

# EXTRACTION OF CELLULOSE AND LIGNIN FROM BIOMASS AND THEIR USE IN REINFORCING POLYMERS AND SYNTHESIS OF PHENOLIC RESINS

Mahesh V. Hosur<sup>1</sup>, Md. Nuruddin<sup>2</sup>, Dereca Hubbard<sup>3</sup>, Alfred Tcherbi-Narteh<sup>4</sup>, and Shaik Jeelani<sup>5</sup>

<sup>1</sup> Department of Materials Science and Engineering, Tuskegee University,  
hosur@mytu.tuskegee.edu

<sup>2</sup> Department of Materials Science and Engineering, Tuskegee University,  
mnuruddin2581@gmail.com

<sup>3</sup> Department of Materials Science and Engineering, Tuskegee University,  
dwatkins4914@mytu.tuskegee.edu

<sup>4</sup> Department of Materials Science and Engineering, Tuskegee University,  
atcherbi-narteh@mytu.tuskegee.edu

<sup>5</sup> Department of Materials Science and Engineering, Tuskegee University,  
jeelanis@mytu.tuskegee.edu

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## ABSTRACT

Lignocellulosic biomass, the world's most abundant renewable resources has been considered as a valuable natural raw material for pulp and paper industry and high performance biocomposites. In addition to this, some useful chemical compounds such as ethanol and lignin modified phenol-formaldehyde resin can be produced. Cell wall of lignocellulosic biomass comprises of cellulose, hemicellulose, lignin, small quantity of pectin and extractives. In the current work, cellulose and lignin were extracted from lignocellulosic biomass sources such as flax fiber, alfalfa fiber and wheat straw. Subsequently, cellulose extracted from wheat straw was reduced to cellulose nanofiber (CNF) using ball milling. It was then used to reinforce epoxy resin. Maximum improvement in flexure strength and modulus of 22.5% and 31.7%, respectively was obtained by the addition of 2 % CNFs. Furthermore, storage modulus was 16-22 % higher than neat epoxy for 2 % loading of CNFs at room temperature, while  $T_g$  improved by 16-17 %. Thermal stability of composite was improved probably due to the catalytic effect of CNFs. Lignin extracted from flax and alfalfa fibers were utilized in synthesizing modified phenol formaldehyde pre-polymers. The resulting materials were subjected to thermogravimetric analysis (TGA) to observe the overall thermal stability and degradation properties of unmodified and modified resole phenol formaldehyde resins. Results from TGA scan and corresponding derivative weight loss thermogram (DTG) for various cured resole phenolic-type resin systems showed a three-stage decomposition profile. Significant mass loss in each system was observed in the following temperature regions; 100-300 °C, 300-600 °C, and above 600 °C.

## 1 INTRODUCTION

Many of the current generation polymeric materials are based on petroleum derived sources. They are not sustainable and are also not degradable. Therefore, researchers are trying to develop bio-based renewable materials of high mechanical and thermal properties as replacements for conventional polymeric systems. Almost all the plants contain cellulose, hemicellulose and lignins as their constituents, which can be extracted and used for preparing many advanced materials. For example, cellulose can be extracted and reduced to nanosize and lignin can be used as one of the precursor materials to synthesize phenolic resin system. Cellulose is an important component of lignocellulosic fibers, which consists of a bundle of cellulose nanofibers (CNFs). Several research studies have been conducted to isolate cellulose nanofibers from plant based materials [1-5]. Scientists and engineers are working together to utilize cellulose nanofibers in various engineering applications.

Cellulose nanofibers have shown excellent mechanical properties (high specific strength and modulus), better biodegradability, high aspect ratio (L/d), renewability, large specific surface area, low coefficient of thermal expansion, environmental benefits, low cost and availability [5-7]. These properties of CNFs made them comparable with other engineering materials such as carbon nanotube, carbon nanofibers, graphene nanoplatelets and nanoclay. CNFs have been considered as effective reinforcing materials for fabrication of green composite materials because of higher mechanical properties and their web-like structure. One of the main disadvantages of using CNFs as reinforcement filler in the polymer matrix is water absorption ability and tendency to be agglomerated. The interaction of hydroxyl groups result in strong hydrogen bond formation between the fibers and also with the moisture. Hydrophilic CNFs show poor dispersion capability in hydrophobic polymer matrix [8]. Therefore, several research studies have been conducted to modify the surface to make them suitable for both hydrophilic and hydrophobic polymer matrix [9, 10]. Cellulose nanofibers (CNFs) can be used as filler materials in a wide range of thermosetting polymers such as epoxy and polyester [11, 12]. Among the thermosetting polymers, epoxy is high performance polymer that shows wide applications from rocket casing to dental filling. Incorporation of CNFs into epoxy polymer matrix has shown to improve mechanical properties such as fatigue resistance, high strength and stiffness of the materials [13, 14]. Nevertheless, the main drawback of epoxy/CNFs composite is the poor adhesion capability of CNFs that causes poor dispersion into the matrix. Therefore, several techniques such as surface modification as well as solvent exchange methods, have been reported to increase the adhesion ability of CNFs [8, 15].

