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SUNFLOWER OIL-BASED WOOD ADHESIVE WITH HIGH MECHANICAL
STRENGTH AND ENHANCED BONDING BY INTRODUCING FILLERS

A Thesis Submitted to the Graduate School
in Partial Fulfilment of the Requirements
For the Degree of
Master of Science

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Pittsburg State University

Pittsburg, Kansas

May, 2023

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STRENGTH AND ENHANCED BONDING BY INTRODUCING FILLERS

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SUNFLOWER OIL-BASED WOOD ADHESIVE WITH HIGH MECHANICAL STRENGTH AND ENHANCED BONDING PERFORMANCE BY INTRODUCING FILLERS

An Abstract of the Thesis by
Arjun S. Chaudhari

Petroleum-based compounds are generally utilized in industries for getting higher mechanical strength for wood application, where the process of synthesis releases toxins into the environment and causes health issues.

Because of this, scientists are trying to make biobased compounds and products. In this research, sunflower polyol was used to make polyurethane (PU) resin. For the formation of polyol, an epoxidation reaction followed by a ring-opening reaction was performed. The presence of hydroxyl groups was confirmed using Fourier transform infrared spectroscopy (FT-IR) and hydroxyl value determination test to confirm the polyol formation. After that, hydroxyl groups of polyol were reacted with diisocyanate to synthesize polyurethane.

Two different techniques were used to cure the adhesive for wood samples. In the first set of samples, heat and pressure were applied simultaneously via hot press for a certain time; after that, samples were placed at room temperature for 24 hours.

For the second set, samples were cured with a manual clamping technique at room temperature for 24 hours. With the hot-press technique, variations in time and temperature were done to find ideal conditions and highest tensile strength.

Adhesion properties were observed with tensile strength testing. The highest tensile strength was observed to be 5.66 MPa without the addition of any filler. Furthermore, silicon dioxide (SiO_2), microcrystalline cellulose (MCC), and titanium dioxide (TiO_2) were introduced as fillers to improve bonding strength. With the introduction of SiO_2 , TiO_2 , and MCC filler, an 86.25%, 27.14%, and 34.15% improvement in adhesive strength was observed, respectively. Apart from that, other characterizations were also done with the help of thermogravimetric analysis (TGA), FTIR, and gel permeation chromatography (GPC) for the analysis of the prepared samples.

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LIST OF ABBREVIATIONS

FTIR	Fourier transformed infrared
TGA	Thermogravimetric analysis
PU	Polyurethanes
SiO ₂	Silicon dioxide
TiO ₂	Titanium dioxide
MCC	Microcrystalline cellulose
GPC	Gel permeation chromatography
SFO	Sunflower oil
ESFO	Epoxide sunflower oil
TEAB	Tetraethylammonium bromide
WCA	Water contact angle
CNT-STD	Control standard

CHAPTER I

INTRODUCTION

1.1 Chemistry of polyurethanes

A polymer is made by joining many small molecules called monomers in a repeating pattern. Polymers can be natural or manmade [1]. Polyurethanes (PUs) play a crucial role in many industries by fulfilling requirements from physical behaviour to chemical properties and from novel applications to sustainability. The first polyurethane was made from a polycondensation reaction between alcohol and isocyanate by E.I. Du Pont and Otto Bayer in 1937 [2]. After modifications, it reached an industrial manufacturing scale in the 1940s. After the invention of polyurethane, it becomes an essential part of modern life. The revolution in the field of polyurethanes and daily life use of polyurethane improved the quality of life.

Polyurethane has various kinds of applications as construction, adhesive, bio-medical, coating, insulation foams, aerospace, sports automobile, etc. [3]. Polyurethane ranked sixth in the worldwide production of polymers in 2018 with a global market of 65.5 billion dollars which is expected to reach 105.2 billion dollars by 2025 [4]. PUs are mostly obtained by the polyaddition reaction between diisocyanates and diol to obtain linear architectures as shown in Figure 1 [5].

Although non-isocyanate polyurethanes (NIPUs) can be made through, for instance, the reaction of cyclic carbonates with polyamines [4], The carbon atom's positive charge within -NCO group's cumulated double-bond system may be a factor in the isocyanate group's high reactivity as shown in Figure 2. The carbon atom has the lowest electron density, whereas the oxygen atom has a higher electron density. The nitrogen atom has an intermediate negative charge. The active hydrogen compound's nucleophilic center attacks the electrophilic carbon atom, and the hydrogen reacts with the nitrogen atom of the -NCO groups [6,7].

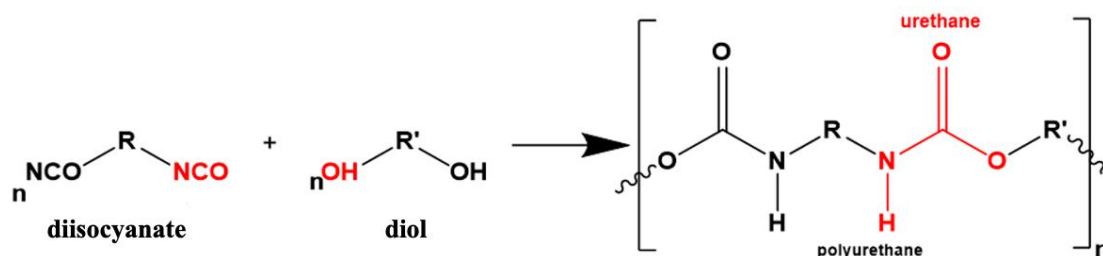


Figure 1: Reaction between isocyanate and polyol

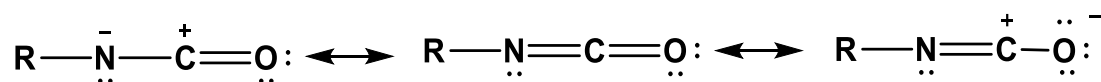


Figure 2: Illustration of resonance structure of isocyanate

One of the critical components of polyurethane is polyols, which include more than two hydroxyl groups [8]. As petroleum stocks play a crucial role in the

typical industrial manufacture of urethane polymers, the current paradigm in polyurethane research has changed toward the investigation of novel synthetic methods leading to renewable bio-based products as a result of the expiration of crude supplies, its accompanying floating price, as well as existing environmental awareness [2]. The majority of the conventional polyols used in polyurethane come from petroleum sources. However, due to the urgent need to decrease the industry's excessive reliance on petroleum-based resources, several cutting-edge research methods for bio-based polyols have been implemented. Scientists are trying to move forward with alternatives to petrochemicals such as vegetable oils, lignin, and other plant-based derivatives [7].

1.2 Applications of polyurethanes

Polyurethane is one of the most significant types of industrial polymers with the fastest-growing worldwide market. There are some primary advantages of PUs such as durability, toughness, and outstanding chemical resistance. PUs are used in almost all polymer application areas, including foams, elastomers, thermoplastics, thermo-rigids, adhesives, coatings, sealants, and fibers. Currently, PUs have one of the greatest market shares in the plastic and CASE (Coating, Adhesive, Sealants, and Elastomers) industries, and the distribution of PUs share various applications [9]. Due to economic conflict and environmental concerns, technologists who are working on PUs and adhesives are investigating innovative chemistry and methods to increase the effectiveness of organic adhesives at minimum volatile organic components [10].

About 82 years have passed since PUs were created. They have become one of the most active classes of polymers. Polyurethanes have a wide range of uses because of the extensive range of tunability allowed in polyurethane chemistry. Due to its exceptional qualities, including a wide range of hardness, flexibility, elasticity and bonding ability. PUs have been used in a wide range of commercial applications [11].

1.3 Wood

Because of its unique qualities and practical uses, wood has been and remains a widely utilized material. It is recyclable and biodegradable [12]. Wood is used in many applications such as furniture, paper, tools, buildings, flooring, particle board, musical instruments, and packaging.

Wood is mainly composed of carbohydrates and lignin. Wood also consists of small inorganic materials. Water is the major component in a living tree and for dry trees, the wood cell wall consists of carbohydrates (65-70%) which are combined with lignin (18-35%). The carbohydrate part of the wood consists of cellulose content ranging from 40-50% and hemicellulose content ranging from 25-35%. Overall, dry wood has an element composition of 44% oxygen, 50% carbon, 6% hydrogen, and a trace amount of inorganics [12]. In this work, oak wood was used for the bonding experiments. According to previous studies and analyses on oak wood, cellulose, hemicellulose, and lignin proportions are 41%, 26.35%, and 25.71%, respectively [13].

1.4 Adhesion

The term "adhesion" refers to the development or outcome of a long-lasting interface, or zone of "intimate" contact, between a piece of wood and a second substance, such as an adhesive, coating, or another piece of wood [14]. As the science of adhesion has progressed, different adhesion theories have been promoted for different materials. Mechanical interlocking, interdiffusion of polymers, intermolecular attractive forces, and covalent chemical bonding have all been put out as explanations for adhesion when using wood as a substrate, either separately or all at once [15].

Wood adhesion is quite difficult because the physio-chemical characteristics of the wood change depending on the wood source. The interaction between the wood and adhesive plays a crucial role in the bonded assembly's overall strength and toughness. Wood adhesion or bonding also depends on the type of wood for example, sapwood is a type of wood which is typically thought to be easier to bond than heartwood due to differences in the extractives [14].

Apart from types of wood, the curing of adhesive is also important. After wetting of substrate, the curing of the substrate must happen. Curing can be accomplished in a variety of ways, including polymerization and cooling-induced solidification. The process of polymerization involves subjecting the adhesive to several treatments, including the addition of a crosslinking polymer, a catalyst, heat, and radiation [16].

1.5 Adhesive

The adhesive is a substance applied on two surfaces to bind them together through the adhesive bonding process. The most common use of adhesives is binding wood and paper [14]. One of the types of adhesive is epoxy adhesive. Because of its simplicity, adaptability, and mechanical qualities, it has a variety of applications in different sectors such as aerospace, automotive, construction, electric, and woodworking industries [17]. Because of the significant amounts of organic solvents present in the formulations of the new adhesive technologies, awareness of their negative environmental impacts has also grown and significant efforts were made to create environmentally friendly products as a result [18].

There are some general categories and types of adhesives such as elastomeric adhesives, thermoplastic resin adhesives, thermosetting-resin adhesives, rubber-based adhesives, animal glue, and epoxy-based adhesives.

1.6 Petroleum-based wood adhesives

One of the most significant markets for adhesives is the bonding of wood. The wood adhesives of today range from formaldehyde-based resins to latex-based systems. The adhesives can be divided into three different groups depending on the hardening processes: drying, curing, or cooling [19]. Depending on the polymer, the curing process can be started by adding a hardener or by changing environmental factors like pH, exposure to moisture, or UV radiation. Unfortunately, adhesives made from petroleum have a detrimental effect on the environment.

