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Cellulose Modification for Use as Reinforcement in Bio-based Composites

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CELLULOSE MODIFICATION FOR USE AS REINFORCEMENT IN BIO-BASED COMPOSITES

by

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(Under the Direction of Rafael L. Quirino)

ABSTRACT

The goal of the research contained in this thesis is to provide an alternative method of developing polymers than the current petroleum-based polymeric products. Vegetable oil-based polymers are a popular alternative due to their low-cost and low toxicity. The carbon-carbon double bonds in the oil are ideal reactive sites for a free radical polymerization. Cellulose is a naturally occurring polymer. Modifying cellulose prior to making composites with tung oil allows a hydrophilic material to mix better with a hydrophobic resin. Vegetable oil-based polymers usually require the reinforcement of fibers to enhance the thermo-mechanical properties that would replace petroleum-based polymers. In this manuscript, the preparation of a nonpolar matrix from the crosslinking of tung oil with co-monomers, divinylbenzene and *n*-butylmethacrylate, and its reinforcement with modified/unmodified cellulose is discussed. The nonpolar regions of the tung oil interact with the nonpolar filler obtained after cellulose modification. The successful modification of cellulose with tung oil was confirmed using FT-IR, DSC, and TGA. The optimal cure schedules were determined by DEA and confirmed through DSC. The thermo-mechanical properties were analyzed using TGA, DSC, and DMA.

INDEX WORDS: Tung oil, Bio-based polymers, Cellulose composites, Thermosets, Free radical polymerization, Renewable polymers

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CHAPTER 1: INTRODUCTION

Resources, in the form of fossil fuels, are valued throughout the United States and the

world, that are slowly depleting and cannot be renewed. The depletion of fossil fuels leads to the

search for renewable resources that have a low carbon footprint. Fossil fuels are used everywhere

and found in a variety of items that are used every day throughout the world. Some products

derived from fossil fuels include oil, coal, petroleum, and others. Annually, approximately 7% of

oil production was used to produce plastics.[1] Plastics are beneficial throughout the world,

because of its use in shelter, health, food, and other needs necessary to modern society. Polymers

are made from oil and gas because of their low cost to the manufacturer, ease of handling, and

good balance of mechanical, electrical, and chemical properties.[7] The use of petroleum in the

production of polymers has led to a depletion of crude oil, fluctuations in oil prices,

environmental concerns.[2] Among the environmental concerns, leads to the discussion of the

polymers disposal, and recyclability.[2]

Bio-based polymers use a variety of renewable starting materials that are more sustainable

and biodegradable than the current petroleum-based polymers in the environment. The current

most widely used starting material for bio-based polymers is vegetable oils.[2] Vegetable oil is the

most popular, due to its ease of availability, low toxicity, and low cost. [2,3] At this time, scientists

can agree that fossil fuels are not a sustainable resource, because fossil fuels will run out

eventually, and deemed a nonrenewable resource. Research into bio-based alternatives is

necessary to limit environmental concerns all the while meeting the demand for polymers when

the price to make petroleum-based polymers are too high.

The most common renewable feedstock for bio-based polymers are natural oils derived

from plants and other sources. Vegetable oils are among the most advantageous because they are

readily available, low cost, low toxicity.[2-4] Vegetable oils contain different fatty acid chains that have a range of 8 to 24 carbon atoms on it.[4] The fatty acid chains also contain carbon-carbon double bonds.[4] In some vegetable oils, like tung oil found in (**Figure 1A**), the conjugation of double bonds aid in polymerization reactivity.[4] The polymerization of vegetable oils occur by a free radical or cationic polymerization reaction.[3,4] According to Zhang, et. al., most vegetable oils need to be modified prior to use in the production of a polymer.[4]

Vegetable oils consists of triglycerides with different fatty acid compositions. Some abundant fatty acid chains found in vegetable oils are α-eleostearic acid, **Figure 1B**, arachidonic acid, linolenic acid, oleic acid, ricinoleic acid, and many more.[5] There are several distinctions that can made about vegetable oils such as the lenth of the fatty acid chains, the position of C=C bonds along the fatty acid chains, and the presence of specific functional groups on the chains.[5] The fatty acid chains comprising over 80% in tung oil is α-eleostearic acid.[5] Castor oil is composed of ricinoleic acid that is unsaturated with a hydroxyl group attached and makes up 85% of the triglycerides formed.[5] Linseed oil is composed of approximately 57% of linolenic acid, this fatty acid chain has three non-conjugated C=C bonds.[5] Olive oils are composed of 80% oleic acid and is a monounsaturated fatty acid.[5]

(A)
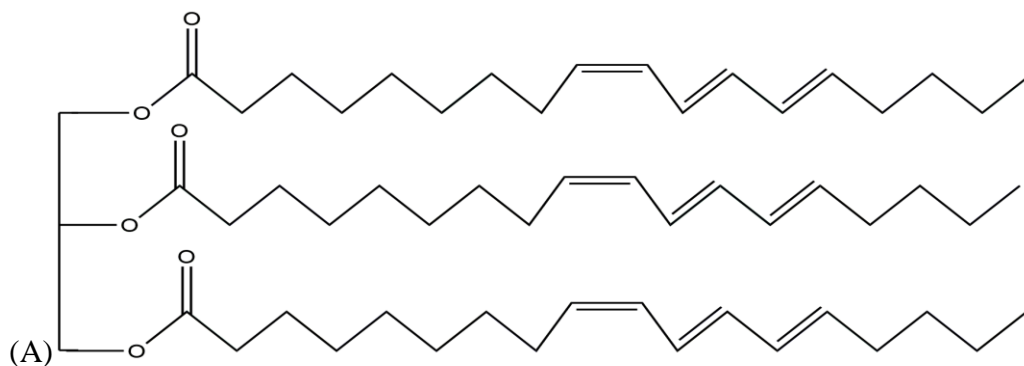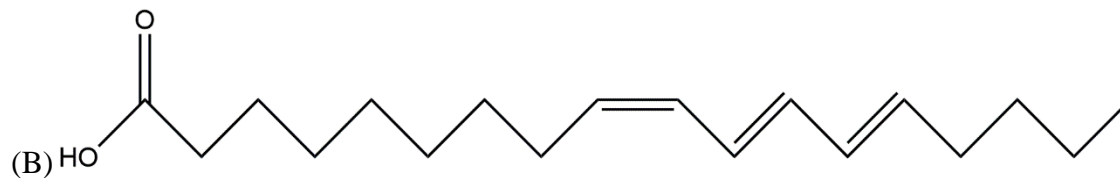
Figure 1. Tung oil is a mixture of various fatty acid chains. The different fatty acid chains are

α-elaeostearic acid (77-82%), which has three naturally conjugated carbon-carbon double bonds,

oleic acid (3.5-12.7%) with one double bond, and linolenic acid (8-10%) that has three non-

conjugated double bonds.[6] (A) Tung oil with the α-elaeostearic acid being the main chain since it

composes ~80%.[5,6] (B) The α-elaeostearic fatty acid chain without the glycerol backbone.