Phenolic resin systems are used in various applications including formable laminates, sheet-molding compounds, electronics, aircraft interior facing, mass transit, oil rigs, cruise ships, and commercial submarines. One of the major advantages to using such polymeric systems is their characteristically low flammability and relatively low smoke generation properties. However, phenolic resin manufacturers have been modifying the material's formulation as a way to order to meet strict demands of fire mandates and regulations. Some of the most common methods that are already used to modify the fire properties of phenolic resins have been to replace the methylene (-CH<sub>2</sub>-) linkage with heteroatoms (oxygen, sulfur, nitrogen, silicon, boron, phosphorous, bromine, and chlorine), insert polyvalent elements (calcium, magnesium, zinc, and cadmium) into the resin as a way to promote complex formation, and enable esterification or etherification reactions of phenolic hydroxyl groups with polybasic acids (phosphorous and boric acid) to incorporate flame retardant moieties [16]. Researchers are even considering incorporating fire retardant nano-additives into the formulation of phenolic resin to achieve desired fire properties as well as an increase in adhesion, barrier, mechanical, and overall thermal properties [17]. Many of these modifications have led to fabrication of phenolic resins with enhanced fire properties, however, research is still being pursued, not only to further enhance properties, but to move towards a less hazardous phenolic resin with comparable flame retardant properties. Recently, an increasingly growing trend of using derivatives of phenol or formaldehyde or lignin extracted from natural biomass resources as partial replacement for the phenol precursor in the formulation of phenolic resins to impart flame retardant properties due to their chemical structure similarities.

In present study, cellulose nanofibers (CNFs) were extracted from wheat straw by delignification and bleaching treatment followed by ball milling technique for using as reinforcing materials. Surface of CNFs was modified by treating it with silane coupling agent. These CNFs were added to epoxy polymer matrix at different loading to fabricate polymer composite. The fabricated composites were characterized by using SEM, Flexure, DMA, FTIR and TGA analysis. Lignin was extracted from wheat straw, pine straw, alfalfa fiber, and flax fiber by formic/acetic acid treatment followed by peroxyformic/acetic acid treatment. Obtained lignin from each source was characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for structural, thermal and chemical composition comparison. In addition, void-free, homogenous, solid novel resole phenolic type resin systems have been synthesized using various ratios of the extracted lignin for the phenol precursor. Resulting novel resole phenolic-type systems were characterized using TGA.

## 2 EXPERIMENTATION

### 2.1 Materials

Wheat straw was used to extract nanocellulose, Alfalfa fibers and flax fibers were used for extracting lignin. Alfalfa fibers were collected from a local field near Tuskegee, Alabama. Wheat straws were obtained from Home Depot store (USA). Flax fibers used in the study were supplied by Alvin Ulrich Company from Canada. Various chemicals used for extraction of lignin are formic acid, acetic acid, hydrogen peroxide, sodium hydroxide, and distilled water were obtained from Sigma Aldrich Inc. Commercial lignin was also USA.

### 2.2 Extraction of Cellulose and Lignin

Cellulose and lignin were extracted from plant fibers according to Nuruddin et al. [18]. In briefly, wheat straw and 90 % formic acid were placed on a hot plate at 110 °C for 2 hours. At the end of the reaction time, the fibers were filtered in a Buchner funnel and washed with formic acid followed by hot distilled water. Post formic acid treated pulp was further treated with peroxyformic acid solution in hot water bath at 80 °C for 2 hours to remove amorphous content (lignin, hemicellulose and pectin). Finally, delignified fibers were filtered to separate cooking liquor (lignin and hemicellulose mixed with formic acid) from cellulose and washed several times with hot water. Delignified fibers were subjected to bleaching by treating them with 35 % H<sub>2</sub>O<sub>2</sub> solution and NaOH solution (to maintain pH: 11-12), and kept in a hot water bath at 80 °C for 2 hours. Finally, the pulp was washed several times with distilled water to ensure complete removal of residual lignin.

Process of lignin extraction from different biomass began first by pulping, where biomass was cut into small sizes and placed in a conical flask. A mixture of 85% organic acid (ratio of formic acid/acetic acid mixture was 70:30 by volume) was added to the biomass in the flask at a liquor to fiber ratio of 1: 8 and allowed to boil on a hot plate for 2 hours. After 2 hours, flask and its contents were allowed to cool to ambient temperature. Fibers were filtered in a Buchner funnel and washed with 80% formic acid followed by hot distilled water. After pulping, FA/AA treated pulp was further delignified by treating it with a mixture of PFA/PAA solution in hot water bath at 80° C for 2 hours. PFA/ PAA solution mixture was prepared by adding 8 ml 35% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) with 85% formic acid/ acetic acid mixture. Finally, the delignified fibers were filtered to separate cooking liquor (lignin and hemicellulose mixed with formic acid) from cellulose and washed with hot water. Delignified fibers were subjected to bleaching by treating with 14 ml 35% H<sub>2</sub>O<sub>2</sub> solution (pH 11-12) in hot water bath at 80 °C for 2 hours. Finally, the pulp was washed with distilled water to remove residual lignin. This process was done again to remove lignin completely. Lignin was isolated by following the procedure suggested by Nuruddin, et al. The lignin dissolved in formic acid was precipitated by adding distilled water (5 times more than volume of concentrated liquor), and the precipitate was filtered in a Buchner funnel. Finally, the precipitated lignin was washed with distilled water and allowed to air dry.