Petroleum-based chemicals are frequently used in industry to get greater mechanical qualities for use with wood; however, the synthesis process releases toxicity into the environment, endangering human health. The majority of them are sourced from limited and non-renewable fossil fuels. Some of them, like formaldehyde-based resins, release low molar mass chemicals during product production, distribution, and end-use that may be hazardous to the environment and human health. Because biopolymers are environmentally friendly and made from renewable resources, there is growing interest in adhesives based on them as a result of growing environmental concerns.

1.7 Renewable source-based polyurethane

Polyols and isocyanates are the primary objectives for modification in polyurethane chemistry. Vegetable oils such as soybean oil [20], corn oil [21], castor oil [22], and canola oil [23] have been studied for polyurethane applications. Vegetable oils are ideal for polyols due to their renewability and low cost, as well as the fact that they contain unsaturated groups that may be changed into reactive sites for polymerization. The synthesis of bio-polyols from renewable resources significantly impacts the polyurethane market. Since the bio-polyols share the same structures and characteristics as current polyols but are made from renewable raw materials rather than petrochemicals, they may be used as drop-in replacements for them [24]. In addition, oil such as castor oil has hydroxyl groups in it and due to that reason, it can be used as a polyol itself [25].

However, there are still several challenges to using bio-based or renewable resources in place of petroleum sources. For example, some of the researched

alternatives are not possible for large-scale production, others are more expensive than fossil derivatives, and some of the final products from these renewable sources are not sufficiently comparable to the conventional ones; consequently, ongoing research and advancements are necessary for this field to have a more significant and long-lasting impact [26].

1.8 Objective of this research

The objective of this research is to find an alternative to petroleum-based wood adhesives by using sunflower oil. In this research, the sunflower oil was converted into an isocyanate-reactive polyol through epoxidation and a ring-opening reaction. Before beginning the process of creating the adhesive, confirmation tests such as FT-IR, hydroxyl value, and GPC were carried out to examine how the bio-based polyol developed. The primary goal of this study was to assess the effect of the SiO_2 , TiO_2 , and MCC fillers on the properties of the prepared sample. Apart from that, the impact on mechanical strength was also carried out by trying various types of curing techniques. This research examined the morphology, density, mechanical characteristics, and thermal stability of the adhesive made from sunflower polyol.

CHAPTER II

MATERIALS AND METHODS

2.1 Materials

2.1.1 Isocyanates

Isocyanates are reactive chemicals that may even interact with water [27]. It is crucial to understand the characteristics of the various polyol and isocyanate utilized structures in order to understand the structural characteristics of polyurethanes created. Elastomers are formed when a diisocyanate, a linear long-chain polyol, and a low-molecular-weight chain extender combine. Additionally, only a small number of isocyanate types are actually employed, despite the fact that there are many different polyols available on the market that may demand a variety of isocyanates.

The two diisocyanates that are used most frequently are toluene diisocyanate (TDI) and methylene bis diphenyl isocyanate (MDI), as well as higher oligomers for improved functionality and cross-linking. Isocyanates have different chemical structures depending on how reactive they are. In general, aliphatic isocyanates are less reactive than aromatic isocyanates. Since it provides a more homogenous reaction kinetics, MDI is usually selected for the formation of PUs. In

comparison to traditional polyisocyanates, it also has the lowest vapor pressure [28].

In this research, MDI was used for the formulation of sunflower oil-based wood adhesive, and it was gifted by Huntsman (The Woodlands, USA). The chemical structure of MDI is shown in Figure 3.

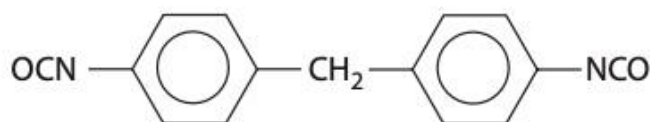


Figure 3: Chemical structure of diphenylmethane diisocyanate

2.1.2 Sunflower oil

The tall plant *Helianthus annuus* L. also known as a sunflower blooms in the late summer and early fall [29]. The sunflower is a short-season plant, with more than 70 species recognized globally, from the genus *Helianthus* to the family Asteraceae. Due to the plant's size and sun-like appearance, the name "sunflower" was given to it. The name is also derived from its movement in the direction of the sun. As the most valuable and economically viable oilseed crop worldwide, sunflower is placed fourth behind soybeans, rapeseed, and safflower [30]. 15% of the fatty acids in sunflower oil are saturated, while 85% are unsaturated and also contain double bonds that can be used to create polyols [31]. The majority of vegetable oil-based polyols are produced by taking advantage of carbon-carbon double bonds to incorporate hydroxyl groups [32]. In this project, for the synthesis

of sunflower oil-based polyol, first double bonds were broken and converted into an epoxide, then a polyol was produced via a ring-opening reaction.

The sunflower oil used to make polyol was purchased from a neighborhood Walmart (Pittsburg, Kansas, USA) and was used without purification. The measured viscosity of 0.07 Pa.s was recorded for the sunflower oil at 25 °C. The chemical structure of sunflower oil is shown in Figure 4.

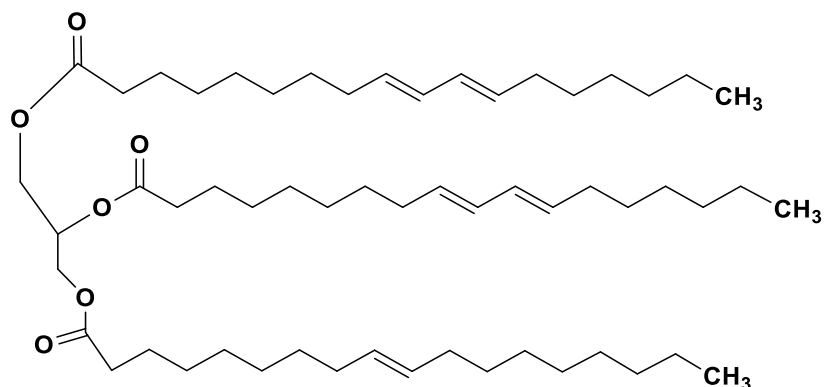


Figure 4: Chemical structure of sunflower oil

2.1.3 Additives

Different kinds of fillers are used in polymer to enhance their thermal, mechanical, and other characteristics. After getting impressive bonding strength with control samples, silicon dioxide (SiO₂), microcrystalline cellulose (MCC), and titanium dioxide (TiO₂) were introduced as a filler to improve bonding strength.

2.1.3.1 Silicon dioxide

The characteristics of the polymer can be enhanced by a significant increase in the interfacial area between fillers and the polymer. For these reasons, a variety of metal oxide nanoparticles, including SiO₂, TiO₂, ZnO, etc., are used. These inorganic fillers are safe, non-toxic, and extremely thermostable. SiO₂ can improve

the composite's thermal and mechanical characteristics [33]. In this research, SiO₂ (AEROSIL 380) was used to increase tensile strength. The chemical structure of SiO₂ is shown in Figure 5.

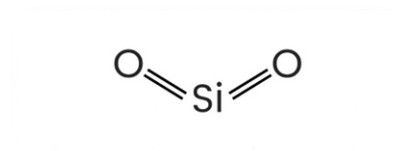


Figure 5: Chemical structure of SiO₂

2.1.3.2 Titanium dioxide

The primary objective is to increase the adhesive's performance through the addition of nano-sized TiO₂ as filler. It has been observed that this has a direct effect on the mechanical, physical, and chemical characteristics of the final adhesive [34,35]. In this research, TiO₂ (particle size 10-15 nm) was used to increase bonding and thermal stability. TiO₂ powder was purchased from (Amazon, USA). The chemical structure of TiO₂ is shown in Figure 6.

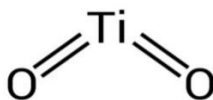


Figure 6: Chemical structure of TiO₂

2.1.3.3 Microcrystalline cellulose

Microcrystalline cellulose is a naturally occurring, non-toxic, completely biodegradable substance that is produced industrially from lignocellulosic biomass, typically farming, forestry, and marine waste [36]. Due to its high degree of crystallinity, MCC is the ideal reinforcing filler due to its low density, high specific

strength, and viscosity, as well as its high thermochemical stability and resilience to expansion in water. For this research, MCC was purchased from Sigma-Aldrich (MO, USA). The chemical structure of MCC is shown in Figure 7.

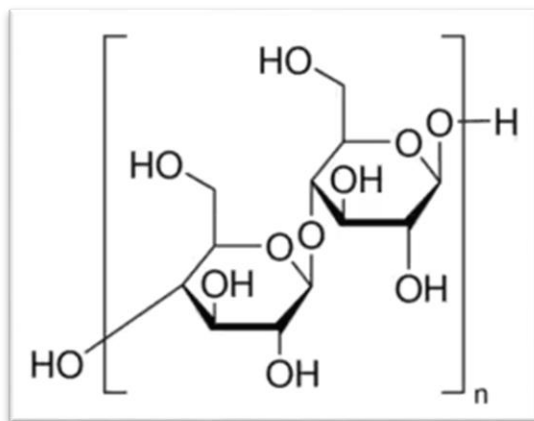


Figure 7: The chemical structure of microcrystalline cellulose

2.2 Synthesis of polyol from sunflower oil

In order to create the bio-based polyol from sunflower oil, an epoxidation reaction and ring-opening reaction with methanol were used.

2.2.1 Epoxidation of sunflower oil

Epoxidation is the process of creating an epoxide by adding an oxygen bridge across a double bond. Epoxide groups have a high degree of reactivity, making them useful as active intermediates in the synthesis of substances of high economic value, including alcohols, glycols, alkalamines, carbonyl compounds, olefinic compounds, and polymers like polyester, polyurethane, and epoxy resin [37]. There are four alternative ways to make epoxies from alkenes (carbon-carbon double bonds), including epoxidation with percarboxylic acid, organic and inorganic peroxides, halohydrins, and molecular oxygen. Acetic acid served as an

oxygen donor, while hydrogen peroxide served as an oxygen transporter. The double bond of oil was converted into an epoxide ring [38]. Important factors for a successful epoxidation process include temperature, catalysts, and environmental factors [39].

