from latex using silica as a filler
- To investigate the effect of experimental variables such as latex concentration, silica content and mixing time on bonding strength and viscosity of the bio-adhesive.
- To investigate the characteristics of the prepared bio-adhesive in terms of bonding strength, viscosity, thermal stability, pH, and foam length

1.4. Significance of the Study

This thesis work is aimed at import substitution of petroleum based adhesives which Ethiopia is importing by way of renewable and locally available adhesive.

For countries like Ethiopia in which 85% of the population depends on agriculture, such type of research is going to upgrade the societal economic status. The first organs to benefit from this study are farmers who can plant the euphorbia tirucalli and supply the raw material for manufacturing the bio-adhesive. In addition, planting more euphorbia tirucalli to extract latex contributes to the reduction in CO_2 from the atmosphere, hence making it environmental friendly. This study will initiate the country to reduce importing petroleum-based adhesives via replacing them with renewable-based adhesive which has higher attribute than the current one which will in turn decrease value of importing and transportation. In this way the country will become self-sufficient. In addition it brings the county to green economy system.

In summary, once the research is done successfully and implemented, it is expected to have the following significances.

- ✓ Reduce cost of production for the manufacturing sectors like furniture, textile and others as they decrease cost for buying the adhesive from aboard.
- ✓ Farmers who cultivate the tree will be benefited financially.
- ✓ Create employment for the local people
- ✓ As it's a pioneer it will be a starting point for further studies.

Therefore, as stated above this thesis work will possess significance on the society, environment and country.

2. Literature Review

2.1. Definition of Adhesive and Adhesion

The dictionary defines an adhesive/glue as a substance capable of holding materials (adherent) together by surface attachment. Adhesion is the state in which two surfaces are held together by interfacial forces, which may be valence forces, interlocking action, or both while an adherent is a substrate held to another substrate by an adhesive(Mwambusi, 2016).

2.2. Historical Background of Adhesive Production

The earliest use of adhesives was discovered in central Italy when two stone flakes partially covered with birch-bark tar and a third uncovered stone from the Middle Pleistocene era (200,000 years ago) were found. This is thought to be the oldest discovered human use of tar-hafted stones (Peter et al., 2006).The birch-bark-tar adhesive is a simple, one-component adhesive. Although sticky enough, plant-based adhesives are brittle and vulnerable to environmental conditions. The first use of compound adhesives was discovered in Sibudu, South Africa.Here,70,000-year-old stone segments that were once inserted in axe hafts were discovered covered with an adhesive composed of plant gum and red ochre (natural iron oxide) as adding ochre to plant gum produces a stronger product and protects the gum from disintegrating under wet conditions(Wadley et al., 2009). The ability to produce stronger adhesives allowed middle stone age humans to attach stone segments to sticks in greater variations, which led to the development of new tools(Wadley, 2014).

The first references to adhesives in literature first appeared in approximately 2000 BC. Further historical records of adhesive use are found from the period spanning 1500–1000 BC. Artifacts from this period include paintings depicting wood gluing operations and a casket made of wood and glue in King Tutankhamun's tomb(Ebnesajjad, 2010). Other ancient Egyptian artifacts employ animal glue for bonding or lamination. Such lamination of wood for bows and furniture is thought to have extended their life and was accomplished using casein (milk protein)-based glues. The ancient Egyptians also developed starch-based pastes for the bonding of papyrus to clothing and a plaster of Paris-like material made of calcined gypsum(Mittal, 2003).From AD 1 to 500 the Greeks and Romans made great contributions to the development of adhesives. Wood veneering and marquetry were developed, the production of animal and fish glues were refined, and other materials were also utilized. Egg-based pastes were used to bond gold leaves

incorporated various natural ingredients such as blood, bone, hide, milk, cheese, vegetables, and grains(Ebnesajjad, 2010).The Greeks began the use of slaked lime as mortar while the Romans furthered mortar development by mixing lime with volcanic ash and sand. This material, known as pozzolanic cement, was used in the construction of the Roman Colosseum and Pantheon(Mittal, 2003).The Romans were also the first people known to have used tar and beeswax as caulk and sealant between the wooden planks of their boats and ships(Ebnesajjad, 2010).

Commercial manufacture dates back to about A.D. 1690 in England and Holland. Numerous patents relating to the manufacture of animal glues were issued during the period 1754–1844. The first manufacture of animal glue in the United States was early in the nineteenth century. The 1920s, 1930s, and 1940s witnessed great advances in the development and production of new plastics and resins due to the First and Second World Wars. These advances greatly improved the development of adhesives by allowing the use of newly developed materials that exhibited a variety of properties. With changing needs and ever evolving technology, the development of new synthetic adhesives continues to the present(Ebnesajjad, 2010).

2.3. Profile on the Consumption of Adhesives

2.3.1. Global Consumption of Adhesives

Global formulated adhesive consumption in 2017 was 14 million metric tons worth USD 51.7 billion. Tonnage is forecasted to expand at a 4.5 % annual rate until 2026. The top five global adhesive suppliers capture one-third of the sales dollars in 2016. Volume in the Asia-Pacific region in 2016 is already up by 10 % over 2015 and is being spurred by strong growth in China and India. South and Central American adhesive consumption has also already surpassed pre-recession levels(Growney, 2018).

The Asia-Pacific region lead in formulated adhesive consumption .The region captured 38% of the global tonnage in 2015 and is projected to surge to a 46% share in 2026. China is by far the largest adhesive user in the region and in 2017 took 54 % of the volume. Chinese adhesive growth is forecast at 9 % per year. Japan and South Korea are the more mature adhesive consumers in the region. Combining for one-fifth of the regional adhesive volume in 2017 the two countries were about one-quarter of the value as they consume a larger share of the higher price and performance products. India consumed only 6 % of the Asia Pacific adhesive tons in

2017 but has the highest rate of adhesive growth. Europe took nearly 30 % of the global formulated adhesive tons in 2017 and 32 % of the dollars. Volume was up modestly from the prior year but is still down about 5 % from 2015. Slow growth is forecast for Western European countries while modest increases are seen for Russia, Turkey, and other Eastern European countries. North America consumed 24 % of the world's volume in 2017and 27 % of the value. As was the case in Europe, volume was up modestly from the prior year but is down some 7 % from 2008. North American adhesive growth is forecast at 3% per year through 2026, similar to that projected for Europe. South and Central American adhesive consumption was only 5 % of the global tons in 2017. Brazil is the largest regional user taking 58% of the 2017 volume. Brazil weathered the 2016 recession better than most and volume in the country is forecast to expand at a 5 % annual rate. Many adhesive end uses in Brazil are growing at a faster rate(Growney, 2018).

2.3.2. Consumption of Adhesives in Ethiopia

In our country Ethiopia due to the growth of different sectors particularly the present housing construction activities, wood working, textile industries, and shoe industries, there is a high demand for adhesive. The country`s requirement of industrial adhesive is met through import**.** A summary of adhesives imported during the period 2000 – 2015 is presented in Fig 2.1.

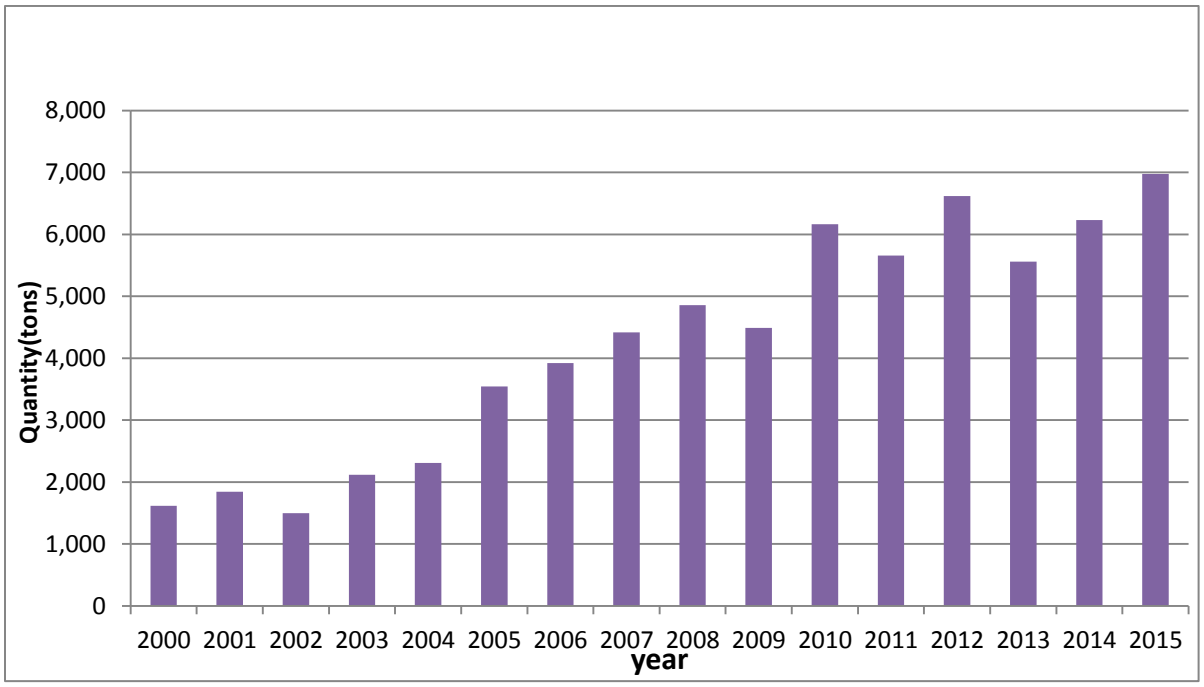


Figure 2. 1: Amount Adhesive imported in Ethiopia (Source: ERCA)

Figure 2.1 reveals that import of adhesives has been consistently increasing from period to period, except a slight decline in the year 2002, year 2004 and year 2011 compared to their respective previous years. The yearly average level of import which was only 1,651 tons during the period 2000-2002 has reached nearly 6,000 tons by the 2010/11.In general, during the past 15 years import volume has shown an annual average growth rate of 17%.

2.4. Theories of Adhesion

The actual mechanism of adhesive attachment is not explicitly defined. Several theories attempt to describe adhesion. No single theory explains adhesion in a general, comprehensive way. Some theories are more applicable for certain substrates and applications; other theories are more appropriate for different circumstances(Allen, 1993). Each theory has been subjected too much study, question, and controversy. However, each contains certain concepts and information that are useful in understanding the basic requirements for a good bond. The most common theories of adhesion are based on adsorption, simple mechanical interlocking, diffusion, electrostatic interaction, and weak-boundary layer (Pocius, 1997).

2.4.1 Adsorption Theory

The adsorption theory states that adhesion results from molecular contact between two materials and the surface forces that develop. Adhesion results from the adsorption of adhesive molecules onto the substrate and the resulting attractive forces, usually designated as secondary or van der Waals forces(Butt et al., 2008). For these forces to develop, the respective surfaces must not be separated more than five angstroms in distance. Therefore, the adhesive must make intimate, molecular contact with the substrate surface. The process of establishing continuous contact between an adhesive and the adherend is known as ‘‘wetting.’’ Good wetting results when the adhesive flows into the valleys and crevices on the substrate surface; poor wetting results when the adhesive bridges over the valleys formed by these crevices(Allen, 1993). Obtaining intimate contact of the adhesive with the surface essentially ensures that interfacial flaws are minimized or eliminated. Poor wetting causes less actual area of contact between the adhesive and adherend, and stress regions develop at the small air pockets along the interface (Pocius, 1997).

2.4.2 Mechanical Theory

The surface of a solid material is never truly smooth but consists of a maze of peaks and valleys. At one time, adhesion was thought to occur only by the adhesive flowing and filling micro-cavities on the substrate. When the adhesive then hardens, the substrates are held together mechanically. According to the mechanical theory of adhesion, in order to function properly, the adhesive must penetrate the cavities on the surface; displace the trapped air at the interface, and lock-on mechanically to the substrate (Pocius, 1997).

2.4.3 Electrostatic and Diffusion Theories

The electrostatic and diffusion theories of adhesion are generally not regarded as highly as the adsorption theory or mechanical theories. However, there are certain applications where each is very appropriate. The electrostatic theory states that electrostatic forces in the form of an electrical double layer are formed at the adhesive-adherend interface. These forces account for resistance to separation. This theory gathers support from the fact that electrical discharges have been noticed when an adhesive is peeled from a substrate(Vaughan, 1997). Electrostatic adhesion theory is regarded as an accepted theory for biological cell adhesion. A simple form of adhesion can also arise from direct contact electrification. This has been demonstrated for thin films of metal sputtered onto polymeric surfaces. The fundamental concept of the diffusion theory is that adhesion arises through the inter-diffusion of molecules in the adhesive and adherend(Pocius, 1997).

2.5. Process of Film Formation during Adhesion

During physical drying where the system is latex, film formation will occur. Film formation is the process of making a coherent film(Packham, 2005). The process can be divided into three stages: consolidation, compaction and coalescence. The first stage, consolidation, is the evaporation of the continuous phase. As evaporation proceeds, the particles will come in contact with each other. In the second stage, compaction, the particles are so close together that they will start to rearrange locally and deformation will occur when they are pressed further together(Petrie, 1999). The forces that are effective during compaction are capillary forces and van der Waals forces. In coalescence, the third stage, the polymer chains in the polymer particles break the interstitial membrane and diffuse into neighboring particles. The inter-particle diffusion leads to the elimination of particle interfaces and it is in this stage that the film

develops mechanical strength. During coalescence a reduction of surface energy occurs, this is the driving force for this stage(Winnik, 1999).

2.6. Classification of Adhesives

For the most part, adhesives used to bond wood together may be separated into two distinct groups: those adhesives such as animal, vegetable, casein, and blood glues which are formulated from materials of natural origin, and those adhesives which are based on synthetic resins derived from petroleum, natural gas, and coal, i.e., products of the petrochemical and related industries (Eckelman, 1977). The properties of various adhesives are discussed below separated according to these two categories.

2.6.1. Natural Adhesives

A. Animal glues

Animal glues are made from the hide and bones of animals such as cattle, sheep, and fish. They are, in fact, hydrolysis products of collagen, i.e., protein-based adhesives. The protein in the animal glues contains a high amount of an amide group (-CONH-), free amino groups (-NH- ,-NH_2) and a carboxylic acid group (-COOH)(Forest Products Laboratory, 1955).

The functional groups interact with each other within and between protein chains. In addition, these functional groups also interact with wood. These interactions provide the strength of animal glues and the adhesion(Blomquist et al., 1981). Proteins in different animal glues have different structures and contain different amounts of these functional groups. Therefore, the properties of different animal glues vary significantly.

Animal glues are sold as solid or liquid. The solid animal glues have to be mixed with water before use. Animal glues were once widely used in furniture. However, they have been replaced by synthetic polyvinyl acetate because of their many undesirable properties such as low moisture resistance, susceptibility to biological degradation, and a relatively high price (Eckelman, 1977).

B. Casein-based Adhesives

Casein is a milk protein. Casein protein precipitates when milk is treated with acid. Separation and subsequent drying of the precipitate generate casein (Skeist, 1990). Casein has high amounts of carboxylic acid groups and can readily dissolve in an alkaline medium such as lime solution or sodium hydroxide solution. The carboxylic acid groups in casein can react with divalent or polyvalent metal ions to form cross-linked networks. The treatment of casein with the metal ions

improves the water-resistance of the resulting plywood. Formaldehyde and di aldehyde starch were used with casein to further improve the water-resistance(Weakley & Mehltretter, 1964). However, the treatment of casein with di aldehyde starch significantly increased the viscosity, which made the application of the modified adhesive onto wood furnish difficult. Another undesirable property of casein-based adhesives is that they stain the wood with rich tannic acid (Eckelman, 1977).

Casein-based adhesives were mainly used for laminated lumbers and doors for interior uses(Huang, 2007). The wood composite panels bonded with casein-based adhesives have moderate dry shear strength, moderate water- and moisture-resistance and cannot be used for exterior applications.

C. Blood-based Adhesives

Blood can also be used as an adhesive. Blood is a byproduct of slaughterhouse and contains a high amount of protein. Lime and sodium hydroxide are typically used to unfold blood protein for adhesive applications(Eckelman, 1977). Formaldehyde and PF resins were used to improve water-resistance, strength and mold resistance of plywood bonded with the blood-based adhesive (Blomquist et al., 1981). Blood-based adhesives have a higher moisture resistance, but a lower strength than the casein-based adhesive.

The blood based adhesive was used in combinations of PF resins or soybean protein for plywood manufacture(Ash & Lambuth, 1957). However, it is no longer used in a commercial scale.