Typically, polymers can be put into two different categories: thermosets or thermoplastics.
Thermoplastics are recyclable because they can be reheated and shaped. The polymer chains
found in thermoplastic have weak intermolecular forces that break down rapidly with an increase
in temperature. Thermosets has a rigid, crosslinked structure, which is a bond that links polymer
chains. Thermosets do not have the ability to be melted down and reshaped. Thermosets have
better mechanical properties, when compared to thermoplastics. It is because of their mechanical
properties that makes it difficult to recycle thermosets. The majority of thermoset polymers are
made from petroleum-based materials. As previously mentioned, petroleum-based materials are
nonrenewable and potentially harmful to the environment. The need for thermosetting polymers
derived from a renewable resource, is a novel process in today's world. It is economically
necessary, because of the fluctuating prices in oil, will drive up the need for an alternative way to
develop polymers. Polymers derived from vegetable oils are flexible, have low glass transition
temperatures, and low stiffness.[6] These properties of vegetable oil-based polymers can be tuned
by changing and adjusting the ratio of co-monomers. These polymers can range from being
flexible to being brittle and stiff materials.

Tung oil is found from tung trees in China,[7,8] and grown in the Southern US in the late 19th century. China contributes to 80% of the worlds production of tung oil.[8] Tung oil is composed of α-elaeostearic acid (77-82%, **Figure 1B**) which has three naturally conjugated carbon-carbon double bonds, oleic acid (3.5-12.7%) with one double bond, and linolenic acid (8-10%) that has three non-conjugated double bonds.[7] Tung oil has good drying capabilities, and is typically used in the paint and varnish industry.[7,8] Tung oil is preferred over many other oils because the conjugated carbon-carbon double bonds found in α-elaeostearic acid (cis-9, trans-11, trans-13-octadecatrienoic acid) make it unnecessary to modify the oil prior to use in polymer making.[7,8] Tung oil can react readily and polymerize upon exposure to oxygen[7], and upon the addition of vinyl or acrylic co-monomers via, cationic, thermal, or free radical polymerization.[5,9,15] Meiorin et. al. cationically copolymerized tung oil with vegetable oil derived monomer to replace styrene and showed the dynamical-mechanical and mechanical properties of the polymers were comparable to using styrene.[7] A study conducted by Bhuyan et. al. showed the crosslinking effect on tung oil-based polymers and was found that the higher the crosslinking density resulted in lower abrasive wear owing to an increase in the hardness of the polymer.[10] Another study examined the properties of polyurethane based tung oil with wood flour upon exposure to a humid environment, and observed that the moisture content found in a polymer was directly proportional to an increase with the filler content (wood flour).[11]

Although bio-based resins are ideal due to the depletion oil, they have to compete with the current production of petroleum-based resins. In order to improve the mechanical properties of bio-based polymers, synthetic fibers and/or natural fibers are added to reinforce the resins. There is some difficulty when binding a polymer with a reinforcement fiber due to an incompatibility between a hydrophobic resin and hydrophilic filler. Until the most recent

presidential election there was a socioeconomical and political push to develop renewable and natural biocomposites, which shifts research from synthetic fiber reinforcement to natural fibers. As previously mentioned by Mosiewicki, polymers exposed to an increase moisture will decrease the mechanical properties of tung oil-based composites.[11] The decrease in mechanical properties is not necessarily a bad thing when it comes to the biodegradability and recyclability of the polymers. Liu et.al. discovered the mixing tung oil with another oil, decreases the viscosity of the mixture and enhances its processability.[8] A previous study using tung oil and carbon nanotube composites, observed that the addition of carbon nanotubes decreased the cure time of the composites.[12] Although the cure time was decreased, the thermo-mechanical properties of the materials were decreased.[12] In order to solve incompatibility issues between the resin-reinforcement, a compatibilizer is used that helps mix a hydrophobic resin with a hydrophilic reinforcement.[13] In a study using cellulose-reinforced biocomposites from tung oil, that the addition of asolectin, found in soybeans, had compatibilizer properties that led to enhanced thermo-mechanical properties.[13]

Upon observation and research into the tung oil-based polymers, the current research on the subject can be taken further. Cellulose (**Figure 2**) is a natural polymer.[14] It is inexpensive and abundant.[14] It is found in all plants (30-50 wt%), can be recovered from wastewater treatment, and is produced by various bacteria.[14] Cellulose has repeating anhydroglucose units with three reactive -OH (hydroxyl) sites.[15] The hydroxyl sites found in cellulose can readily react with various chemicals to provide a derivative with unique properties.[15] Cellulose is becoming popular in the polymer industry due to the materials low cost, biodegradability, accessibility, and mechanical properties.
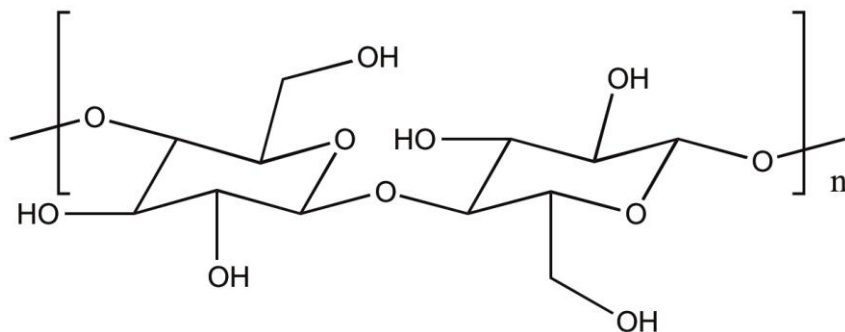
Figure 2. Structure of cellulose

In Gibbons et. al. lignin was modified prior to polymerization with tung oil.[15] In wood, cellulose and lignin are attached chemically.[1] From this knowledge, the same principle from Gibbons et.al. can be applied to this research. The research in this manuscript aims to provide a way to polymerize hydrophilic cellulose and hydrophobic tung oil. By modifying the cellulose (**Figure 3**) and replacing the hydroxyl units with the chains from tung oil, it would have the ability to bond to the nonpolar resin of tung oil. It can be hypothesized that the nonpolar groups in tung oil and modified cellulose can form a intermolecular carbon-carbon bonding network. This polymeric network would have enhanced thermo-mechanical properties. The modification of the hydroxyl units of cellulose with tung oil chains was partially confirmed by FT-IR Spectroscopy. The modification of cellulose with tung oil was successful, but there was a partial conversion of the hydroxyl groups on cellulose with tung oil chains.
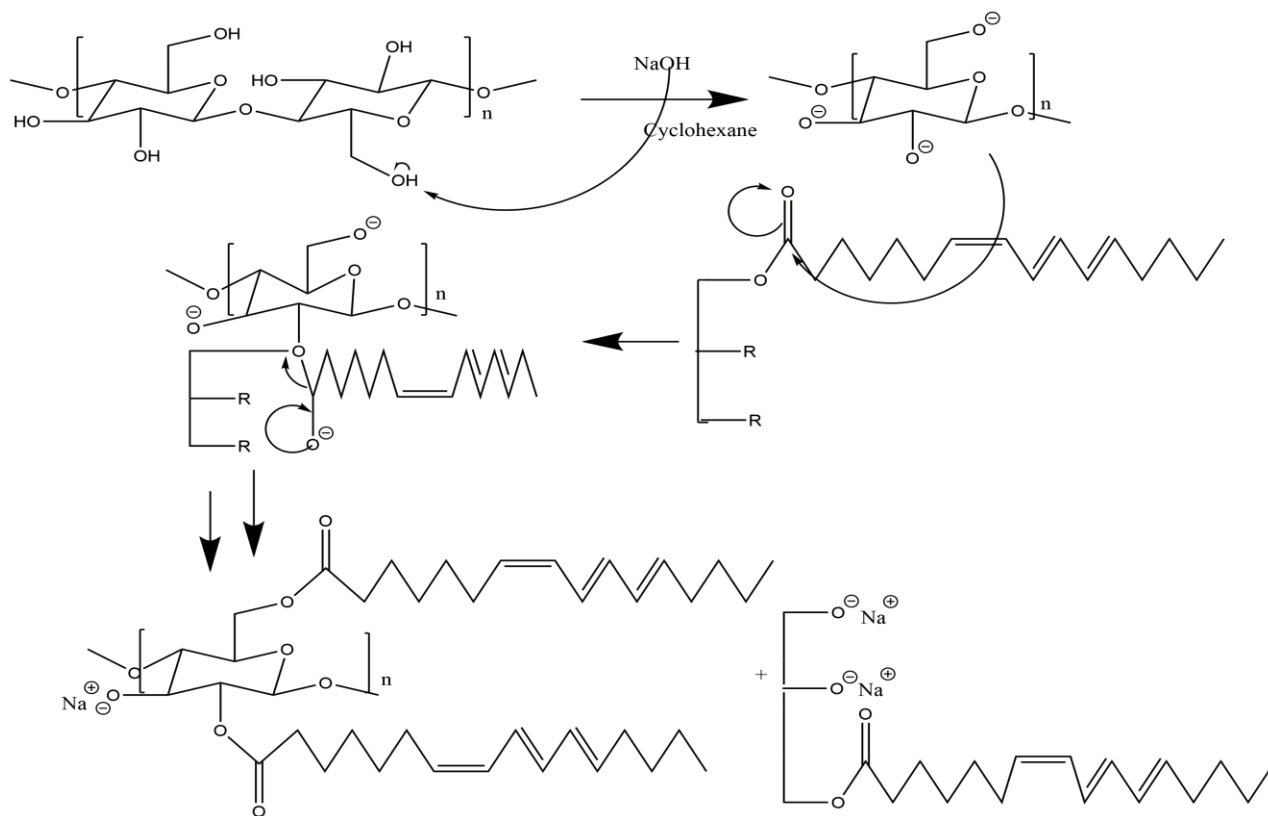
Figure 3. Cellulose modification under basic conditions (NaOH) with tung oil; separating the hydroxyl groups from the repeating cellulose units.