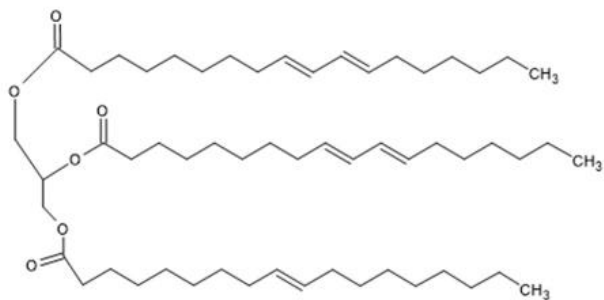
A three-necked flask was filled with 300 g of SFO and 150 mL of toluene (50% wt. of SFO). After that, 75 g of amberlight IR 120 H resin (catalyst) was added. The resulting mixture was then stirred for 15 minutes to ensure homogeneity. After that, 44 mL of acetic acid was added gradually using a dropping funnel for the subsequent 30 minutes while being stirred. 180 mL of 30% wt./wt. of H_2O_2 was added between the temperature range of 5-10 °C. A dropwise manner was employed as a safety measure to avoid any overheating based on by exothermic nature of epoxidation processes [40]. The temperature was raised and kept at 70 °C for the following eight hours after the H_2O_2 solution was added. After that, the resin was decanted using a filter, and the system as a whole was cooled to room temperature.

The mixture was filtered by washing it with 10% brine in a separatory funnel. Periodically adding brine and stirring the mixture allowed the aqueous layer to separate from the oil. As a drying agent, anhydrous sodium sulfate was added and mixed into the mixture. The residual solvents in the mixture were extracted by rotary evaporation using both low and high vacuum pressures after the sodium sulfate was filtered out. The epoxide sunflower oil (ESFO) was synthesized, and it was examined using confirmatory tests such as FT-IR, epoxy number, and GPC.

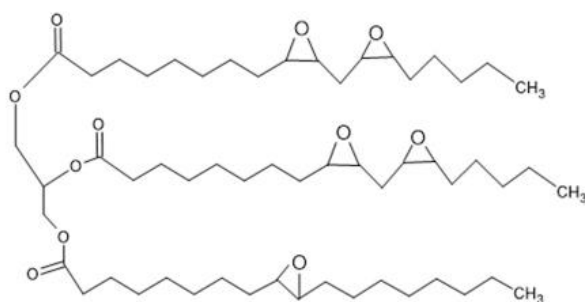
2.2.2 Ring-opening of ESFO into polyol

The basic structure of an epoxy ring consists of oxygen bonded to two adjacent carbons. The presence of an electrophilic strained epoxy ring in the ring-opening reaction allows a nucleophilic attack by a beta-substituted hydroxyl group [39]. Mono-alcohols, diols, and carboxylic acids are the nucleophiles that have been studied the most for ring-opening; however, weaker nucleophiles such as amines, water, and thiols have been investigated and demonstrated to be low reaction rates [41,42].

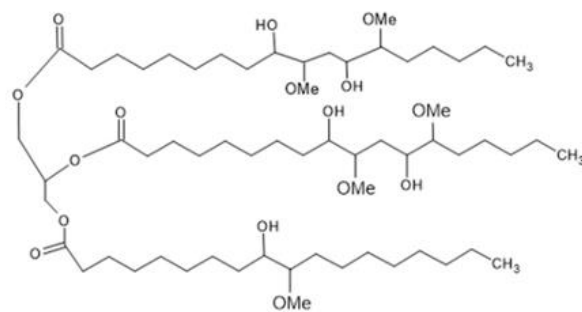
In this research, methanol and epoxidized sunflower oil were employed with a molar ratio of 7:1. The amount of tetrafluoroboric acid (HBF_4) measured, was equal to 50% weight of water, plus 0.05% of methanol and epoxidized oil. A three-necked flask connected to a condenser and dropping funnel was used to prepare the reaction mixture of methanol and tetrafluoroboric acid at a temperature of around 70 °C. The previously synthesized ESFO was added dropwise after several minutes of mechanical stirring. After the addition of ESFO, the solution was refluxed for 1 hour in presence of a condenser to prevent the evaporation of methanol. Then, Lewatit MP 64 ion exchange resin was added and mechanically stirred in the mixture to neutralize the acid. After ensuring $\text{pH}=7$, the solution was filtered to remove the resin, then treated for rotary evaporation. To confirm the generation of the hydroxyl group, further characterization of the synthesized polyol was carried out. The illustration of the ring-opening and epoxidation of sunflower oil is presented in Figure 8 [43].



Sunflower oil



Epoxide sunflower oil



Sunflower polyol

Figure 8: Ring-opening and epoxidation reaction of sunflower oil

2.3 Characterization of sunflower oil-based polyol

2.3.1 Iodine value

One of the most significant and preliminary experiments in this research was to determine the iodine value of sunflower oil. This is so that the iodine number can be used to determine the number of double bonds present in an unsaturated compound. A double or triple bond found in an unsaturated substance can be successfully reacted with iodine. The existence of highly unsaturated fatty acids would be demonstrated by a high iodine value [39]. In this experiment, the Hanus titration method was used to determine the number of double bonds in the sunflower oil used in the production of polyols.

2.3.2 Epoxide number

For the determination of epoxy oxygen content, glacial acetic acid and tetraethylammonium bromide were used. This test was done to confirm the formation of the epoxide groups from the double bond. To perform this test, 0.5 g of epoxidized sunflower oil was dissolved in 50 mL of tetraethylammonium bromide (TEAB) solution. Titration with 0.1 N perchloric acid was performed after adding a drop of crystal violet indicator to the solution. The titration ended when the color changed from blue to green, and the measured volume was used to determine the amount of epoxy present in the epoxidized sunflower oil. Before starting further reaction for polyol, this test was repeated 2 more times and the average value of a total of 3 tests was taken.

2.3.3 Hydroxyl value

The hydroxyl number (-OH value) is used to calculate the number of hydroxyl groups in a compound. The -OH value of polyol provides important information about the functionality and the required amount of isocyanates for an effective chemical reaction. To find the -OH value of sunflower polyol, following ASTM-D 4274, the phthalic anhydride pyridine (PAP) technique was used. In a glass bottle, 10 mL of a hydroxyl solution was mixed with 0.5 g of the sunflower polyol. The bottles were loosely capped and placed in a preheated oven at 100 °C for 70 minutes. During that time, the solution was shaken every 15 minutes. The mixture was then brought to room temperature, and 10 mL of HPLC-grade water and 20 mL of isopropanol were added. These additions were then mixed for nearly 10 minutes. After that, 1 N NaOH was added and titrated until a pink color appeared. The amount was measured and used to determine the hydroxyl number.

2.3.4 Acid value

The identification of acid value was accomplished using the IUPAC 2.202 standard procedure. About 1 g of the material was dissolved in 30 mL of the solvent mixture (isopropanol, toluene, and phenolphthalein indicator). 0.1 N potassium hydroxide was added gradually until a pink color shift was observed. The volume was measured and used to determine the acid values. The acid value after the formulation of the sunflower polyol was 0.37 mg KOH/g.

2.3.5 Fourier-transform infrared spectroscopy

FT-IR is a quick technique for identifying the existence of various functional groups in a compound. The presence of the absorbance peaks can be used to

identify changes in the final product. The spectrum results of synthetic materials were achieved in this experiment using the PerkinElmer Spectrum Two Spectrophotometer at room temperature (Figure 9).



Figure 9: Fourier-transform infrared spectroscopy (Spectrum Two, PerkinElmer)

2.3.6 Viscosity

Viscosity is a measurement of the resistance of the flow of a substance. Viscosity is related to molecular weight, where higher molecular weight leads to higher viscosity. In addition, a lower level of viscosity correlates to ease of further reaction. For the measurement of viscosity, an AI 2000 dynamic stress rheometer (TA instrument, USA) as shown in Figure 10 was used. The viscosity was measured at 25 °C with shear stress increasing from 1 to 200 Pa. The dynamic rheometer was equipped with a cone plate having an angle of 2° and a cone diameter of 25 mm.



Figure 10: AR 2000 dynamic stress rheometer

2.3.7 Gel permeation chromatography

GPC, also known as size exclusion chromatography was used to evaluate compounds in a mixture by distributing them based on molecule size. After epoxidation and the ring-opening process, sunflower epoxide and polyol production from the oil was investigated and confirmed using this characterization method. The Water GPC instrument was used as shown in Figure 11 with 4 phenogel 5 μ columns (300 mm \times 7.8 mm) containing various pore sizes of 50, 102,

103, and 104 Å. THF was used as a solvent, and the flow rate was 1 ml/min at 30 °C.

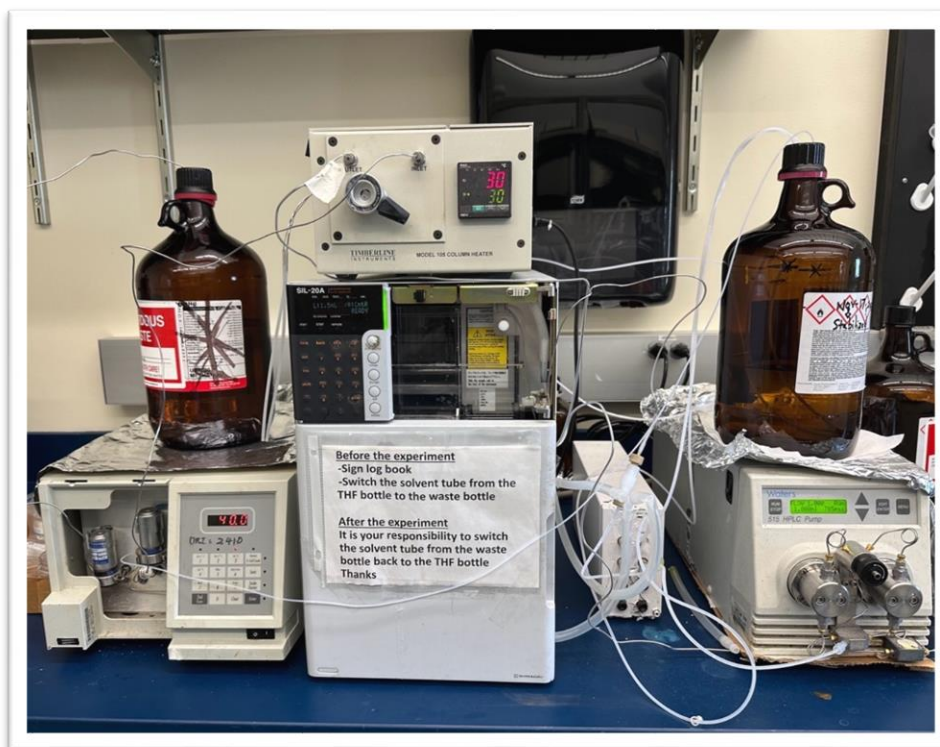


Figure 11: Gel permeation chromatography

2.4 Sample preparation

For the preparation of the control sample of sunflower oil-based wood adhesive, initially, sunflower polyol and MDI were transferred into a beaker. After the addition of MDI, the mixture was sonicated for the next 10 minutes for proper dispersion, and the final adhesive solution was formed. For the preparation of the wood specimen, oakwood was cut in the dimension of 25 mm x 75 mm x 1 mm (width x length x thickness). Around 140 g/m² adhesive was applied on the 25 mm x 25 mm (length x width) area. Prepared samples were pressed by a hot-press

instrument. A hot-press instrument as shown in Figure 12 (Model 3891 Carver, Inc., Wabash, IN, USA) was used. The variations in press time and temperature were performed. TiO_2 , SiO_2 , and MCC were used as fillers to increase the bonding strength. Each filler was used with different proportions for the formulation of various types of adhesives.