D. Starch Based Vegetable Adhesives

Although starch glues still are used in the United States, they are used little in the wood industry. Of particular importance, they have been replaced by urea-resin adhesives in gluing interior-type hardwood plywood and furniture(Rieman, 1992). They are included here largely as a matter of historical interest. As the name implies, the principal component of these adhesives is starch which may be obtained from a variety of plants including corn, potatoes, rice and cassava. The root of the cassava plant is the source of tapioca. Prior to World War II, extensive cassava plantations were maintained by major glue companies in what is now Indonesia. During the war, these plantations were lost, substitutes were found, and production of glues which relied on this plant decreased accordingly(Williani, 1921). Vegetable glues are ordinarily sold in powdered form and must be mixed with water. Other chemicals such as alum may be added to improve their properties. These mixtures are heated to prepare them for use--heating flour paste, for

example, renders the flour soluble. Vegetable glues are relatively inexpensive and have a relatively long pot life. They set through loss of water, which may be quite slow, so that glued assemblies must often remain clamped overnight. Vegetable glues were widely used during World War I in such applications as veneering. They lack moisture resistance, however, stain certain veneer species, and are attacked by micro-organisms(Eckelman, 1977).

E. Protein Based Adhesives

The principal protein-based vegetable glue is manufactured from either soybean meal or the vegetable protein isolated from it. Soybean glue has properties and characteristics which are similar to those of casein glue, but lacks its water resistance(Rathi & Domb, 2018). Soybean glue may be hot-pressed, and in the past was widely used for interior grade Douglas-fir plywood. Soybean protein is also used in a blend, consisting primarily of blood and soybean proteins. They are prepared by mixing with cold water, lime, caustic soda, and other chemicals; applied and pressed at room temperatures, but more frequently hot-pressed, especially when blended with blood protein These are mixed and used like the hot-press blood glues (Eckelman, 1977)..

2.6.2. Synthetic Adhesives

Synthetic resins are man-made polymers which resemble natural resins in physical characteristics but which can be tailored to meet specific requirements. These resins impart to glue lines and joints the highest water resistance attained to date. Synthetic resins are typically derived from petrochemicals. There are two types of synthetic resins: thermosetting resins and thermoplastic resins(Mittal, 2003). Thermosetting resins become insoluble and infusible materials after being heated at a certain temperature, which is an irreversible process. Thermoplastic resins soften or melt when they are heated, and solidify again when they are cooled. The softening and solidifying are reversible and can be repeated many times (Eckelman, 1977). Major thermosetting and thermoplastic adhesives are described in detail in the following sections.

2.6.2.1. Thermosetting Adhesive

The most commonly used commercial thermosetting adhesives in manufacturing sectors include phenol-formaldehyde resin, urea-formaldehyde, melamine-formaldehyde and phenol-resorcinol-formaldehyde(Sellers, 2001).

A. Phenol-Formaldehyde (PF) Adhesive

PF resins are prepared by addition and condensation reactions of phenol and formaldehyde in the presence of either an acid or base catalyst. Under either an acid catalysis or a base catalysis, the initial reaction is the same, i.e., addition of formaldehyde to phenol to form methylol substituted phenols(Fan et al., 2014). The addition reaction can occur at the *ortho*- and *Para*-position of the phenolic hydroxyl group. The resulting methylol-substituted phenols react with each other through a condensation reaction to form linear or branched polymers. PF resins prepared with an acid catalyst are called volacs and those prepared with a base catalyst are called resoles (Koch, 1987).

PF resins are mainly used for production of exteriorly used structural wood composite panels such as plywood and laminated veneer lumber (LVL) because of their good durability and high strength even under harsh weather conditions. PF resins after cured have a dark color, which negatively affects the aesthetics of wood composite products(Skeist, 1990). Therefore, PF resins are normally not used for production of interiorly used wood composite panels.

B. Urea-Formaldehyde (UF) Adhesive

UF resins are derived from urea and formaldehyde in the presence of a catalyst. The reactions between urea and formaldehyde first generate a mixture of mono-, di-, tri- and tetra-methylol urea that further condense to form cross-linked polymer networks(Salkova, 2010). The molar ratio of formaldehyde to urea is above one, typically around 1.5 to 2. The pH value of the UF resins should be lower than 7 for curing. UF resins can be cured at elevated temperatures (95-130 ^{o}C) with ammonium salts of strong acids as catalysts. UF resins can also be cured at room temperature using strong acids as catalysts (Skeist, 1990). But the strong acids could degrade wood and lower bonding strength (Hse et al., 1994).

UF resins are colorless and inexpensive, and have a faster curing rate, i.e., a shorter curing time than PF resins. They are widely used for making interior plywood, particleboard and medium density fiberboard. UF resins have a lower water-resistance than PF resins and can easily be hydrolyzed by water to release formaldehyde. Depending on the water-resistance requirements, some melamine may be incorporated into the UF resins to improve their water-resistance (Eckelman, 1977).

C. Melamine-Formaldehyde (MF) Adhesive

Melamine is derived from urea and is widely used for making MF resins. Melamine has three amino groups that can react with formaldehyde to form MF resins. The molar ratio of melamine to formaldehyde is about 1:2.5(Li et al., 2016).

MF resins are more resistant against hydrolysis. In other words, wood composite panels bonded with MF resins are much more water-resistant than those bonded with UF resins. MF resins are widely used for making wood composite panels for covered exterior applications. MF resins are also widely used for saturating paper. MF resins are more brittle than UF resins, thus resulting in brittle joints, blunt tools and hard cleaning of mixing equipment(Hse et al., 1994). Because of the high cost of melamine, the annual consumption of MF resins is much less than that of PF and UF resins in the wood adhesive market. The small amount of melamine is often incorporated into UF resins to form melamine-urea-formaldehyde (MUF) resins. MUF resins are more water-resistant than UF resins. MUF resins are used to make wood composite panels for covered exterior applications, such as finger joints, and edge-glued lumber(Ishak, 2012).

D. Epoxy Adhesive

Epoxy resins are based on compounds containing at least two epoxy functional groups. These compounds polymerizes in the presence of a hardener and a catalyst. One of the widely used epoxy resins is bisphenol A diglycidyl ether (BADGE) that is derived from bisphenol A (a condensation product of phenol and acetone) and epichlorohydrin(Kothe et al., 2016). Epoxy resins are widely used in coatings, casting, encapsulation and laminates because they are capable of forming good bonding to many materials. The epoxy functional group can react with a wide variety of functional groups such as hydroxyl groups, amino groups, and carboxylic acid groups. Epoxy resins are thus widely used as crosslinking agents for various substrates in both an organic medium and an aqueous medium(González et al., 1988).

Epoxy resins have some outstanding physical properties, such as low cure shrinkage, good wetting ability, excellent chemical and corrosion resistance, superior strength and weather durability. The disadvantages of epoxy resins are inherent brittleness, high cost, high cure requirements for obtaining high strength, and environmental issues related to the emission of volatile organic compounds(Ratna, 2003).

2.6.2.2. Thermoplastic Adhesives

A. Polyvinyl acetate (PVA)

PVA, the "white glue", is typically prepared from an emulsion polymerization of vinyl acetate. The PVA glue is typically sold as an aqueous emulsion. PVA is the most commonly used glue in furniture assembly(Gražulevi et al., 2015). Once the PVA glue is applied to wood, it set quickly (typically within 15 min) at ambient temperature and the high strength of adhesive bonds is quickly achieved. The PVA glue line is almost invisible, which is a desirable feature of an adhesive for furniture manufacture. However, The PVA glue has poor gap-filling properties and its water-resistance and heat-resistance are also not good. For improving the water- and heat-resistance, various cross linkable monomers such as N-(hydroxymethyl)acrylamide have been added in the polymerization of vinyl acetate to modify PVA glues so that the modified PVA glue can form cross-linked polymer networks once cured(Liu et al., 2005).

B. Hot Melt Adhesives

Hot melt adhesives are resins which are normally solid but melt upon heating so that they may be applied as a drop or a bead of glue. Upon cooling, they immediately regain their adhesive properties. Ordinarily, hot melts are not used in structural applications where high strength is required but rather, are commonly used to attach decorative materials such as edge banding to panels and table tops. The adhesives themselves are based on various polymers including the polyolefin, the vinyl acetate olefin copolymers, polyamides, and the polyurethanes (Eckelman, 1977).

2.7. Issues Associated with Petroleum-based Adhesives

2.7.1. Dependence on Non-Renewable Raw Materials

The raw materials for making UF and PF resins are mostly derived from non-renewable natural gas and petroleum. The finite reserve and expanding consumption of petroleum and natural gas will definitely affect the availability of the raw materials for making these formaldehyde-based adhesives in a long run(Huang, 2007).

2.7.2. Emission of Carcinogenic Formaldehyde

Formaldehyde has been re-classified as a human carcinogen by International Agency for Research on Cancer(IARC, 2004). It is well established that formaldehyde is released in the production and use of wood composites bonded with these formaldehyde-based adhesives,

especially UF. The emission of formaldehyde mainly comes from residual free formaldehyde in adhesives and the hydrolytic product of the adhesives. Cured UF resins are susceptible to hydrolysis in the presence of water or moisture to release formaldehyde. Acidic environment and elevated temperatures can speed up the hydrolysis. Cured PF resins are more resistant to hydrolysis than cured UF resins. Thus, residual free formaldehyde is mainly responsible for the formaldehyde emission from PF resins and PF-bonded wood composite panels(Carvalho, 2012).
The non-renewable nature of the raw materials for making currently used formaldehyde-based adhesives and the hazardous issues associated with formaldehyde emission have generated a need for the development of a formaldehyde-free wood adhesive from renewable materials (Huang, 2007).

2.8. Production process of bio adhesive from natural latex

The production of bio-adhesive from natural latex basically consists two major sections. These are extraction of latex and mixing of the extracted latex with filler. Extraction of latex consists the following procedures: crushing, soaking, pH adjustment, heating filtration, and, concentration.

1. **Crushing**: it is the process of reducing the size of the plant material into small size. The plant material should be used as a wet.

2. **Soaking**: it is the process of adding water to the crushed material to extract the liquid latex
3. **pH adjustment:** At acidic or neutral condition, latex coagulates due to the growth of bacteria. Therefore, to prevent this ammonia solution should be added to make it basic solution. pH should be in the range of 8-11(Cornish et al., 1999).
4. **Heating**: process of heating the slurry to prevent from sticking.
5. **Filtration**: it is the process of separating liquid latex from bagasse by vacuum filter suction.
6. **Concentration:** it is the removal excess water from the liquid latex by evaporation.
7. **Mixing of latex with additives:** it is the process mixing latex with fillers. Cellulose, silica and kaolin are most commonly used fillers to enhance latex property(Camacho et al., 2018**).**

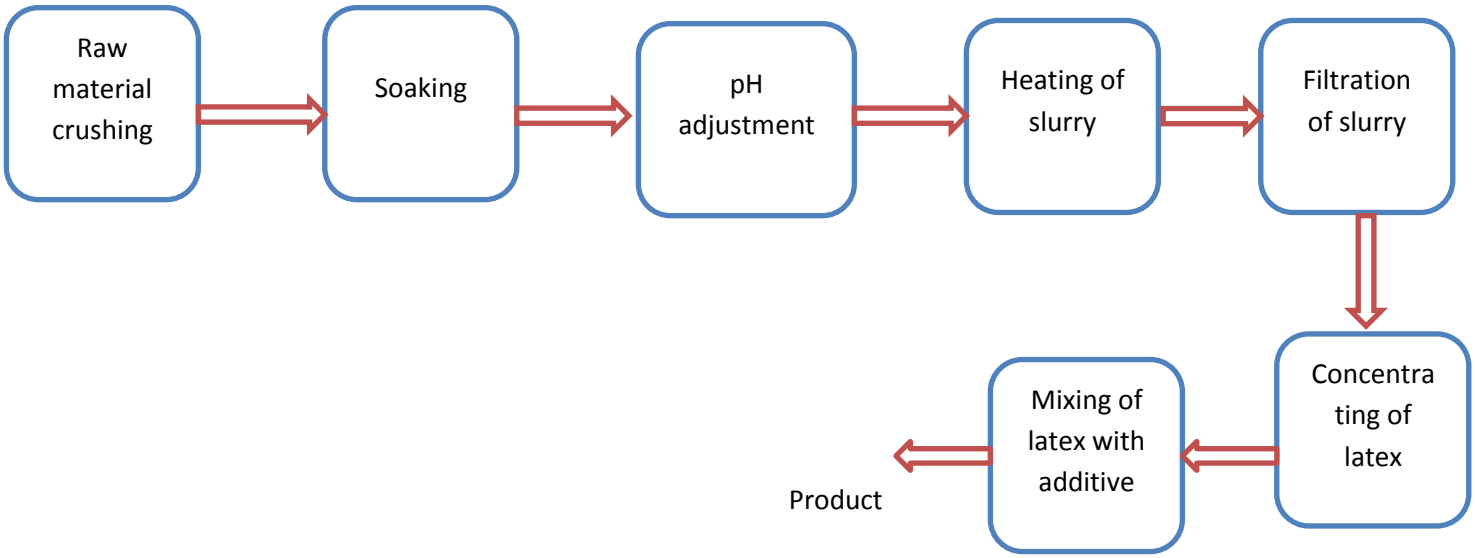


Figure 2. 2: Process flow diagram of bio-adhesive production from natural latex

2.9. Application of silica in adhesive production

Silica is the name given to a group of minerals composed of silicon and oxygen, the two most abundant elements in the earth's crust. Silica is found commonly in the crystalline state and rarely in an amorphous state. It is composed of one atom of silicon and two atoms of oxygen resulting in the chemical formula SiO_2.

Silica has long been used in adhesives and sealants to provide thixotropic and reinforcement. Powder silica through its structure of aggregated particles reduces the flow properties of a fluid. This property results in an increase in viscosity, reduced flow and leveling, and reduced sag. By replacing more traditional thickeners, such as cellulosic, associate thickeners and clays, viscosity can still be maintained, but with the added benefit of reinforcement. The same structure that controls viscosity response also sets up an internal network of inorganic particles that improve the bulk properties of the dried film(Camacho et al., 2018).

2.10. Modification of natural rubber latex using different fillers for bio-adhesive production

Natural latex which is a renewable resource can be used as adhesive due to its tacky nature. However, due its low viscosity and poor bonding strength relative to synthetic adhesives, it cannot be used directly as an adhesive. Therefore, in order to modify its property different fillers were used.

(Khan & Poh, 2010) investigated the effect of silica loading of using coumarone- indene as the tackifying resin on viscosity and shear strength. Silica loading was varied from 10–50 parts per hundred parts of rubber (phr), whereas the coumarone-indene concentration was fixed at 40 phr. Toluene was used as the solvent. Their result shows that viscosity of the adhesive increases gradually with increase of silica loading due to the concentration effect of the filler. Shear strength show maximum value at 40 phr silica.

In other study starch and ZnO were used to modify natural rubber latex. Cassava starch was modified chemically into hydrolyzed, dextrinized and oxidized starch and added to natural rubber blend which increased its adhesiveness. According to their result the reinforcer (ZnO) added to natural rubber increased its bonding strength on paper, wood and bottle label. The reinforced natural rubber adhesive and the three modified starch adhesive incorporated into rubber showed good bonding strength compared to natural rubber(Juliet et al., 2018).

2.11. Importance of Adhesives in Industry

Adhesives are everywhere in the highly technological manufacturing world today, and it is no surprise that adhesives are one of the most important substances used in industry(Frihart , 2005).

The main areas using industrial adhesives are the following:

1. Construction: floor tile and continuous flooring installation, ceramic tile installation, countertop lamination, manufacture of prefabricated beams and trusses, carpet adhesives, flooring underlayment adhesives, installation of prefinished panels, joint cements, drywall lamination adhesives and covering installations(Piekarczyk & Grec, 2012).

2. Consumer adhesives: model and hobby supplies, decorative films, school and stationery products.

3. Packaging: carton-side seam and closures, composite bonding of disposable products, bags, labels, cups, cigarette and filter manufacture, specialty packages (cosmetics, toiletries), composite containers and tubes(Ashley et al., 1995).

4. Tapes: packaging, industrial, surgical, masking, and consumer tapes.

5. Transportation: auto, truck and bus assemblies, weather strip and gasket bonding, aircraft and aerospace structural assemblies(Dinte & Sylvester, 2017).

6. Other rigid bonding: shake-proof fastening; furniture manufacture; manufacture of millwork, doors, and kitchen cabinets ; appliance assembly and trim attachment; TV, radio and electronics assembly and machinery manufacture and assembly.

7**.** Other non-rigid bonding: apparel laminates; shoe assembly, sports equipment, book binding, rug backing, flock cements, air and liquid filter manufacture, etc. (Petrie, 1999).

2**.12. Adhesive Bond Failure Modes**

There are two basic ways in which an adhesive bonded joint may fail:

- By fracture of the adhesive layer (cohesion failure).
- Interracially between the adhesive and one of the adherends (adhesion failure).

If the bond failure occurs between the adhesive layer and one of the adherends, it is called adhesive failure [Fig.2.3 (a)]. A failure in which the separation occurs in a manner that both adherent surfaces remain covered with the adhesive is called cohesive failure in the adhesive layer [Fig.2.3 (b) and (c)](Kinloch, 2014). Sometimes the adhesive bond is so strong that the failure occurs in one of the adherends away from the bond. This is called a cohesive failure in the adherent. Bond failures often involve more than one failure mode and are ascribed as a percentage to cohesive or adhesive failure. This percentage is calculated based on the fraction of the area of the contact surface that has failed cohesively or adhesively(Schofield, 2007).

