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Study of a Carbon Fiber Reinforced Polymer Composite Using a Biobased Polyurethane as a Thermosetting Resin

Teddy Mageto
Pittsburg State University, t.mageto.7@gmail.com

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STUDY OF A CARBON FIBER REINFORCED POLYMER COMPOSITE USING A BIOBASED POLYURETHANE AS A THERMOSETTING RESIN

A Thesis Submitted to the Graduate School
In Partial Fulfillment of the Requirements
For The Degree of Master of Science

Teddy Brian Kaba Mageto

Pittsburg State University

Pittsburg, Kansas

May 2023

STUDY OF A CARBON FIBER REINFORCED POLYMER COMPOSITE USING A BIOBASED POLYURETHANE AS A THERMOSETTING RESIN

Teddy Brian Kaba Mageto

APPROVED:

Thesis Advisor ______________________________

Dr. Ram Gupta, Department of Chemistry

Committee Member ______________________________

Dr. Serif Uran, Department of Physics

Committee Member ______________________________

Dr. Khamis Siam, Department of Chemistry

Committee Member ______________________________

Dr. Timothy Dawsey, National Institute for Materials Advancement

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STUDY OF A CARBON FIBER REINFORCED POLYMER COMPOSITE USING A BIOBASED POLYURETHANE AS A THERMOSETTING RESIN

An Abstract of the Thesis By
Teddy Brian Kaba Mageto

Carbon Fiber Reinforced Polymer (CFRP) composites have garnered increasing interest in recent years especially in the aerospace and automobile industries where they are gradually replacing metals as structural materials. This is owing to their light weight, high strength, high modulus, and excellent strength-to-weight ratio. Polymers are typically used as thermosetting resins in these composites. However, the synthesis of polymers currently is conducted utilizing petrochemical-based materials which leads to adverse effects on the environment. To this end, in this work a biobased polyurethane (PU) was used as a thermosetting resin in a CFRP. The biobased PU was synthesized by the reaction of a sunflower oil-derived polyol with isocyanate. The CFRPs were then fabricated using increasing layers of carbon cloth ranging from 1 to 5. Mechanical testing of these composites was then carried out. Tensile test data showed an increase in maximum load before failure with an increase in the number of carbon cloth layers, with values of 1828 N, 5240 N, 7193 N, 10164 N, and 10774 N for composites made from 1, 2, 3, 4 and 5 layers of carbon cloth respectively. Young's modulus values showed a similar increase, with values of 44.7 GPa, 55.7 GPa, 56.4 GPa, 57.2 GPa and 63.9 GPa for composites made from 1, 2, 3, 4 and 5 layers of carbon cloth respectively being realized. Flexural testing data showed that there is an increase in the flexural modulus with an increase in the number of carbon cloth layers, with values of 315 GPa, 390 GPa, 656 GPa, 707 GPa, and 833 GPa for composites made from 1, 2, 3, 4 and 5 layers of carbon cloth respectively. A similar trend was observed in the hardness values of the composites, with values of 88D, 89D, 94D for composites made from 1, 2, and 3 layers of carbon cloth and values over 100D for the composites made from 4 and 5 layers of carbon cloth. Our composites show excellent chemical resistance properties with minimal degradation after immersion in water, acidic and basic solvents for 48h. This work suggests that CFRPs can be prepared using biobased polyurethanes.

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CHAPTER I

INTRODUCTION

1.1 Composite Materials

Composite materials are a class of materials which combine two or more distinct materials of differing properties. These materials do not dissolve or blend into each other, and as such can be easily distinguished from each other once the composite material has been fabricated. In general, composites are made up of two materials: (i) the reinforcement material (typically fibers) which carry most of the loads and provide most of the overall stiffness of the composite, and (ii) the matrix/binder material which transfers loads between the individual fibers and protects the reinforcement material from damage by mechanical abrasion or environmental factors [1]. These properties of the respective material components work synergistically to thus provide a material with enhanced properties compared to just using the components individually. Furthermore, the design flexibility of composites is also quite high by virtue of the basic composite parameters facilitating the geometrical arrangement of reinforcement fibers and the adjustment of fiber content [1]. Fiberglass is one of the most common composite materials that is used today, comprised of glass fibers as a reinforcement material embedded in a polymeric matrix.

1.2 Carbon Fiber Reinforced Polymer Composites

Carbon fiber reinforced polymer composites (CFRP) are a class of composite materials that are comprised of carbon fiber, as the reinforcement material, and a polymer matrix, as binder material, which transfers loads within the composite laminate fibers. The matrix is typically composed of a thermosetting or thermoplastic polymer, with epoxy resins being the most widely used [2].

CFRPs have attracted increasing attention as a class of materials for structural applications owing to their low density, exceptional strength-to-weight ratio, corrosion and fatigue resistance, low thermal expansion coefficient and high specific modulus [3–12]. As a result, CFRPs have found extensive use in the aerospace and automotive industries as structural materials and are gradually replacing traditional metallic structural materials in these industries. The Boeing 787 Dreamliner, for example, utilizes CFRPs, and other advanced composites, in nearly 50% of its airframe [13]. This application specifically targeted the utilization of CFRPs in areas of the aircraft under high tension loads, which is mainly the fuselage. This is due to the ability of CFRPs to efficiently handle tension loads, as compared to aluminum which is especially sensitive to tension loads but handles compression loads exceptionally well [13]. Through this expanded use of composite materials throughout the airframe, scheduled and non-routine maintenance due to fatigue and corrosion is greatly reduced, compared to a primarily aluminum-constructed airframe. Additionally, overall aircraft weight is greatly reduced through the incorporation of a composite primary aircraft structure.

Recent research in the development of biobased thermosets for CFRPs have mainly utilized vanillin as a renewable biomaterial. Wang et. al. fabricated a high-performance, biobased, degradable polyurethane thermoset for application in readily recyclable carbon fiber composites [14]. The researchers synthesized an acetal diol from the lignin derivative vanillin, which was then reacted with hexamethylene diisocyanate trimer to prepare the biobased polyurethane thermoset. The fabricated composites exhibited tensile strength of 381 MPa and Young's modulus of 16.3 GPa. In another study conducted by Zamani et. al., a multifunctional Schiff base monomer was synthesized from the reaction between vanillin and a phosponitrilic chloride trimer, after which it was cured using a diamine to form a Schiff base polymer that was utilized in the fabrication of CFRPs [15]. This CFRP exhibited flexural modulus of 54.2 GPa, Young's modulus of 47.3 GPa and tensile strength of 455 MPa. Liu et. al. synthesized a biobased high-performance epoxy vitrimer by curing a commercial biobased resin with an imine containing hardener and utilized the vitrimer as a matrix for a CFRP [3]. The hardener was a biobased compound from vanillin and 4-aminophenol. The fabricated CFRPs exhibited excellent mechanical properties, with Young's modulus of 12.9 GPa and tensile strength of 449 MPa.

1.2 Issues Facing CFRPs

Despite their numerous benefits, CFRPs do have inherent disadvantages. One main challenge is the high cost of fabrication of CFRPs. The production of carbon fibers involves the conversion of raw materials such as polyacrylonitrile into long, thin strands of carbon through a series of chemical and mechanical processes. The carbon fibers produced as a result must be woven into fabric and then impregnated with a polymer matrix material to form the composite. This production process is complex, energy-intensive, and labor-intensive, which in turn causes CFRPs to be more costly than the traditional metallic materials such as steel and aluminum.

Development of CFRPs can also have adverse effects on environmental sustainability. CFRPs utilize polymers that are currently produced using petrochemical-based starting materials which in turn leads to production of greenhouse gases because of the petrochemical-based processing of these raw materials. Additionally, CFRPs have limited recyclability compared to their traditional metallic counterparts. This is attributed to their complex structure, which makes it more difficult to recycle when compared to steel or aluminum, which can easily be melted down and reused. This brings about a situation where used CFRPs are disposed of in landfills which contributes to environmental pollution.

The sensitivity to environmental conditions is another challenge faced by CFRPs as they are highly susceptible to damage from moisture, heat and UV light. These environmental factors can degrade the structural integrity of the composite. Furthermore, the polymer matrix that is utilized in the CFRP can also be prone to degradation when exposed to certain chemicals such as acids and gasoline. Overall, this makes CFRPs more difficult to manufacture and utilize in certain applications and environments, such as those with extreme temperatures. Other general challenges faced by CFRPs include delamination, low resistance to impact, poor fatigue resistance, surface energy mismatch between the polymer matrix and reinforcement material, and poor wettability [16].