Figure 12: Hot-press instrument (Instron, USA)

2.5 Characterization of bio-based adhesive

2.5.1 Thermogravimetric analysis

For the determination of the thermal stability of adhesive made from sunflower polyol, the TGA (Q500, Discovery, Trios, USA) instrument as shown in Figure 13 was used. Adhesive samples were heated under a nitrogen atmosphere from 25 to 600 °C at a temperature ramp of 10 °C per min.



Figure 13: Thermogravimetric analysis (TGA550, TA instruments)

2.5.2 Shear strength measurement

Dry shear strength measurement was conducted using an Instron Model 3367 (Instron, USA) as shown in Figure 14 with a 10 mm/min crosshead speed. The given figures for the shear strength under maximum load are the averages obtained from measurements made on three separate specimens. The ASTM Standard Procedure D2339-98 was used to measure the strength.



Figure 14: Shear strength measurement instruments

2.5.3 Differential scanning calorimetry (DSC)

A Differential scanning calorimetry instrument was used for thermal analysis to evaluate changes in the physical characteristics of samples and their temperature over time. DSC can be used to measure glass transition temperatures (T_g), crystallization temperature (T_c), and melting temperature (T_m). In this research,

all DSC tests were performed using DSC Q100 instruments (TA Instruments, USA) as shown in Figure 15. During all tests, the temperature range was set to -50 to 250 °C with a 10 °C /min ramp rate.



Figure 15: Differential scanning calorimetry instrument

2.5.4 Water contact angle

For measuring the hydrophobicity of adhesive samples, water contact angle (WCA) measurement was performed using Ossila Contact Angle Goniometer (as shown in Figure 16). For this experiment, a droplet of 10 μL distilled water was dropped on the surface of the sample at room temperature.



Figure 16: Ossila water contact angle instrument

2.5.5 Atomic force microscope

For the characterization of the surface roughness of adhesive samples, an atomic force microscope instrument was used. This instrument was used to obtain high-resolution images of the surface. The AFM instrument (as shown in Figure 17) was purchased from AFM Workshop (South Carolina, USA).



Figure 17: Atomic force microscope instrument

CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of sunflower oil-based epoxy and polyol

3.1.1 Iodine value

The Hanus technique was employed to measure the iodine value and calculate the value of unsaturation or the number of double bonds in sunflower oil and its derivatives. The iodine value of sunflower was 100 g I₂/100 g oil, which indicates that 0.39 molecules of double bonds were present in 100 g of the sunflower oil sample. After the epoxidation and ring-opening reactions, the measured iodine value for the epoxide and polyol was 0.02 g I₂/ 100g and 0.01 g I₂/ 100g respectively.

3.1.2 Hydroxyl number

The hydroxyl number is one of the most essential polyol factors because it controls isocyanate reactivity and quantity required for polyurethane production. In this research, the calculated -OH value for sunflower polyol was 190.74 mg KOH/g.

3.1.3 Epoxide value

The percent oxirane value calculates a compound's epoxide group amount. In this research, after the epoxidation reaction of sunflower oil, the epoxide number was measured for epoxide sunflower oil: it was 4.91%. This reaction was done with

hydrogen peroxide and acetic acid in the presence of the catalyst. After the ring-opening reaction, the epoxide number for polyol was observed to 0.1%, which confirms the conversion of the epoxy ring into hydroxyl groups.

3.1.4 Fourier-transform infrared spectroscopy

The existence of various functional groups in particles was determined by FTIR. This method was employed as one of the efficient ways of verifying the synthesis of the polyol and epoxide from sunflower oil. One of the common indications of unsaturation can be found in the range of 2989–3029 cm^{-1} in the FTIR spectra of some fats and vegetable oils [44]. FTIR spectra of sunflower oil, epoxide sunflower oil, and sunflower polyol are shown in Figure 18. The peak which was observed around the wavelength at 3008 cm^{-1} indicates the presence of a =C-H in the sunflower oil based on the stretching vibration from the =C-H bonded to it [45, 46]. That peak disappeared following the ring-opening reaction and a new peak appeared around 834 cm^{-1} . This current peak is associated with the bending from the epoxy group in the C-O-C ring [40].

To confirm the formulation of sunflower polyol, the wide peak was observed around 3477 cm^{-1} . This wide peak illustrates the stretching vibration generated by present hydroxyl groups in a molecule [47– 49]. This FTIR peak confirms the formulation of sunflower oil-based polyol and gave evidence to start further synthesis for making sunflower polyol-based adhesive.

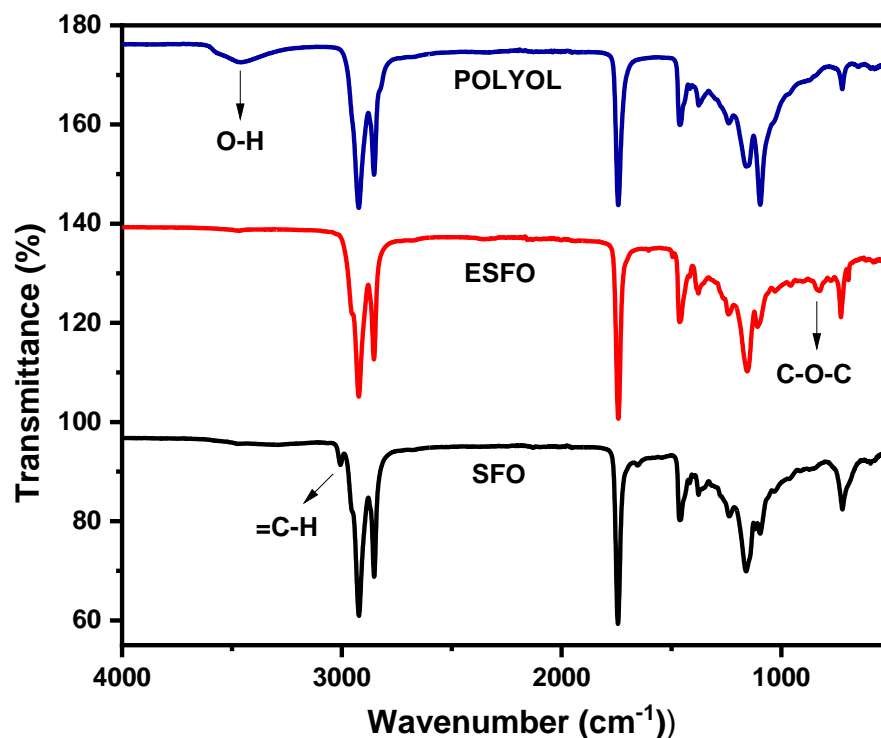


Figure 18: FTIR spectra for sunflower oil (SFO), epoxide sunflower oil (ESFO), and sunflower polyol (SFO-Polyol)

3.1.5 Gel permeation chromatography

This scientific technique can be utilized for monitoring the process of a reaction. Analytes can be divided based on the range of weights for a particular GPC column. Smaller compounds are more likely to spend more time in the column and have an extended retention time because of the porous beads in the column. On the other hand, larger molecules will have fewer routes of entry, stay in the column for a brief period of time, and be simplified to elute. As shown in Figure 19, the green peak represents the sunflower polyol that comes out first at 22.2 minutes. The retention time for the epoxide and sunflower oil is 22.5 and 22.7 minutes

respectively. The lowered retention time of the sunflower polyol compared to its initial and intermediate products suggests that the polyol has formed.

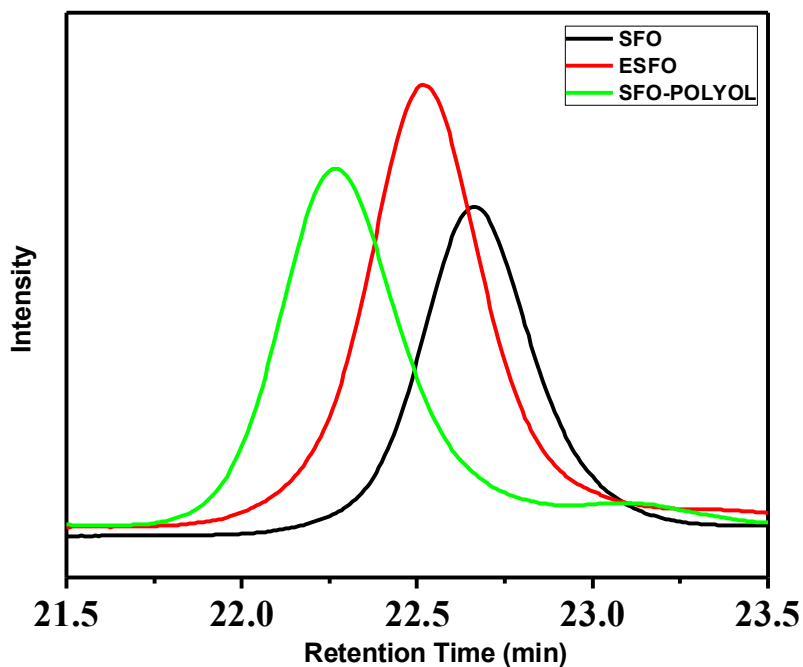


Figure 19: GPC results for sunflower oil (SFO), epoxide sunflower oil (ESFO), and sunflower polyol (SFO-Polyol)

3.2 Viscosity measurement

Viscosity is an evaluation of a material's flow for movement, and it can have a big impact on how easily samples can be processed. The measured viscosity of sunflower oil was 0.071 Pa.s, which gradually increased and reached 0.16 Pa.s and 1.61 Pa.s for epoxide sunflower oil and sunflower polyol, respectively. Viscosity from sunflower oil to polyol gradually increased, indicating that molecular weights increased during the conversion processes. For the formulation of wood adhesive, after the addition of MDI into the polyol, a change in viscosity was

observed. The viscosity of the control sample of the wood adhesive solution was 1.79 Pa.s.