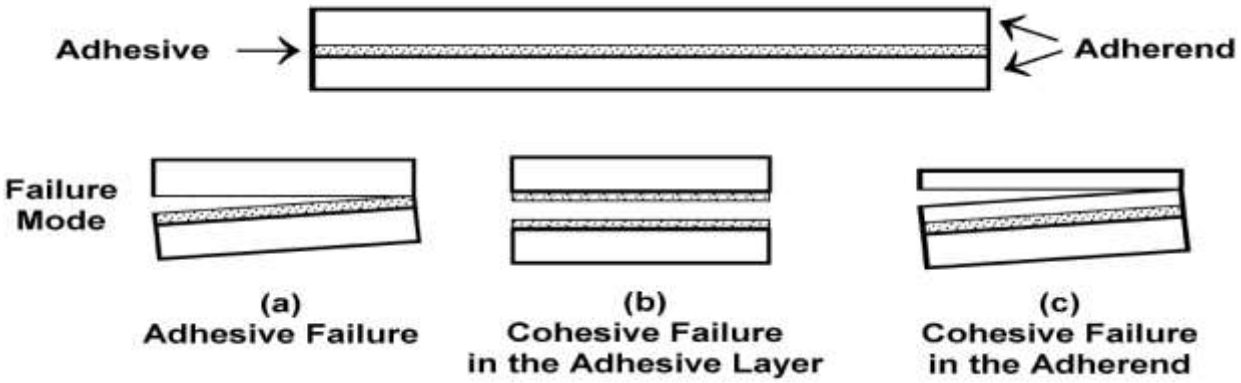


Figure 2.3: Schematics of adhesive bond failure modes

There are five most common reasons for joint failure.

1. **Inappropriate adhesive**: When selecting an adhesive, you have to consider (at a minimum) the substrates being joined, the environment it will be applied & used in, and how long it will have to be operational.

2. **Environmental Factors:** Even if the type of adhesive is appropriate for the application, an unplanned or unexpected change in the environment can cause the adhesive to fail. Heat, cold, moisture, and the introduction of chemicals are all potential culprits.
3. **Surface Preparation:** Careful consideration must be given to the cleanliness of the two substrates. Grease, oil, dust, or dirt is a few examples that can cause poor bonding(Söğütlü, 2017).
4. **Improper curing of the adhesive:** Adhesives require specific actions in order to cure. Some of those include time, air flow, and the amount of pressure used during application. If any or all of these requirements aren't followed, failure is possible.
5. **Lack of elasticity and strength:** Flexibility and adhesion levels are critical components to think about when selecting an adhesive. The specific type and amount of stress on the joint must be accounted for. Above are some examples of joint stress(Mark Swanson, 2015).

2.13. Testing of Adhesives

1. Bonding strength

Bonding strength is defined as the maximum force born by unit bonding area, which mainly depends on the own strength of adhesives (cohesive power) and the adhesive strength (adhesive power) between adherends and adhesives(Li & Ren, 2011). In other words, bonding strength refers to the ability of an adhesive to stick to a surface and bond two surfaces together. It is measured by assessing the maximum tensile stress needed to detach or unstick the adhesive .It is the most important of all the test parameters which shows how much your glue is strong. Minimum lap shear strength requirement as specified by ASTM D 4690 is 2.344MPa (Lambuth, 1977).

2. Viscosity

The measure of the viscosity of the glue solution is important. It shows how the glue flows. The test for viscosity, or fluidity, is based on the idea that the greater the tenacity of the glue, the greater will be its cohesiveness, and the less will be its flowing power. In other words, the higher will be its viscosity. The viscosity test is not entirely accurate in itself, but taken in connection with the bonding strength test it forms a very satisfactory basis for grading(Forest Products Laboratory, 1955). It has been adopted by several prominent Western manufactories as the sole means of determining glue strength. On itself, it is insufficient for this purpose, but, considered

in conjunction with bonding strength, it is of great value in grading the glue. It must not be inferred from this that the higher the viscosity, the stronger the glue. The operating viscosity limits of adhesives are very diverse ranging from 500 to 75,000 cps depending on the application(Lambuth, 1977).

3. Foam

Foam, in glue, arises from the incorporation of minute bubbles of air with the solution, when it is beaten rapidly. There may be present in the solution, substances which render the emulsion more or less permanent; or the emulsion may be only temporary, the foam receding and disappearing in a few moments. The same defects which fictitiously increase the viscosity, contribute materially to the foam in glue. Foam is undesirable in glues as it decreases strength by creating bubble. Foam of adhesives shall be not more than 2 .5 cm(Forest Products Laboratory, 1955).

4. Alkalinity and Acidity of Adhesive

It is a measurement used to specify how acidic or basic the adhesive solution is. The acidity or alkalinity shall be determined in terms of pH and must be within the range of 5.5 to 7.5(Forest Products Laboratory, 1955).

5. Thermal Stability

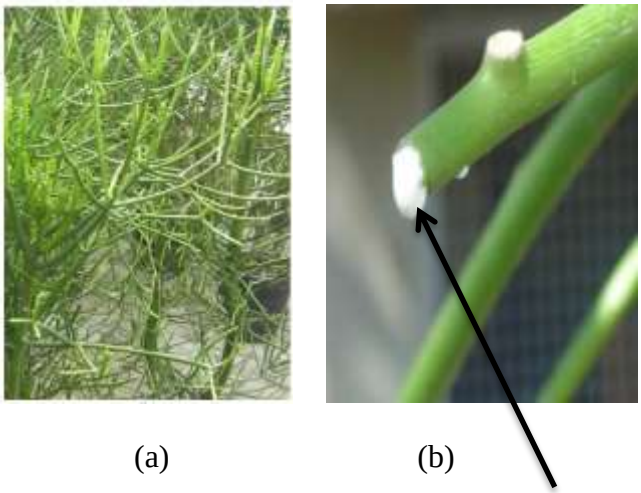
The ability of an adhesive to maintain high bond strength even across wide variations of temperature is important. This is because the bonded wood, during use, will definitely be exposed to fluctuation in environmental conditions which may affect the coefficient of thermal expansion of the adherends as well as the adhesive(Okemini & Dilim, 2015).

2.14. Introduction to Euphorbia Tirucalli Tree

2.14.1 Plant Description

Euphorbia tirucalli(Kinchib) belongs to the genus *Euphorbia*, one of the 8,000 species within family Euphorbiaceae(Gupta et al., 2013). It is a shrub or a small tree that can grow up to 7 – 12 m high. It is present in most (sub) tropical areas with a propensity for semi-arid areas. Its pencil-like branches have inspired its vernacular name, the pencil-tree. *E. tirucalli* is generally evergreen since its stems and branches remain green for a number of years; eventually the main trunk and older branches get a brown bark appearance, however. The tree is rarely fed on by herbivores, nor has it many natural enemies. It bears white poisonous latex, which accounts for its low herbivore pressure and medicinal features. Most of these features are shared by a number

of other, so-called coralliform euphorbias occurring in its center of origin, e.g. *E. intisy*, or *E. fiha* (or as it is known by its synonymous *E. plagiantha*). However, *E. tirucalli* is rather unique because it can grow very fast, and produce a lot of biomass even under very marginal soil and extreme climatic conditions(Panchal, 2017). This can at least partly be explained by its rather unique combination of CAM stems and its leaves which allow it to assimilate CO_2 during 24 h per day. And apparently it does this well than some of its closest relatives in the sub tribe Euphorbiinae. The species is easily vegetative propagated through stem cuttings. It quickly spread from Africa into the other continents which have subtropical to tropical climates. The species epithet is derived from tirucalli, a local name given to the plant on the Malabar Coast of India. There is a hypothesis that the plant came to that part of the world with Portuguese travelers who had traveled from Portugal to East Africa and then further to India(Mwine & Damme, 2011).



(a) (b)

Figure 2. 4: a) Euphorbia tirucalli tree b) latex

2.14.2 Ecology and Geographical Distribution of Euphorbia Tirucalli

E. tirucalli is probably the best known and most widespread of all trees Euphorbia species (Gildenhuys, 2006). According to the same author, the plant's origin is not known but Van Damme (1989) and Schmelzer and Gurib-Fakim (2008) believe it originated from tropical East Africa and it is endemic in countries such as Angola, Eritrea, Ethiopia, Kenya, Malawi, Mauritius, Rwanda, Senegal, Sudan, Tanzania, Uganda and Zanzibar. The tree is currently widely distributed in southern Europe, Asia and the Americas having been steadily introduced due to its ornamental and medicinal features. *E. tirucalli* can survive in a wide range of habitats.

Van Damme (2001) states that the plant can grow under conditions in which most crops and other trees cannot grow. They include: tropical arid areas with low rainfall, on poor eroded soils, saline soils and high altitudes up to 2000 m but cannot survive frost. Its distribution is therefore limited by low temperatures(Mwine & Damme, 2011).

2.14.3. Latex and Its Chemical Composition

E. tirucalli contains white milky latex in all its parts, including the roots. Latex is sticky and a stable dispersion (emulsion) of polymer micro particles in an aqueous medium. It is found in nature, but synthetic latexes can be made by polymerizing a monomer such as styrene that has been emulsified with surfactants. Latex as found in nature is a milky fluid found in 10% of all flowering plants (angiosperms)(Agrawal & d Kotaro Konno, 2009). It is a complex emulsion consisting of proteins, alkaloids, starches, sugars, oils, tannins, resins, and gums that coagulate on exposure to air. It is usually exuded after tissue injury. In most plants, latex is white, but some have yellow, orange, or scarlet latex. Since the 17th century, latex has been used as a term for the fluid substance in plants. It serves mainly as defense against herbivorous insects. The latex contains about 28% solid matter whose composition is: 21 to 27% water-soluble substances, 59 to 63% resin-soluble substances and 12 to 14% rubber-like substances(Mwine & Damme, 2011).

3. Materials and Methods

The experimental work was carried out in the laboratory of Addis Ababa University, Addis Ababa Institute of Technology specifically at the School of Chemical and Bio Engineering and Defense Engineering College (Debrezeit).

3.1. Materials

3.1.1. Chemicals

All of the chemicals used in this experiment were purchased from different chemical shops in Addis Ababa. Ammonia and Acetic acid were purchased from Atomic chemical shop and toluene and silica were bought from Yeshadam trading. List of chemicals used and their purposes are shown below.

- Ammonia solution(25% conc) - to prevent latex from coagulation by adjusting pH
- Acetic acid(99.8% conc) - to adjust pH of latex
- Toluene(99.5% purity) - as plasticizer and solvent for dissolving rubber particles with silica
- Silica powder(99% purity) - to improve adhesive strength and viscosity (reinforcement agent)
- Distilled water - solvent for extraction of latex

3.1.2. Equipment

The equipments used to conduct the experiment were:

- Universal tester machine (DIN 50106)- to measure lap shear strength of the adhesive via joined woods
- pH meter(JENWAY 3505) – to measure pH of latex
- Vibrio viscometer - to measure viscosity
- Oven - to dry samples
- FTIR-Spectrophotometer - to identify functional groups available in latex
- Electrical Onion grinder – to crush raw material
- Vacuum filter - to separate liquid latex from bagasse
- Rotary evaporator - to remove water from latex/to concentrate latex
- Electronic balance - to measure mass of different materials
- Pycnometer - to measure density

- Refrigerator - to preserve harvested ET branches
- Beaker – as a main equipment to prepare the adhesive
- Sand paper – to make the surface of wood specimen rougher and to remove dust
- Ruler – to measure height of foam of adhesive

3.2. Methods

3.2.1. Raw Material Collection, Transportation and Storage

Euphorbia tirucalli branches were harvested from Shire Enadasilse, Tigray, Ethiopia by cutting them using knife in size of 8cm. Then, the harvested plant materials were transported to Addis Ababa institute of technology school of Chemical and Bio Engineering laboratory by coating them using wet cloth with in one day. Finally, the collected branches were washed using water to remove dusts and stored in refrigerator for three day to prevent from drying until the experiment started out.

3.2.2. Extraction and Characterization of Latex

3.2.2.1. Latex Extraction

Latex extraction was carried out according to the method of Cornish with minor modifications (Cornish et al., 1999). After harvesting and preserving, 100g branch of *Euphorbia tirucalli* was cut into small pieces using electrical onion grinder for 2 minutes. After this, 200ml of distilled water was added to the grinder to extract the liquid latex from the crushed material. Then, the mixture transferred into 1000ml beaker and its pH was measured and it is found to be 6.34 then the pH adjusted using ammonia solution to be 11 in order to it prevent from coagulation. The mixed material is allowed to heat in a hot plate at 35^0C for 45 minutes to prevent sticking of the latex with the bagasse. Next to this, the slurry was transferred onto a 1 mm mesh porcelain Buchner funnel without filter paper, and the homogenate (mixture of liquid latex and distilled water) was filtered through by slow vacuum filter suction and bagasse left on the funnel as a cake. The surface of the slurry was made even and pressed slightly with a tablespoon for efficient filtration. The remaining ground branches (bagasse) were returned to the extraction unit to extract the retained latex. The slurry was again transferred onto the Buchner funnel and the homogenate filtered. The homogenate from both filtrations were concentrated to remove the added water using vacuum rotary evaporator operated at – 0.5bar and 60^0C. Finally, the collected

latex was quantified. The overall extraction of experimental procedure is shown diagrammatically below in Figure 3.1.

The percentage yield of latex in wet basis was calculated by:

$$\text{Percentage of latex yield (wet basis)} = \frac{\text{Mass of liqiud latex obtained}}{\text{Mass of euphorbia triculli used}} \times 100 \ldots\ldots\ldots \text{(3.1)}$$

a) Branches of ET b) Crushed ET c) Extraction of latex d) Heating of mixture

e) Vacuum filtraion f) Rotary evaporation g) Concentrated latex

Figure 3.1: Experimental procedure for latex extraction from Euphorbia tirucalli tree branch

3.2.2.2. Characterization of latex

It is necessary to determine the physic-chemical properties of the raw material before conducting the main experiment. Thus, the characterization includes determination of dynamic viscosity, density, pH, total solid content and FTIR analysis of the latex. For raw material characterization latex was extracted by mechanical tapping which is free from ammonia solution. The methods applied to characterize the properties of latex are briefly discussed below.

A. Determination of Dynamic Viscosity (μ)

The dynamic viscosity of latex was determined using Digital Vibrio viscometer. The dynamic viscosity was determined at 20°C (room temperature) according ASTM D 1084 procedure. 45 ml

of sample was placed into the holder. Then, the Vibrio viscometer tips were inserted to the sample to measure the dynamic viscosity and the reading was taken from the controller display. It was done in triplicates to minimize error.

B. Determination of Total Solid Content (TSC)

The total solid content of the latex was determined using ISO 123 method. This is determined by loss of volatile components. Three samples of latex with mass of 10, 15 and 20gm were taken and filled into a known weight of crucible. Then, the crucibles with their latex were placed in an electric hot air oven maintained at 104^0C and the weight of each sample was measured every four hours. After 4 h, it is allowed to cool in dissector then measured the amount of latex and returned to the oven at the same temperature as in the previous step. The procedure was repeated until a constant weight was obtained and the percentage total solid content of the latex was determined.

Then, percentage of total solid content as mass fraction of the initial latex was determined using equation 3.2.

$$\text{Total solid content}(\%) = \frac{M_1}{M_0} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Where, M_0 is mass of latex before drying

M_1 is mass of latex after drying

C. Determination of pH value

The pH of latex was measured according to ASTM E70 procedure.30ml of the fresh sample was taken and putted in to a clean dry 100 ml beaker. Before staring measuring the pH, the pH electrode was first calibrated .Then, to make a pH measurement, the electrode was immersed into the sample solution until a steady reading was observed. Finally, the reading was taken from the display.

D. Determination of Density

The density was determined according to ASTM D1076 method using pycnometer. A clean and dry 100ml pycnometer was used. Then, the free pycnometer was weighed to give a mass of W_1 and next latex was poured into the pycnometer apparatus. The bottle was again weighed to give a mass W_2 which is the weight of pycnometer with latex and the difference in weight between W_1 and W_2 gave the weight of latex. Finally, the density of the latex was calculated according to equation 3.3.

Density of latex (g/ml) = $\frac{W_2 - W_1}{Vp}$ …….3.3

Where W_1 weight of free pycnometer, W_2 sum of weight of pycnometer and latex and V_p is volume of pycnometer used

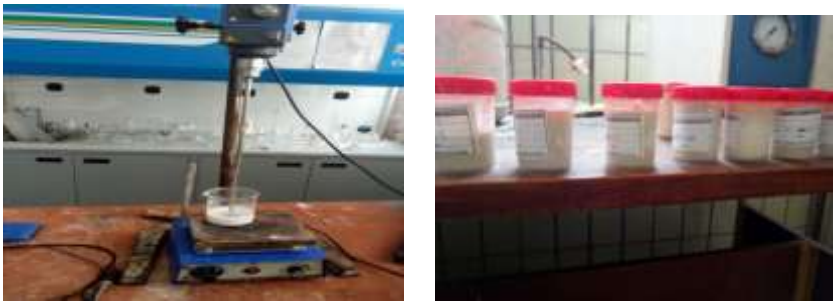
E. FTIR Spectroscopy for latex Characterization

Initially, liquid latex free from ammonia solution was allowed to dry for 24 hours under the sun. Then, 1 mg of the dried latex sample was taken for FTIR determination. Finally, the Sample was analyzed using FTIR (PerkinElmer) in the 400 to 4000 cm^{-1} wave length range. This experiment was done in Addis Ababa University, college of natural science department of chemistry.