1.3 Polyurethanes

Polyurethanes are polymers that are synthesized from diisocyanate or polyisocyanate monomers and an oligomeric polyol [17, 18] first developed by Dr. Otto Bayer and partners [19]. The hydroxyl groups of the oligomeric polyol react exothermically with the isocyanate groups of the polyisocyanate monomer thereby resulting in the formation of multiple urethane linkages, hence forming polyurethane [20]. A functionality $\geq$ 2 is required for both the polyol and isocyanate to synthesize polyurethane [19]. **Figure 1** shows the basic chemical reaction between polyol and isocyanate to form polyurethane. Both the polyol and the isocyanate determine the final properties of the synthesized polyurethane and as such, any variation in the polyol or isocyanate can cause drastic changes in the final product [21]. In general, the polyol tends to have longer chains than the isocyanate thus facilitating better mobility and ultimately providing flexibility to the synthesized polyurethane [21]. Isocyanate, on the other hand, is a short chain molecule which facilitates higher crystallization, thereby forming compact, packed segments that are hard and rigid [21]. It is this combination that gives polyurethanes their versatility for a large range of applications.

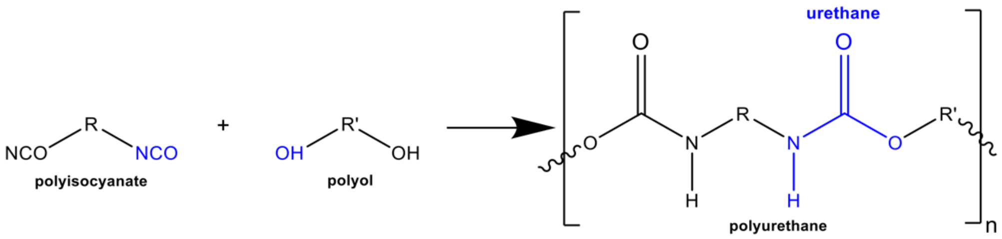

Figure 1: General polyaddition reaction between isocyanate and polyol to form polyurethane

1.3 Applications of polyurethanes

Polyurethane-based materials continue to generate a high demand in the market owing to their exceptional abrasion resistance, excellent stretchability, and high elasticity, with the global polyurethane market expected to grow up to \$81.74 billion by 2028 [20]. The dominance of polyurethane in many industrial applications comes down to its high degree of customization, as its properties can be drastically altered by making changes in functionality, molecular weight, and chain length. **Figure 2** gives a breakdown of polyurethane utilization across different applications in the United States as of 2021, with furniture and construction sectors having the market majority.

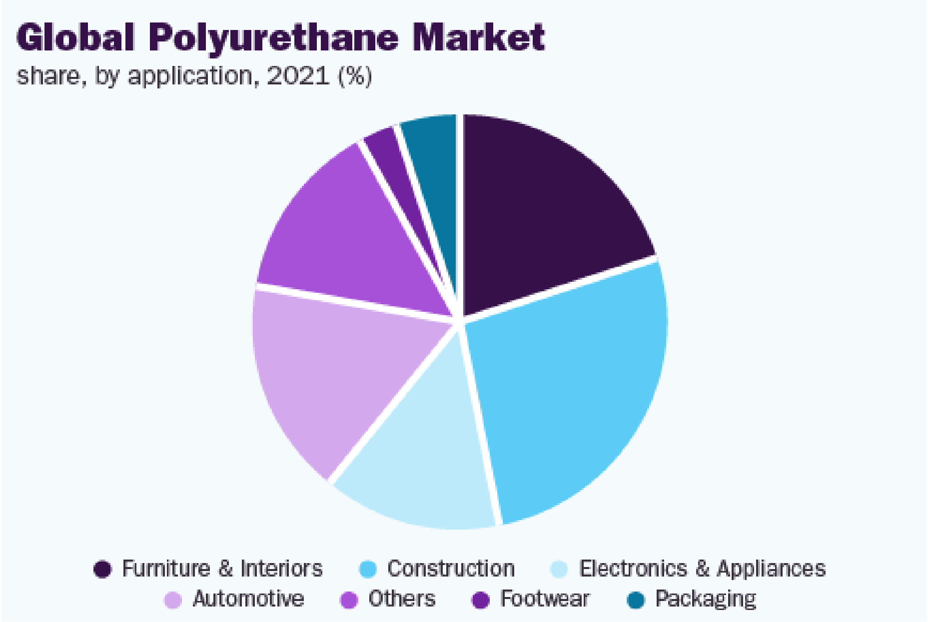

Figure 2: Global market consumption of polyurethane in 2021 [22]

One of the key applications for polyurethane is in the automotive industry, where polyurethane is applied in the manufacture of car seat cushions. Flexible polyurethane foams hold the largest market share for polymeric foams as a result [21]. Furthermore, polyurethane can also be utilized structurally for enhanced impact resistance for car bumpers as well as in windows, car doors and ceilings. In replacing metallic materials in this way, the overall weight of the car is lowered thereby enhancing the efficiency of performance and increasing the fuel economy as a result [21]. Another of the major applications of polyurethanes can be found in the coatings, adhesives, sealants, and elastomers (CASE) industry. Polyurethane-based adhesives provide excellent bonding strength, while the polyurethane-based sealants provide exceptionally tight seals. As a result of this excellent adhesion, along with excellent drying capabilities, good abrasion resistance, and high corrosion and chemical resistance, polyurethane has found marked applications as a coating material for wood, textiles and glass [21]. Polyurethanes have found other applications for medical applications (tubing, surgical drapes, wound dressing), marine applications (marine coatings, boat insulation, noise control) and in the textile/apparel industry [21].

1.4 Importance of Biobased Polyurethanes

The development of polyurethanes using biobased materials has garnered exceptional research attention in recent years. This is because the starting materials used in the development of polyurethanes currently are largely derived from petroleum-based resources which are known to be unsustainable [23]. As a result of this sustainability issue, crude oil resources worldwide are experiencing concerning depletion, global crude oil prices continue to rise and fall unpredictably, and the adverse environmental effects of over-reliance on petrochemical processes in polyurethane-producing industries are exacerbated. To this end, development of biobased polyurethanes is a promising avenue to pursue in the mitigation of this overlying sustainability issue.

The focus of the development of biobased polyurethanes is the raw materials from which they are synthesized: polyols and isocyanates. Polyols derived from biobased materials have garnered significant research attention in recent years, with vegetable oils, lignocellulose such as wood, microalgae, polysaccharides, and biomass being the main starting materials utilized to synthesize different types of polyols as is shown in **Figure 3** [24]. Biobased polyols derived from vegetable oils are the most popular both in academia and industry [25–30]. This is owing to relatively low cost of vegetable oils (such as soybean oil, castor oil, canola oil and corn oil) as well as the unsaturated groups present in the vegetable oil structure which can be modified into more reactive forms [24]. Likewise, continued research into the development of biobased isocyanates is ongoing. Isocyanate is industrially synthesized via phosgenation of primary amines, which has adverse environmental and health impacts owing to the toxicity of phosgene [17]. To this end, isocyanates based on biomass, specifically wood, algae sources, solid waste, and agriculture products, have been found to be the most promising pathway for the synthesis of biobased isocyanates [17]. The demand for chemical and energy products that are highly ecofriendly can be met by converting biomass sources into renewable functional molecules such as acids, alkenes and alcohols [17].

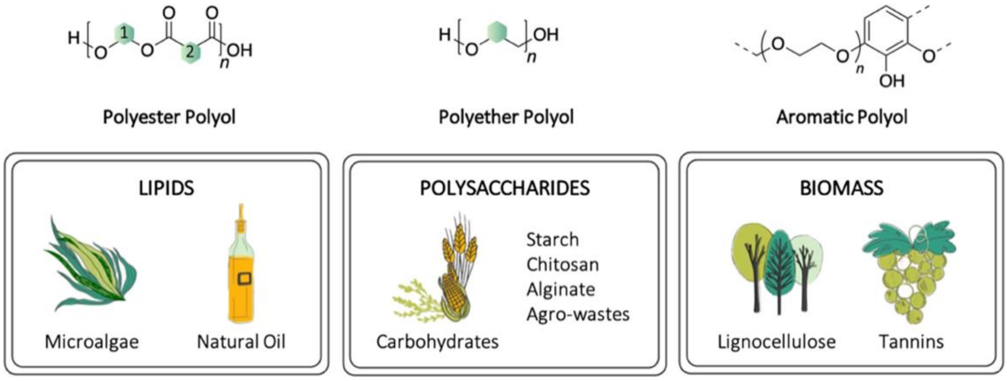

Figure 3: Different types of polyols and their corresponding renewable sources [24]

However, despite the benefits of the development and utilization of these biobased materials in the place of their petroleum counterparts, there are also several challenges facing their further development and application. One major disadvantage is cost of production, where some biobased materials ultimately cost more than the conventional petrochemical-based materials thereby negating its application in industry. Furthermore, in some cases the biobased products cannot practically be produced at a large scale thus hampering commercial development and use. Finally, there is an issue where the biobased materials perform significantly worse than the already available petroleum-based products which severely limits their adoption into the current commercial market.