An increase in viscosity was observed, after adding various fillers such as SiO₂, TiO₂, and MCC to the wood adhesive solution. To obtain excellent adhesive qualities, the viscosity of the adhesive should be modified. A less viscous adhesive spreads and fills wood more readily. However, it should not be too low as it will have trouble covering the wood. A different proportion was taken of each filler for the formulation of wood adhesive samples. Samples loaded with 5 and 10 (wt.% to polyol) with each filler were tested for viscosity. The viscosity of the samples loaded with 5 and 10 (wt.% to polyol) SiO₂ filler was 3.94 Pa.s and 22.07 Pa.s, respectively. For TiO₂, viscosity was 2.44 Pa.s and 5.55 Pa.s for 5 and 10 (wt.% to polyol) samples, respectively. The viscosity of the samples loaded with 5 and 10 (wt.% to polyol) MCC filler was 2.43 Pa.s, and 5.74 Pa.s, respectively.

3.3 Contact angle measurement

For measuring the contact angle, the prepared adhesive sample was applied on the surface of a specimen and placed at room temperature for 24 hours. To measure contact angle, a droplet of 10 µL distilled water was dropped on the surface of the sample. The same as the viscosity measurement, the contact angle test was also done on samples loaded with 5 and 10 (wt.% to polyol) with each filler. The contact angle for the control sample was 65.80°. The contact angle of the sample loaded with 5 and 10 (wt.% of polyol) SiO₂ filler was 71.00° and 82.48°, respectively. TiO₂ filler's contact angle was 69.14° and 84.89° with 5 and 10 (wt.% of polyol), respectively. For MCC filler, a significant change was observed.

Samples made from 5 and 10 (wt.% of polyol) MCC filler were tested and contact angle was 85.02° and 99.23° , respectively. As shown in Figure 20, an increment in contact angle was observed with increasing the wt% of fillers for all three fillers.

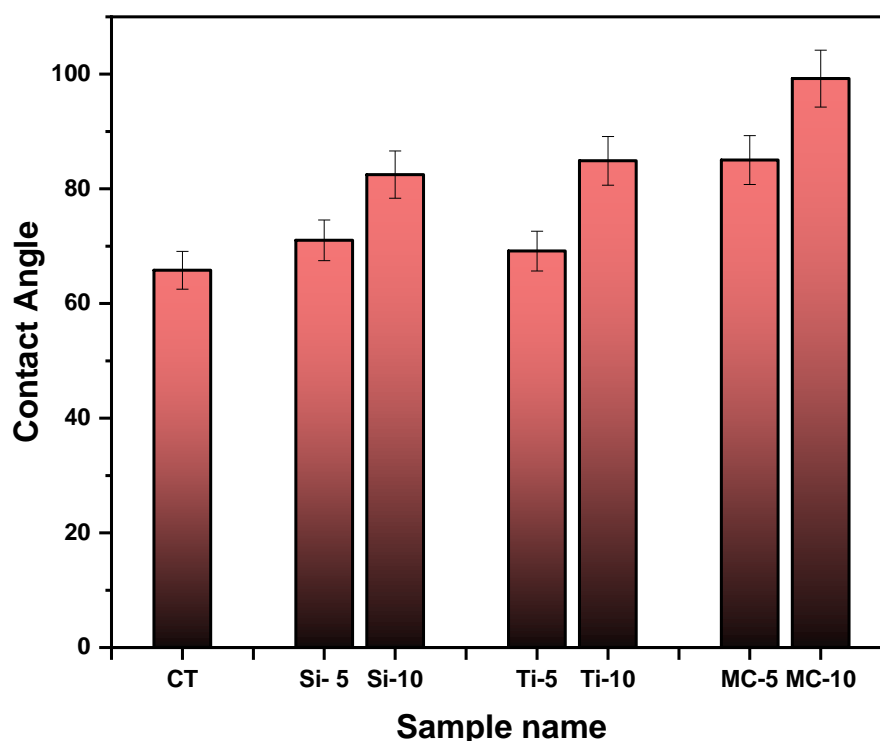


Figure 20: Contact angle results

3.4 Thermogravimetric analysis

Figure 21 represents the degradation behavior of the control standard sample (CNT-STD) and all samples with fillers of different amount (MCC-5%, MCC-10%, TiO_2 -5%, TiO_2 -10%, SiO_2 -5%, SiO_2 -10%) against the temperature. All the samples possessed one-stage degradation. Up to 100°C all the volatile materials and moisture evaporated from the samples. It can be demonstrated from

Figure 21 that the initiation of degradation of the CNT-STD starts around 287 °C. However, the incorporation of fillers such as MCC, SiO₂, and TiO₂ enhanced the initial degradation temperature marginally.

For instance, the initiation of degradation for MCC-5% and MCC-10% was found to be 296 °C and 298 °C. Increase in the thermal stability of the filler-based adhesives such as MCC-5% and MCC-10% was due to the presence of MCC in the adhesive. Similarly, samples SiO₂-5% (302 °C), SiO₂-10% (298 °C), TiO₂-5% (287 °C), and TiO₂-10% (290 °C) reflected increased initial degradation temperatures compared to CNT-STD. Interestingly, all the filler-based samples reported an increased initial degradation temperature, which confirms the enhanced thermal stability of the filler-based samples.

The final degradation of all the samples takes place around 450 °C. As temperature rises, degradation of chemical bonds such as C-O and N-O starts breaking and after 450 °C samples left a very small amount of residue. Noticeably, residual amounts left after the final degradation of all the filler-based adhesives were more than that of the CNT-STD sample (6.8%). A residual weight of 12.06%, 7.5%, 9.0%, 17.0%, 10.46% and 13.6% were shown by the filler-based samples MCC-5%, MCC-10%, SiO₂-5%, SiO₂-10%, TiO₂-5%, and TiO₂-10%. The incorporation of filler content enhances the residual masses left after the final degradation.

The above results show that the incorporation of fillers into all the samples lead to the increased thermal stability of all the samples compared to the CNT-STD.

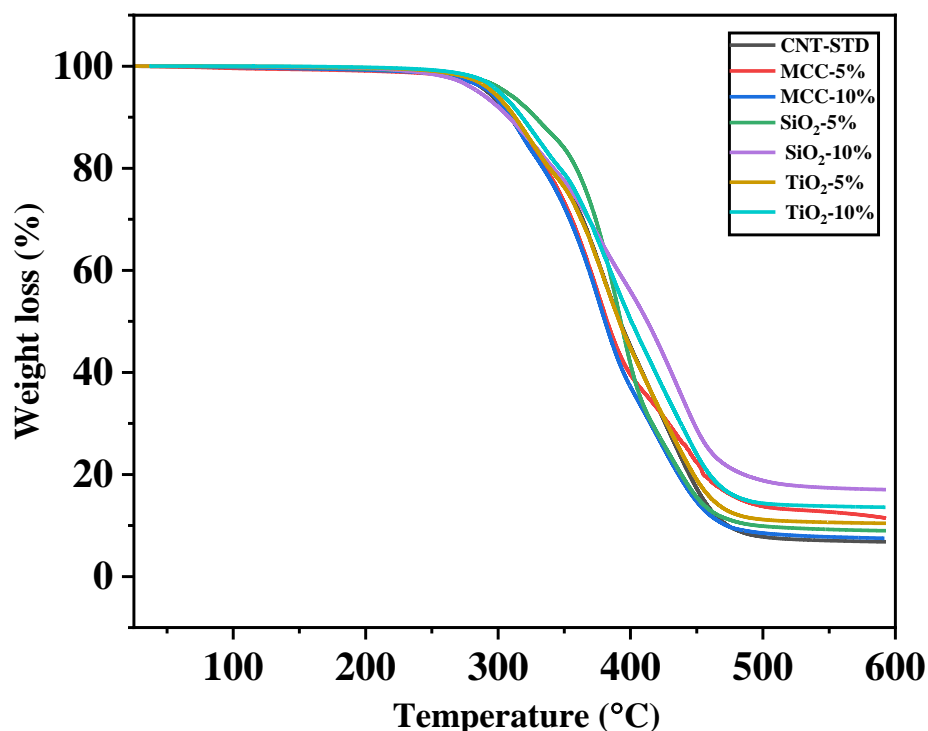


Figure 21: Thermogravimetric analysis results

3.5 Differential scanning calorimetry analysis

Figure 22 demonstrates the thermogram of the CNT-STD and all the samples. During the heating cycle sample, CNT-STD reported a peak of around 35 °C, which might appeared due to the softening of the sample. Likewise, samples MCC-5%, MCC-10%, SiO₂-5%, SiO₂-10%, TiO₂-5%, and TiO₂-10% recorded a glass transition temperature 42 °C, 38 °C, 36 °C, 39 °C, 36 °C and 40 °C, respectively. All the MCC, SiO₂, and TiO₂-filled samples reported an increased value of T_g compared to the pristine CNT-STD. This increase in the glass

transition temperature of MCC, SiO₂, and TiO₂-filled samples was exhibited as a result of restriction provided by these molecules to the molecular chain movement.

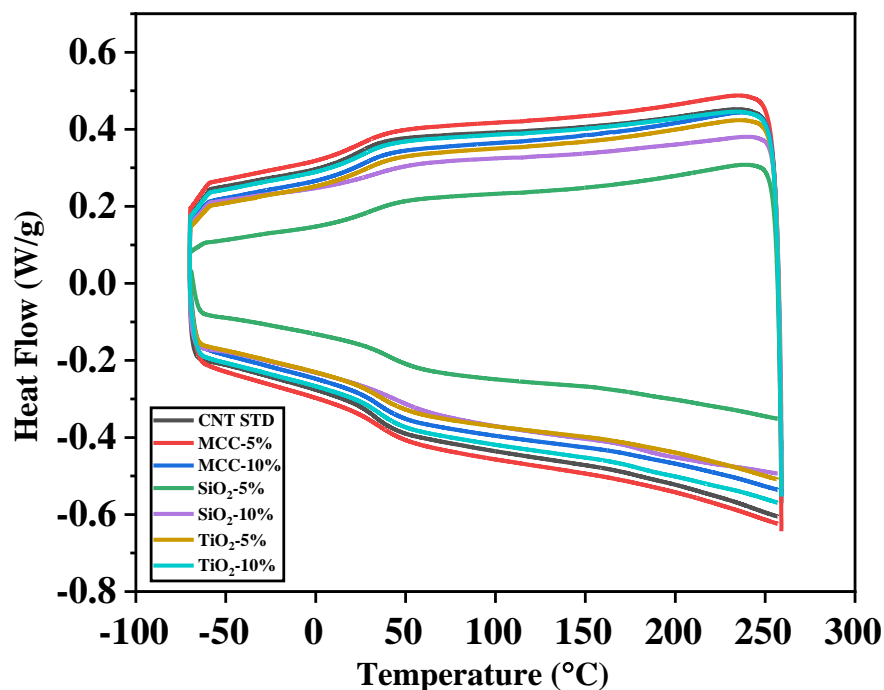


Figure 22: Differential scanning calorimetry analysis results

3.6 Single-lap shear strength

In this research, the sunflower oil-based wood adhesive samples were made by first combining sunflower polyol and MDI in a beaker at a 2:1 molar ratio. For the preparation of the wood specimen, oakwood was cut in the dimension of 25 mm x 75 mm x 1 mm (width × length × thickness). Around 140 g/m² adhesive was applied on the 25 mm × 25 mm (length × width) area. For the curing of all samples, two different techniques were used: manual clamping and hot-press. To prepare control samples, which were made without the addition of filler, the hot-

press technique was used with the variations in time and temperature as shown in Figure 23.