3.2.3. Production and Characterization of Bio-Adhesive

3.2.3.1. Production of Bio-Adhesive

The production of bio-adhesive was carried out in a beaker equipped with mechanical stirrer as shown in Figure 3.2. The process used to prepare adhesive was mixing of latex with silica. Initially, latex at different concentration was prepared in such way that: high ammonia liquid latex was allowed to dry in a sun for 24 hr and then the dried latex was shredded using a spoon to facilitate dissolution. Then, the solid latex mixed with a different amount of distilled water to prepare the required different concentration (30, 40 and 50%). After preparation of different concentrations of latex solution, a specified amount of 10ml toluene was added to the beaker. And next, lumped silica was crushed into powder form using a mortar and pestle before incorporation into the latex solution. Then, the powder silica was added at different levels according to the design presented in Table 3.1 into the latex solution and the agitator was adjusted at 300rpm to mix homogenously. 50gm of adhesive was prepared in each run.



(a) (b)

Figure 3. 2: a) Experimental setup for preparation of bio-adhesive b) product (bio-adhesive)

Mixing ratio of components required for preparing the bio- adhesive is present below.

Table 3. 1: Typical formulation used for the production of bio adhesive

Ingredient	**Phr(parts per hundred rubber)**	
Latex	100	(Khan & Poh, 2010)
Silica	10-30	

Detail calculation of each material requirement and conversion of Phr into wt.% are presented in appendix C. The overall process block diagram for preparation of bio-adhesive from *Euphorbia tirucalli* latex is shown below in figure 3.3.

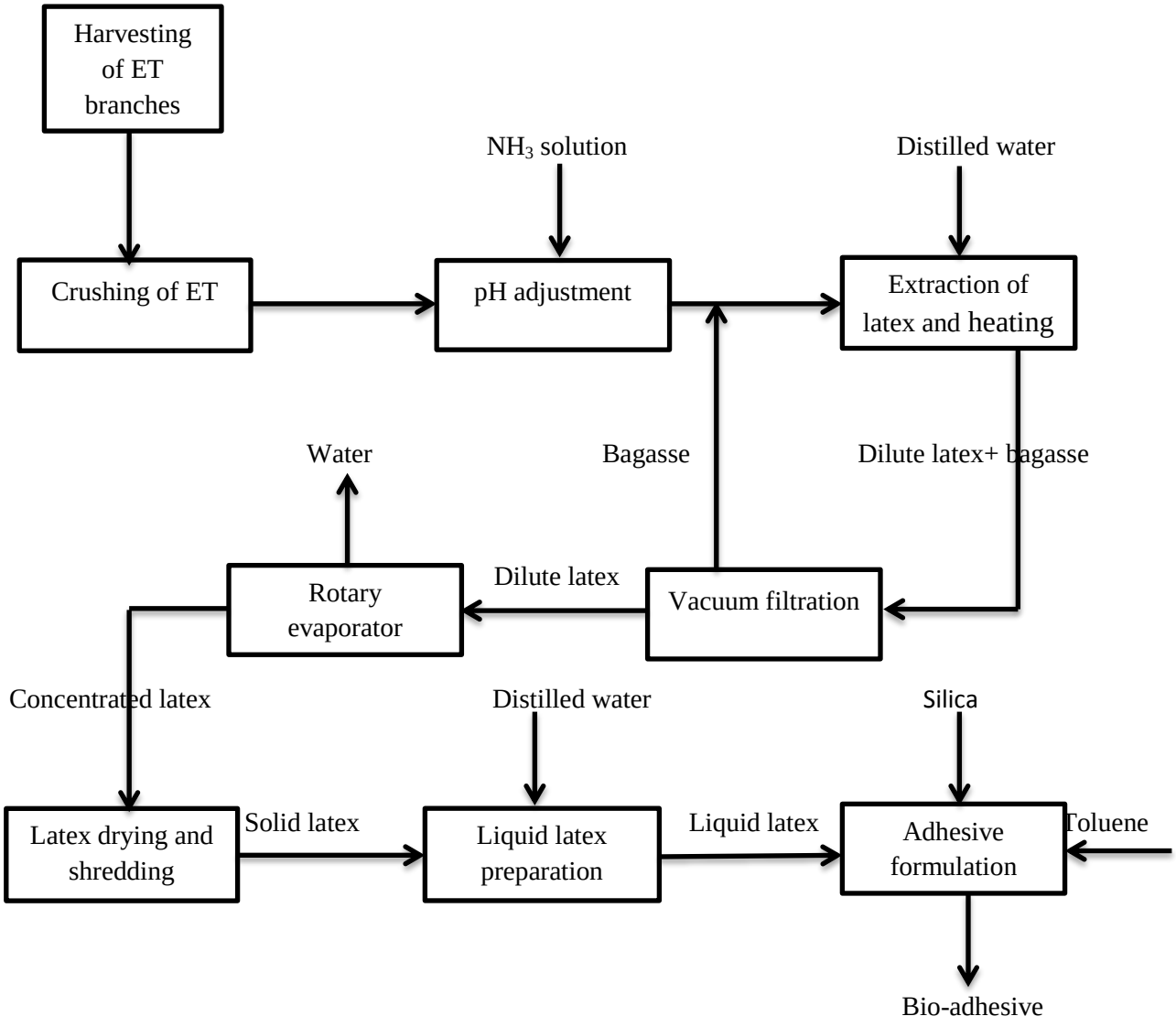


Figure 3.3: Block diagram for preparation of bio-adhesive from Euphorbia tirucalli latex

3.2.3.2. Characterization of Bio-Adhesive

It is necessary to characterize the produced bio-adhesive to check whether it met the requirements of adhesive standards. Thus, the adhesive was characterized using different properties. It consists the determination of viscosity, lap shear strength, pH, thermal stability test, and foam length. In this study viscosity and lap shear strength were taken as responses. The remaining properties were determined by taking sample adhesive from the experimental run which gave maximum bonding strength.

1. Viscosity Test

The viscosity of the bio-adhesive was determined using digital vibrio viscometer in reaction Engineering laboratory, AAiT School of chemical and Bio Engineering. The viscosity was determined at 20°C (room temperature) according to ASTM D1084 procedure. 45 ml of sample was placed into the holder. Then, the vibrio viscometer tips were inserted to the sample to measure the dynamic viscosity and the reading was taken from the controller display. The same procedure was applied for each run to determine the viscosity. Diagrammatically it is shown below in Figure 3.4.

Figure 3. 4: Experimental setup for viscosity measurement

2. Bonding Strength Test

Bonding strength of the prepared bio-adhesive was evaluated by measuring the lap shear strength according to the procedures of ASTM D 903-49. Medium density fiber wood was used as the adherend for adhesive strength tests throughout this study. Wood specimens with dimensions of 25mm (Width), 100mm (Length) and 4mm (thickness) were cut and then coated with aluminum foil to prevent them from dust. These wood pieces were polished using sand paper, and then a

constant amount of adhesive slurry (30 mg/cm^2) was applied on to 3cm by 2.5 cm area of one end of the wood pieces using brush. Then, the glued woods were allowed to dry for 15 min at room temperature before assembly and next bonded as a lap joint, by applying a load of about l kg for 24 hr. Before testing, the lap joints were conditioned for 7 days at room temperature to attain its strength. Finally, tensile strength (N) of the assembly was measured by a shear strength test using universal tester machine (DIN 50106) at crosshead speed of 1 mm/min for each joints. Then, readings were taken from computer display .This experiment was done in defense engineering college (Debrezeit) material testing laboratory.

Upon analysis of specimens using the universal testing machine, the value of lap shear strength was calculated by using equation 3.4.

$$\text{Lap shear strength (N/m}^2\text{)} = \frac{F}{A} \quad \ldots\ldots 3.4$$

Where, F is tensile force required to detach the joined woods

A is the lap (glued) area, A = a*b

Where, a is length of the glued wood specimen (2.5cm) and b is width of the glued wood specimen (3cm).

(a) (b)

Figure 3.5: a) lap joint of woods b) Experimental setup for lap shear strength test using UTM

3. Thermal Stability Test

The thermal stability of the prepared bio-adhesive was determined according EN 14257:2006 procedures to find out the degree to which its bond strength can withstand temperature variations. First, three pairs of bonded wood samples were prepared and all of the pairs were glued using the adhesive which gives maximum bonding strength selected from the experimental

run(Run#15). Then, two pairs were kept in an electric oven the one at temperature of 50^0C and the other at 100^0C for 2 hours while the third pair was kept in a refrigerator at 0^0C for 2 hours. Finally, the lap shear strength of each pair was measured according to the procedure described in section 3.2.3.2. Percentage of retention was calculated based on equation 3.5.

$$\text{Percentage of retention (\%)} = \frac{\text{Lap shear strength at specified temperature}}{\text{Lap shear strength at } 20^0\text{c}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

Lap shear strength at 20^0C is the maximum lap shear strength obtained.

4. Foam

Foam of the prepared bio-adhesive was determined according the following procedure. 30 gm of the adhesive solution was placed in 500ml beaker container and agitated with universal stirrer at 1500 rpm for 1min. Then, allowed to stand at room temperature for 10 minutes. Finally, the height of the foam was measured using ruler(Forest Products Laboratory, 1955).

5. Determination of pH of Adhesive

The pH of adhesive was measured according to ASTM D1583 procedure.25gm of the sample was taken and putted in to a clean dry 100 ml beaker. Before staring measuring the pH, the pH electrode was calibrated. Then, to make a pH measurement, the electrode was immersed into the sample solution until a steady reading was observed. Finally, the reading was taken from the display.

3.3. Experimental Design

3.3.1. Full Factorial design

Factorial design was used to investigate the effect of each factor. In a factorial experiment all the possible combinations factor levels would be tested and it would be possible to determine the effect of individual factors and to assess the effect of change of two or more variable at a time (Zivorad , 2004).

The analysis was performed by utilizing Design Expert software using general factorial design method. This method of experiment design helps to differentiate the significance of the main and the interaction factors. The soft-ware also used to develop the mathematical model that will describe the effect of main and interaction factors on the Response. In this study, the experimental design involved in studying three independent variables (factor) with three levels each. Latex concentration, silica load and mixing time were selected as independent variables to see their influence on the quality of the product.

Bonding strength (lap shear strength) and viscosity were selected as responses in this study. Design Expert® version11.1.0.1 was used for regression analysis of the data and to estimate the coefficient of the regression equation. According to the design summary of the software 27 runs were sufficient to provide information about the effect factors on the responses. The equations were validate by the statistical test called ANOVA with the significance of each term in the equation is to estimate the goodness of fit in each case. Levels of each factor are tabulated in the following table below. Levels of the factors were set based on review of different literatures as shown in Table 3.2.

Table 3.2: Coded and actual levels of each factor

Factors	**Unit**	**Coded symbol**	**Level 1 (-1)**	**Level 2 (0)**	**Level 3 (1)**	**Reference**
Latex concentration	%(w/w)	A	30	40	50	
Silica load	phr	B	10	20	30	(Khan& Poh, 2010)
Mixing time	minute	C	15	30	45	(Bressler, 2016)

4. Results and Discussion

4.1. Extraction and Characterization of Latex

4.1.1. Latex Extraction

From the experimental work done according to Cornish method discussed in section 3.2.2.2., the following results are obtained. Based on the obtained results, the percentage latex yield was calculated by using equation 3.1.

Mass of liquid latex obtained = 21.6gm

Initial mass of plant material used = 100gm

Percentage of latex yield (wet basis) $= \frac{\text{Mass of liqiud latex obtained}}{\text{Intial mass of plant material used}} \times 100$

$$= \frac{21.6}{100} \times 100 = 21.6\%$$

From this result, it can be concluded euphorbia tirucalli plant can be used as a source of latex for bio-adhesive production as it gives good yield.

4.1.2. Characterization of Latex

A. Determination of Total solid content (TSC)

The total solid content of latex was determined using the methods described in section 3.2.2.2. The calculations of total solid content of the samples were determined using equation 3.2 and the obtained results are summarized in Table 4.1.

Table 4. 1: Total solid content of latex

	Sample mass in grams		
	Sample 1	Sample 2	Sample 3
Initial mass	15	20	10
Mass after 4hrs.	11	14.4	7.5
Mass after 8 hrs.	9.6	13.4	6.3
Mass after 12 hrs.	4.7	6.7	3
Mass after 16hrs.	4.6	6.5	2.9
Total solid content after 16 hrs. (%)	30.66	32.5	29

The total solid content of the three latex samples having mass of 15, 20 and 10grams were 30.66, 32.5 and 29.0 percent respectively. The mean of the three samples gives 30.7±1.75%. The result obtained is almost in agreement to that of the literature since (Kapaczewski , 1947) who reported a total solid content of 28%.From this finding ,it can be concluded latex has low viscosity due to low total solid content. Therefore, it needs modification to it use as an adhesive.

B. Determination of pH value of latex

The pH value of latex was determined by pH electrode as measuring experimental procedure was stated in section 3.2.2.2. The pH value of latex was triplicated and the results obtained are summarized in Table 4.2 below.

Table 4. 2: pH value of latex

Run	pH value	Mean
1	6.34	6.33±0.015
2	6.35	
3	6.32	

The result shows that the natural extracted latex is slightly neutral. At acidic or neutral condition, latex will coagulate due to the growth of bacteria. Therefore, to prevent this ammonia solution should be added to make it basic solution.

C. Determination of Dynamic Viscosity

Vibrio viscometer was used to determine the dynamic viscosity of the latex according to method discussed in section (ASTM D1084).An average of 14.7mPa.s dynamic viscosity at a temperature of 20^0C was obtained. The determination of latex viscosity was triplicated and the results obtained are summarized in Table 4.3 below.

Table 4.3: Viscosity of latex

Run	Viscosity(mPa.s)	Mean
1	14.9	14.7±0.2
2	14.5	
3	14.7	

Viscosity indicates the flow property of any liquid. The result obtained indicated that the naturally occurred latex is less viscous .Therefore; it cannot be used directly as adhesive. It needs modification to use it as an adhesive.

D. Determination of Density

Pycnometer was method was used to determine the density of latex as the detail experimental procedures were stated in section 3.2.2.2. Based on the obtained results, density of latex was calculated by using equation 3.3.

The results obtained from the experimental work are:

Weight of free pycnometer at 20^0C (W_1) = 40.3gm

Sum of weight of pycnometer and latex at 20^0C (W_2) = 136.2gm

Volume of pycnometer (V_p) = 100ml (known)

Density of latex (g/ml) = $\frac{W_2 - W_1}{Vp}$

$$= \frac{136.2-40.3}{100} = \frac{95.9gm}{100ml} = 0.959\text{gm/ml}$$

From this result, it can be concluded that liquid latex is dense.

E. FTIR Spectroscopy Analysis of Latex

Fourier Transform Infrared Spectrophotometer (FTIR) is the most powerful tool for identifying the types of chemical bonds (functional groups) present in compounds. The wavelength of light absorbed is characteristic of the chemical bond as can be seen in the annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. In this case FTIR was done to determine which component of the latex is responsible for the tacky nature of the latex. From the results shown in Figure 4.1, the latex from Euphorbia tirucalli shows the FTIR bands characteristic of cis-1,4 polyisoprene at 1637 and 834 cm^{-1} which are due to C=C stretching and C-H bending respectively(Dinsmore & Smith, 1948).cis-1,4 polyisoprene (rubber) is the most common polymer available in plants latex which has tacky nature(Kang et al., 2014). Latex specific bands were also attributed to some non-isoprene compounds such as: Amine (3372 cm^{-1}), carboxyl (2928 cm^{-1}), -CH_2 (1447 cm^{-1}), and ester (1243 cm^{-1})(Liengprayoon & Vaysse, 2015). Functional groups of amine confirmed that the

existences of proteins in the latex. Proteins also contribute for tacky nature of the latex. On the other hand, ester and carboxyl groups are mostly present on lipid molecules.