1.5 Purpose of This Research

In this study, CFRPs were fabricated from carbon cloth and a biobased polyurethane thermosetting resin. The biobased polyurethane used in this study was synthesized via a facile one-step reaction between isocyanate and a sunflower oil-derived polyol. There are several biobased thermosetting materials that have been reported [14, 31, 32], however the focus of these studies has mainly been on the biodegradability of the thermoset as well as the recyclability of the CFRP and not on the mechanical properties of the CFRP. As such, the main aim of this study was to investigate the effect of incorporating a biobased polyurethane thermoset as a CFRP polymeric matrix on both the mechanical properties and chemical properties of the fabricated CFRPs, with a primary interest in the effect on mechanical properties.

CHAPTER II

MATERIALS, METHODS AND PREPARATION

2.1 Materials

2.1.1 Sunflower Oil

Sunflower oil is derived from the seeds of the sunflower (*Helianthus annuus*) and is the fourth most economic oilseed in the world after soybean, rapeseed and safflower [33]. In terms of chemical composition, sunflower oil possesses about 85% unsaturated fat and 15% saturated fat with the former containing double bonds which are encouraging for the synthesis of polyols [34]. This work targeted the carbon-carbon double bonds in the triglycerides [35] in the chemical structure of sunflower oil as shown in **Figure 4** to produce a greater number of reactive sites for the synthesis of a bio-based polyol. The double bonds were broken, and sunflower oil was converted to an epoxidized sunflower oil. This was then followed by a ring opening reaction using methanol to produce the bio-based polyol (chemistry of these reaction mechanisms are explained in detail in the synthesis section). This work used sunflower oil purchased from a local Neighborhood Walmart (Pittsburg, KS, USA) with a measured viscosity of 0.06 Pa·s at 25 ℃.

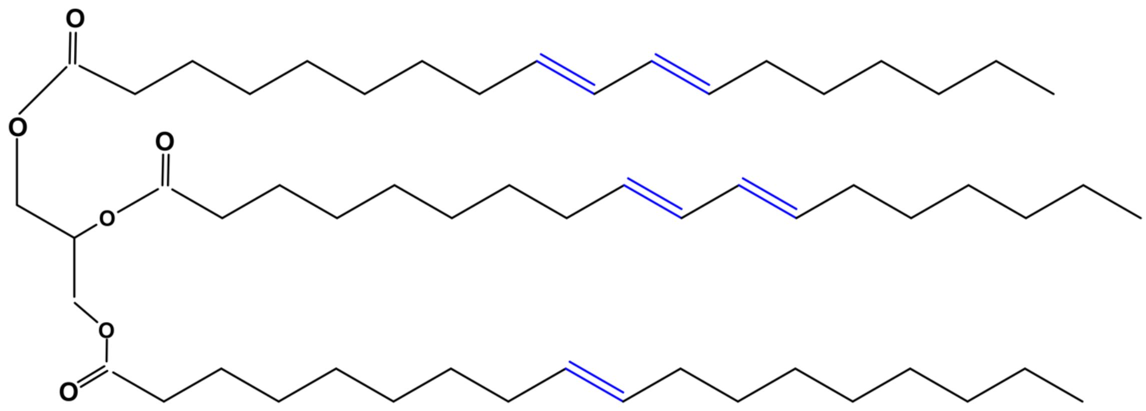

Figure 4: Chemical structure of sunflower oil

2.1.2 Isocyanate

The presence of the reactive NCO groups (-N=C=O) in isocyanates is crucial as these are complimentary reactive groups for the addition reaction with hydroxyl groups in the synthesis of polyurethanes [19]. The high reactivity of the isocyanate groups towards hydroxyl groups facilitates efficient polyurethane synthesis [19]. This work utilized Rubinate M isocyanate, a Methylene diphenyl diisocyanate (MDI), provided by Huntsman (The Woodlands, TX, USA). MDI is utilized due to its favorable homogenous reaction kinetics and low vapor pressure making it less hazardous [35]. MDI has a functionality of 2.7, viscosity of 0.21 Pa·s, weight equivalence of 135, specific gravity of 1.23 at 25 ℃ and a reactive NCO group presence of 31%. **Figure 5** shows the chemical structure of MDI.

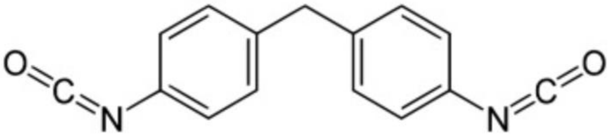

Figure 5: Chemical structure of MDI

2.1.3 Carbon Fiber Cloth

Carbon fiber (CF) cloth acts as the reinforcement material for the CFRPs fabricated in this work providing continuous fiber reinforcement for the overall composite. Additionally, plain weave CF cloth is easy to work with as it maintains its fiber orientation to a great extent, which is important to the performance of the overall composite as the properties provided by CFs are highly directional [36]. This study utilized plain weave 3k 6 oz. / 203 GSM Toray T300 carbon fiber fabric which was purchased from Composite Envisions (Wausau, WI, USA).

2.2 Characterization of Sunflower Oil, Epoxidized Sunflower Oil, and Sunflower Polyol

2.2.1 Hydroxyl (OH) Number

Determining the hydroxyl number for a given polyol is essential as the hydroxyl group is primarily responsible for the reaction between the polyol and isocyanate to form polyurethane bonds. In this work, phthalic anhydride/pyridine (PAP) was used to determine the hydroxyl number according to ASTM D4274 standard.

2.2.1 Epoxide Number

Determination of the epoxide number is undertaken to confirm the formation of epoxide groups from the sunflower oil double bonds. To this end, the epoxy oxygen content (EOC) was determined using tetraethylammonium bromide (TEAB) and glacial acetic acid. Epoxidized sunflower oil (0.3-0.5 g) was dissolved in 50 ml of TEAB solution, after which a drop of crystal violet indicator was added, and the resulting solution was titrated with 0.1 M perchloric acid. The titration end point was indicated by a change in color from blue to green. The epoxy content in the epoxidized sunflower oil was calculated using the recorded volume. This test was conducted three times and an average value was determined and utilized for further calculations necessary for the ring opening experiment.

2.2.2 Viscosity Measurements

Polyol viscosity is an important parameter as the viscosity value dictates important characteristics for the synthesized polyol. A lower viscosity would enable the polyol to mix in a homogenous manner within a given matrix. Furthermore, viscosity is directly proportional to the molecular weight of a given material which has several critical implications for the physical properties of the resulting polyurethane. An AR 2000 dynamic stress rheometer (TA Instruments, USA) was utilized to determine viscosity for sunflower oil, epoxidized sunflower oil and sunflower polyol.

Figure 6: AR 2000 dynamic stress rheometer

2.2.3 Iodine Value

Iodine value provides an indication of the content of double bonds present in an unsaturated compound by determining the amount of iodine that will react with 100 g of the given sample. The higher the iodine value, the greater the amount of unsaturated fatty acids present. Iodine value of the sunflower oil utilized in polyol synthesis was determined via the Hanus method.

2.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR detects the functional groups present in a given compound, as well as determining the chemical bonds present. The change in peaks of the functional groups assists in examining and understanding the reaction process. FTIR results were determined by a PerkinElmer Spectrum Two™ FT-IR Spectrometer.

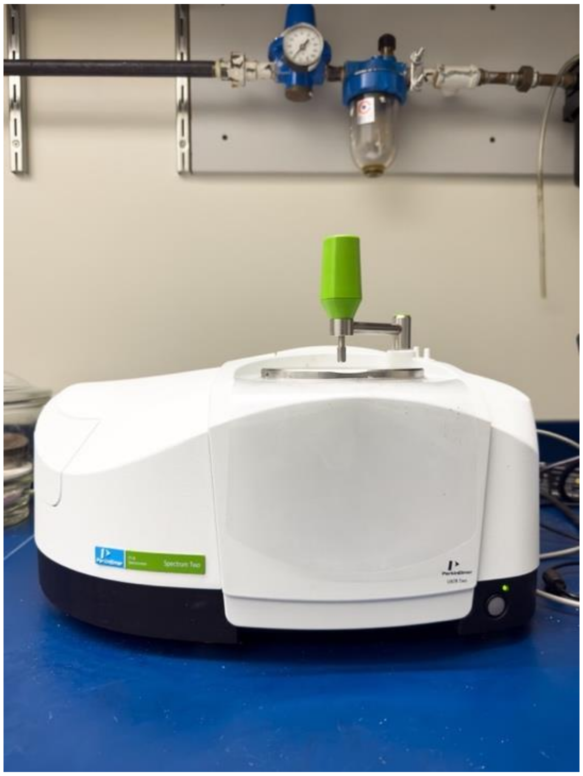

Figure 7: PerkinElmer Spectrum Two™ FT-IR Spectrometer

2.2.5 Gel Permeation Chromatography (GPC)

GPC determines changes in molecular weight by observing the changes in retention time of GPC peaks, with an increase in molecular weight corresponding to a reduction in the retention time of the given GPC peak. GPC characterization was carried out using a Waters Gel Permeation Chromatograph (Waters Corporation, Milford, MA, USA).