The resins polymerization was monitored by dielectric analysis (DEA) and further analyzed by differential scanning calorimetry (DSC) to verify the completion of the curing. The composites and resins were tested by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Various curing times of the tung oil resins and composites were analyzed under the same parameters listed above. These curing times were compared between the different composites to observe the thermo-mechanical properties of each.

The manuscript provided will be broken up into chapters. In chapter 2, will discuss the materials, procedures, and analysis parameters for the modification of cellulose, composite polymerization, and instruments. In chapter 3, will be the analysis of the curing times of tung oil

and modified cellulose composites, along with a discussion of the results from the

instrumentation used like the DEA, DSC, TGA, and DMA. In chapter 4, will be a critical

perspective of the overall results obtained in the work presented here and future directions for

future studies on improving the filler-resin interaction in bio-based composites.

CHAPTER 2: EXPERIMENTAL METHODS

The following section will include the experimental methods used to modify cellulose and the polymerization of modified cellulose with tung oil. The section will include the characterization methods used for modified cellulose and the final polymer composites, along with all parameters used on each instrument employed.

2.1 MODIFICATION OF CELLULOSE BY A TRANSESTERIFICATION REACTION

2.1.A. Materials for the Modification of Cellulose

The materials used for modifying cellulose were tung oil (TO) (Sigma-Aldrich, St. Louis, MO), acetone (BDH Analytical Chemicals, Radnor, PA), 50% w/w sodium hydroxide solution (NaOH), cellulose (Sigma-Aldrich, St. Louis MO), and cyclohexane (Fischer Chemical, Pittsburgh, PA). The FT-IR spectroscopy studies were performed on a thermos nicolet iS10 with a smart performer (Waltham, MA). Differential scanning calorimetry (DSC) studies were conducted on a Q250 DSC instrument from TA Instruments, New Castle, DE under nitrogen, and approximately 10 mg of sample was heated from -20 °C to 200 °C at a rate of 10 °C/min. A Q50 thermal gravimetric analyzer (TGA) instrument (TA Instruments, New Castle, DE) was used to study the thermal properties of all materials involved in this work. The weight loss of approximately 10 mg samples was measured as a function of temperature under air, from room temperature to 500 °C.

2.1.B. Procedure

Cellulose is a naturally occurring polymer.[13] The hydroxyl groups found on cellulose makes it hydrophilic. The intent of this work is to chemically modify to append reactive alpha-eleostearic acid chains from tung oil, rendering cellulose more hydrophobic and capable to crosslink with a tung oil-based polymer resin. It has been hypothesized that the modification of cellulose would enhance resin-reinforcement interactions by the production of a hydrophobic reinforcement that is chemically

compatible with the resin. This would allow the hydrophobic polymeric resin and the hydrophobic modified reinforcement, to interact favorably.

The methodology used in the current work was adapted from the study by Gibbons, et. al. in which the functionalization of lignin was successfully accomplished by trans-esterification with tung oil. In a round-bottom flask, 51.0 g of cellulose was mixed with 163.0 mL of tung oil, and 200.0 mL of cyclohexane, and 3.8 mL of 50% wt/wt NaOH was added to the flask and mixed with a stirring rod. The experiment was set up under reflux conditions at 50-60°C for 2 hours. The solid was filtered and all unreacted oil was washed off extensively with acetone. The final yellow product was dried under vacuum overnight at 70°C before characterization.

The modification of cellulose occurs in a multistep mechanism, shown in detail in **Figure 3**. First the hydroxide from NaOH deprotonates the hydroxyl group on the cellulose. The resulting alkoxide groups perform a nucleophilic attack on the carbonyl groups of tung oil, breaking the connection between the fatty acid and the glycerol unit of tung oil. This process results in addition of the fatty acid chains to the cellulose structure.

2.1.C. Characterization of Modified Cellulose

In order to characterize the structure of the newly modified cellulose, FT-IR was used for a comparison of the product with unmodified α-cellulose, and tung oil (**Figure 9**). The FT-IR spectra shown in this work have been collected using an attenuated total reflectance, ATR, accessory. DSC was used to check for the presence of water in the sample. The DSC experiments were carried out from -20°C to 200°C, at a heating rate of 10°C/min, followed by cooling to -20°C, and a second heating cycle to 200°C at 10°C/min. The TGA was also employed to obtain the thermal stability profile of the modified cellulose in comparison to unmodified alpha-cellulose. The TGA experiments were performed from room temperature to 500°C at a heating rate of 10°C/min. The TGA provided insight into the weight loss of the sample when heated over a temperature range.

2.2 Tung oil-Based Composites with Modified Cellulose

    2.2.A. Materials

n-butyl methacrylate (BMA), tung oil (TO), and di-tert-butyl peroxide (DTBP) were purchased from Sigma-Aldrich (St. Louis, MO). Divinylbenzene (DVB) was purchased from TCI America (Portland, OR). All reactants were used as received. The thermoset resins were cured in a convection oven. In order to establish the appropriate cure conditions, curing was initially monitored over a 24-hour period using an Epsilon 230/1 Dielectric Analyzer (Netzch Instruments, North America LLC, Burlington, MA). The thermal properties of all composites were assessed by DSC and TGA using the same parameters indicated previously. The mechanical properties of the composites were analyzed using a Q800 DMA (TA Instruments, New Castle, DE). It used a three-point bend fixture, under iso-strain mode, and a frequency of 1 Hz.