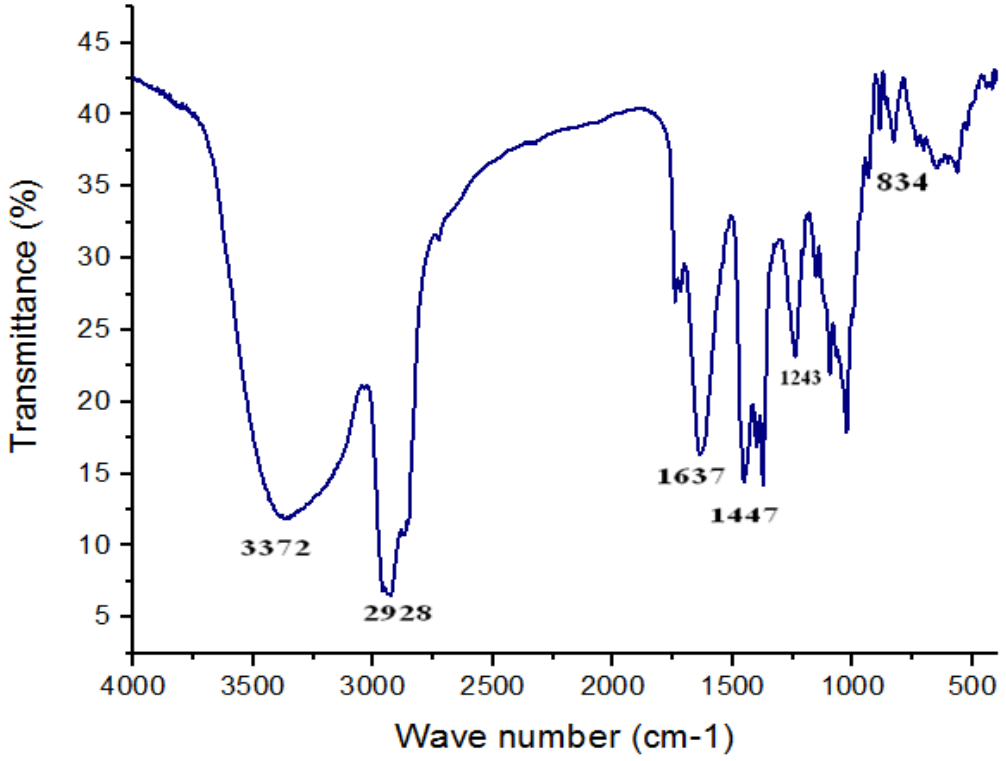


Figure 4.1: FT-IR spectra of euphorbia tirucalli latex

4.2. Experimental Results of Responses

The viscosities and lap shear strengths obtained from each run are given in the following table.

Table 4.4: Experimental results of responses

	Factor 1	Factor 2	Factor 3	Response 1	Response 2
Run	**A: Latex concentration (%)**	**B:Silica load (phr)**	**C:Mixing time (min)**	**Viscosity (mPa.s)**	**Lap shear strength (MPa)**
8	30	10	15	398	1.2
11	40	10	15	469	1.6
27	50	10	15	539.6	2.1
5	30	20	15	439.3	1.9
1	40	20	15	505	2.4
15	50	20	15	567.5	2.8
24	30	30	15	476	1.4
4	40	30	15	537	2
23	50	30	15	597	2.3
19	30	10	30	397.3	1.8
17	40	10	30	468	2.1
3	50	10	30	538	2.6
10	30	20	30	439	2.4
16	40	20	30	503	3
7	50	20	30	567.2	3.28
26	30	30	30	476.6	1.7
14	40	30	30	537.8	2.6
12	50	30	30	594	2.9
20	30	10	45	399	1.8
22	40	10	45	467.5	2.1
21	50	10	45	540	2.6
9	30	20	45	439.6	2.4
18	40	20	45	504.7	3
6	50	20	45	564	3.26
13	30	30	45	478	1.7
25	40	30	45	537.2	2.6
2	50	30	45	597.4	2.9
Pure latex	30	---	---		0.88

As presented in Table 4.4 maximum lap shear strength (3.28MPa) with a corresponding viscosity of 567.2mPa.s was obtained when 50% latex concentration mixed with 20phr silica for 30 minutes (run #15). This may be due to good interaction between silica and latex. Minimum lap shear strength (1.2MPa) with a corresponding viscosity of 398mPa.s was observed when 30% latex concentration mixed with 10phr silica for 15 minutes (run #1). This may be due to low

amount silica and insufficient mixing between silica and latex. Bonding strength of pure latex was also done to check its strength without addition of silica and it was found that lap shear strength of 0.88MPa as shown in table 4.4.

4.3. Statistical Analysis of the Experimental Results

Data obtained from the experiment were analyzed with the help of design expert software. ANOVA was conducted for fitting the model and to examine statistical significance of the model terms for each response. The analysis was carried out to investigate how the viscosity and lap shear strength of the adhesive were affected by the latex concentration, silica load and mixing time in the adhesive. The statistical analysis of data and three-dimensional plotting were performed using the software. The adequacies of the models were determined using model analysis, R^2, Adjusted R^2, Precision R^2, Adjusted precision and F-test analysis as outlined.

4.3.1. Data Analysis for Viscosity

As shown from the ANOVA Table 4.5, the data was tested by different values. By entering the data obtained from the experimental runs, the resulting ANOVA table for 2FI model for viscosity was displayed. The adequacy of the developed models was tested at 95 % confidence interval and the results of the linear response surface model fitting in the form of ANOVA were given in Table 4.5. The ANOVA results (Table 4.5) indicated that the model F-value of 8085.77 implies that the model is significant. In other words, it implies that most of the variation in the response could be explained by the regression equation and that the model was significant. Furthermore, the probability $p<0.0001$ also suggested that the model was significant. There is only a 0.01% chance that a Model F-Value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B and AB, are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. Viscosity is significantly affected by linear terms of the parameters (latex concentration and silica load) and the linear interaction between latex concentration and silica load at ($p < 0.0001$).

Table 4. 5: Analysis of variance (ANOVA) for viscosity

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	96492.72	6	16082.12	8085.77	<0.0001	significant
A-Latex concentration	75091.04	1	75091.04	37754.31	<0.0001	
B-Silica load	21033.01	1	21033.01	10574.98	<0.0001	
C-Mixing time	0.1606	1	0.1606	0.0807	0.7792	
AB	365.20	1	365.20	183.62	<0.0001	
AC	2.34	1	2.34	1.18	0.2909	
BC	0.9633	1	0.9633	0.4843	0.4945	
Residual	39.78	20	1.99			
Cor Total	96532.49	26				

4.3.1.1. Model adequacy checking

The "Pred R-Squared" of 0.9992 is in reasonable agreement with the "Adj R-Squared" of 0.9995."Adeq Precision" Measures the signal to noise ratio. A ratio greater than 4 is desirable. For this case the ratio of 275.5386 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.6: Model adequacy measures for viscosity

Std. Dev.	1.41	**R^2**	0.9996
Mean	502.81	**Adjusted R^2**	0.9995
C.V. %	0.2805	**Predicted R^2**	0.9992
		Adeq Precision	275.5386

The regression coefficient (R^2) quantitatively evaluates the correlation between the experimental data and the predicted responses. Results of R^2= 0.9996 and Adj-R^2= 0.9995 obtained explicates that the predicted values were found to be in good agreement with experimental values. Since the R^2 value is closer to 1.0 it indicates that the regression line perfectly fits the data. Similar to that in this investigation, R^2 obtained was 0.9996, which was close to 1. Results imply that the predicted values were found to be in good agreement with experimental values (R^2= 0.9996 and Adj-R^2= 0.9995). The model's goodness of fit was checked by regression coefficient (R^2). In this

case, the value of the coefficient (R^2 = 0.9996) from table 4.6 indicated that only 0.04 % of the total variance was not explained by the developed regression model. The obtained R^2 values suggest good adjustments to the experimental results. The adjusted determination coefficient (Adj-R^2= 0.9995) was also satisfactory for confirming the significance of the model. Pred R-Squared indicating that the model will probably explain a high percentage (about 99.92%) of the variability in new data.

4.3.1.2. Model Equation for viscosity

The model equations, which relate the response viscosity of adhesive to the independent variables in terms of the coded and actual factors are given below.

Final Equation in Terms of Coded Factors:

Viscosity=+502.81* +64.59* A+34.18* B-0.0944* C-5.52*AB-0.4417*AC+0.2833*BC

Final Equation in Terms of Actual Factors:

Viscosity=+129.74815* +7.65056* Latex concentration+5.56833*Silica load+0.073704*Mixing time-0.055167*Latex concentration*Silica load-0.002944*Latex concentration*Mixing time+0.001889*Silica load * Mixing time

4.3.1.3. Diagnostics Test

The normal probability plot is a graphical method used to check whether the error occurred during the experimental analysis is normally distributed throughout the experiment. The normality assumption of analysis of variance is valid if all the data points lie along the straight line of normality plot. As shown in Figure 4.2 below, the normal probability plot indicates the residuals following by the normal % probability distribution, in the case of this experimental data the points in the plots shows fitted to the straight line in the figure, this shows that the quadratic polynomial model satisfies the assumptions analysis of variance (ANOVA) i.e. the error distribution is approximately normal.

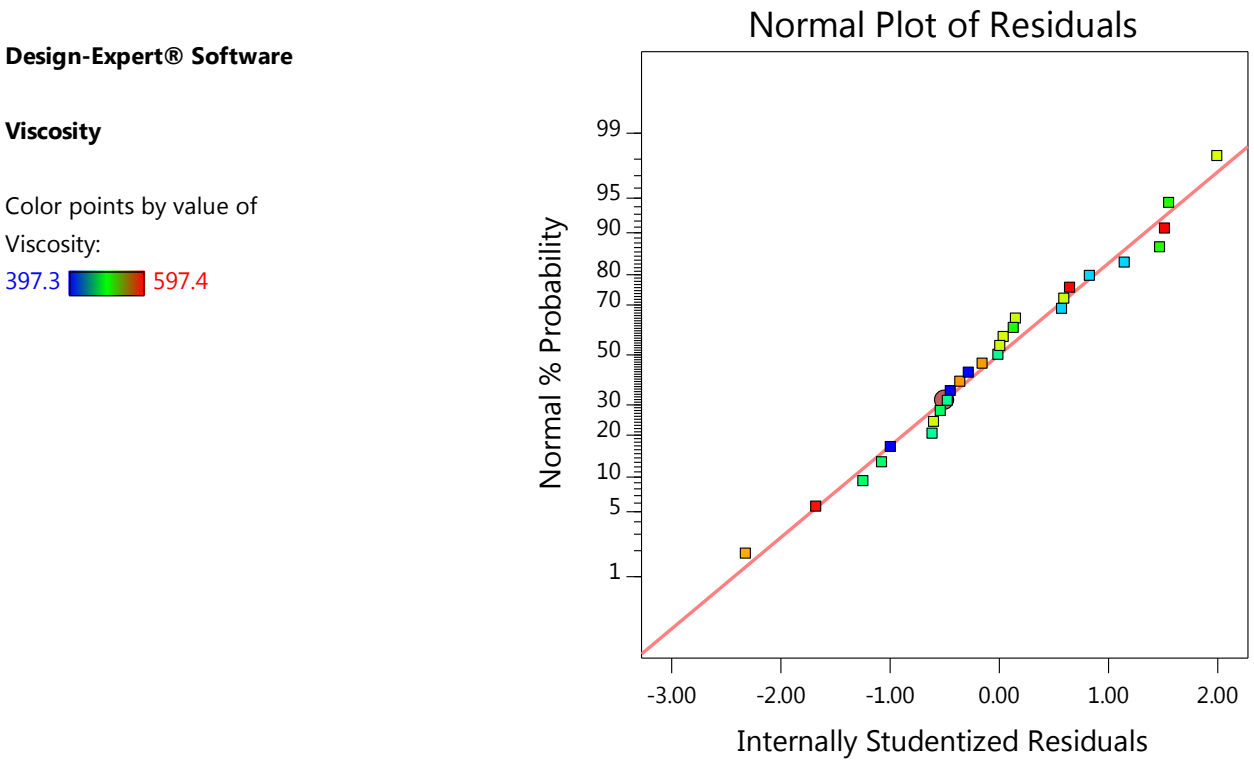


Figure 4. 2: Normal probability plot of residuals for viscosity

4.3.2. Data Analysis for Bonding Strength (Lap Shear Strength)

The same procedure has been applied on this response as that of viscosity. By entering the data obtained from the experimental runs, the resulting ANOVA table for the quadratic model for lap shear strength was displayed. The adequacy of the developed models was tested at 95 % confidence interval and the results of the linear and quadratic order response surface model fitting in the form of ANOVA was given in Table 4.7. The ANOVA results (table 4.7) indicated that the model F-value of 92.45 implies that the model is significant. In other words, it implies that most of the variation in the response could be explained by the regression equation and that the model was significant. Furthermore, the probability $p<0.0001$ also suggested that the model was significant. There is only a 0.01% chance that a Model F-Value this large could occur due to noise. P- values less than 0.05 indicate model terms are significant. In this case A, B, C, AB, A^2, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. Lap shear strength was affected by linear terms of the parameters (latex concentration, silica load and mixing time) and quadratic of the latex concentration, silica load

and mixing time at ($p < 0.0001$); the interaction between latex concentration and silica load with effect of at ($p<0.005$).

Table4. 7: Analysis of variance (ANOVA) for lap shear strength

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8.19	9	0.9099	92.45	< 0.0001	significant
A-Latex concentration	3.98	1	3.98	404.01	< 0.0001	
B-Silica load	0.2689	1	0.2689	27.32	< 0.0001	
C-Mixing time	1.22	1	1.22	123.64	< 0.0001	
AB	0.0533	1	0.0533	5.42	0.0325	
AC	0.0027	1	0.0027	0.2743	0.6072	
BC	0.0008	1	0.0008	0.0847	0.7746	
A^2	0.0561	1	0.0561	5.70	0.0289	
B^2	2.21	1	2.21	224.38	< 0.0001	
C^2	0.4056	1	0.4056	41.21	< 0.0001	
Residual	0.1673	17	0.0098			
Cor Total	8.36	26				

4.3.2.1. Model adequacy checking

Table 4. 8: Model adequacy measures for lap shear strength

Std. Dev.	0.0992	R^2	0.9800
Mean	2.31	Adjusted R^2	0.9694
C.V. %	4.29	Predicted R^2	0.9462
		Adeq Precision	35.2888

The Predicted R^2 of 0.9462 is in reasonable agreement with the Adjusted R^2 of 0.9694; i.e. the difference is less than 0.2. High multiple correlation coefficient (R^2) value of 0.9800, which is very close to 1, signifies a good model explanation where only 2% of total variation was not explained by the model. The Predicted R^2 of 0.9462 is in reasonable agreement with the Adjusted R^2 of 0.9694; i.e. the difference is less than 0.2. It indicates a good correlation between the observed and predicted values. Adequate Precision measures the signal-to-noise ratio, with a ratio greater than 4 considered as desirable. The Adequate Precision ratio of 92.45 obtained in this study indicates an adequate signal and this model can be used to navigate the design space.

4.3.2.2. Model Equation for Lap Shear Strength

The model equations, which relate the response lap shear strength of adhesive to the independent variables in terms of the coded and actual factors are given below.

Final Equation in Terms of Coded Factors:

Lap shear strength=+2.96*+0.4700*A+0.1222*B+0.2600*C+0.0667*AB+0.0150*AC-0.0083*BC-0.0967*A^2-0.6067*B^2-0.2600*C^2

Final Equation in Terms of Actual Factors:

Lap shear strength, =-4.08222*+0.108000*Latex concentration+0.229889*Silica load+0.083778*Mixing time+0.000667*Latex concentration * Silica load+0.000100*Latex concentration * Mixing time-0.000056*Silica load * Mixing time-0.000967* Latex concentration^2-0.006067*Silica load^2-0.00115* Mixing time^2

4.3.2.3. Diagnostics Test

The normal probability plot is a graphical method used to check whether the error occurred during the experimental analysis is normally distributed throughout the experiment. The normality assumption of analysis of variance is valid if all the data points lie along the straight line of normality plot. As shown in Figure 4.3 below, the normal probability plot indicates the residuals following by the normal % probability distribution, in the case of this experimental data the points in the plots shows fitted to the straight line in the figure, this shows that the quadratic polynomial model satisfies the assumptions analysis of variance (ANOVA) i.e. the error distribution is approximately normal.