Figure 8: GPC instrumental setup

2.3 Testing Methods For CFRPs

2.3.1 Tensile Test

Tensile testing is used to determine the amount of force that is required to break a composite specimen and the extent to which the specimen elongates to that breaking point. Tensile testing was carried out by the National Institute for Aviation Research following the ASTM D 3039/D 3039M standard test method for tensile properties of polymer matrix composite materials as shown in the testing setup in **Figure 9**.

Figure 9: Tensile test experimental setup

2.3.2 Flexural Test

Flexural testing is another method used to determine the amount of force required to break a composite specimen, this time in bending. Often the data obtained is used to select materials for parts that must support loads without bending. Flexural testing was carried out following the ASTM D790-84a standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials.

Figure 10: 3-point bending test experimental setup

2.3.3 Hardness Test

The hardness of a material is its ability to resist deformation by distortion, scratching, indentation, and penetration. Hardness values for each composite were determined via the Shore D hardness test.

Figure 11: Type D Durometer for the Shore D hardness test

2.3.4 Chemical Resistance Test

Resistance to degradation by chemical elements is crucial for materials that are to be utilized for aerospace applications. To this end, chemical resistance was determined by immersing the composites in room temperature distilled (DI) water, DI water at 60 ℃, 0.1 M HCl aqueous solution at 25 ℃, and 0.1 M NaOH aqueous solution at 25 ℃ for 48h. The samples were then allowed to dry in air for 72 hours. Each CFRP sample used in this test was of dimensions 30 mm × 25 mm. Samples were weighed before immersion and after drying to determine the weight loss caused by the chemical degradation of the biobased polyurethane thermoset.

2.4 Preparation Details

2.4.1 Synthesis of Sunflower Polyol

The synthesis of sunflower polyol (SFP) used in this work was carried out through epoxidation of sunflower oil followed by ring-opening of the epoxidized sunflower using methanol. For the epoxidation reaction, 300 g of sunflower oil, 75 g of amberlite resin, and 150 ml of toluene (1:0.5:1.5 molar ratio) were mechanically stirred in a 3-necked flask in a water bath with controlled heating. This mixture was stirred continually while simultaneously reducing the reaction temperature to about 5-10 ℃. Acetic acid (43.9 ml) and 180 ml hydrogen peroxide (30%) were then added dropwise into the mixture one after the other. This is done to prevent overheating typical of epoxidation reactions due to their exothermic nature [37]. Once all the reagents were completely added, the mixture was stirred for 7 hours at 70 ℃ then cooled to room temperature after which the resin was filtered out. The mixture was then purified by washing with 10% brine in a separatory funnel. The mixture was then allowed to stand to facilitate the removal of the aqueous layer from the oil. Anhydrous sodium sulfate was added and stirred into the mixture to act as a drying agent. The drying agent was then filtered out and excess solvents were removed from the resulting mixture via rotary evaporation at low and high vacuum pressures. Confirmatory tests such as FTIR, GPC and epoxy number analysis were carried out to confirm the successful synthesis of epoxidized sunflower oil (ESFO).

For the ring opening reaction, methanol was utilized in a mole ratio of 7:1 with ESFO along with catalytic amounts of tetrafluoroboric acid. The amount of tetrafluoroboric acid was equal to 50% of the weight of water, plus 0.05% of methanol and ESFO. The reaction between methanol and acid was performed at 70 ℃ in a three-necked flask attached to a condenser and a dropping funnel. The previously synthesized ESFO was then added dropwise into the mixture after several minutes of mechanical stirring and the reaction was refluxed for an hour. Once the mixture had cooled, Lewatit MP 64 was added to neutralize the mixture and to prevent hydrolysis. Following complete neutralization, the mixture was filtered to remove the resin after which rotary evaporation was carried out. The synthesized SFP was characterized using confirmatory tests to confirm the formation of hydroxyl groups.

2.4.1 Synthesis Of Polyurethane

In a conical flask, 25 g of sunflower polyol was mixed with 12 g of isocyanate and mechanically stirred until the mixture was homogenous. This mixture was then evaporated in a rotary evaporator at 60 ℃ and 80 RPM for 10 minutes to obtain liquid polyurethane. Evaporating the mixture in this way was carried out to get rid of any moisture in the mixture as well as further reacting of the sunflower polyol and isocyanate. Furthermore, evaporating at 60 ℃ ensured that the resulting liquid polyurethane did not become too viscous.

2.4.1 Preparation of CFRPs

5 CFRPs were fabricated with increasing layers of carbon cloth for each test that was conducted. Each carbon cloth layer was of dimensions 15 cm × 10 cm. The liquid polyurethane prepared by the process outlined in the previous subsection was then applied on each carbon cloth layer. The composites were fabricated via a hot press

method at 130 °C and 700 lbf for 1.5 hours. After the hot press was complete the composites were allowed to cool in air at room temperature. Once cooled, each composite was then cut into samples of dimensions 13.5 cm × 2.5 cm using a stationary band saw. The thickness of each composite varied as a result of utilizing increasing layers of carbon cloth in its fabrication. The full dimensions of each sample are presented in **Table 1.** The composite samples follow a naming convention where each is named according to how many layers of carbon cloth the resultant composite sample had (i.e., COMP01 has one carbon cloth layer, COMP02 has two carbon cloth layers etc.)

Table 1: CFRP Dimensions

Specimen	Dimensions
COMP01	13.5 cm × 2.5 cm × 0.028 cm
COMP02	13.5 cm × 2.5 cm × 0.049 cm
COMP03	13.5 cm × 2.5 cm × 0.069 cm
COMP04	13.5 cm × 2.5 cm × 0.086 cm
COMP05	13.5 cm × 2.5 cm × 0.107 cm

CHAPTER III

RESULTS AND DISCUSSION

In general, the synthesis of epoxides from carbon-carbon double bonds (olefins) can be achieved via epoxidation with i) organic and inorganic peroxides, ii) percaboxylic acid, iii) molecular oxygen, or iv) halohydrins [38, 39]. Of these synthesis routes, epoxidation with percaboxylic acid is the most widely used. This work utilized the epoxidation with percaboxylic acid route, where hydrogen peroxide acts as an oxygen donor and acetic acid acts as an oxygen carrier. This reaction leads to the formation of peracetic acid which is involved in the breaking of the double bonds into an epoxide ring. Following the epoxidation reaction, it is necessary to break the formed epoxy rings to facilitate the formation of hydroxyl groups. An epoxy ring has a basic structure of an oxygen atom bonded to two adjacent carbon atoms. The ring-opening reaction involves the nucleophilic attack for a beta-substituted hydroxyl group due to the presence of the strained epoxy rings that are electrophilic [40]. **Figure 12** shows a schematic of the synthesis of SFP via epoxidation and ring-opening of sunflower oil and epoxidized sunflower oil, respectively.

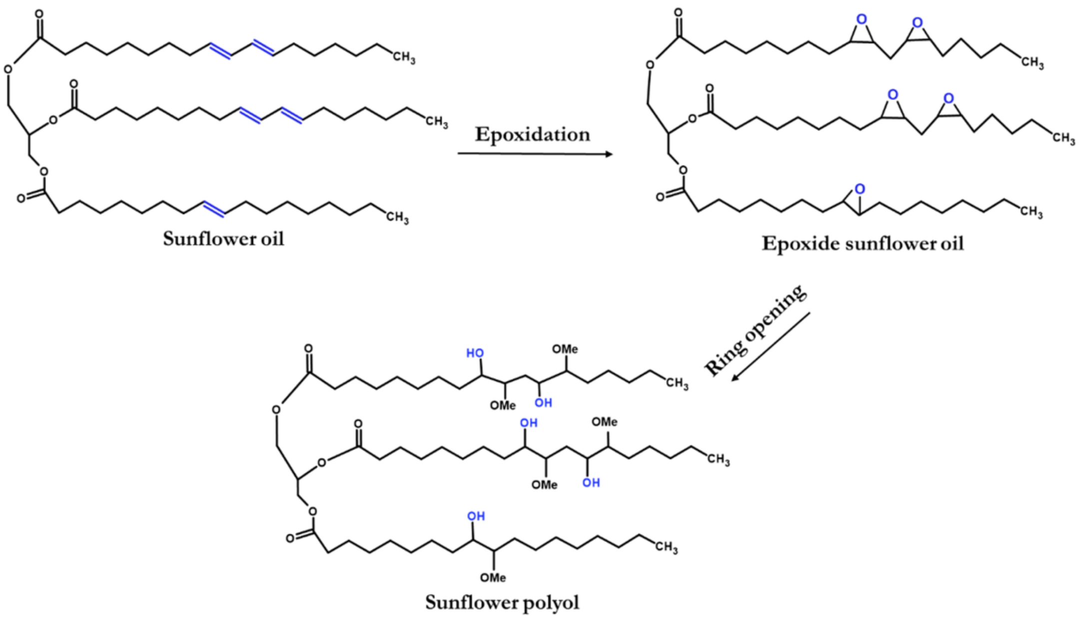

Figure 12: Reaction steps in the synthesis of sunflower polyol from sunflower oil

Characterization of SFO, ESFO and SFP was carried out to determine iodine value, viscosity and OH number, with results shown in **Table 2**. The iodine value of sunflower oil was determined to be 100 g I_2/100 g oil, which indicates that 0.39 moles of double bonds were present in 100 g of sunflower oil. This value was then utilized in stoichiometric calculations to determine the exact amount of reagents required for the epoxidation reaction. It can be observed that the measured iodine values for ESFO and SFP were determined to be negligible after the epoxidation and ring-opening reactions respectively. This indicates the successful conversion of the sunflower oil double bonds into a more reactive form for the synthesis of the polyol and, ultimately, the polyurethane thermoset matrix. The percent epoxide number was determined to be 5.7% for ESFO, and 0.01% for both SFO and SFP. The decrease in epoxide number from ESFO to SFP indicates that the epoxide rings were successfully converted to hydroxyl groups as a result of the ring-opening reaction.