### 2.3 Isolation of cellulose nanofibers (CNFs)

In our laboratory, a new technique has been developed to isolate CNFs by ball milling [17]. In briefly, Approximately 10 gm of bleached cellulose was soaked in 10 ml of 80 % ethanol solution and the fiber was allowed milling for 120 minutes in a Mixer/Mill 8000DTM (SPEX Sample Prep, USA) using zirconia ceramic grinding vial and ball with diameter 12.7mm. After ball milling, the mixture was repeatedly washed with distilled water and centrifuged until the pH of the cellulose reaches between 6 and 7. Finally, the suspension of ball milled cellulose nanofibers (CNFs) were freeze dried.

### 2.4 Surface modification of cellulose

1% silane coupling agent (total weight of fiber) was mixed with 80/20 v/v ethanol/water mixture and then 5g freeze dried CNFs was added to the mixture. 1% acetic acid was added dropwise to maintain PH near 3.5, and then the mixture was magnetically stirred at 500 rpm for 90 minutes, maintaining the room temperature. After completion of the reaction time, the CNFs suspensions were repeatedly centrifuged and washed with distilled water until the PH became 6. Then samples were freeze dried to use it as filler materials.

## **2.5 Fabrication of nanocomposites**

Pre-calculated amount of part-A and CNFs were mixed manually in a beaker and then ultrasonicated for 20 minutes at 40 °C, using “Sonics Vibra-cell” (Sonics & Materials Inc., USA) set at 30 seconds pulse on, 20 seconds pulse off, and amplitude of 40. Then the sonicated mixture was magnetically stirred at 500 rpm for 5 hours at 40 °C temperature to ensure complete dispersion of CNFs in the polymer matrix. After the end of the stirring, part B was mixed with CNFs modified part A in the ratio of 10:3 (part A: part B). The resultant mixture was stirred again using high speed mechanical stirrer for 5 minutes to ensure complete mixing. Then the mixture was kept in a vacuum oven to remove bubbles formed during mixing of part A and part B. After removal of bubbles, the resin was poured into the metal molds for desired shape and kept in the oven at 60 °C for 1 hour and 120 °C for 3 hours. For neat samples, calculated amount of part A and part B were mixed in the ratio of 10:3 by using mechanical stirrer and followed the same procedure as mentioned for CNFs modified samples.

## **2.6 Preparation of Resole Phenolic and Novel Resole Lignin Phenolic Resins**

Lignin extracted from these flax and alfalfa fibers were chosen for the synthesis of resole lignin phenol formaldehyde resin-type systems (FL-PF and AL-PF) with the addition of each lignin sample at various percentages (40, 50, and 60 %), partially replacing the phenol precursor to compare with the unmodified resole phenol formaldehyde resin (PF). The PF, 40 % FL-PF, 50 % FL-PF, 60 % FL-PF, 40 % AL-PF, 50 % AL-PF, and 60 % AL-PF pre-polymers were subjected to a multi-temperature schedule to obtain the overall cured resins. Synthesis of phenol formaldehyde resin proceeded by first adding sodium hydroxide (NaOH) and distilled water to a 100-mL beaker. The aqueous basic solution was slightly swirled until complete dissolution. Paraformaldehyde and phenol were added to the beaker and the beaker was then placed in a heated water bath, 75-80 °C. The solution of the beaker were brought to reflux and then allowed to react for 2 hours under constant mechanical stirring to produce the resole phenolic pre-polymer solution. The beaker was then removed from the water bath and the pre-polymer solution was dehydrated in a vacuum oven heated to 65 °C for 30 minutes. The resulting pre-polymer solutions were immediately poured into molds for cure. The lignin phenol formaldehyde resin was synthesized and cured in a similar manner as the procedure for phenol formaldehyde resin with the exceptions of using phenol and lignin extracted from flax fiber (FL), or lignin extracted from alfalfa fiber (AL), as partial replacement in the starting phenolic precursor. Molds containing the pre-polymer solutions were placed in an oven and cured for 24 hours at 65° C followed by a temperature increase to 85° C for 24 hours, 110° C for 1 hour, 130° C for 1 hour, and subjected to a final temperature increase of 160° C for 1 hour. After the thermal cure cycle, the samples were slowly cooled to room temperature and stored for thermal characterization.

## **3 CHARACTERIZATION TECHNIQUES**

### **3.1 Flexure test**

Three point bending flexure test was conducted according to ASTM D790-02, using Zwick-Reoll Z 2.5 machine. The test was conducted under displacement control mode with a crosshead speed of 1.2 mm/min. The sample size was maintained according to the ASTM; size was 96 mm × 12.5 mm × 4.5 mm (span length×width×thickness). The span length to thickness ratio of 16:1 was maintained, and at least 5 samples of each type nanocomposites were tested at room temperature.

### **3.2 Scanning electron microscopy (SEM)**

Scanning electron micrograph of ball milled CNFs was taken using JEOL JSM-6400 scanning electron microscope (SEM) at 20 kV accelerating voltage. Morphological studies of neat epoxy and CNFs reinforced epoxy polymer nanocomposites were conducted using JEOL JSM-6400 scanning electron microscope (SEM) at 15 kV accelerating voltage. Surface of each sample was sputtered with a thin layer of gold particle before SEM conducted.