Hot-press was used under three different temperatures, 100 °C, 130 °C, and 150 °C. At each temperature, a set of 3 samples was cured with 5 different time durations. After being hot-pressed, the bonded wood was allowed to settle overnight before being evaluated for shear strength with an Instron machine with a 10 mm/min crosshead speed. The tensile shear strength was calculated using the following equation, where F_{max} is the highest applied force (in N), A is the adherend surface area (mm^2), a is the width (mm), and b is the length (mm).

$$\text{Tensile shear strength (MPa)} = F_{max} / A = F_{max} / a \times b$$

With 5 minutes of hot-press time, a set of 3 wood samples was cured at 100 °C, 130 °C, and 150 °C. The average shear strength of a 5 minute hot-press time duration for 100 °C, 130 °C, and 150 °C temperatures was 5.66 MPa, 4.55 MPa, and 3.73 MPa, respectively. These results indicate a downward trend with an increment in temperature. The average shear strength with a 10-minute hot-press time duration for 100 °C, 130 °C, and 150 °C temperatures was 4.65 MPa, 4.23 MPa, and 2.88 MPa, respectively. With respect to the same for 15 minutes hot-press time, results were 4.75 MPa, 3.80 MPa and, 2.72 MPa. The last two-time variations were 30 minutes and 60 minutes with 100 °C, 130 °C, and 150 °C. For 30 minutes results were 4.65 MPa, 4.45 MPa, and 4.32 MPa. The average shear

strength with a 60 minute hot-press time duration for 100 °C, 130 °C, and 150 °C was 5.11 MPa, 4.23 MPa, and 3.77 MPa, respectively.

After testing all samples, as shown in Figure 23, the highest shear strength for control samples, 5.66 MPa was observed with a 5 minute hot press at 100 °C temperature. This temperature and time were considered ideal for all remaining sample testing.

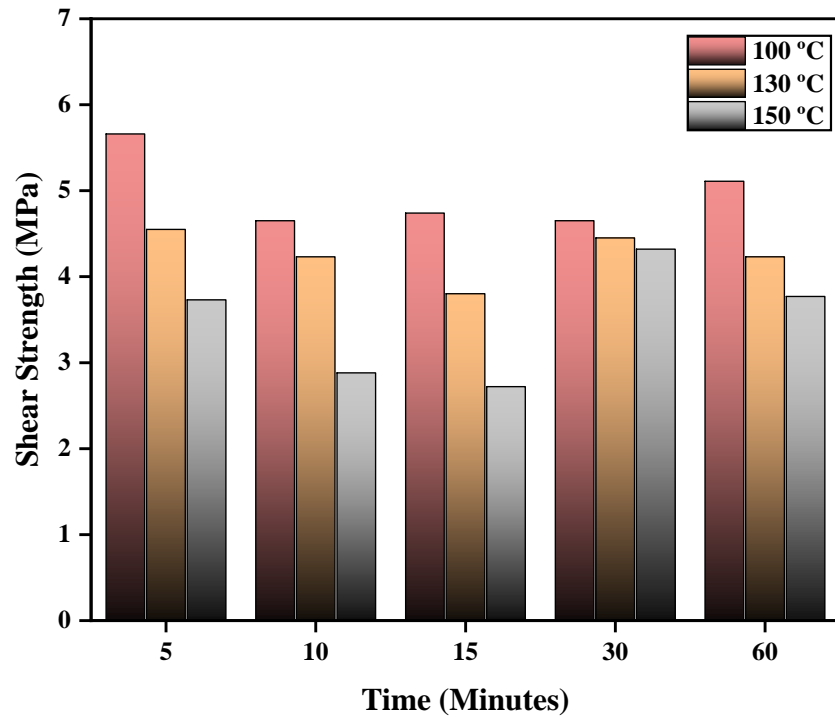


Figure 23: Shear strength results for control samples

3.6.1 Single-lap shear strength for SiO₂ filler

After achieving remarkable bonding strength with control samples and variations in curing time and temperature with hot-press, titanium dioxide, silicon dioxide, and cellulose microcrystalline were added as fillers to further enhance the bonding strength. Along with the hot-press technique, a manual clamping technique was used to obtain results relating to real-life applications. For the preparation of wood adhesive samples, different proportions of SiO₂ filler were used. As per the highest result of a control sample, all samples were cured for 5 minutes at 100 °C temperature via the hot press.

For the samples made with SiO₂ filler and cured with the hot-press technique, an upward trend was observed up to 5 wt.%, and then a decrease in results was observed as shown in Figure 24. With 1 wt.% SiO₂ filler, the bonding strength was 6.41 MPa, which represents a 13% increase with respect to a control sample. For 3 wt.% SiO₂ filler, the bonding strength was 7.68 MPa. With 5 wt.% SiO₂ filler, the bonding strength was 10.49 MPa, which indicates an 86.25% improvement as compared to a control sample. After increasing the wt.% of SiO₂ filler decrease in the shear strength was observed. Samples made with 7 wt.% and 10 wt.% SiO₂ showed shear strength of 6.83 MPa and 3.99 MPa, respectively.

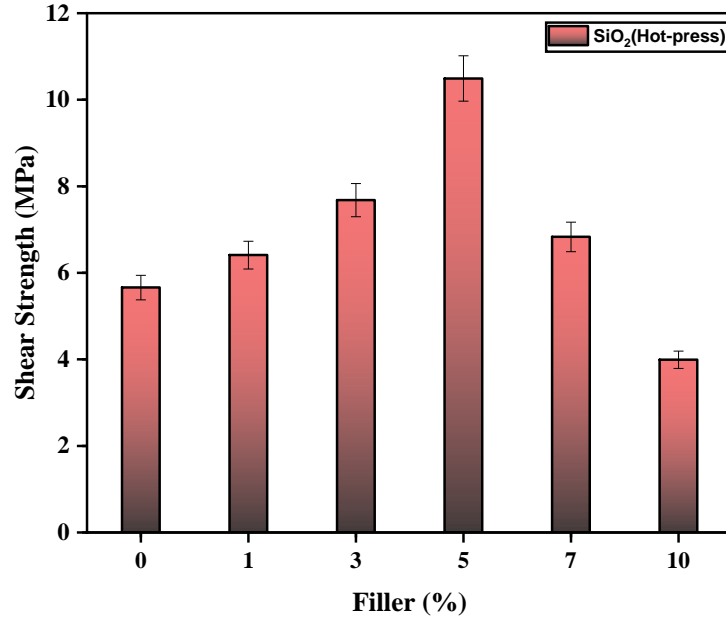


Figure 24: Shear strength results for samples [SiO₂ filler (Hot-press)]

Samples made with SiO₂ filler and with manual clamping technique observed an upward trend as well, with the same pattern decrease in shear strength observed after increasing the SiO₂ proportion over to 5 wt.% as shown in Figure 25.

7.28 MPa and 7.49 MPa bonding strength was observed with 1 wt.% and 3 wt.% SiO₂ loaded samples with manual clamping technique. Apart from that, with 5 wt.% SiO₂ loaded sample obtained 9.16 MPa bonding strength with a 62.50% increase as compared to the control sample. Samples made with 7 wt.% and 10 wt.% SiO₂ proportion obtained 5.99 MPa and 3.41 MPa bonding strength, respectively.

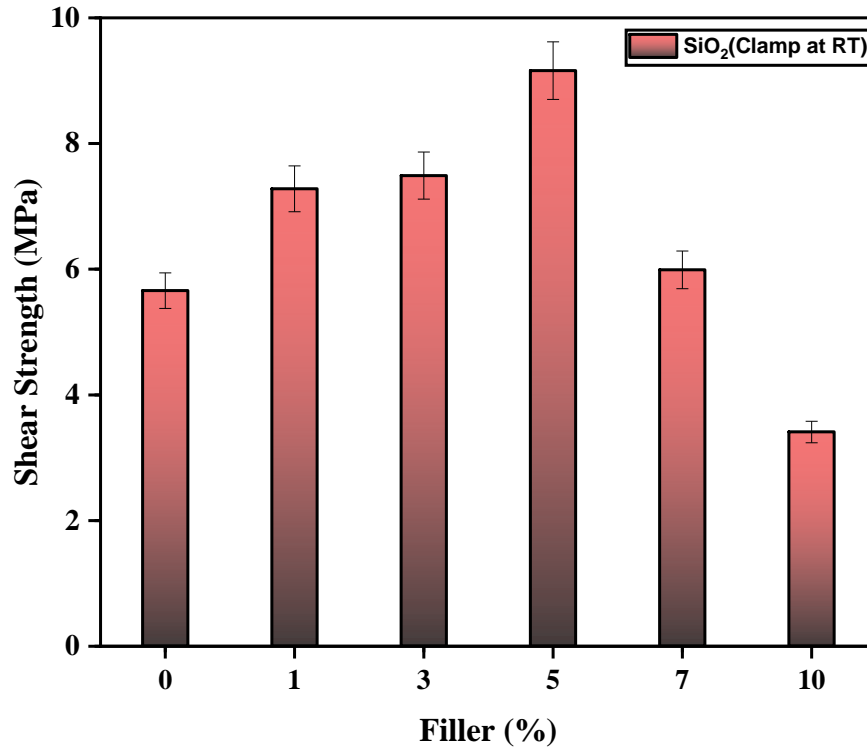


Figure 25: Shear strength results for samples [SiO₂ filler (Clamp RT)]

3.6.2 Single-lap shear strength for TiO₂ filler

After testing all samples for SiO₂ fillers with both curing techniques, all samples for the remaining two fillers were cured using manual clamping at RT. An upward trend was observed in TiO₂ as shown in Figure 26, with filler-loaded samples with manual clamping up to 10 wt.% content of TiO₂ and afterward, decrement in bonding strength was observed by the increasing proportion of TiO₂.