FTIR was then utilized to confirm the chemical structure of the starting, intermediate, and final products while GPC was utilized to confirm the molecular weight of the synthesized polyol as well as the starting and intermediate products. FTIR spectra of SFO, ESFO and SFP are given in **Figure 13**. A =C-H peak can be observed at 3011 cm^{-1} for SFO which disappears in ESFO and SFP spectra. There is a C-O-C bond present at 851 cm^{-1} confirming the presence of an epoxy group as is expected for ESFO. This epoxy group is not present in the SFP spectrum, and instead, a hydroxyl group emerges at 3472 cm^{-1}. As can be observed from the GPC curves in **Figure 14**, SFO and ESFO had peak retention times of 22.75 s and 22.62 s respectively, while SFP had a peak retention time of 22.27 s. This reduced retention time observed in the GPC curves suggests a molecular weight increase from the starting materials to the final synthesized polyol. The peak observed at 20.78 s on the SFP plot is possibly due to the formation of dimers and trimers as a result of the variation in the fatty acids present, as well as the oligomerization of a small portion of the polyol during conversion. An ESFO peak is absent in the GPC curve for SFP, which thereby confirmed that all the ESFO was used up in the formation of the polyol. FTIR and GPC results thus confirm that the polyol is obtained.

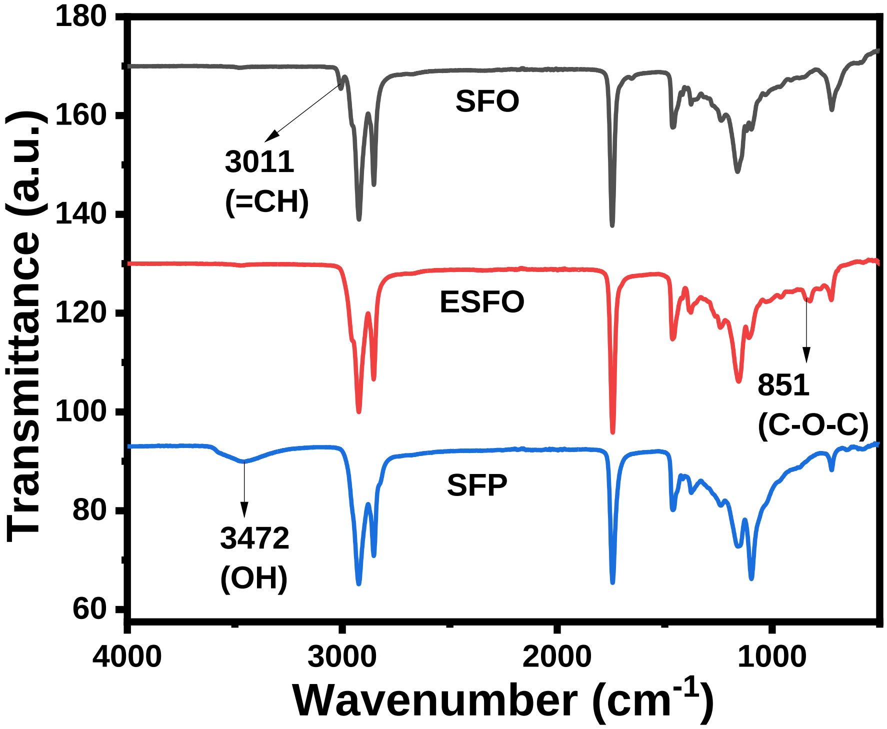

Figure 13: FTIR spectra of sunflower oil (SFO), epoxidized sunflower oil (ESFO) and sunflower polyol (SFP)

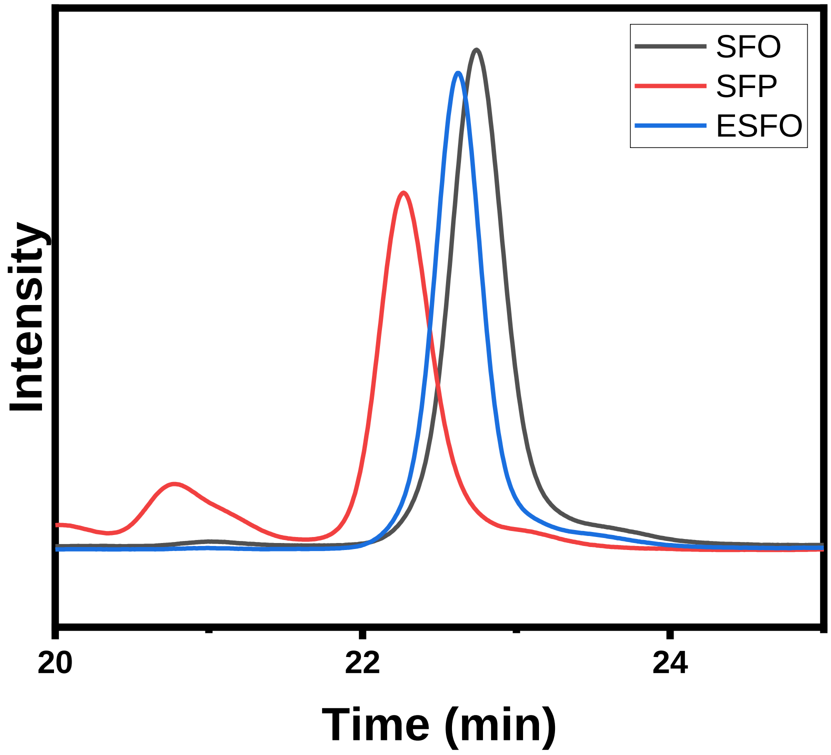

Figure 14: GPC of SFO, ESFO and SFP

Table 2: Characterization test results for SFO, ESFO and SFP

Test	SFO	ESFO	SFP
Iodine value	100 g I_2/ 100 g oil	0.02 g I_2/ 100 g oil	0.01 g I_2/ 100 g oil
Epoxide number	0.01 %	5.7 %	0.01 %
OH number	0.5 mg KOH/g	0.5 mg KOH/g	180 mg KOH/g
Viscosity	0.06 Pa·s	0.1 Pa·s	1.6 Pa·s

Table 3 details the results of tensile testing conducted for each of the composite samples. From the load vs. displacement curves presented in **Figure 15**, it can be observed that the maximum tensile load increases with an increase in carbon cloth layers

per composite sample. This is to be expected, as a greater amount of carbon fiber reinforcement would imply a stronger overall composite material. Owing to the direct proportionality between tensile strength and maximum tensile load, the tensile strength shows a similar increase in value across the composite samples. In general, tensile strength is determined by the strength and volume content of the fiber reinforcement. This is owing to the greater strength exhibited by the fibers as opposed to the polymer matrix, as such, the fibers determine the ultimate tensile strength. The increase in tensile strength in this work is thus brought about the increase of the carbon fiber content in each composite sample. Ultimate tensile strength is given by the following equation:

$$F_{TU} = \frac{P_{max}}{A} \qquad (1)$$

where F_{TU} is ultimate tensile strength, P_{max} is the maximum tensile load and A is the cross-sectional area of the composite sample ($A = w \times t$, where w is the composite width and t is the composite thickness).

From the stress-strain curves presented in **Figure 16**, it can be observed that all the fabricated composites show no indication of plastic deformation, and instead suddenly fracture. As such, it can be concluded that the fabricated composites are brittle materials. This is further confirmed by observing the failure modes of the composites after testing, whereby all composites display brittle failure as is shown in **Figure 17** using COMP01 as an example. Young’s modulus values are observed to increase across the fabricated CFRPs, corresponding to an increase in overall stiffness of these composites. Overall, the values for Young’s modulus are high which implies that although stiffness increases with increase in carbon reinforcement, all the fabricated composites are stiff in nature and are thus highly resistant to bending when subjected to a given tensile load.