    2.2.B. Procedure

Tung oil resins were prepared using 5.0 g of tung oil, 3.0 g of BMA and 2.0 g of DVB and 0.5 g of the free radical initiator, di-tert-butyl peroxide (DTBP) in a 20 mL scintillation vial. A homogeneous mixture was obtained after the contents of the vial were thoroughly mixed. The crude resins were cured at a pre-set temperature schedule determined after the DEA study. The same procedure was employed for the preparation of composites reinforced with modified or unmodified cellulose. The modified or unmodified cellulose was previously dried overnight under vacuum, at 70°C. 3.0 g of cellulose was added to the vial prior to cure. The vial was placed in the convection oven for the designated temperature and times according to the specific cure schedule used. **Figure 5** provides a general schematic of polymerization by the free radical initiator, DTBP, and under heat. Although the schematic only shows the initiator in the figure, the monomers BMA and DVB are incorporated into the polymer network. The radical from the initiator, will break double bonds and share electrons with the radical to form new covalent bonds.

Figure 4: (A) Chemical structure of butyl-methacrylate (BMA). **(B)** Chemical structure of divinylbenzene (DVB). **(C)** di-tert butyl peroxide (DTBP).

(A)

(B)

Figure 5: (A) A schematic with the free radical initiator, DTBP, and the overall process for polymerization. The crosslinking monomers, BMA and DVB are not included in the schematic for simplicity. **(B)** A tung oil chain that shows the addition of the co-monomers which show that with polymerization the co-monomers will add where double bonds used to be.

2.2.C. Characterization of Composites

The composites were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dielectric cure monitoring (DEA), and dynamic mechanical analysis (DMA) in order to

assess their thermo-mechanical properties. Section 2.2.C provides the parameters used to analyze the composites with TGA and DSC.

Dielectric cure monitoring was used over a 24-hour period for determining the optimal cure schedule for samples reinforced with modified cellulose. 15.0 g of tung oil, 9.0 g of BMA, 6.0 g of DVB, and 9.0 g of dried modified cellulose were added to a container. The DEA probe was submerged into the crude resin, and the container was closed before being heated in a convection oven. The ion viscosity of the resin was measured at frequencies ranging from 0.01-10,000 Hz.

Dynamic mechanical analysis was conducted on the pure resin, and composites reinforced with non-modified cellulose, and with modified cellulose. Each sample was cut having a width 10 mm x 20 mm x2 mm (width x length x thickness). For each experiment, the temperature was varied from -60°C to 150°C at a heating rate of 3°C/min.

Chapter 3: Results and Discussion

The following section will discuss the characterization of unmodified/modified cellulose composites and the resin, and the optimization of the cure schedules. Additionally, composites containing modified cellulose were examined using DSC, TGA, DEA, and DMA, and the results were compared to those obtained from reinforced resin and composites prepared with non-modified.

3.1. Modified Cellulose Characterization

3.1.A Infrared Spectroscopy Analysis

In order to observe that the cellulose was modified, FT-IR was used on unmodified cellulose, modified cellulose, and tung oil. There are several significant peaks in **Figure 6A** to take note of that indicates the successful modification of the cellulose. Cellulose has an OH peak above 3000 cm[1]. Tung oil has a carbonyl peak, or a carbon-oxygen stretch, at 1750 cm^{-1} and a C-C double bond peak at 1650 cm^{-1}. In the modified cellulose, there is a carbonyl peak at 1750 cm^{-1} and a C-C double bond peak at 1500 cm^{-1}. This indicates the successful addition of the fatty acid chains of tung oil adding onto the cellulose. The disappearance of the OH peak confirms that the hydroxyl groups have been functionalized. A peak that is below 3000 cm^{-1} found in tung oil and modified cellulose is consistent with CH_2 peaks. Another important peak to note for the modified cellulose and unmodified cellulose is the peak at 1000 cm^{-1} and is considered to be a -C-O-C- bond, which is common for cellulose. Although there are residual hydroxyl groups on the cellulose, the experiment is successful because the IR spectra confirms that the fatty acid chains from tung oil successfully interacted with cellulose.

(A)

(B)   (C)
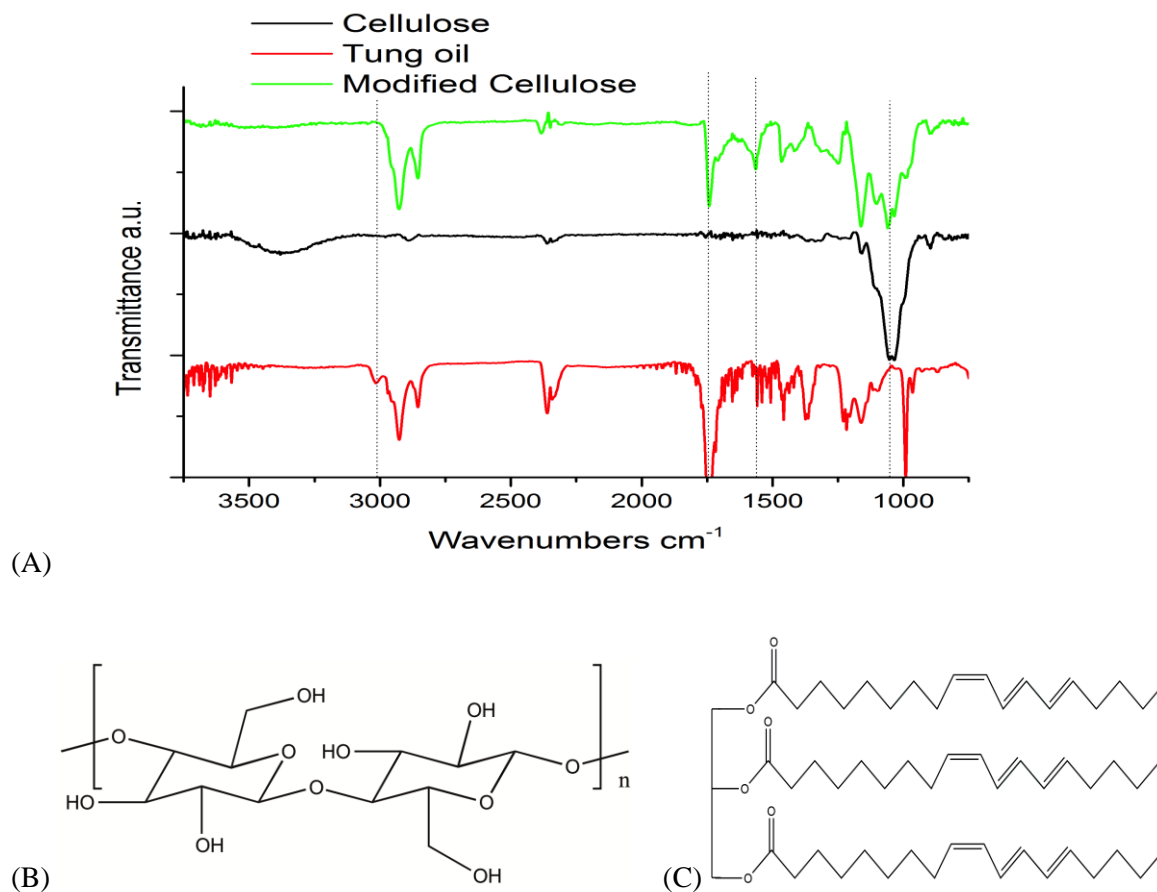
Figure 6. (A) FT-IR of cellulose, modified cellulose, and tung oil. (B) Cellulose (C) Tung oil. The structures for cellulose and tung oil are included so that they can be used in reference when examining the FT-IR.