### 3.3 Transmission electron microscopy (TEM)

A drop of dilute cellulose nanofibers (CNFs) suspension was deposited on the 300 mesh Formvar/Carbon coated support film grids. The excess liquid was absorbed by a piece of filter paper and then allowed to dry at room temperature. When the sample has been dried, then it was observed using ZEISS EM10 Transmission Electron Microscope (Thornwood, NY) operated at 60 KV accelerating voltage.

### 3.4 Fourier transfer-infrared (FTIR) spectroscopy

Structural characterization was conducted on CNFs, surface treated CNFs, neat epoxy and CNFs reinforced epoxy polymer composite, using Shimadzu FTIR 8400s equipped with MIRacle™ ATR, and samples were scanned from 550-3500  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

### 3.5 Dynamic mechanical analysis

Dynamic Mechanical Analysis (DMA) of nanocomposites was conducted according to ASTM D4065 using TA Instrument DMA Q-800. The tests were performed in a three-point bending mode at amplitude of 15 $\mu\text{m}$  and oscillation frequency of 1 Hz. The temperature range was 30 to 150° C at a heating rate of 5 °C/min. The sample size of the samples was 60mm×12.5mm×4.5mm, and at least 3 samples of each nanocomposite were tested. Storage modulus and tan-delta as a function of temperature were obtained from this experiment. Glass transition temperature was obtained from Tan-delta curve.

### 3.6 Thermogravimetric analysis (TGA)

Thermal stability of polymer nanocomposites and neat epoxy were studied using thermogravimetric analysis Q-500 from TA Instruments Inc. (DE). Approximately 10-12 mg Samples were taken for the test. TG scans were performed at 10° C/min from 25- 600° C under nitrogen environment with a purge flow rate of 60 mL/min. For phenolic resin systems, Cured unmodified and unmodified phenolic resins were tested over a temperature of 35° C to 800° C, at heating rates of 2,5,10, and 15° C/minute. Testing was performed under nitrogen purge in order to examine the thermal stability and decomposition kinetics of the cured resins. Platinum pans were used to hold samples weighing  $20 \pm 5$  mg. The parameters studied are the temperature corresponding to the percent of degradation at various temperatures including 100, 200, 400, 600, and the percentage char yield at 750 °C as well as the thermal events obtained from TGA data. In addition, solid state thermal decomposition kinetic parameters were calculated using the Flynn-Wall Expression. Three scans were run on each sample to confirm repeatability and reproducibility of the individual scans.

## 4 EXPERIMENTAL RESULTS

### 4.1 Morphological characterization of CNFs and nanocomposites

Fig. 1 shows the SEM and TEM images of extracted web like CNFs. The maximum and minimum diameters were calculated from TEM images using MaxIm DL5 software. The maximum and minimum diameter of ball milled CNFs were approximately 45 nm and 17 nm respectively. A morphological study on the fracture surface of neat epoxy and CNFs modified epoxy polymer composites are presented in Fig. 2. It is apparent from the SEM images that, the fracture surface of CNFs modified nanocomposites is rougher than the neat samples. Among the nanocomposites, 2% CNFs reinforced ones showed roughest fracture surface indicating the highest resistance to crack propagation by the materials as shown in Fig. 2c. In contrast, the exposed fracture surface of neat epoxy and 3% CNFs incorporated samples exhibit relatively smoother surface than 2% CNFs incorporated samples (Fig. 2a and 2d). Addition of higher loading causes cluster of agglomerated CNFs. This agglomeration was formed might be due to two factors. One is, 3% loading CNFs was more than enough to crosslinked with epoxy polymer resulted in unreacted CNFs in the form of agglomeration. Another important factor is the higher tendency of hydrogen bonding between the hydrogen groups on the surfaces of CNFs. The crack for 3% CNFs reinforced samples initiated from a zone where the CNFs appear to be agglomerated to form a cluster.

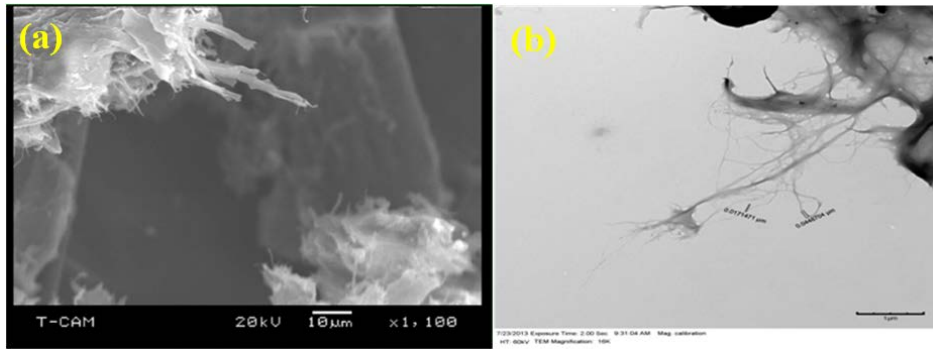


Figure 1: (a) SEM, and (b) TEM images of Cellulose nanofibers (CNFs).