Table 3: Tensile test results

Specimen	Young’s Modulus (GPa)	Maximum Tensile Load (N)	Tensile Strength (MPa)
COMP01	44.7	1828	246
COMP02	55.7	5240	398
COMP03	56.4	7193	406
COMP04	57.2	10164	428
COMP05	63.9	10774	484

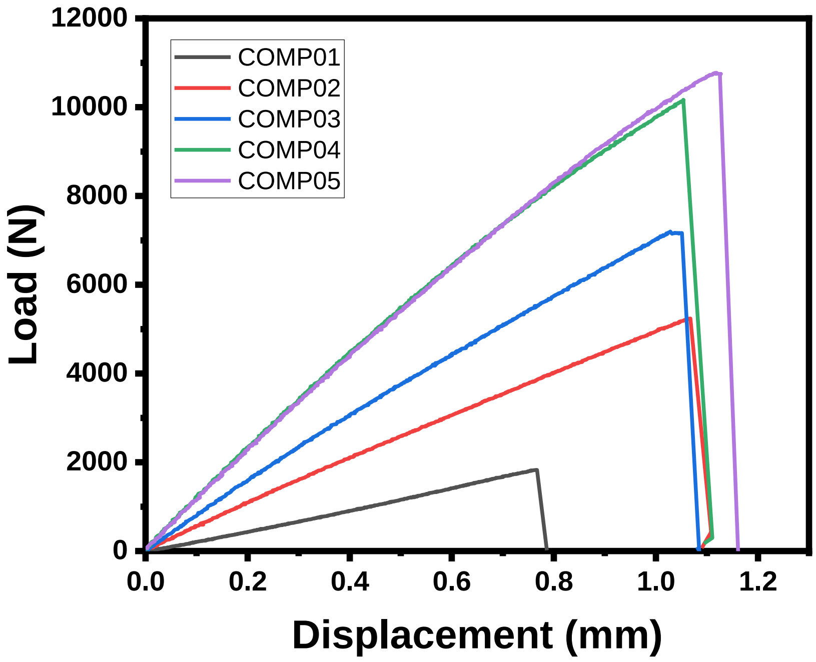

Figure 15: Load vs. displacement curves

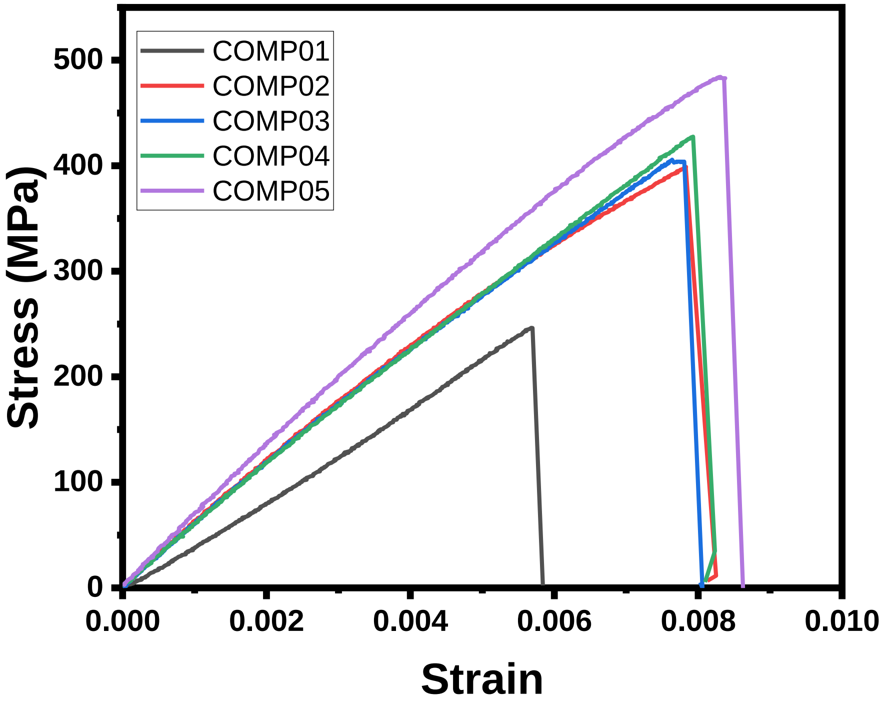

Figure 16: Stress-strain curves

Figure 17: Brittle failure mode for COMP01 after tensile testing

Flexural testing was carried out on the composite samples to determine the flexural modulus for each CFRP. Flexural modulus is a physical property that indicates the ability of a given material to bend, i.e., the rigidity or stiffness of the material. This assists in the design of the composite in reference to its final application as some applications may require flexible materials that resist damage when subjected to bending forces while others require rigidity for structural support. **Figure 18** shows the load vs extension curves of the fabricated CFRPs. As can be observed in the figure, the slope of the straight-line portion of each plot increases from COMP01 to COMP05. This gradient increase is consistent with the increase in the flexural modulus values calculated using the following equation:

$$E_B = \frac{L^3 m}{4bd^3} \qquad (2)$$

where E_B is the flexural modulus, L is the support span, m is the slope of the Load vs crosshead plot generated by the testing software, b is the specimen width and d is the specimen thickness. **Table 4** shows the calculated flexural modulus values for each composite. In general, the higher the flexural modulus of a given material, the harder it is for that material to bend under an applied force. The increase in carbon fiber reinforcement caused the increase in the flexural modulus observed. COMP05 is the most rigid of the fabricated CFRPs with a flexural modulus value of 833 GPA. Furthermore, this increase in stiffness also serves as an explanation as to why the extension at break generally decreases from COMP01 to COMP05 while fracture load increases as stiffer materials will require a greater load to cause fracture but will not extend as much because of the higher stiffness.

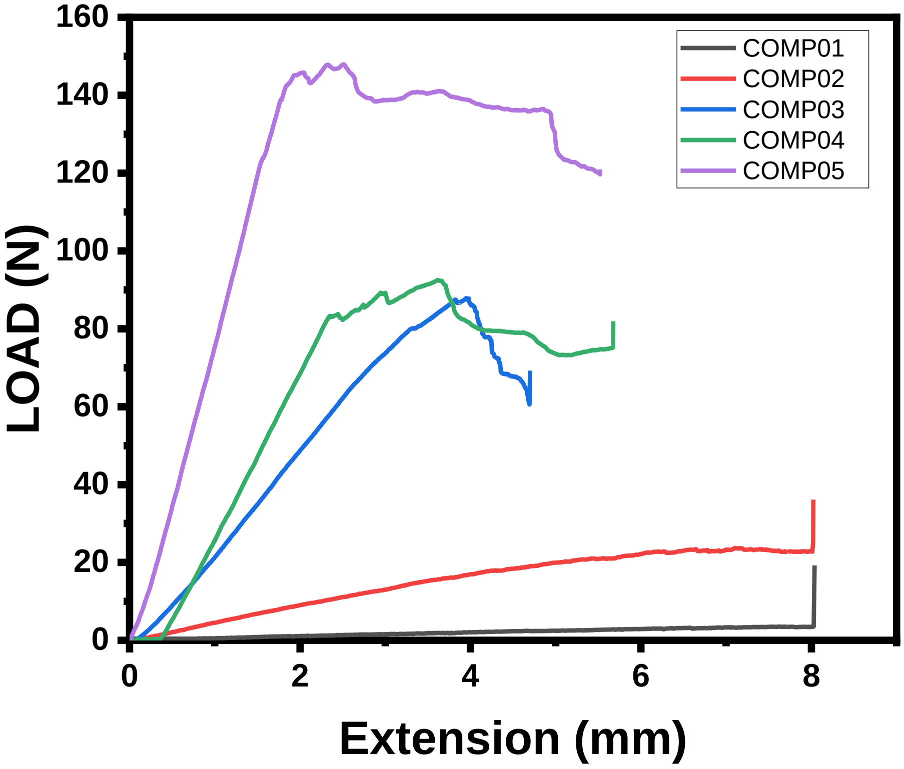

Figure 18: Load vs extension curves for the fabricated CFRPs

Table 4: Flexural modulus of the fabricated CFRPs

Specimen	Flexural Modulus (GPa)
COMP01	315
COMP02	390
COMP03	656
COMP04	707
COMP05	833

Hardness testing is a critical mechanical test that is carried out to determine the resistance of a given material to plastic deformation. As such, hardness testing is imperative for overall quality control of a material as it determines whether the composite will both perform and sustain itself in its projected application. As shown in **Figure 19**, all the composites exhibited high values for Shore D hardness, with the lowest of these values being 88D for COMP01. This indicates that the composites show high resistance to indentation by the durometer. **Table 5** shows the hardness values for each of the composites. It can be observed that COMP04 and COMP05 both had hardness values greater than 100D, indicating that the indenter for the durometer did not penetrate these two composites at all. This suggests that all the composite specimens are highly resistant to indentation.