3.1.B. Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) is a thermal analysis technique that measures heat flow in a sample and an empty reference pan while the temperature is varied over a pre-selected range. The DSC curve in **Figure 7** shows that cellulose and modified cellulose exhibit an exothermic peak at approximately 125°C, which indicates the release of heat/energy to maintain equilibrium with the reference pan.
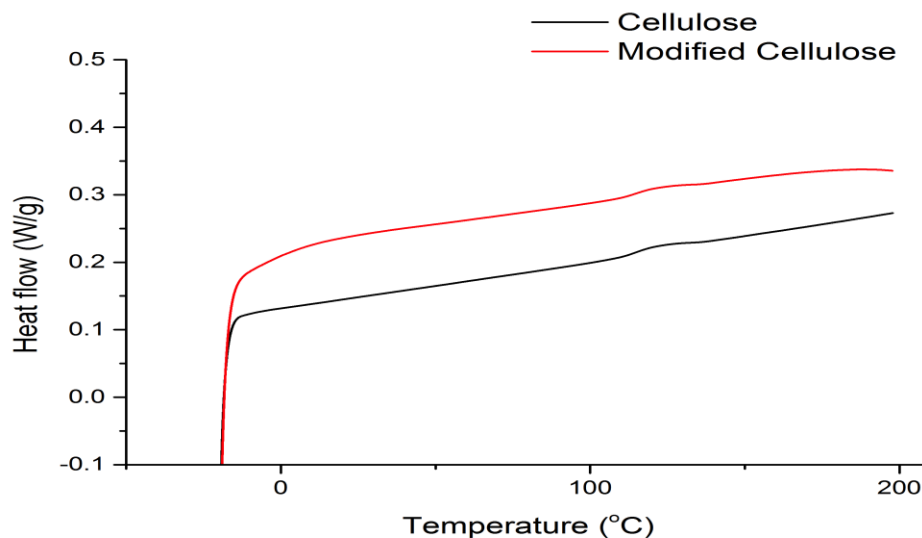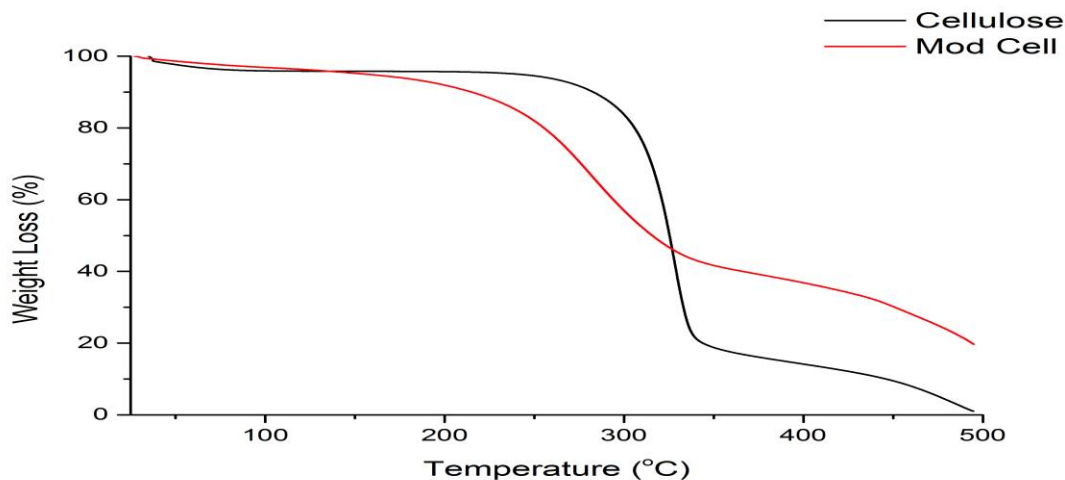
Figure 7. DSC of cellulose and modified cellulose

3.1.C. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measures the weight change in a sample through an increase in temperature. Cellulose is known to be less stable thermally than the modified cellulose, which is due to its ability to absorb water. From **Figure 8**, it is shown that with an increase in temperature, both samples, begin to lose weight at approximately 100°C. This could be attributed to water being released. As temperature increases, the weight loss of modified cellulose takes a large dip then levels off a little bit and then decreases more. Cellulose remains leveled off from approximately 150-275°C and then there is a major loss in weight. Cellulose and modified cellulose seem to have similar weight loss at approximately 350-500°C. Although they have similar behavior, there is a 20% difference between the two curves. This difference is related to the difference in structure between cellulose and modified cellulose. The main degradation step of modified cellulose starts at a lower temperature than the non-modified cellulose. Non-modified cellulose is fully degraded at 500°C, meanwhile modified cellulose has about 20 wt% left at this temperature. This can be due to changes in the cellulose after modification leading less hydrogen bonding, and possible pre-polymerization of the tung oil chains added to the cellulose.

Figure 8. TGA of cellulose and modified cellulose

3.2. Characterization of Composites

3.2.A. Optimization of Cure Schedule

In order to develop an optimum cure schedule used for the composites investigated in this work, samples containing the modified cellulose were prepared according to Section 2.2 and heated in a convection oven over a period of several hours at 100°Celsius, 110°Celsius, and 120°Celsius. Samples were removed from the over at 3-hour intervals for a total of 12 hours. Visual comparison of the samples revealed that the composites had a more solid appearance and less bubbles when left in the oven for longer times. The samples at 110°Celsius and 120°Celsius were solid with minimal bubbles after 12-hours. In light of these results, three cure schedules were tested. The cure schedules can be found in **Table 1**. In previous studies, it was noted that, in order to result in a completely cured thermoset, tung oil-based resins similar to the one used in this work required a final cure step of 2 hours and 50 minutes at 140°C.[15]

Table 1. Cure schedule used to make composites.

I	II	III
30 min. at 110ºC	30 min. at 120ºC	30 min. at 110ºC
12 hours at 110ºC	12 hours at 120ºC	6 hours at 110ºC
30 min. at 140ºC	30 min. at 140ºC	30 min. at 120ºC
2 hours and 50 min. at 140ºC	2 hours and 50 min. at 140ºC	6 hours at 120ºC
-	-	30 min at 140ºC
-	-	2 hours and 50 min at 140ºC

3.2.B. Dielectric Analysis on Optimum Cure Schedules

Dielectric analysis (DEA) cure monitoring uses electrical properties from polymers to provide information that can be used to make assumptions about the physical properties of a polymer such as the degree of cure, viscosity, and storage modulus. The DEA uses a sensor with parallel plates that is submerged in the crude resin and an electric field is applied to the sample. The ions in a sample migrate from one electrode to another. As a thermosetting polymer, the co-monomer mixture starts in the liquid state, reflecting a high conductivity (or low resistivity), but as the polymerization reaction progresses, polymer chain formation results in a more rigid and crosslinked material, with increasing low conductivity.