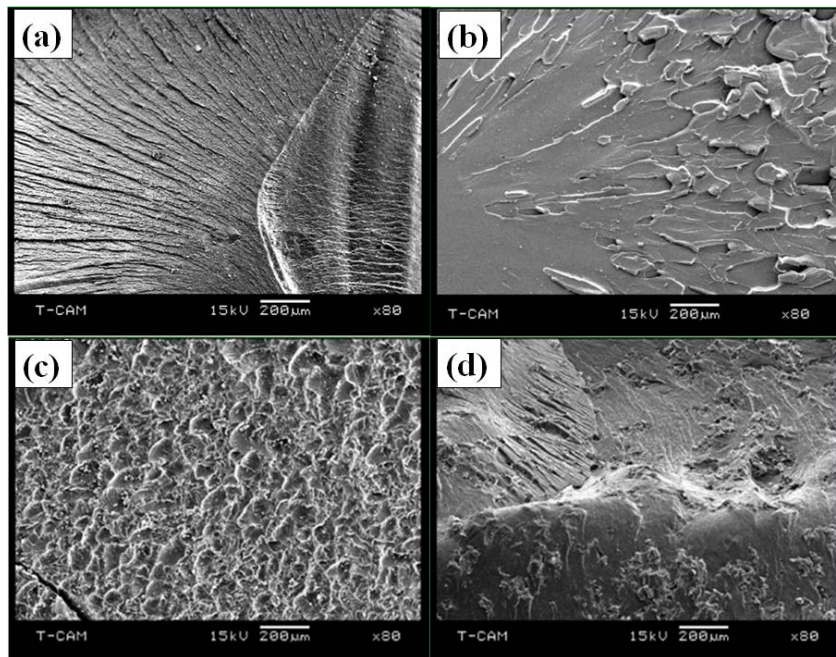


Figure 2: Fracture surfaces of (a) neat epoxy, (b) epoxy/1% CNFs, (c) epoxy/2% CNFs and (d) epoxy/3% CNFs.

#### 4.2 Flexure test

Flexure properties of nanocomposites are characterized by subjecting neat epoxy and CNFs reinforced nanocomposites under three point bending load. The stress-strain curves as shown in the Fig. 3, obtained from flexure test show significant non-linearity, although no remarkable yield point was observed in the curves. Flexure test results obtained from various samples are compared in the Fig. 4. From Fig. 4, it can be seen that incorporation of cellulose nanofibers into epoxy polymer matrix exhibited significant improvement of flexure strength and modulus. The highest flexure strength and modulus were achieved from 2% CNFs/epoxy nanocomposite (22.5% and 31.7% higher than neat epoxy). In contrast, a reduction in flexure properties at 3% loading might be due to the strong attractive forces between cellulose nanofibers leading to cluster or agglomeration of CNFs. Due to poor dispersion of CNFs at 3% loading as shown in Figure 2d, CNFs agglomerates in the resin system leading to the reduction of load transfer between CNFs and epoxy polymer.

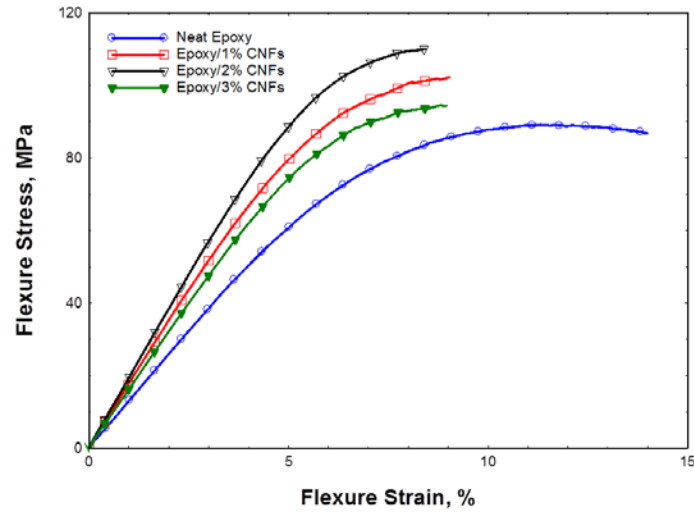


Figure 3: Flexural stress–strain response of neat epoxy and CNFs incorporated epoxy nanocomposites.

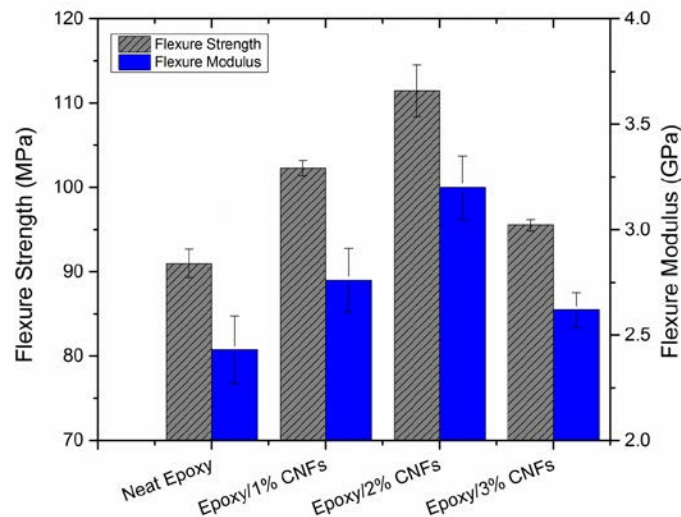


Figure 4: Comparative value of flexure strength and modulus of neat epoxy and CNFs incorporated epoxy nanocomposites.