5.86 MPa and 6.38 MPa bonding strength was obtained with 1 wt.% and 3 wt.% TiO₂ loaded samples and with 5 wt.%, 7 wt.%, and 10 wt.% obtained 6.74 MPa, 6.88 MPa, and 7.18 MPa bonding strength, respectively. 7.18 MPa with 10

wt.% TiO_2 was the highest bonding strength result among all samples made from various proportions of TiO_2 . For 15 wt.% and 20 wt.% loaded samples, the obtained bonding strength was 6.96 MPa and 5.40 MPa which represent a downward trend.

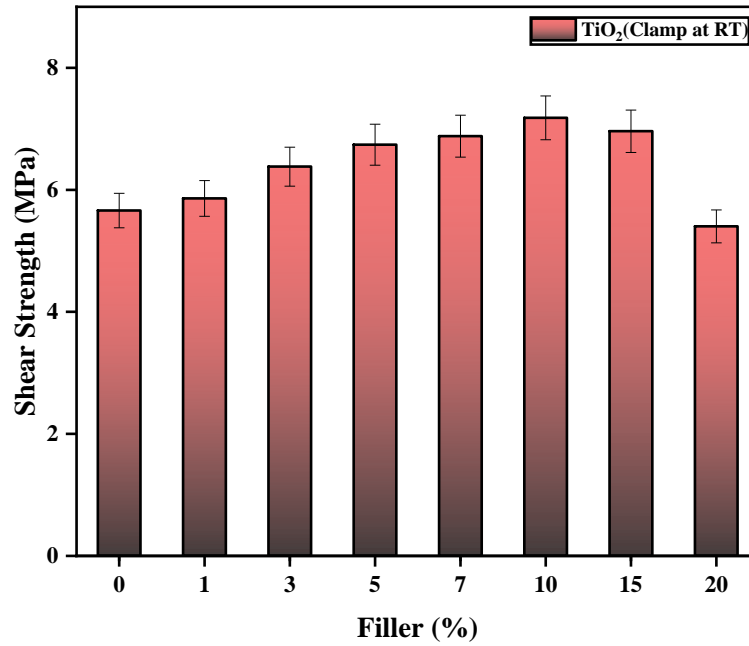


Figure 26: Shear strength results for samples [TiO_2 filler (Clamp RT)]

3.6.3 Single-lap shear strength for MCC filler

In the same manner as TiO_2 filler, a manual clamping technique was used to cure the samples made with microcrystalline cellulose filler. The variation in the proportion of MCC filler range from 1 wt.% to 20 wt.%. Apart from that, the same trend as TiO_2 filler was observed as shown in Figure 27, in bonding strength with MCC filler.

5.86 MPa and 6.26 MPa bonding strength was obtained with 1 wt.% and 3 wt.% MCC loaded samples with manual clamping technique. Along with that, 6.76

MPa, 7.44 MPa, and 7.61 MPa bonding strength were obtained with 5 wt.%, 7 wt.%, and 10 wt.% MCC loaded samples respectively. For 15 wt.% and 20 wt.% loaded samples, the bonding strength was 7.02 MPa and 5.48 MPa.

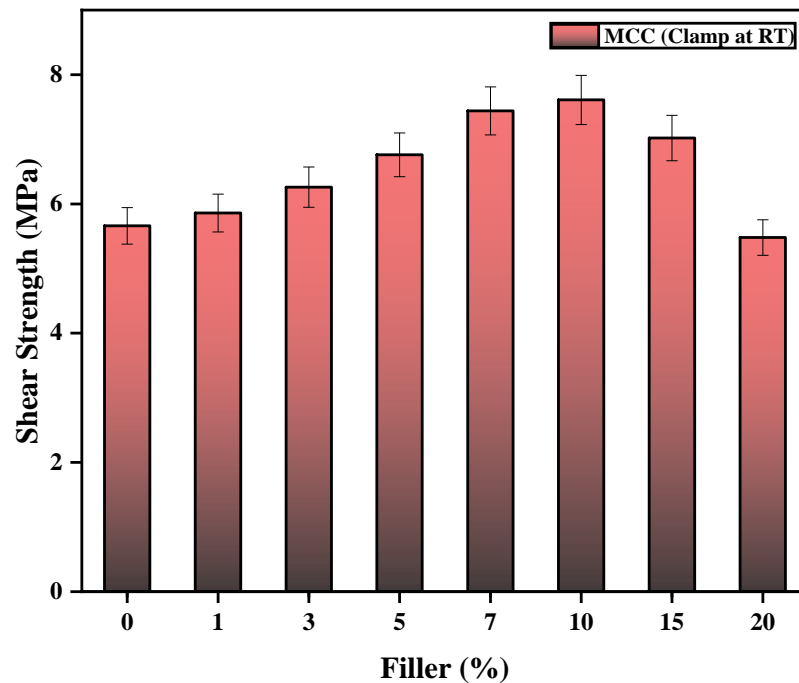


Figure 27: Shear strength results for samples [MCC filler (Clamp RT)]

3.7 Atomic force microscope analysis

Morphological characterization of adhesive samples was conducted using atomic force microscope instruments. By increasing the content of each filler, an increment in surface roughness was observed as compared to the control sample. AFM roughness images of all samples are shown in Figures 28-34. The figure 28 image represents the roughness of the control sample and the surface roughness for the control sample was 5 nm. Surface roughness of 5 wt.% and 10 wt.% SiO₂

loaded sample was 19nm and 25 nm respectively. With TiO_2 5 wt.% and 10 wt.% loaded samples, surface roughness was 25 nm, and 35 nm, respectively.

Compared to SiO_2 and TiO_2 filler, the sample made with MCC filler indicates higher roughness. 55 nm roughness was observed for the sample made with 5 wt.% MCC and for 10 wt.% MCC loaded sample roughness was 110 nm.