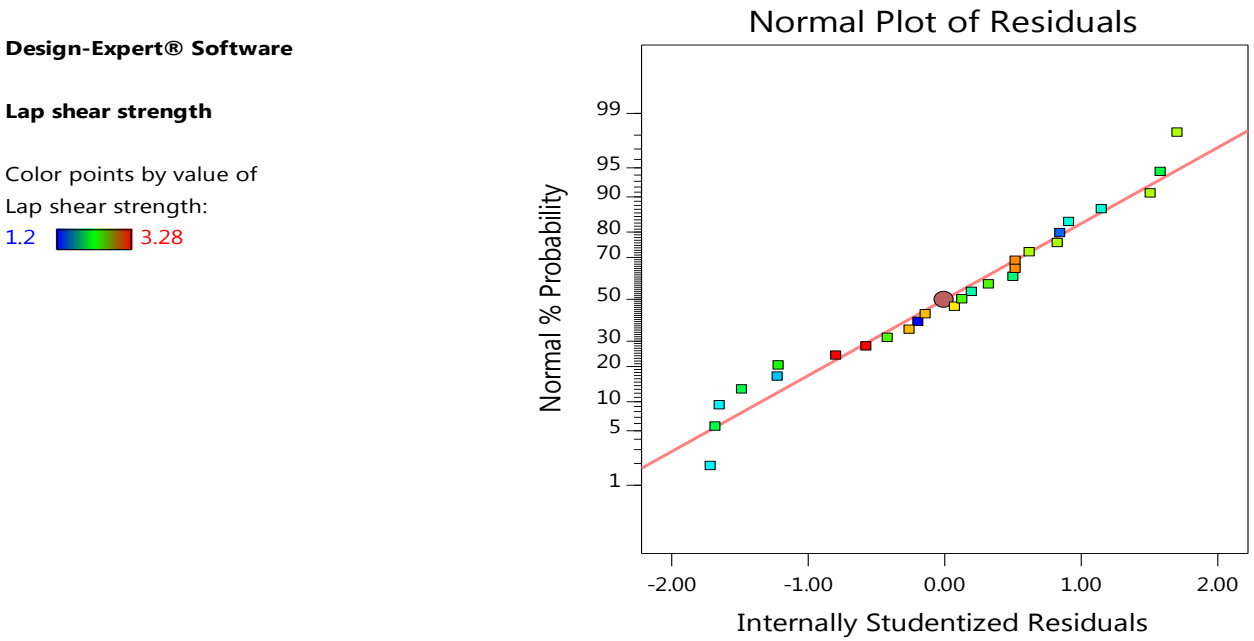


Figure 4. 3: Normal probability plot of residuals for lap shear strength

4.4. Effects of Experimental Variables on Lap Shear Strength and Viscosity

4.4.1. Effects of Experimental Variables on Lap Shear Strength

4.4.1.1. Effect of latex concentration

The lap shear strength of the adhesive at different latex concentration by setting silica load and mixing time constant have been investigated and the results are plotted in Figure 4.4. As shown in the figure the lap shear strength of adhesive was affected by latex concentration, as the latex concentration increase from 30% to 40% and from 40% to 50% a steady increase in lap shear strength was observed. This may be due to the case that as latex concentration increases, amount solid latex in the solution increases and results an increase in the availability of more tacky solid latex. In other word as latex concentration increases, amount of water in the solution decreases and as a result dilution effect of water decreases. As shown in the graph minimum lap shear strength was observed at latex concentration of 30 % which is 2.4MPa and maximum lap shear strength was observed at latex concentration of 50% which is 3.28MPa.

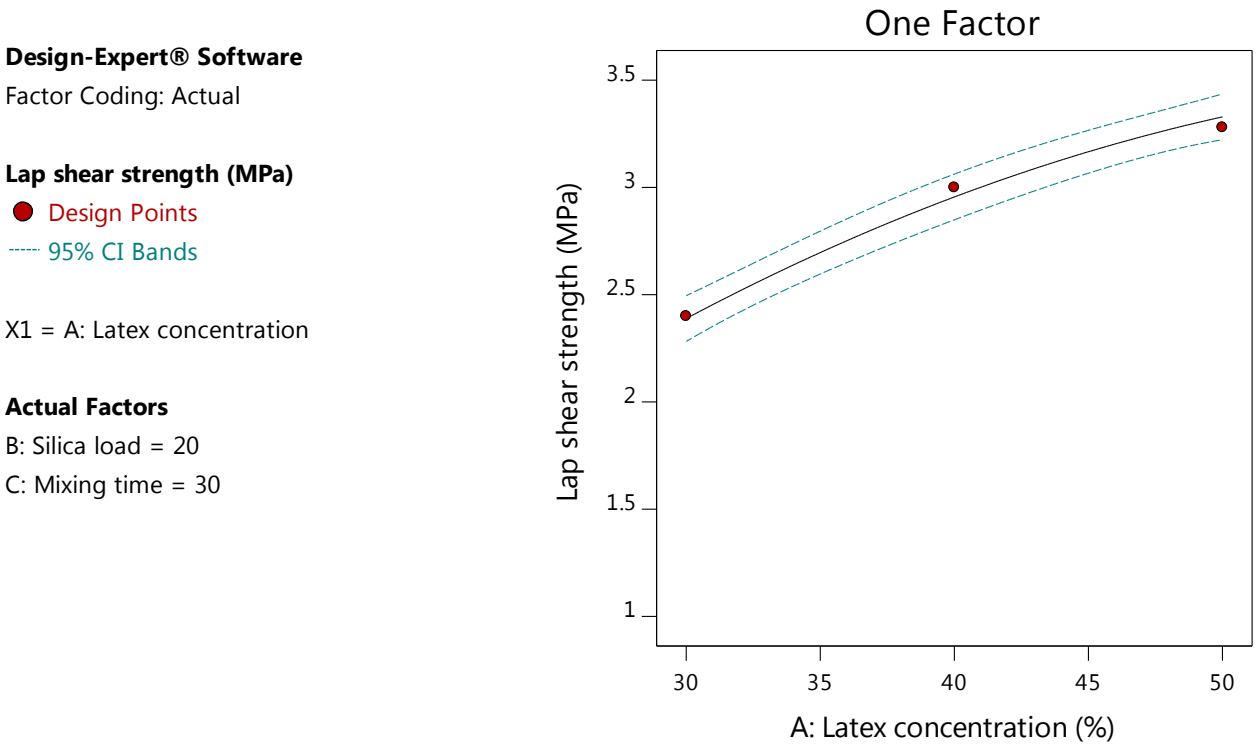


Figure 4. 4: Effect of latex concentration on lap shear strength of the bio-adhesive

4.4.1.2. Effect of silica load

The resulting plot of silica load versus the lap shear strength, when latex concentration and mixing time were constant, is shown in Figure 4.5 below. From the plot as silica load increases from 10phr to 20phr, lap shear strength increased from 2.1MPa to 3MPa. This may due to increasing interaction between silica and latex i.e., greater filler reinforcement occurs. Beyond 20phr, decrease in lap shear strength was observed which may be due to dilution effect of excess silica. This trend shows that there is an optimum level of silica load which results in maximum bond strength. Therefore, as shown from the graph maximum lap shear strength was found at 20phr which is 3MPa.

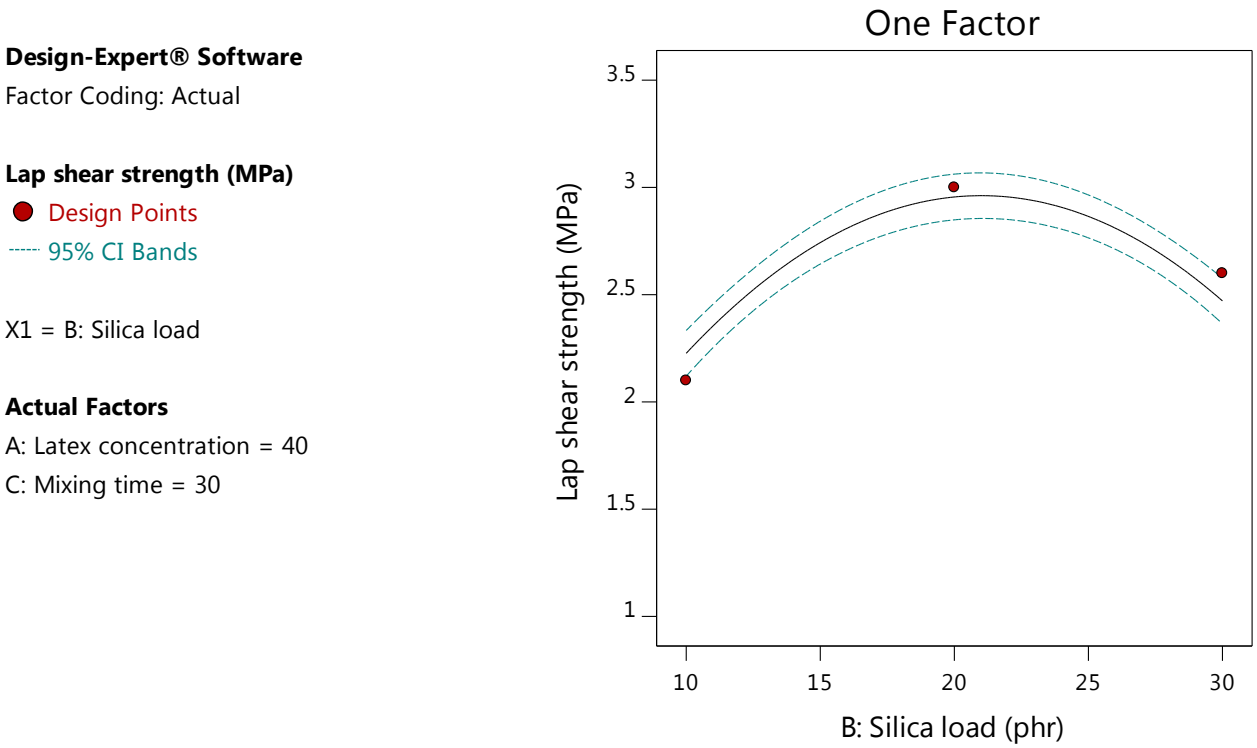


Figure 4. 5: Effect of silica load on lap shear strength of the adhesive

4.4.1.3. Effect of Mixing Time on Lap Shear Strength

Figure 4.6 shows the effect of mixing time on the lap shear strength of adhesive at constant latex concentration and silica load in the center point. From the plot as mixing time increases from 15min to 30min, lap shear strength increased significantly from 2.4MPa to 3MPa. Beyond 30min, no significant difference in lap shear strength was observed which means the uses of excess mixing time on lap shear strength has no any effect. The result of the lap shear strengths of the adhesive as a function of mixing time indicate that effective mixing of silica with latex was achieved within 30 min of mixing, and there were no significant differences in lap shear strength between the 30 and 45minute treatments. Therefore, as shown from the graph maximum lap shear strength was found at 30minutes of mixing time.

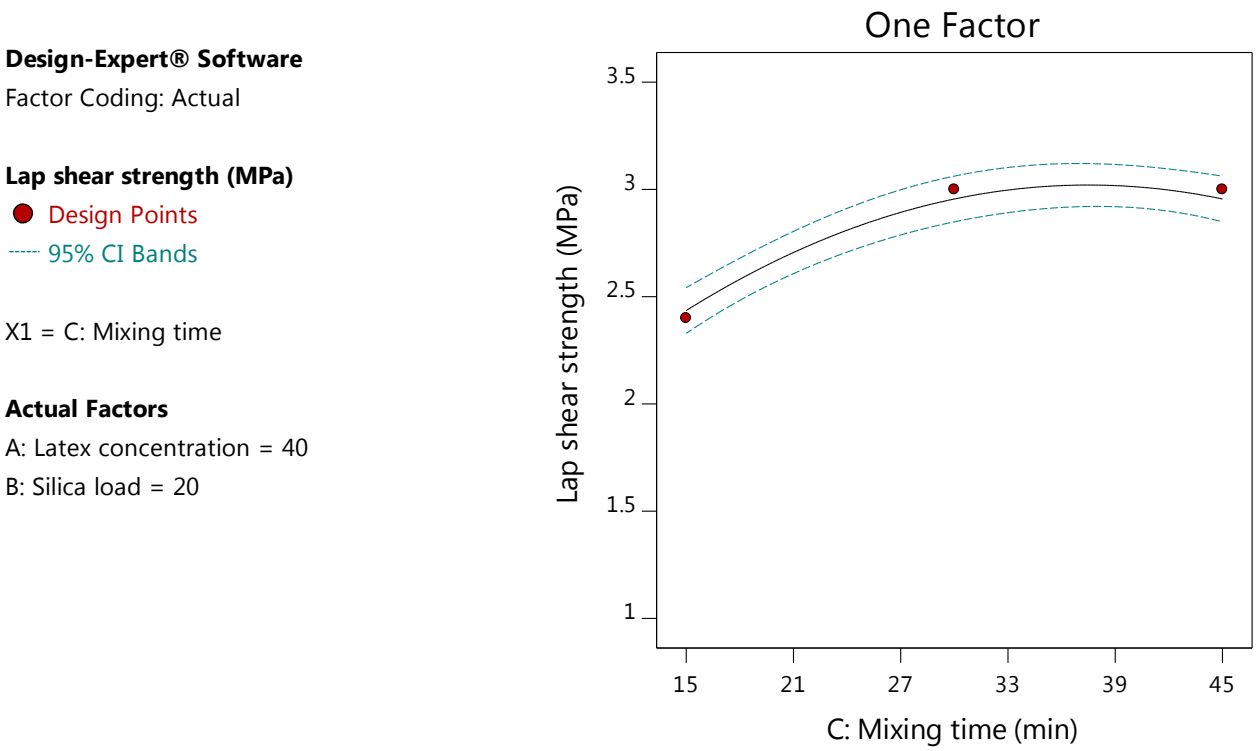


Figure 4.6: Effect of mixing time on lap shear strength of the adhesive

4.4.1.4. Interaction Effect among the Three Parameters on lap shear strength

From Design Expert® version11.1.0.1 output, interaction effect between;

- Latex concentration and silica load
- silica load and mixing time
- Latex concentration and mixing time on lap shear strength of the adhesive are discussed below.

There was no interaction between silica loads and mixing time as presented in Table 4.7.This implies that irrespective of mixing time, optimum silica load can give higher lap shear strength and irrespective of silica load, optimum mixing time can give higher lap shear strength. Similarly as can be noticed from Table 4.7 there was no interaction effect between latex concentration and mixing time. But, there is an interaction effect between latex concentration and silica load. As shown in Figure 4.7, an increasing trend is observed at the center point of silica load with increasing of latex concentration. However, a decreasing in lap shear strength is observed on both below and above center point of silica load with increasing of latex concentration. So, increasing latex concentration with increasing silica content up to optimum level increases lap

shear strength. This may be due to the occurrence of good reinforcement between increasing latex concentration and optimum silica content.

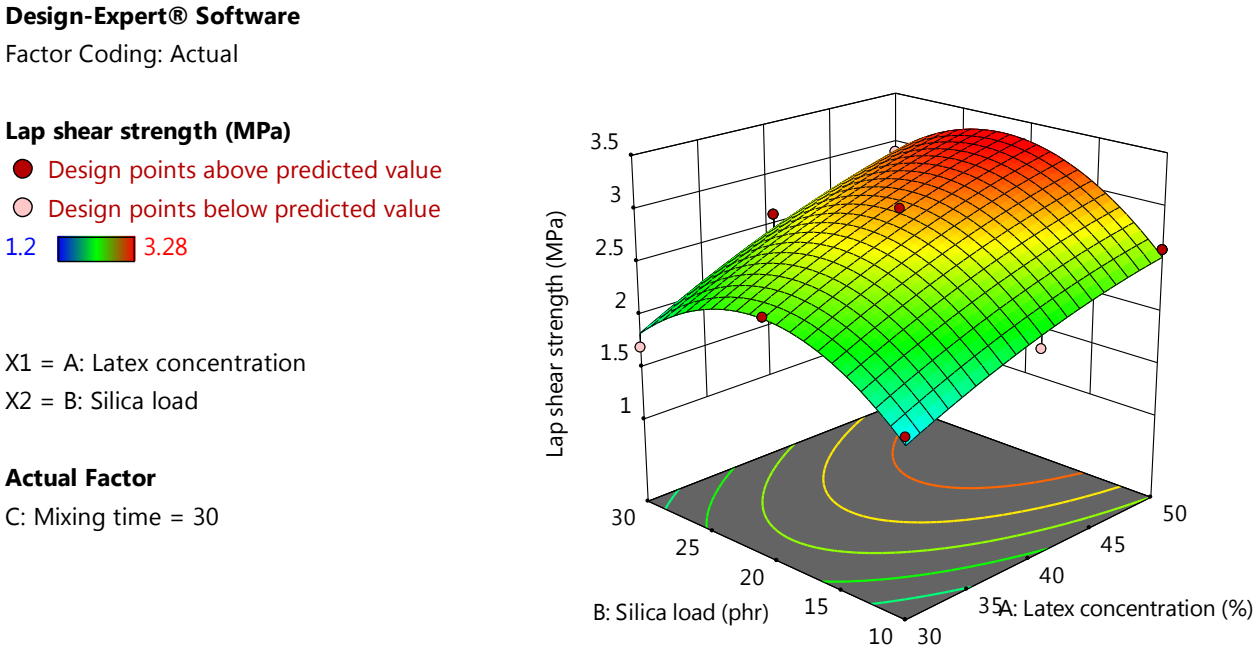


Figure 4.7: 3D representation of interaction effect between latex concentration and silica load on lap shear strength

4.4.2. Effects of Experimental Variables on Viscosity

4.4.2.1. Effect of Latex Concentration

Figure 4.8 shows the effect of latex concentration on the viscosity of the adhesive at constant silica load and mixing time at center point. Viscosity increases significantly as the latex concentration increases, as expected, since molecular weight of latex is very high. This is due to the case that as concentration increases the amount of solid latex in the solution increases and results a higher molecular weight. Molecular weight is a factor that directly affects the solution viscosity of polymers (in this case adhesive)(Berat et al., 2017). As shown in the graph minimum viscosity was observed at latex concentration of 30% which is 439mPa.s and maximum viscosity was observed at latex concentration of 50% which is 567.2mPa.s