Uniform dispersion of CNFs ensures more surface area of cellulose nanofibers to be exposed to the matrix and better interaction between CNFs and epoxy polymer. Silane treated CNFs contain amino functional groups that are strong nucleophile. Therefore, these amino functional groups of CNFs attack epoxide group of epoxy SC-15 and form strong covalent bond by ring opening reaction. As a result, higher cross-linking between epoxy molecules is formed that results in an interlocking structure in the matrix and reducing the mobility of epoxy polymer chains through the system. Chemically interlocked resin and CNFs structure may facilitate stress transfer between matrix/fiber and fiber/fiber. Strong covalent bonds between fibers and polymers must be broken before the sample fails while subjecting to loading. Higher crosslinking means formation of higher covalent bonds between fibers and polymer matrix. Thus, flexure strength and modulus of nanocomposites increased after addition of CNFs. After initiation of crack due to loading, the propagation of the crack can be restricted by the presence of CNFs. Thus, the direction of crack propagation is changed in the presence of CNFs.



### 4.3 Viscoelastic properties of epoxy nanocomposites

The viscoelastic properties of neat epoxy and CNFs reinforced nanocomposites are evaluated as a function of temperature. Figure 5 shows the comparison of dynamic mechanical properties such as storage modulus and tan-delta as a function of temperature. Storage modulus measures the energy stored in the materials after deformation while subjected to cyclic loading. Fig. 5a represents the storage modulus of nanocomposites as a function of temperature. It can be seen that the addition of CNFs increases the storage modulus as compared with neat epoxy. Maximum storage modulus was achieved for 2 % loading of CNFs (16-22 % higher than neat epoxy) at room temperature. The polymer chain initiates to move with increasing the temperature leading to decrease in stiffness. As mentioned earlier, CNFs covalent bonded with epoxy polymer by crosslinking that restricted the movement of the polymer chain. In contrast, lower value of storage modulus for 3 % loading of CNFs can be attributed the agglomeration of CNFs due to strong interaction between CNFs.

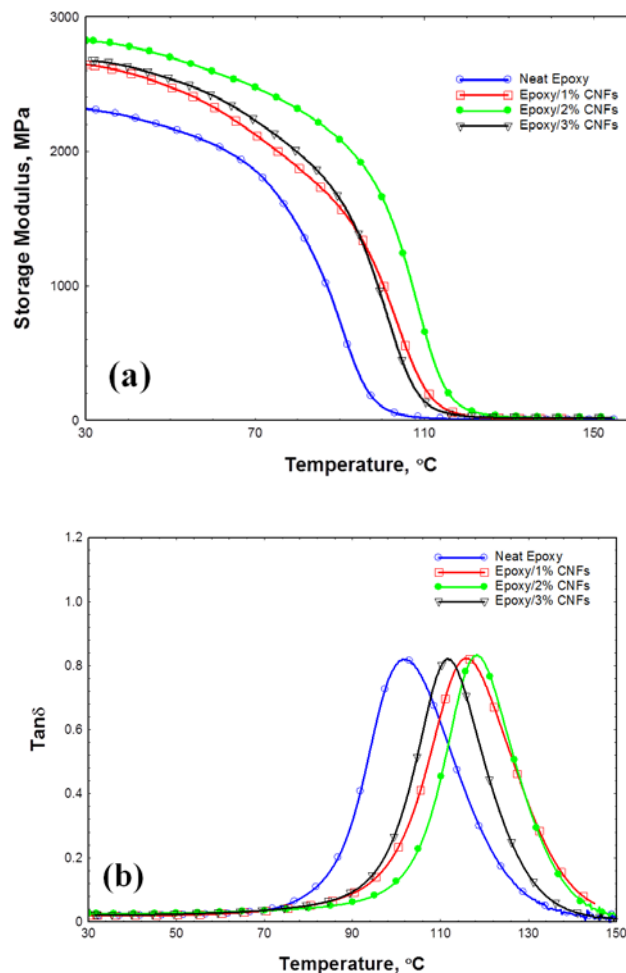


Figure 5: (a) Storage modulus versus temperature curve and (b) Tan $\delta$  versus temperature curves of neat epoxy and epoxy/CNFs nanocomposites.

Fig. 5b shows the Tan-delta curve of neat epoxy and different percentage of CNFs incorporated epoxy composite samples. Tan-delta value represents the damping properties of the materials and can be expressed as the ratio of loss modulus over storage modulus. The peak of tan-delta curve represents the glass transition temperature ( $T_g$ ). From Fig. 8, it can be observed that the value of  $T_g$  increases with the addition of CNFs up to 2%. About 16-17 % improvement of  $T_g$  was achieved at 2 % loading of CNFs compared with neat epoxy polymer composite. Good dispersion of CNFs was achieved for 2 % loading CNFs into the polymer matrix leading to sufficient crosslinking between matrix and cellulose



nanofibers and ensures severe restriction of movement of polymer chain when temperature increases. Thus, the matrix/CNFs crosslinked network initiates to move at a relatively higher temperature than neat epoxy sample leading to higher  $T_g$  value. Salam et al. reported that improved interfacial bonding between CNTs and epoxy polymer leads to higher  $T_g$  value [19]. This  $T_g$  value shifted towards lower temperature possibly because of agglomeration tendency of CNFs.