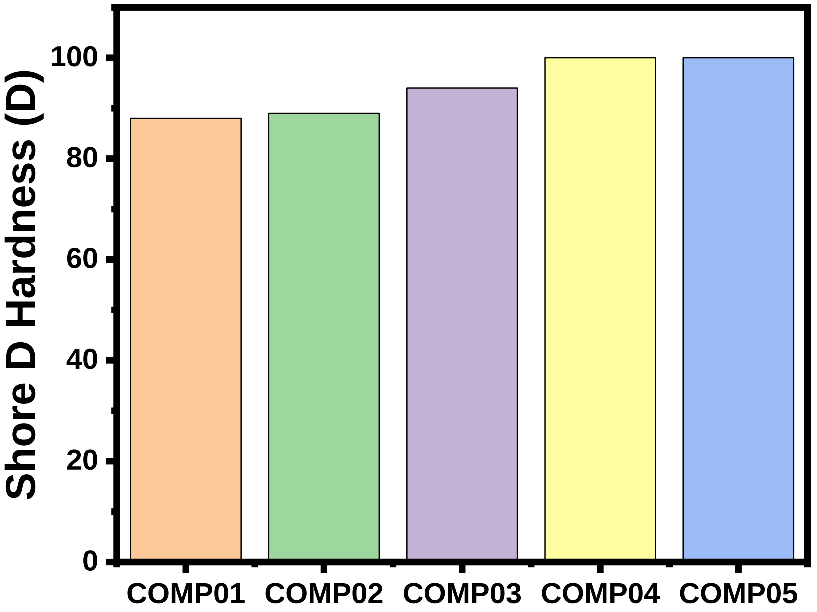

Figure 19: Shore D hardness test results for the fabricated CFRPs

Table 5: Shore D Hardness values for the prepared composite samples

Specimen	Shore D Hardness (D)
COMP01	88
COMP02	89
COMP03	94
COMP04	100+
COMP05	100+

The resistance of the biobased polyurethane thermoset to chemical degradation by water, acid and alkali was also tested. As mentioned in Chapter 2, this involved immersing the fabricated CFRPs in room temperature distilled (DI) water, DI water at 60 ℃, 0.1 M HCl aqueous solution at 25 ℃, and 0.1 M NaOH aqueous solution at 25 ℃ for 48h as is shown in **Figure 20**. Degradation was determined by measuring the change in mass of the CFRP samples before immersion into the varying chemical environments and after removal from the respective solutions and drying in air. This data is visualized in **Figure 21-24** where it can be observed that the mass is basically maintained across the samples in the varying chemical environments. This confirms that minimal degradation of the polyurethane thermoset occurs in alkaline, acidic and aqueous environments. **Figure 25** and **Figure 26** show the samples before and after immersion further confirming the minimal degradation of the thermoset with the CFRPs maintaining their structural integrity and appearance.

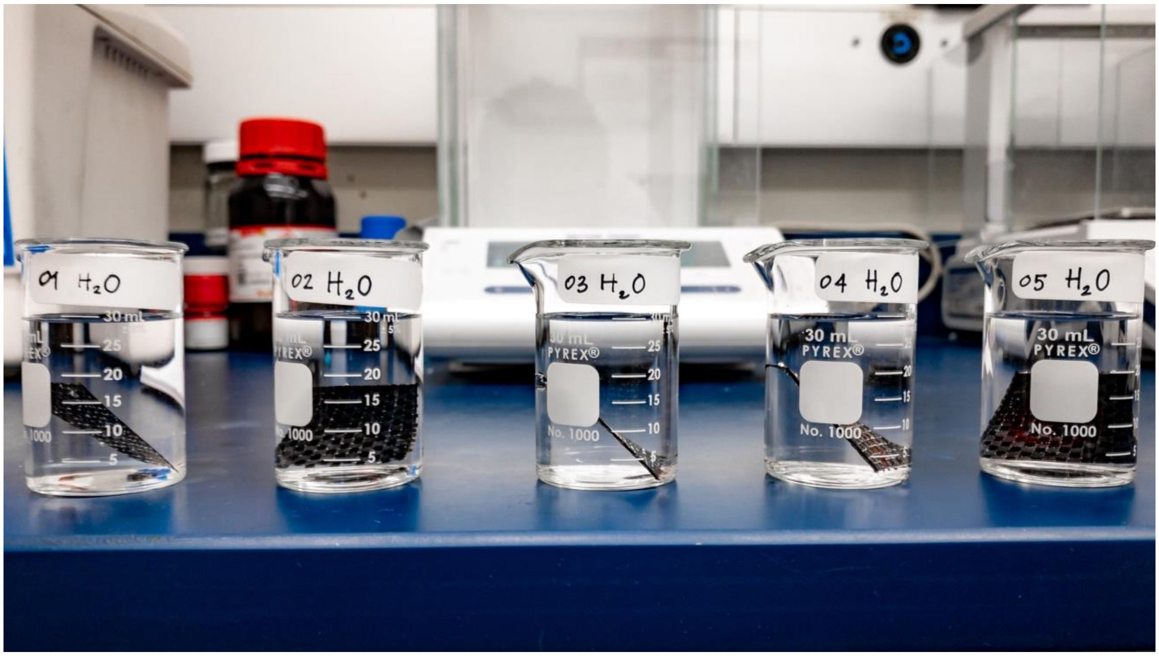

Figure 20: Chemical resistance test set up at the start of testing in room temperature water

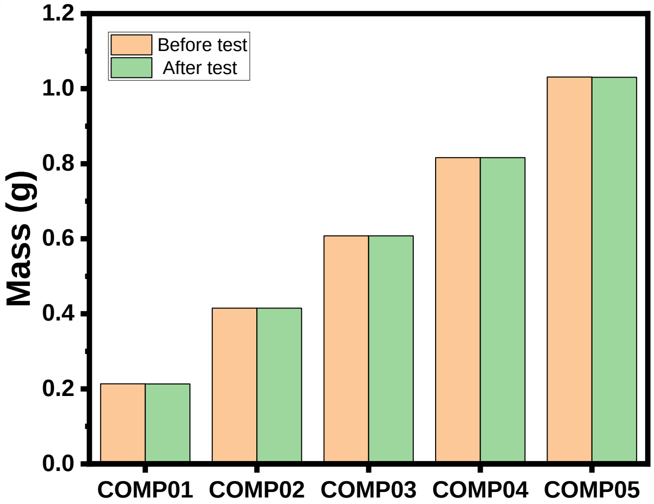

Figure 21: Mass of fabricated CFRPs before and after chemical resistance test in room temperature water

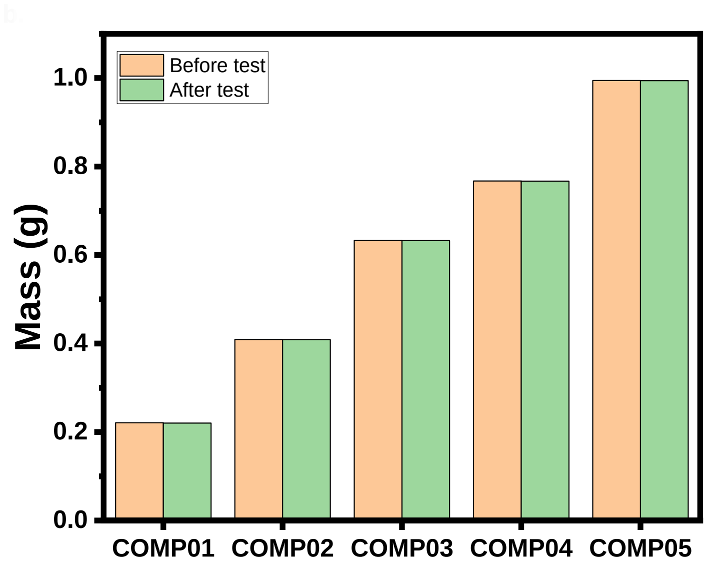

Figure 22: Mass of fabricated CFRPs before and after chemical resistance test in water at 60 ℃

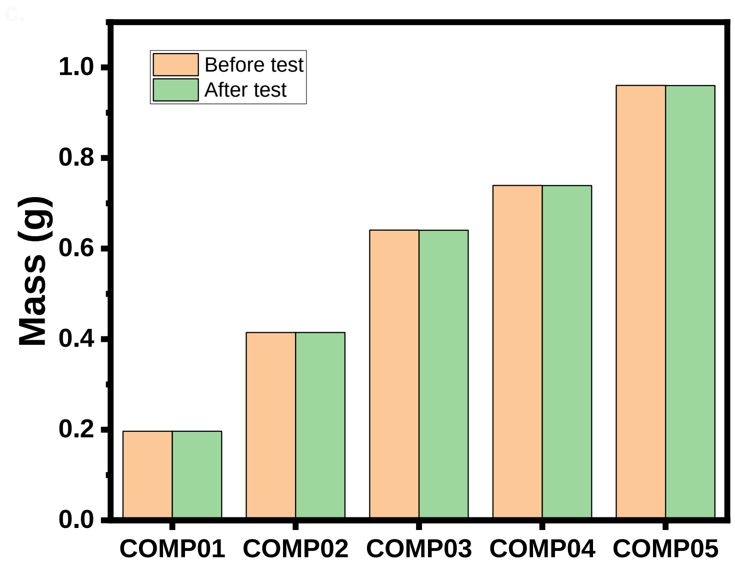

Figure 23: Mass of fabricated CFRPs before and after chemical resistance test in 0.1 M HCl