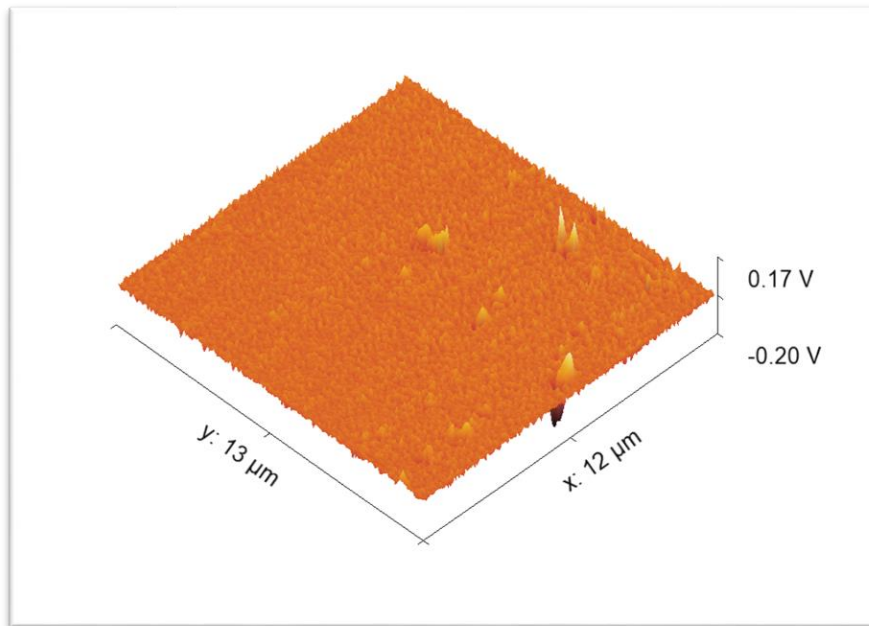


Figure 28: AFM image of the control standard sample

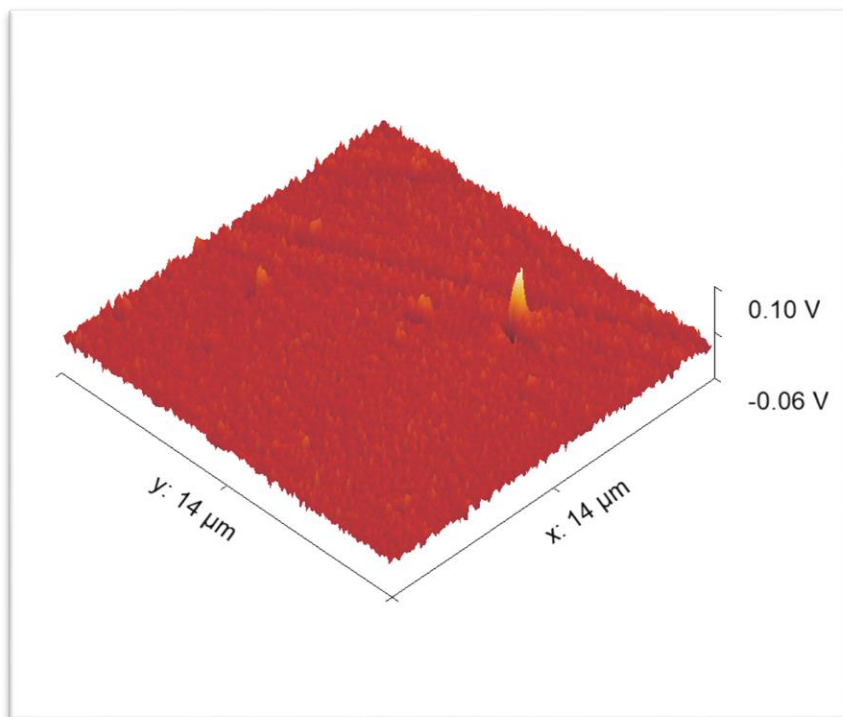


Figure 29: AFM image of the sample with 5 wt.% SiO₂

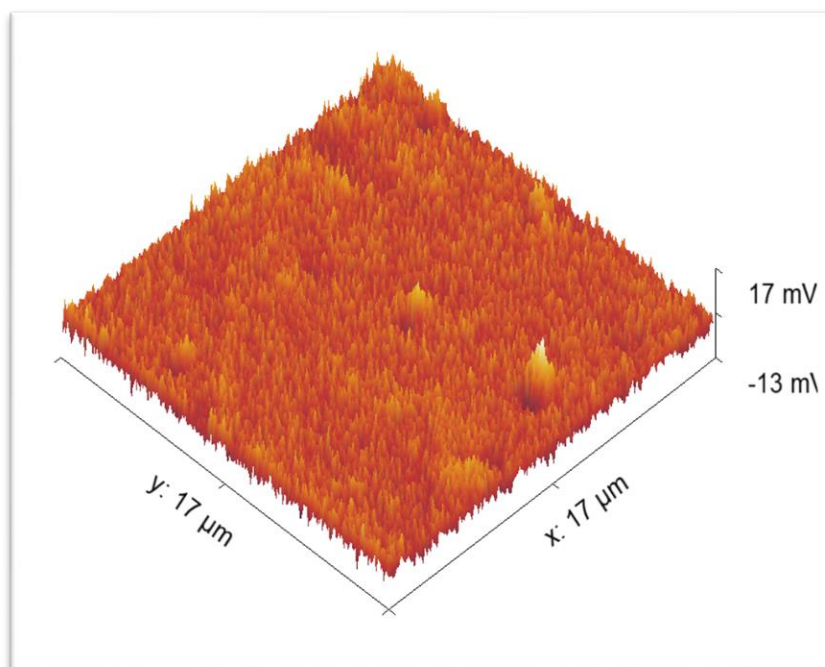


Figure 30: AFM image of the sample with 10 wt.% SiO₂

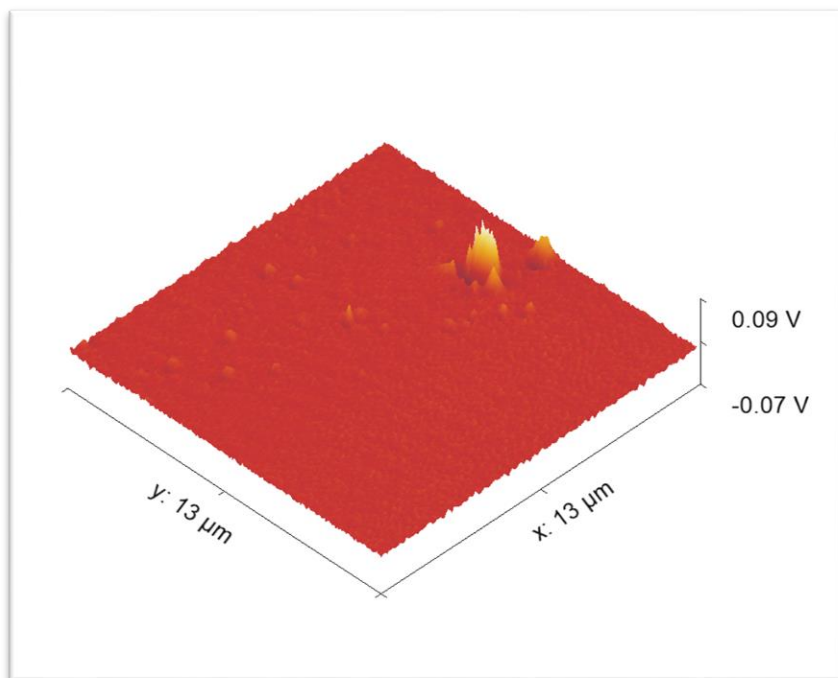


Figure 31: AFM image of the sample with 5 wt.% MCC

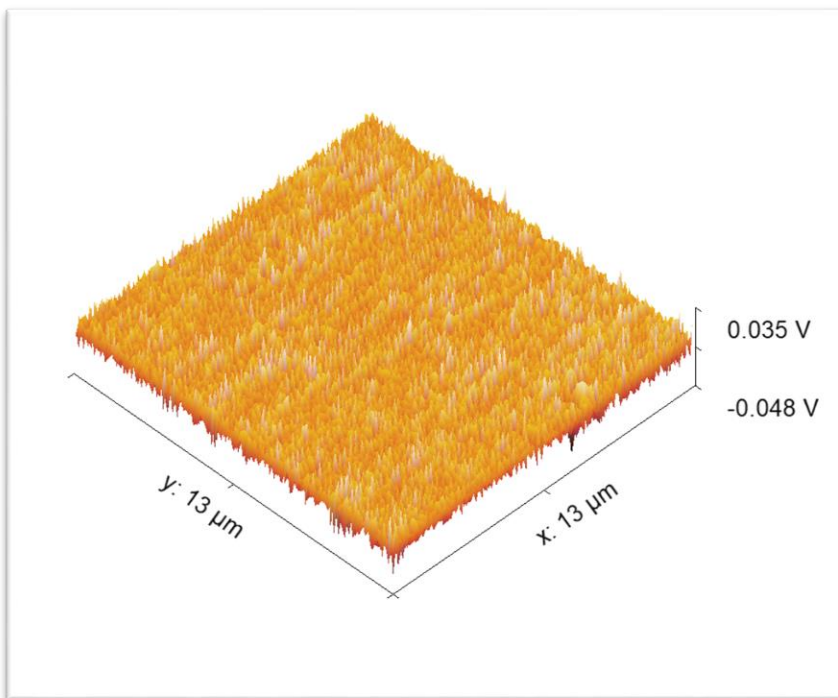


Figure 32: AFM image of the sample with 10 wt.% of MCC

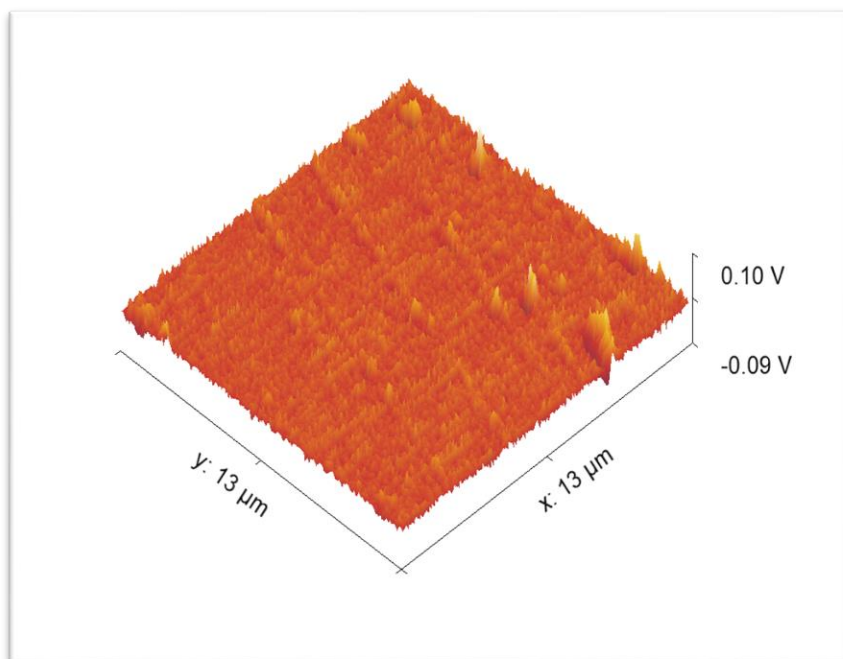


Figure 33: AFM image of the sample with 5 wt.% TiO₂

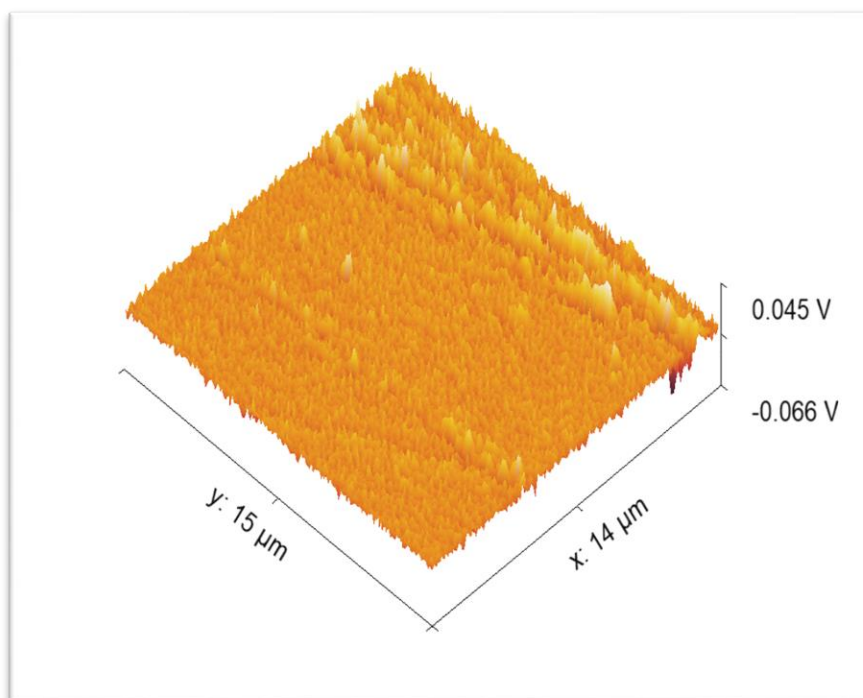


Figure 34: AFM image of the sample with 10 wt.% TiO₂

CHAPTER IV

CONCLUSION

In this research, bio-based wood adhesive was formed using sunflower oil, which represents an alternative to petroleum-based adhesive. Epoxidation reaction followed by the ring-opening reaction was performed to form sunflower oil-based polyol. To confirm the formation of polyol, confirmatory tests such as FTIR, GPC, and -OH value were performed. The control samples of wood adhesive were prepared with a single-step process of adding isocyanates into polyol. Along with that, three fillers were introduced for enhancing thermal and mechanical properties, and for curing the samples, hot-press, and manual clamping, two different techniques were used. 10.49 MPa was the highest shear strength result obtained for the sample made with 5 wt.% SiO₂ filler. Along with tensile strength, fillers also made a significant change in hydrophobicity. As compared to the control sample 51% increment in contact angle was observed with a 99.23° result. To conclude, sunflower oil was a suitable raw material for the synthesis of high-performance bio-based wood adhesives.

CHAPTER V

FUTURE WORK

- I.** The current study could be expanded to examine the impact of various cross-linkers and fillers on the general functionality and commercial aspects of wood adhesives based on vegetable oils.
- II.** Comparison can be made between sunflower oil-based adhesives and other vegetable oils-based wood adhesives.
- III.** Synthesis, based non-isocyanates routes can be an alternative to isocyanate-based wood adhesive for reducing toxicity level in a wood adhesive.
- IV.** Along with dry shear strength, wet shear strength measurement can be also tested after placing samples in water for a certain time.

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