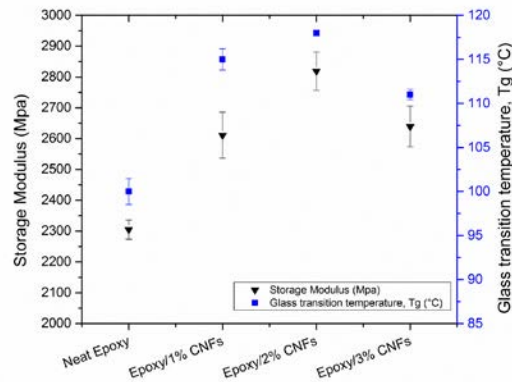


Figure 6: Comparative study of storage modulus and glass transition temperature ( $T_g$ ) of nanocomposites.

#### 4.4 Thermal stability of nanocomposites

Thermal stability of neat epoxy and cellulose nanofibers incorporated epoxy polymer composites was evaluated by thermo-gravimetric analysis (TGA). Summary of thermal stability of all samples are evaluated in terms of onset of decomposition, ( $T_i$ ) and maximum decomposition temperature as shown in Table 1. From Table 1 and Fig. 7, it can be seen that the onset temperature varied significantly with the addition of CNFs into epoxy polymer matrix. Onset temperature of neat epoxy was 311 °C and was increased to 327 °C after incorporation of CNFs.

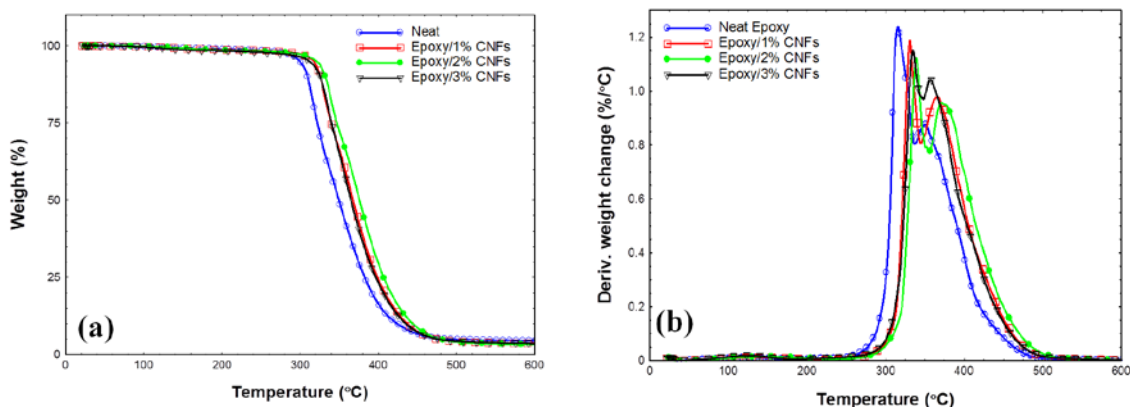


Figure 7: (a) Weight % versus temperature, and (b) derivative of weight % versus time curves of neat epoxy and epoxy/CNFs nanocomposites.

From the curves shown in Fig 7b, it is seen that the decomposition of all samples show two distinct peaks. The first decomposition peak was noticed around 323-342 °C with 13-26 % weight loss, which was mainly due to the decomposition of lower molecular weight materials. The second decomposition peak was around 362-376 °C with 48-60 % weight loss of the samples, which was the result of decomposition of highly crosslinked materials [20]. Cellulose nanofibers (CNFs) enhance both first and second decomposition temperature with a maximum of 19 and 14 °C respectively over

neat system. This improvement of thermal stability can be attributed to the probable catalytic effect of CNFs that enhances the cross-linking reaction between polymers and curing agent.

#### 4.5 TGA and DTG of Phenolic Resins at Various Scanning Rates

The results of TG and DTG for the various cured resole phenolic-type resin systems for the rate of weight loss showed that each system degraded/decomposed into three temperature regions as seen in Figures 8-9. The first region ranging between 100-300 °C which can be attributed to the removal of the terminal groups, and further condensation reactions of methylol groups or post curing reactions of phenolic resins [21-23]. Weight loss is seen in this range as a result of loss of water and paraformaldehyde due to the reaction of hydroxymethyl groups leading to further cross-linking [21]. The second region is evident at 300-600 °C which is attributed to the main weight loss region for resole resins containing lignin content greater than 40% due to the decomposition of bridged methylene into both phenol and the cresol homolog. In addition, water loss is present formed from condensation reactions of methylene and phenolic-OH [23]. However, the unmodified resin exhibited its second region was due to the main weight loss region for pure resole phenol formaldehyde or modified resole resins containing lignin less than 40%. This results to further degradation of phenols and methylene bridges to carbonaceous structures such as carbon monoxide and methane [21, 22]. The aromatic structures, in both, the unmodified and modified resole resins is stable during the second temperature region and starts to do degrade at temperatures above 600 °C [21]. At temperature above 600 °C, aromatic skeleton begins to degrade exhibiting minimum weight loss. During the first thermal event, unmodified and modified showed similar thermal stabilities. Yet, once the second thermal event began, the PF resin exhibited the overall greatest thermal stability followed by 40 % FL-PF, 50 % FL-PF, 40 % AL-PF, 50 % AL-PF, 60% AL-PF and finally 60 % FL-PF resins. Modified resole lignin phenolic resins, excluding the 50 % AL-PF resin, had a higher mass loss in the first and second thermal events which may be attributed to the breakdown of side chains present in lignin and a decrease in thermal stability showed unstable three-dimensional network [21]. Hence, the introduction of lignin in the resole phenolic resin system decreased the thermal stability. This remains a major challenge for the substitution of phenol using lignin extracted from various biomass resources in to the resin. Yet, there are hopes that the thermal properties can be improved by purifying the extracted lignin before the resin is synthesized. By first purifying the extracted lignin, it is suggested that aliphatic sugars can be removed and aromatic structures can be increased improving the cross-linking during synthesis of resulting resole lignin phenolic resins [22].