Ion viscosity is the ability of free ions to move around a sample, while under the influence of an electric field that also varies with temperature. Ion viscosity has a tendency to decrease with an increase in temperature. Temperatures will have increased until the desired cure temperature is reached (adjusted from cure schedules I-III), and remained at a constant temperature of 140ºC, until the 24-hour reaction is complete. When polymerization is reached, the reaction rate increases with temperature. Polymerization

begins 30 min to 1 hour into the experiment. When the ion viscosity slope plateaus, the electrical and physical properties do not change, and the curing of the sample has been completed. In **Figure 9** shows the ion viscosity graph, it shows a dip in the graph and then a subsequent increase until it plateaus.
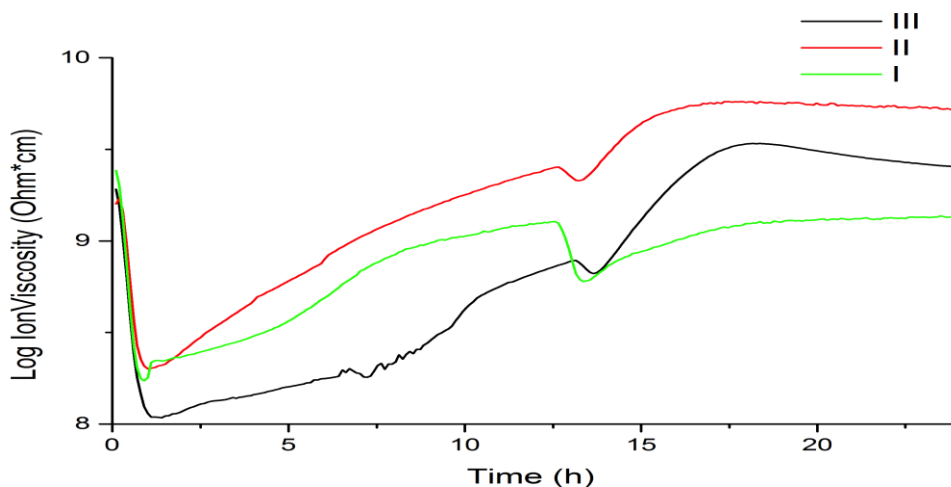
**Figure 9.** DEA curved for the different Cure Schedules described in Table 1.

Each cure schedule found in **Table 1** was run on the DEA in order to see which cure schedule would be best for making the composites. It is worth noting that the decreases in ion viscosity in **Figure 9** are related to the samples heating up prior to polymerization. Indeed, during heating, ions in the sample have more opportunity to move around. When the polymerization reaction begins, ion viscosity increases, indicating a stronger resistance to ion movement in the sample. From **Figure 9**, it is shown that eventually each curve starts leveling off at a different temperature, indicating that polymerization is close to completion. For the I, it is obvious that the polymerization is not complete at the end of the experiment, configuring an unsuitable cure schedule. At II, the polymerization is complete after approximately 16 hours. For III, polymerization completion takes approximately 20 hours, which is not surprising considering that cure schedule has additional times that II.

DEA is highly sensitive and provides a better insight on the cure of polymer resins than DSC or TGA. From the data presented in Figure 12, it can be determined that there may be some unreacted material left in I. In order to confirm the DEA results, DSC and TGA has been performed.

3.2.C. Cure Verification by Differential Scanning Calorimetry

The use of DSC allows insight into the cure kinetics and thermal events of materials as a function of temperature. The sample of analysis can either absorb or release heat/energy. This release or absorption result in either an exothermic, or an endothermic peak. The absence of an exothermic peaks indicates a fully cured polymer sample. An uncured sample typically exhibits an exothermic peak that indicates further polymerization reactions (crosslinking).

DSC is used to confirm the DEA data to show the completion of polymerization in the composites and resin. From **Figure 10**, it is shown that the modified cellulose composite and the resin were fully cured. For the cellulose, in **Figure 10**, there is an exothermic peak from 75-100°C. This shows that the cellulose composite using cure schedule III, is not fully cured. This comes as a surprise and will be repeated in order to confirm the results. From **Figure 11**, using cure schedule II, the resin and cellulose composite gives off exothermic peaks from 75-100°C. The modified cellulose composite seems to be fully cured until approximately 150°C which gives an endothermic peak, indicating the absorption of heat and then levels off. Further analysis into the peaks found will be done using TGA and DMA, and the results will be discussed in sections 3.2.3 and 3.2.4.
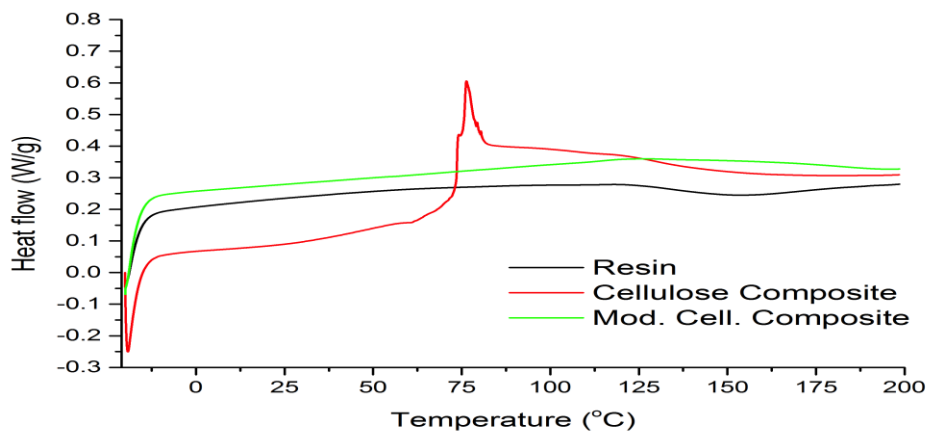
Figure 10. DSC for III for the Resin, Cellulose, and Modified Cellulose Composites
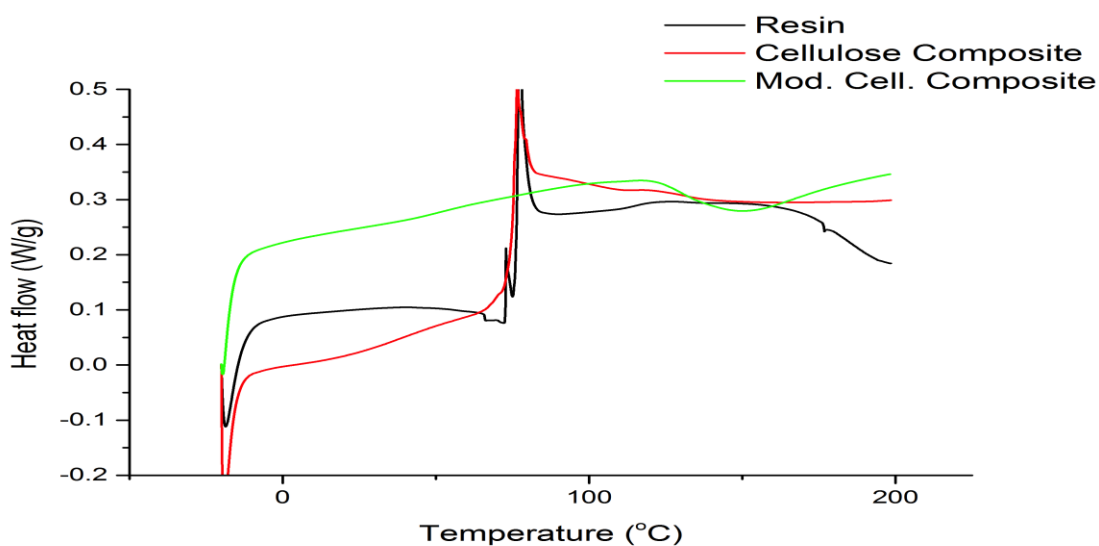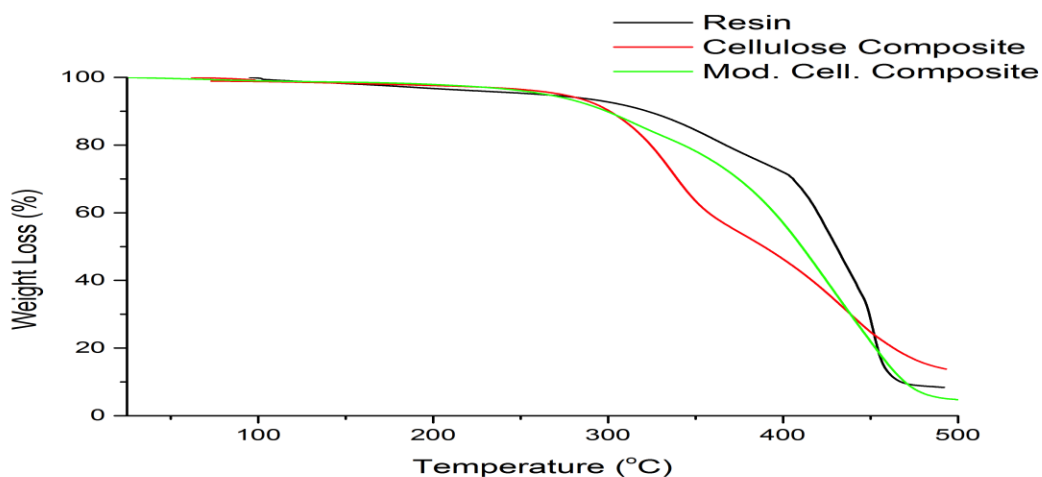