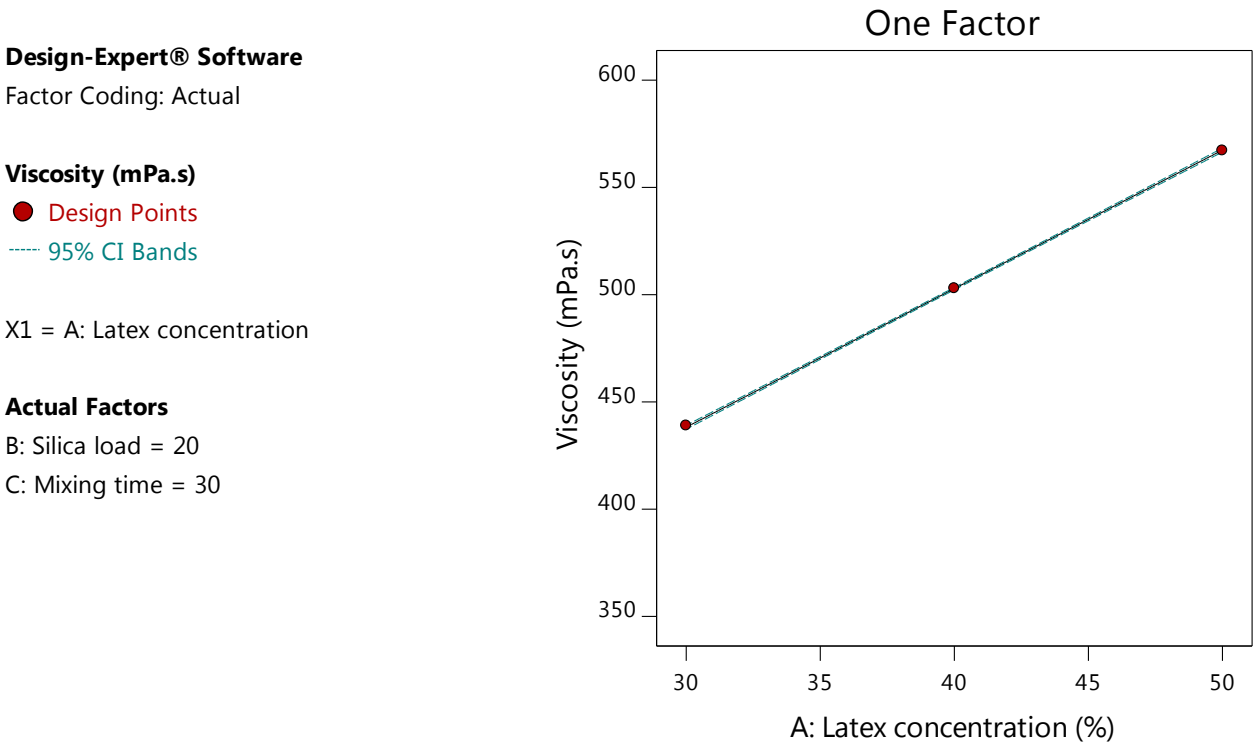


Figure 4.8: Effect of latex concentration on viscosity of the bio-adhesive

4.4.2.2. Effect of silica load on viscosity

Figure 4.9 shows the effect of silica loading on the viscosity of the adhesive at constant latex concentration and mixing time in the center point. As shown in the figure the viscosity of adhesive was affected by silica loading, as the amount of silica content increase from 10phr to 30phr a steady increase of viscosity was observed. This is due to the case that as silica load increase, total solid content on the solution becomes higher and results an increase in viscosity. As shown in the graph minimum viscosity was observed at silica load of 10phr which is 468mPa.s and maximum viscosity was observed at silica load of 30phr which is 537.8mPa.s.

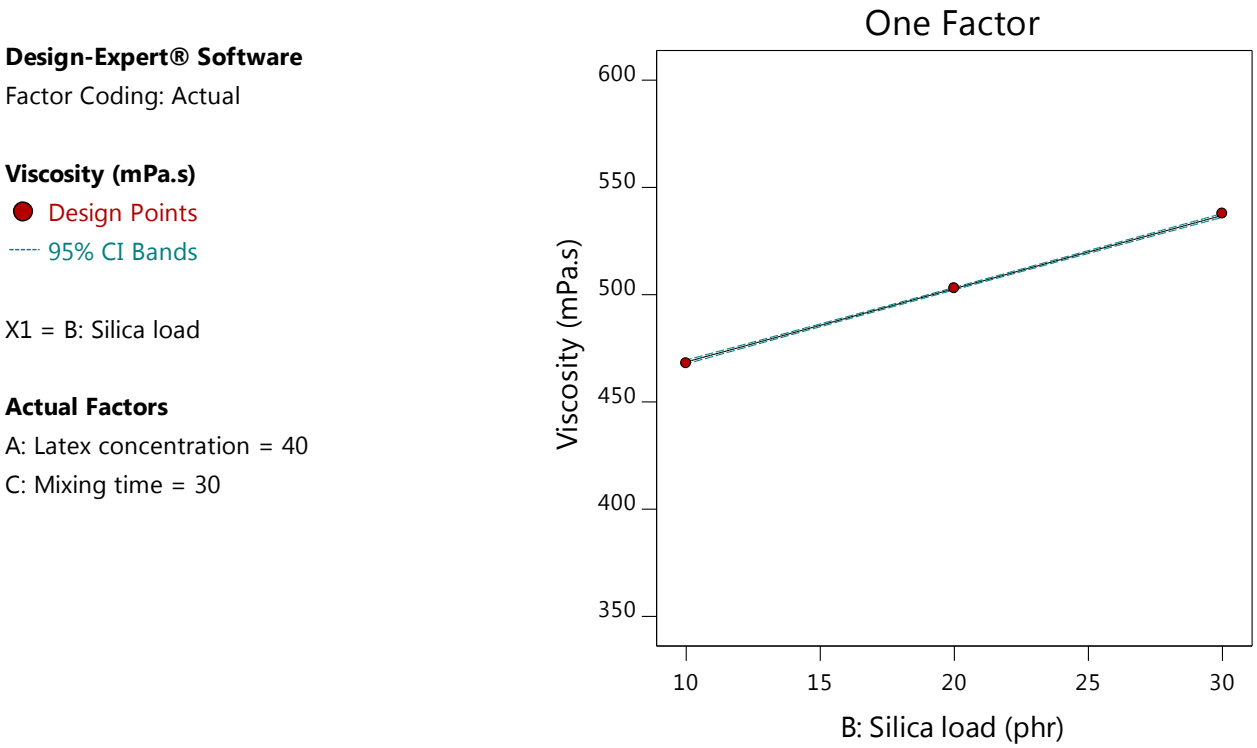


Figure 4. 9 Effect of silica load on viscosity of the bio-adhesive

4.4.2.3. Effect of Mixing Time on Viscosity

Figure 4.10 shows the effect of mixing time on the viscosity of adhesive at constant latex concentration and silica load in the center point. As shown in the graph below a straight horizontal line is observed. Thus, as time increases from 15 to 30minutes and from 30 to 45 minutes, there was no significant difference in viscosity. This shows that mixing time has no any effect on viscosity of the adhesive.

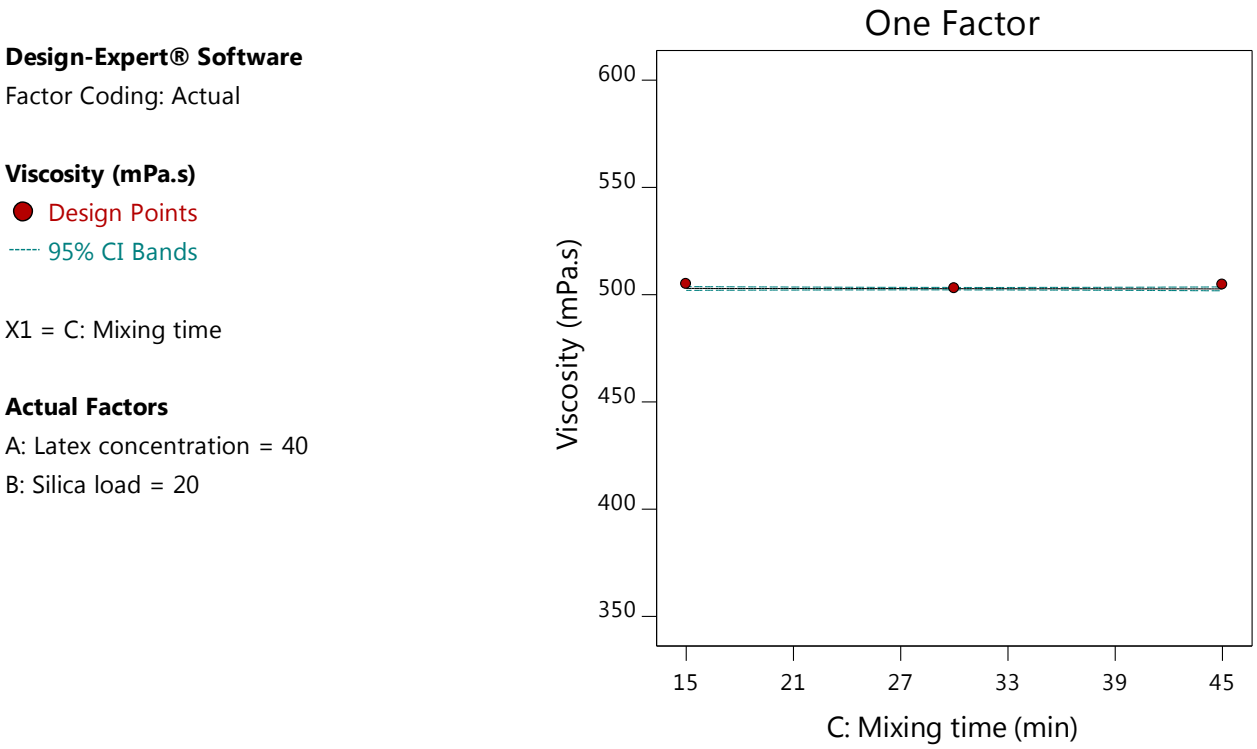


Figure 4. 10: Effect of mixing time on viscosity of the adhesive

4.4.2.4. Interaction Effect among the Three Parameters on Viscosity

From Design Expert® version11.1.0.1 output, interaction effect between;

- Latex concentration and silica load
- silica load and mixing time
- Latex concentration and mixing time on viscosity of the adhesive are discussed.

There was no interaction between silica load and mixing time as presented in table 4.5. This implies that irrespective of mixing time, higher silica load can give a higher viscosity and irrespective of silica load, there is no change in viscosity with time. Similarly as can be noticed from Table 4.5 there was no interaction effect between latex concentration and mixing time. But, there is an interaction effect between latex concentration and silica load. As shown in Figure 4.11, as both latex concentration and silica load increase viscosity also increases. This is may be due to increase of solid content in the adhesive solution. In other words, concentration of the adhesive solution becomes high (increase in molecular weight.) i.e. there is less water and results in increase viscosity.

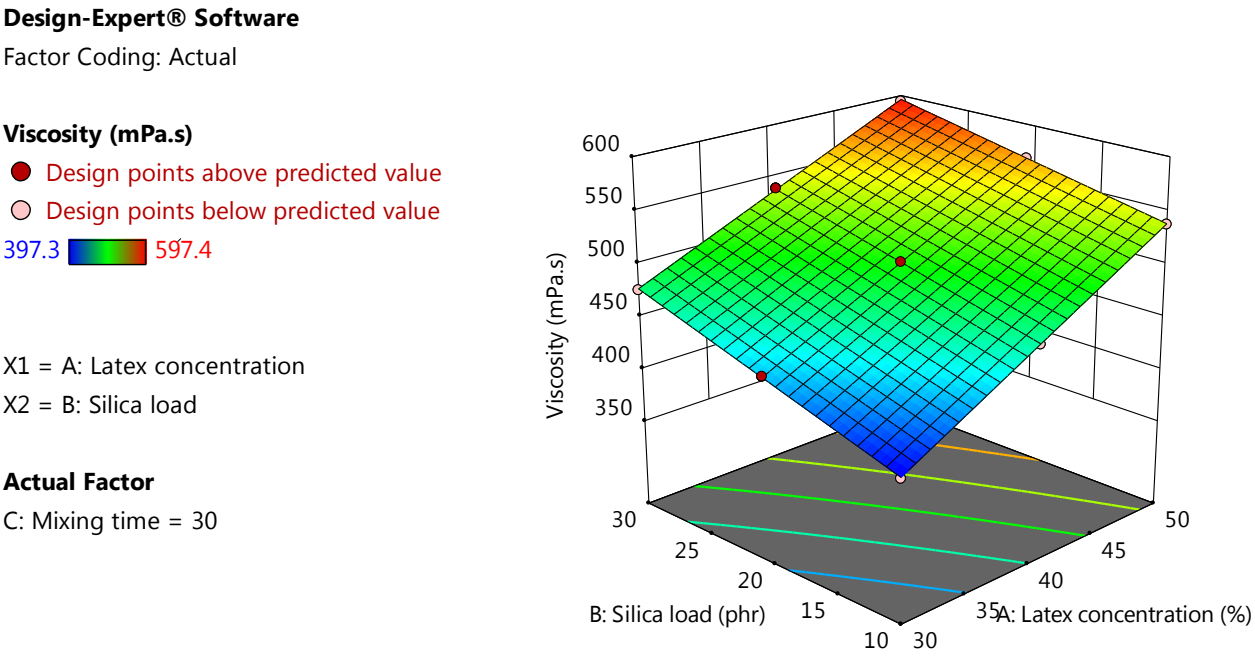


Figure 4.11: 3D representation of interaction effect between latex concentration and silica load on viscosity

4.5. Characterization of the Prepared Bio-Adhesive

Sample from product of Run #15 which was carried out at 50% latex concentration, 20phr, and 30 minutes was selected for characterization as it gave the maximum lap shear strength. The following results are obtained based on the procedures discussed in chapter three. The minimum requirements that an adhesive should fulfill are presented in appendix F. In this study standards are taken based on wood specimen.

Table 4.9: Characteristics of the produced bio-adhesive

Parameters	**Values**
Lap shear strength	3.28MPa
Viscosity	597.2mPa.s
pH value	7.3
Foam	0.3 cm

The prepared bio-adhesive was compared with synthetic adhesives in terms of bonding strength (lap shear strength) and hence the results confirmed that the bio-adhesive is comparable. Lap shear strength of some synthetic adhesives is presented in appendix E.

4.5.1. Thermal Stability Test

Table 4.10 shows shear strength of lap joints of wood samples glued with the prepared bio-adhesive measured at different levels of temperature. Percentage of retention was calculated based on equation 3.5. It expresses by what percent does the adhesive fails when it heats at different temperature.

Table 4. 10: Lap shear strength values of wood joints joined by the prepared bio-adhesive at different temperature

Temperature (^{0}C)	**Lap shear Strength(MPa)**	**Percentage of Retention (%)**
0	3.12	95
20	3.28(Control)	---
50	2.6	79.2
100	0	0

Lap shear strength at 20^{0}C was taken as a control. From the above shown results at 0^{0}C, no significant change in lap shear strength was observed and its percentage of retention is 95%. At heating temperature of 50^{0}C, a significant decrease in lap shear strength was observed. However, as the value (2.6MPa) is greater than the minimum requirement of lap shear strength (2.34MPa) it can be used this adhesive up to 50^{0}C temperature operating condition. As the heating increased from 50 to 100^{0}C, the paired wood joints were detached each other totally. This implies that the prepared bio-adhesive cannot be used at elevated temperature. This may be due to breakdown of interaction forces among particles.

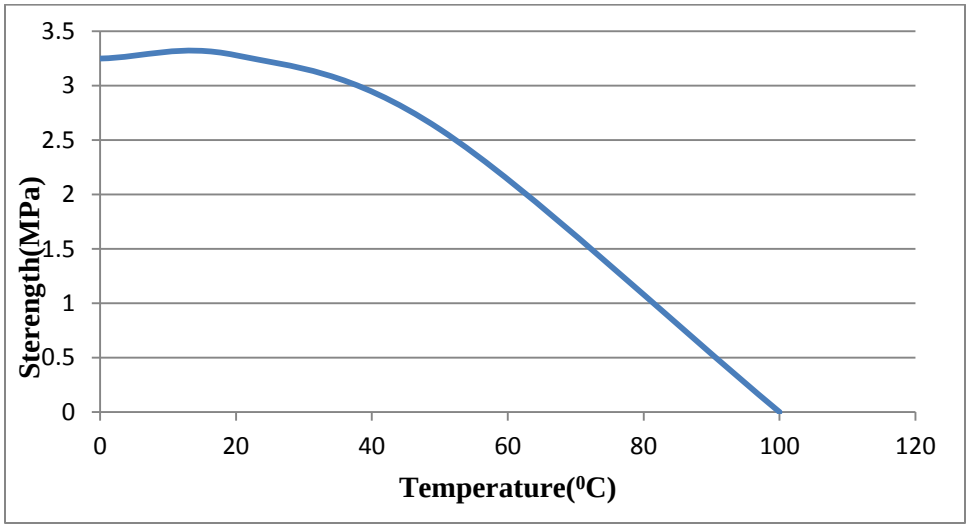


Figure 4. 12: Effect of temperature on thermal stability of the adhesive in terms lap shear strength (wood joints)

5. Conclusion and Recommendation

5.1. Conclusion

Bio-based adhesive derived from latex of Euphorbia tirucalli was developed in this study. Characterization of latex like viscosity, pH, density, total solid content and functional group were determined. These analyses hence made characteristics data available for use as reference in future scientific studies. Results from latex characterization (14.7mPa.s viscosity and 0.88MPa bonding strength) confirmed that the extracted latex has low viscosity and bonding strength and as a result silica was added to modify its properties. A maximum of 3.28MPa of lap shear strength (Bonding strength of the adhesive) with corresponding viscosity of 567.2mPa.s is achieved. Form the findings, it was seen that mixing of latex with optimum silica content gave better results on both lap shear strength and viscosity.