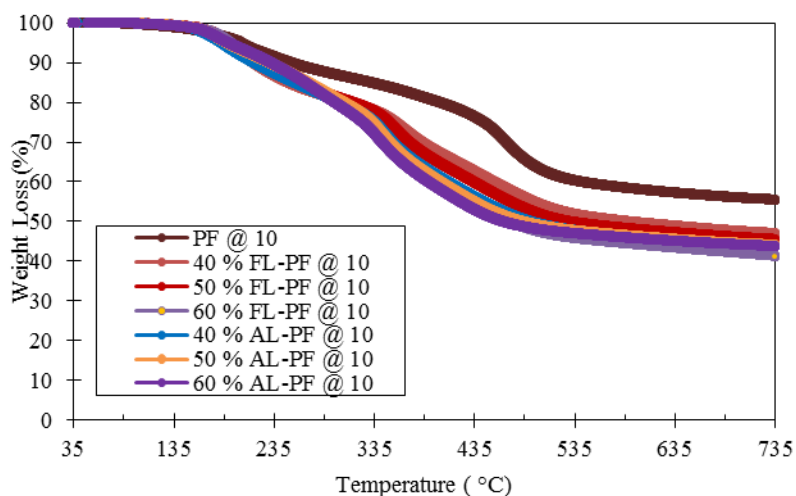


Figure 8: TGA plots of unmodified and modified resole phenolic resins using lignin extracted from flax or alfalfa fiber at 10 °C/min.

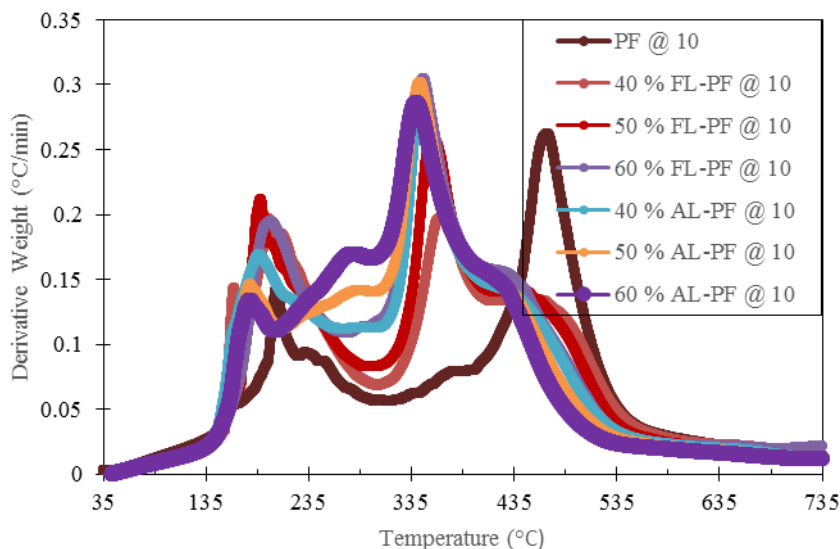


Figure 9: Derivative TGA curves of lignin from flax fiber, alfalfa, pine straw, and wheat straw obtained under nitrogen atmosphere at 10 °C/min.

## 5 CONCLUSIONS AND FUTURE WORK

In this study, silane treated cellulose nanofibers were incorporated into the DGEBA epoxy resin in order to improve both mechanical and thermal properties of nanocomposites. The chemical reaction and structural analysis was evaluated by FTIR analysis. Incorporation of CNFs into matrix increases flexure strength, flexure modulus, storage modulus, glass transition temperature and decomposition temperatures. Maximum improvement was observed for 2 % loading of CNFs as it facilitates maximum crosslinking with epoxy polymers. The highest flexure strength and modulus were improved by 22.5 % and 31.7 % after addition of 2 % CNFs. Furthermore, storage modulus was 22.3 % higher than neat epoxy for 2 % loading of CNFs at room temperature, while  $T_g$  was improved approximately 18 %. Thermal stability of composite was improved probable due to the catalytic effect of CNFs. Cellulose nanofibers (CNFs) enhance both first and second decomposition temperature with a maximum of 19 and 14 °C respectively over neat system.

Unmodified and modified resole phenolic resins using lignin extracted from flax and alfalfa fibers were successfully synthesized and cured. Therefore, partially substituting the phenol precursor with extracted lignin for resole resins is possible. However, the introduction of lignin in the resin formulation decreased the overall thermal stability which led to lower decomposition temperatures, and a reduced amount of char yield at elevated temperatures, but can be improved by purifying extracted lignin before resins synthesis.

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