Figure 11. DSC for II for the Resin, Cellulose, and Modified Cellulose Composites

### 3.2.D. Cure Verification by Thermogravimetric Analysis

The thermal properties of the composites were evaluated by TGA using the same parameters described in Section 2.1.C. The samples cured under cure schedules II and III (**Figures 15 and 16**) are thermally stable until approximately 275°C. Beyond this point, the composite prepared with non-modified

cellulose degrades sooner than the one prepared with modified cellulose or the unreinforced resin. The composites exhibit a multi-stage degradation. From room temperature until 100°C, the weight loss can be attributed to water being evaporated, in the samples. From 100-300°C represents the evaporation of unreacted materials or the rupture of weaker bonds. The last stage for the samples from 300-450°C, shows the fasted degradation which is suggested by the steepest slope. This last stage indicated the cross-link network is degrading rapidly as the sample become charred. The rate of degradation and thermal stability of the samples is highly dependent on the polymer composition.

In the beginning stages of degradation from **Figures 12** and **13**, shows composites with a high cross-link are more thermally stable. With cellulose being less stable than the resins, for cure schedules II and III, stability comes from the resin and the modified cellulose composite. The composites prepared with non-modified cellulose degrade the fastest. The general trend for the thermal stability of composites, from **Figures 12** and **13**, is as follows: non-modified Cellulose composite>Modified Cellulose composite> unreinforced Resin. The unreinforced resin is the most stable, which is not surprising since it has the lowest amount of the less thermally stable cellulose less added.

Figure 12. TGA for the cure schedule III of the Resin, Cellulose, and Modified Cellulose Composites
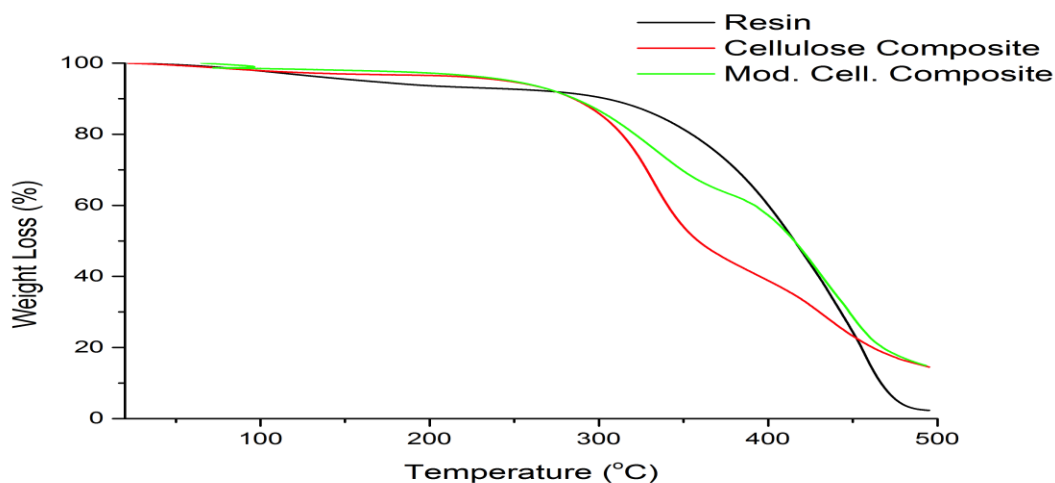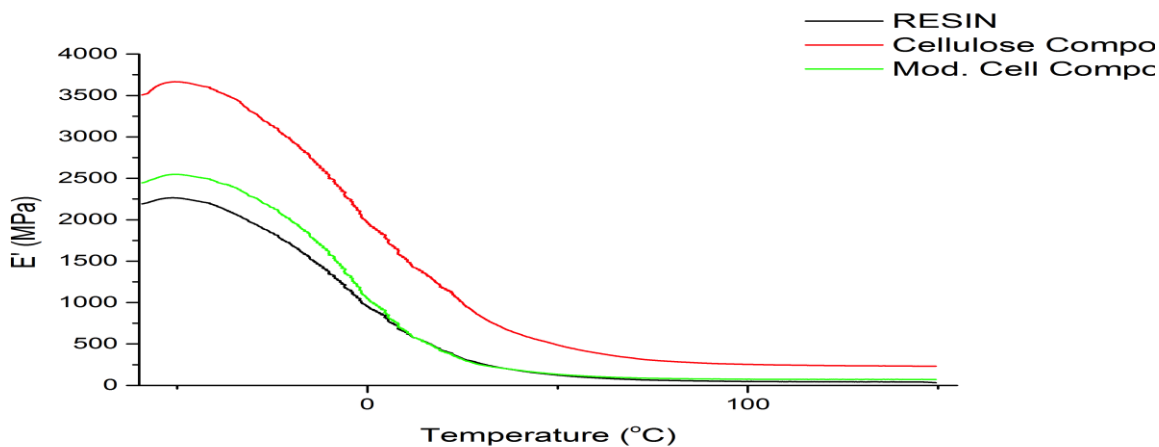
Figure 13. TGA for cure schedule II of the Resin, Cellulose, and Modified Cellulose Composites

3.2.E. Composites Mechanical Properties

Dynamic mechanical analysis (DMA) was used to examine the mechanical properties of the composites and resin for cure schedules II and III. Refer to Section 2.2.C for a description of the parameters used for analysis. There are three distinct viscoelastic regions found in composites: the glassy state, glass transition state, and rubbery plateau states. For cure schedule III, the resin and modified cellulose composites display similar mechanical properties in the glassy states until -10ºC, then they start to transition into glass transition states. Regardless of the viscoelastic state, the cellulose composites had the highest storage modulus when compared to the resin and modified cellulose composite. In the DMA analysis, it was surprising to discover that the resin and modified cellulose had a storage modulus that decreases as temperature increases. From 0ºC to 50ºC, there is a sharp decrease in the storage modulus in the samples found in **Figure 14**, and at this temperature range the samples are transitioning from a brittle, rigid states, to a more fluid, glass transition state. From 50ºC to the end of the experimental temperature 150ºC, the storage modulus for the samples plateaus as it goes into a rubbery plateau region. The rubbery plateau region is indicative of cross-linked polymers. Prior to this region, the polymer's stiffness decreases with an increase in temperature. A polymer's crosslink network gives a rigid structure that does

not flow past a certain point, rubbery plateau, which is due to steric hindrance despite the increasing temperature. A polymer's stiffness or elasticity and the E' does not change until the temperature is high enough for sample degradation.