During the preparation of the adhesives, the effects of latex concentration, silica load, and mixing time on the adhesive bond strength and viscosity were studied. It was found that viscosity of the adhesive is significantly affected by latex concentration and silica load. However, no significant difference was observed with variation of mixing time on viscosity. In the case of lap shear strength all the studied factors i.e. latex concentration, silica load and mixing time were significant. From the statistical analysis it can be concluded that as latex concentration increases up to 50% total solid content, lap shear strength also increases. Increasing silica load up to 20phr was found to increase lap shear strength of the adhesive. However, beyond 20phr a decrease in lap shear strength was observed. This trend shows that there is an optimum level of silica load which results in maximum bond strength. It was also found that the result of the lap shear strength of the bio- adhesive as a function of mixing time indicate that effective mixing of silica with latex was achieved within 30 minutes of mixing.

The results obtained show that adhesive production using latex as feedstock was a considerable potential specially in terms of availability, renewability and producing environment-friendly product.

In general, from the findings it can be concluded that the prepared bio-adhesive has comparable quality with synthetic commercial synthetic adhesives and hence it can be used in place of synthetic adhesives.

5.2. Recommendations

The bio-adhesive prepared from *Euphorbia tirucalli* latex gives good quality in terms of bonding strength as the commercial adhesives do. However, further work should be done on:

- Assessment of toxicity hazards to humans presented by collection, preparation and service of the Euphorbia tirucalli latex adhesive
- Assessment of the costs and feasibility of latex extraction and adhesive preparation

In this study the strength of the prepared bio-adhesive was only tasted on wood specimens. Therefore, in order to check its applicability on other materials it is recommended to test the adhesive on other substrates such as ceramics, glasses, papers and others.

As it is discussed in chapter four, there is a lot of waste from the extraction section. This waste is called bagasse. Another research should be done to convert the bagasse into valuable product. Since the bagasse is biomass it can be used to produce renewable energy such as biogas and briquette.

In this thesis, latex was extracted by milling the branches of *Euphorbia tirucalli* using electrical onion grinder. However, this equipment is not efficient to give higher yield and there is also a possibility of contamination with fragments during crushing. Therefore, to improve the yield and purity equipment like waring blender should be used.

Even though the prepared bio adhesive is good in bonding strength, it is not applicable for elevated operating temperature (above 50^0C). Therefore, it is recommended that further work should be done on improving thermal stability of the adhesive.

Toluene was used as plasticizer in this study by setting at constant value. Future studies should consider toluene as a factor to investigate its effect on viscosity and bonding strength (lap shear strength) of the adhesive.

Moreover, as this research is new in its kind further works should be done on selection and considering of other filler and factors.

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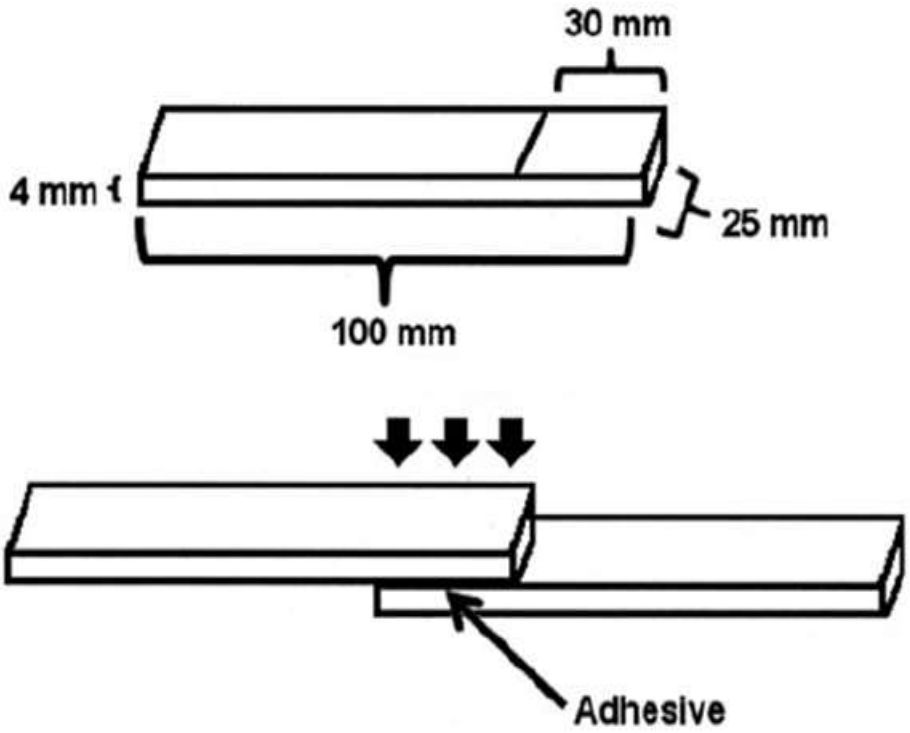
Appendices

Appendix A: Schematic of wood specimen preparation for lap shear strength test (ASTM D906 method)



Appendix B: Fit Summary and diagnostics of responses (viscosity and lap shear strength)

Viscosity: Fit summary

Source	Sequential p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0.9952	0.9937	
2FI	**< 0.0001**	**0.9995**	**0.9992**	**Suggested**
Quadratic	0.2467	0.9995	0.9991	
Cubic	0.2791	0.9996	0.9985	Aliased

Viscosity : Diagonasitcs

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Viscosity

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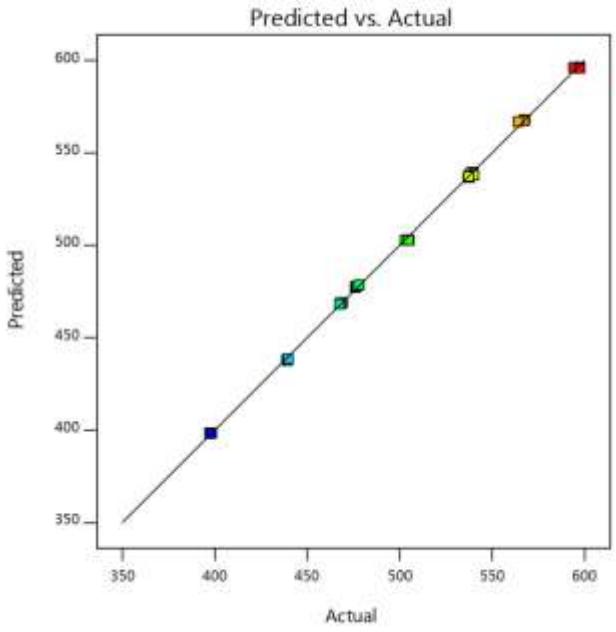

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Viscosity

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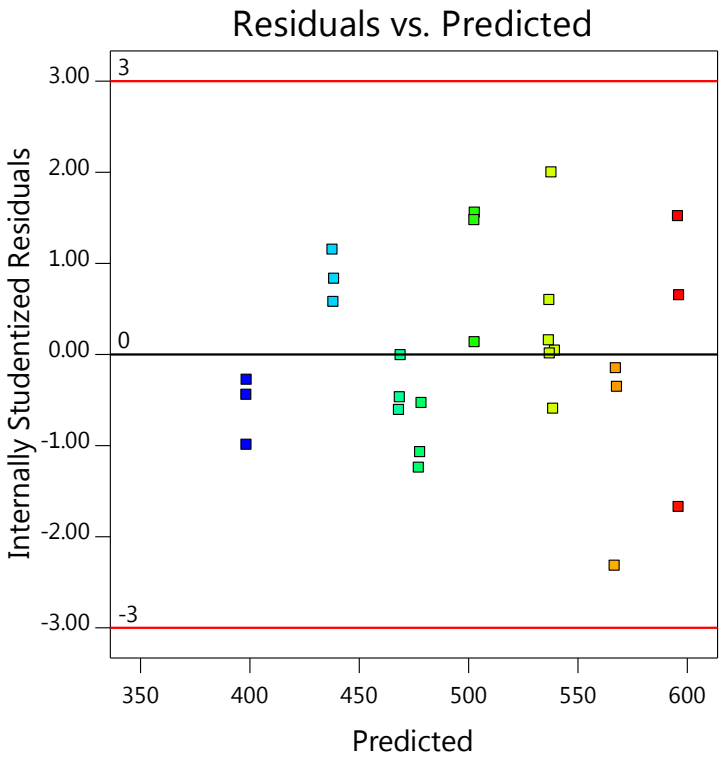
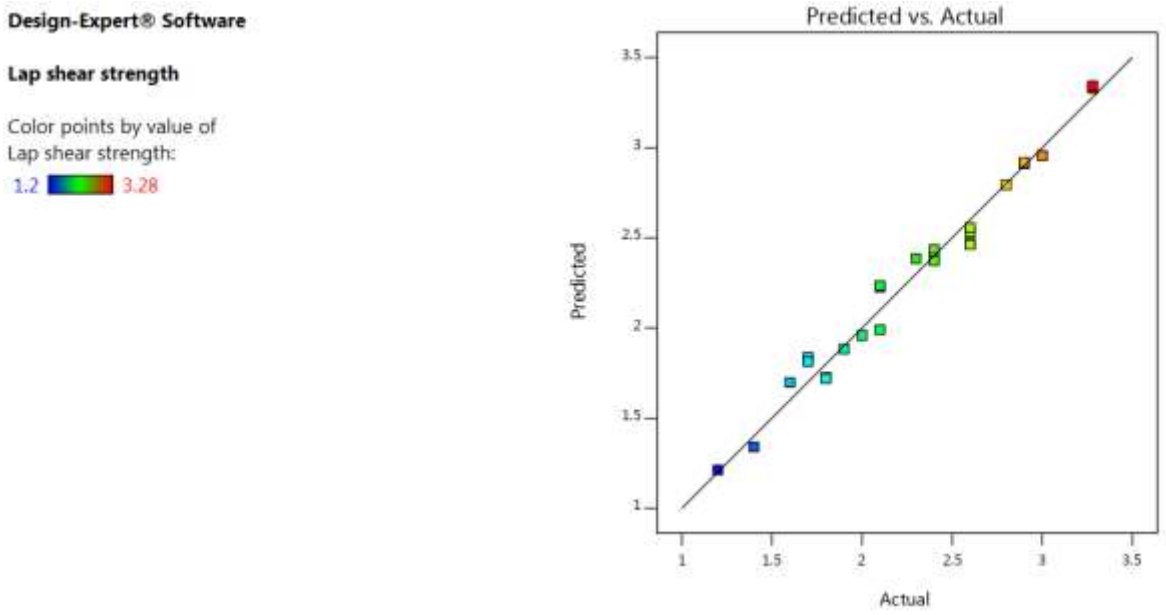
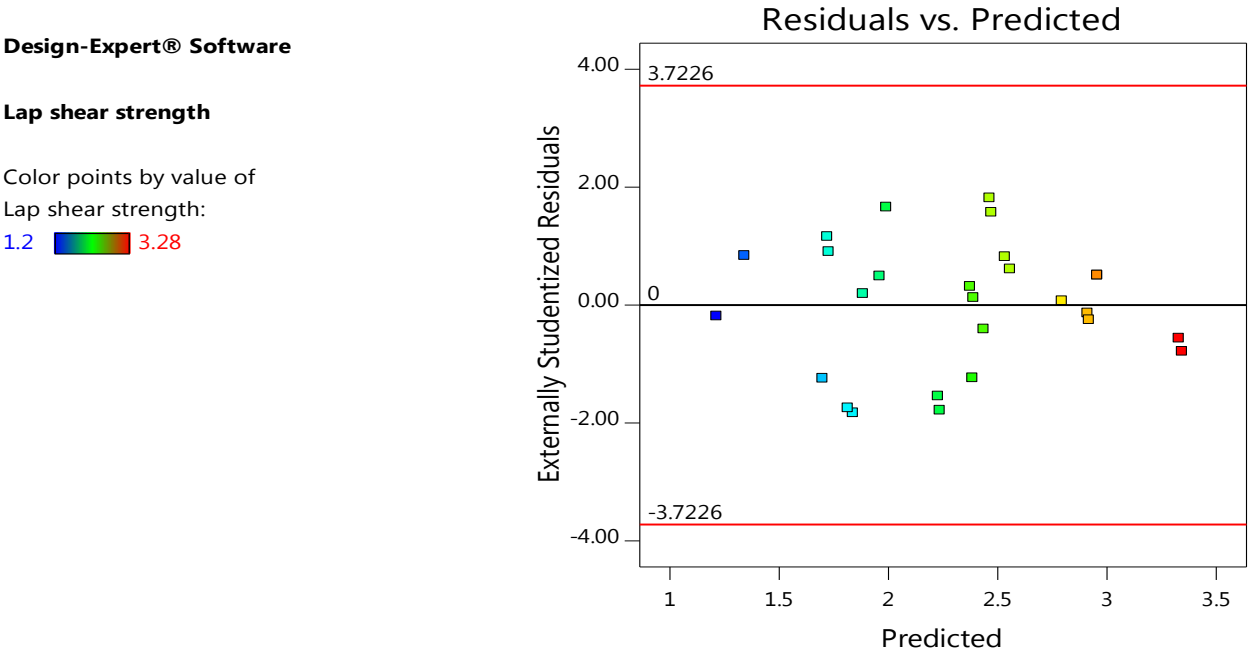


Lap shear strength: Fit summary

Source	Sequential p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0.6085	0.5368	
2FI	0.9389	0.5586	0.3465	
Quadratic	**< 0.0001**	**0.9694**	**0.9462**	**Suggested**
Cubic	0.0014	0.9926	0.9691	Aliased

Lap shear strength: Diagnostics





Appendix C: Calculation of amount of requirement of each component for bio-adhesive formulation

C_1: Latex concentration determination

Required latex concentration (%wt.) = $\frac{\text{Mass of shredded latex}}{\text{Total mass of solution}} \times 100$

For 30% concentration, mass of shredded latex = 0.3*total mass of solution

For 40% concentration, mass of shredded latex =0.4*total mass of solution

For 50% concentration, mass of shredded latex = 0.5*total mass of solution

NB: total mass solution is known for all concentrations. It is selected based on the amount required to run the experiment.

C_2: Amount of additives required Calculations are based on phr.

Ingredient	**phr**
Latex	100
Silica	10-30

Amount shredded latex and water was determined by the following relations

Required latex concentration (wt. %) = $\frac{\text{Mass of shredded latex}}{\text{Total mass of solution}} \times 100$

Since total mass of solution and latex concentration are known, amount required shredded latex can be calculated easily using equation.

Amount of silica added was calculated using the following equation

Percentage of silica to be added (wt. %) = $\frac{\text{Mass of silica}}{\text{Mass of adhesive to be prepared used}} \times 100$

Since mass of adhesive to be prepared and percentage of silica to be added known, it is easy to calculate mass of silica required using the above equation

Density of toluene = 0.87g/ml (as conversion factor into mass)

C_3: conversion of phr into wt. %

Conversion of 10phr into wt. %

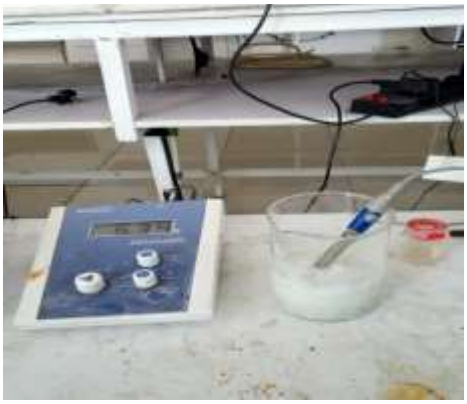
Total phr = 100+10=110 phr

Wt. % silica = $\frac{10}{110}$ *100 = 9.09% and the same procedure for other levels was used.

Appendix D: Pictures of some laboratory works

Prepared wood specimens

Bagasse



pH measuring of latex

Solid latex

Appendix E: Lap Shear Strength of Some Commercial Synthetic Adhesives

Adhesive name	**Lap shear strength (MPa)**
Coral	5.42
Bulllond	3.01
Ponal	3.46
Fevicol	2.54

(Mwambusi, 2016)

Appendix F: Minimum requirements of adhesive

Parameters	**Values**
Lap shear strength	≥2.34MPa
Viscosity	≥500mPa.s
pH value	5.5-7.5
Foam	<2.5cm

It is cited in chapter section 2.10.