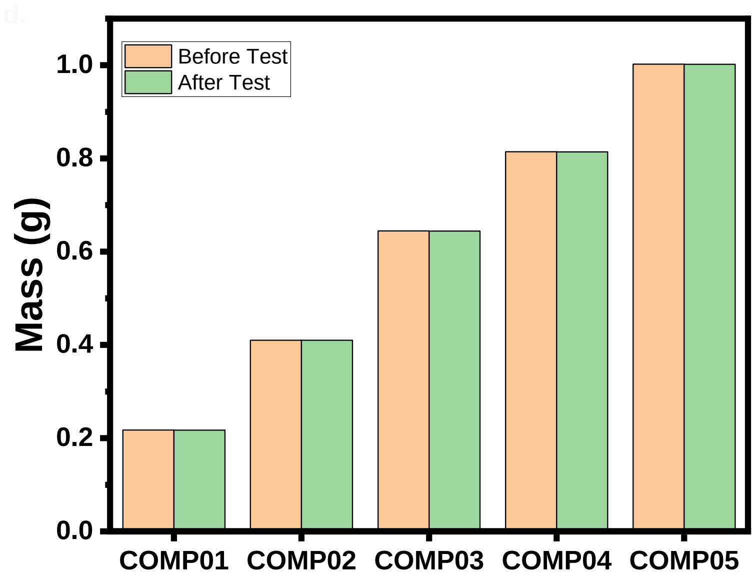

Figure 24: Mass of fabricated CFRPs before and after chemical resistance test in 0.1 M NaOH

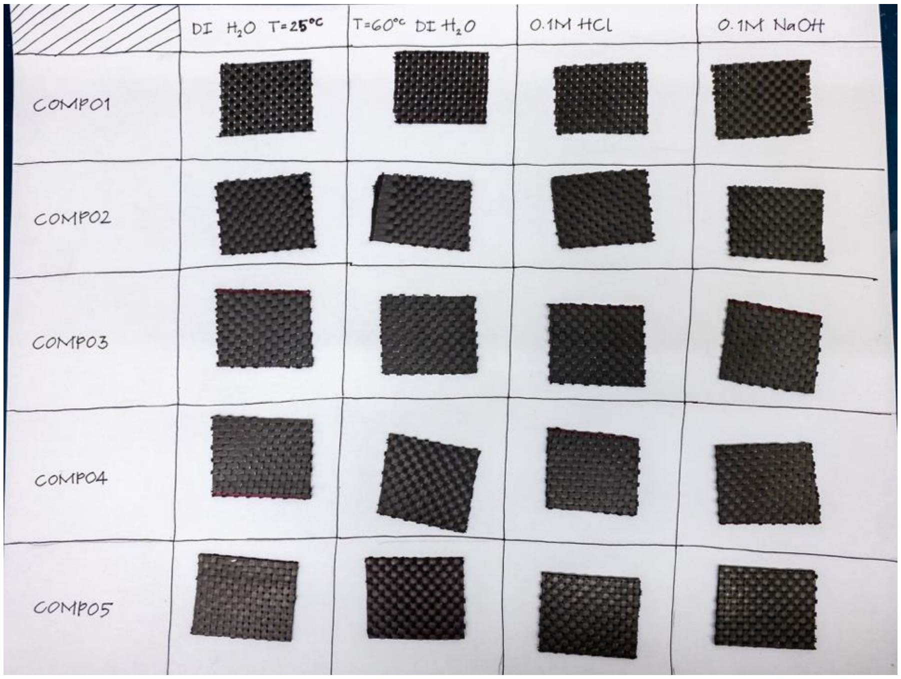

Figure 25: Chemical resistance test samples before immersion into solution

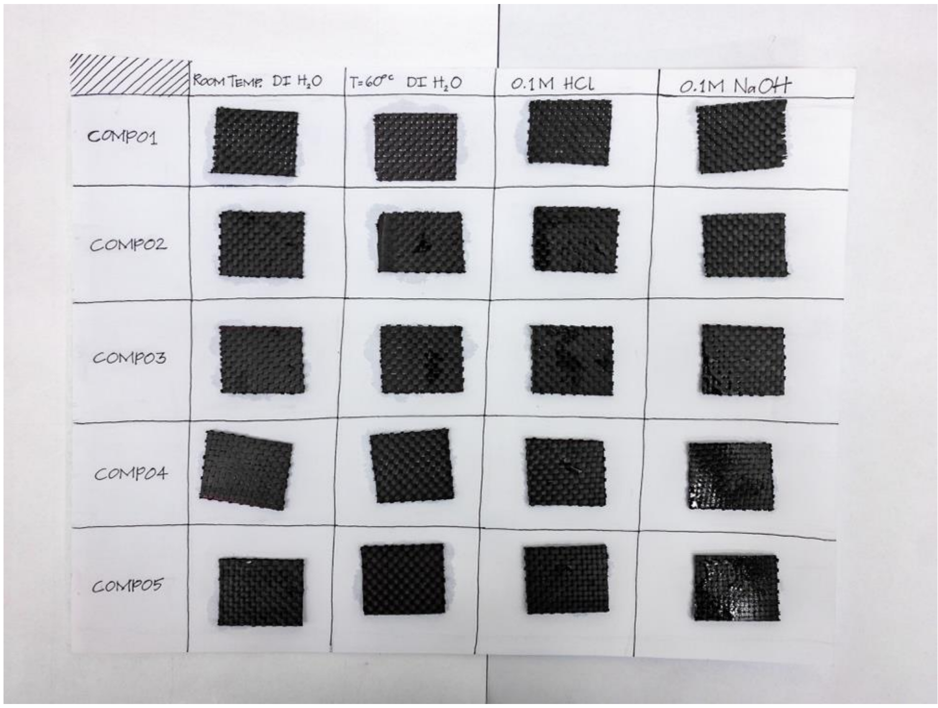

Figure 26: Chemical resistance test samples just after removal from solution

Table 6 gives a comparison between the major results of this work and those of other biobased CFRPs studied in recent years. As can be observed, the CFRP made in this work outperforms the comparative works across the major mechanical performance parameters, indicating that the utilization of sunflower polyol in the synthesis of the biobased polyurethane thermoset can result in a CFRP that exhibits excellent mechanical properties.

Table 6: Comparison of major results of this work with other biobased CFRP works.

Composite Specimen	Young's Modulus (GPa)	Tensile Strength (MPa)	Flexural Modulus (GPa)	Reference
GTE-VA-CF	12.9	449	-	[3]
CRFC-HMDO	16.3	381	-	[14]
Schiff base CFRP	47.3	455	54.2	[15]
COMP05	63.9	484	833	This work

CHAPTER IV

SUMMARY

CFRPs continue to gradually replace traditional metal materials in sectors such as aerospace, sports equipment, automotive among others due to their attractive properties such as high modulus and corrosion resistance. The polymer matrices incorporated into these composites, however, are synthesized from materials that are derived from petrochemical sources which leads to adverse effects on the environment. This work sought to synthesize a biobased polymer thermoset to be utilized in the fabrication of CFRPs and to investigate the mechanical properties of the fabricated CFRPs. Sunflower oil was utilized as a renewable starting material in the synthesis of a polyol, which is more reactive and therefore useful for the synthesis of a biobased polyurethane thermoset. The polyol is synthesized via epoxidation of sunflower oil, followed by a ring-opening reaction of the epoxidized sunflower oil. Through confirmatory tests such as hydroxyl number and FTIR, the sunflower polyol was determined to have been successfully synthesized and was thus used in the synthesis of a polyurethane thermoset for CFRP applications.

The synthesized CFRPs exhibited excellent mechanical properties. Tensile testing revealed high Young’s modulus values in the range of 44.7-63.9 GPa, with similarly high values for tensile strength being observed. As is expected, the increase in carbon fiber reinforcement and the subsequent increase in the amount of polyurethane thermoset utilized leads to an overall composite that is remarkably resistant to deformation. This is further confirmed by the flexural test in which flexural modulus values in the range of 315-833 GPa are achieved. Hardness testing revealed that the fabricated CFRPs are remarkably resistant to indentation, with values above 85 D being observed in all the composites. Chemical resistance testing confirmed that the synthesized polyurethane thermoset is resistant to varying aqueous chemical environments, with the composite samples showing negligible degradation after being immersed in acid, alkali and water environments for 48 h. In conclusion, this work suggests that biobased polyurethanes derived from sunflower oil can be utilized in the fabrication of CFRPs.

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