Figure 14. DMA graph for the Resin, Cellulose, and Modified Cellulose Composites for cure schedule III.

The result found in **Figure 14** and **Table 2**, the modified cellulose composite and resin have weak mechanical properties. The cellulose composite displayed the best mechanical properties, which was unexpected. The mechanical property trend between the resin and the modified cellulose composite are similar, if not identical. The modified cellulose was used as a reinforcement that was supposed to enhance the mechanical properties.

Table 2. Data obtained from DMA for composites made with cure schedule III. [a] The Glass transition temperatures were evaluated from the tan δ curves, [b,c] storage modulus of the E' curves, evaluated from DMA analysis of the resin, cellulose, and modified cellulose composites using cure schedule III.

Sample Type	Glass Transition (ºC)[a] T_g	Storage Modulus E' (25ºC)[b]	Storage Modulus E' (T_g+50ºC)[c]
Resin	25.81ºC	324.8 MPa	63.14 MPa
Cellulose	37.43ºC	982.4 MPa	270.4 MPa
Modified Cellulose	19.98ºC	323.5 MPa	90.10 MPa

Based on **Figure 15**, the modified cellulose composite had the best damping properties, followed by the resin. The width of the tan δ curves, increases between the resin and cellulose composite. This could indicate that the addition of cellulose may disrupt the heterogeneity or homogeneity nature of the polymers. This could also indicate the cellulose fibers are not distributes throughout the polymer. The modified cellulose displays the opposite, upon comparison of the resin and cellulose composite. From **Table 2**, the modified cellulose had the lowest T_g, despite the belief that the compatibility would increase. It may have had a low crosslink density within the polymer, which may be why there was not an enhancement in thermo-mechanical properties. The lack of increase in the resin and modified celluloses thermo-mechanical properties (T_gs), the cellulose composite had an increase in mechanical properties based on the storage modulus (**Figure 14**).
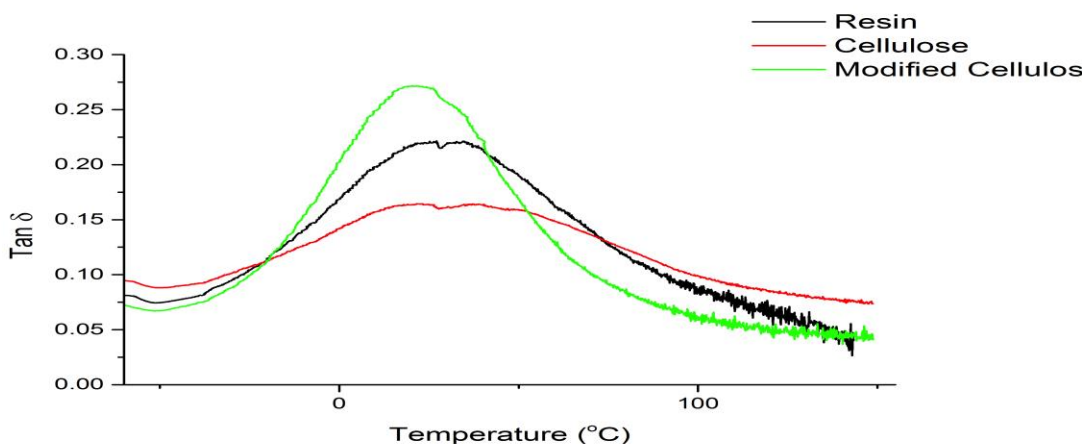
Figure 15. DMA graph of the tan δ curves for the Resin, Cellulose, and Modified Cellulose Composites for Cure Schedule III.

Through the use of DMA analysis, the mechanical properties of the modified and unmodified cellulose composites and the resins for cure schedule III. **Figure 14** shows the storage modulus for the cellulose, modified cellulose, and resin made using cure schedule III. The graph shows that the resin was less thermally stable than the modified cellulose composite. Cellulose composites showed an improved storage modulus. From this data, it can be inferred that the modified cellulose composites could be weaker due to the excess amounts of NaOH used when modifying the cellulose. The NaOH could be breaking down the hydrogen bonds within the cellulose fibers. The tan δ curve, **Figure 15**, examines the change in storage modulus and loss modulus. The broader the tan δ curve the more heterogeneous the polymer is. From **Figure 15**, it is seen that the modified cellulose composite is homogeneous, or uniform, throughout the polymer. The cellulose composite and resin have a much wider curve, therefore it is more heterogeneous, than the modified cellulose composite, this could happen due to the polar and nonpolar reactions of the unmodified cellulose.

CHAPTER 4: CONCLUSIONS

This thesis concludes with the successful modification of cellulose with tung oil chains, and its polymerization in order to enhance the resin-reinforcement interface. The enhancement between the resin and reinforcement can lead to an increase in thermo-mechanical properties in bio-based composites. For comparison, modified/unmodified cellulose composites were made along with resins made from tung oil. The composite and resin were examined to study the effects of the thermo-mechanical properties based on the chemical modification of a starting material.

The cellulose was modified by a transesterification reaction that limits harmful waste products. The modified cellulose is environmental friendly and is a renewable material. To observe the successful modification of cellulose was analyzed by FT-IR, DSC, and TGA.

The thermomechanical properties were enhanced through the use of co-monomers such as butyl methacrylate (BMA) and divinylbenzene (DVB), that was cured in a convection oven. The polymerization with the free radical initiator was monitored by dielectric analysis (DEA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) in order to obtain an optimal cure schedules. The thermo-mechanical properties of the resin and modified/unmodified cellulose composites were analyzed by the thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The unmodified cellulose composite for the cure schedule III, showed an increase in mechanical properties, when compared to the resin and modified cellulose composites. The modified cellulose composites seemed to be less favorable when compared to the cellulose and resin but showed a more uniform structure as shown by the tan δ curve. Additional analysis will be conducted using cure schedule II.

At the time of the writing of this thesis, the modified cellulose polymer has not been made before and is a novel contribution to the scientific community. The modified cellulose composites should be used over other composites due to its ease of availability and its use of materials that are more natural than the current petroleum-based polymers on the market today. The cellulose composite showed an

improved storage modulus but is a more heterogeneous throughout. The modified cellulose composite had a less favorable storage modulus but is homogeneous throughout. The research conducted in this manuscript will be further improved by trying to remodify the cellulose without the excess NaOH used. This research provides viable and promising initial research in regard to the enhancement between the resin-reinforcement compatibility. The research concluded here can be used for future experiments that will contribute the global goal of bio-based polymers that are bio-renewable and environmentally friendly.

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