

Utilization of tall oil to enhance natural fibers for composite applications and production of a bioplastic

Michael George, Paolo G. Mussone, David C. Bressler

Department of Agricultural, Biorefining Conversions and Fermentation Laboratory, Food and Nutritional Science, University of Alberta, Edmonton

Correspondence to: D.C. Bressler (E-mail: dbressle@ualberta.ca)

ABSTRACT: Tall oil is one of the side products from the kraft pulping process of lignocellulosic material. The most abundant acid found in this crude viscous material is abietic acid. Strangely, in the past, the utilization of tall oil has been limited to incineration for cogeneration of power. In this study, tall oil rosin acids (TORAs) were used in two different applications. First, it was used to enhance the hydrophobicity and thermal properties of hemp fibers. Second, TORAs were used to supplement epoxy for the production of a polymeric material. The reaction conditions from a model study were mimicked using a crude tall oil rosin acid mixture to enhance hemp fibers. Treated hemp fibers were characterized with increased surface hydrophobicity and improved thermal properties. Also, IR and X-ray photoelectron spectroscopy confirmed successful chemical modification and grafting of carbon rich moieties onto the surface of the fibers, respectively. Furthermore, TORAs were used to supplement epoxy resin and produced plastics with comparable properties to pure epoxy based plastics. Specifically, 25% (w/w) replacement exhibited little difference in thermal stability and curing when compared to virgin epoxy plastics. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44327.

KEYWORDS: biomaterials; biopolymers and renewable polymers; cellulose and other wood products; crosslinking; fibers

Received 29 April 2016; accepted 4 August 2016

DOI: 10.1002/app.44327

INTRODUCTION

Recently, there has been an increasing demand for natural and renewable products applicable to the industrial space because of the concerns surrounding waste disposal, the depletion of non-renewable resources, and environmental issues. Renewable resources have the potential to replace petrochemical-based platforms through the design of bio-based systems that can compete with the former in terms of cost. The use of biomass or byproducts from the biomass processing for production of composites and plastics has been identified as one of the key areas of interest.^{1–3}

The idea of using natural fibers as a possible reinforcement for polymeric matrices has been around for a long time. Natural fibers offer advantageous properties in that they are biodegradable, low weight; they are obtained from a renewable source, less abrasive on processing equipment, and have comparable specific mechanical properties with glass fiber.³ On the other hand, natural fibers are limited by a high propensity to absorb moisture from the environment, have limited thermal stability, and the polar surfaces of the fibers form a poor interface with non-polar polymeric matrices.³

Researchers have proposed numerous methods for modification of these fibers to improve on the associated limitations.

Chemical,⁴ physical,³ and biological methods⁵ have been presented extensively in the literature for enhancing natural fibers. Also, of late, a lot of research has been done using compatibilizers to enhance natural fibers. In one particular study, Tajvidi and Take-mura (2009)⁶ studied the effect of compatibilizers on the thermal stability and degradation of composites made of polyethylene reinforced with kenaf fibers, wood flour, newsprint, and rice hulls. They reported that the use of the compatibilizers (maleic anhydride) reduced the rate of degradation of the material because of better interfacial adhesion. However, these methods are in some cases not practical. As outlined by George *et al.* (2016),⁷ in a comprehensive review with a section specific to the life cycle assessment of natural fiber composites, the methods best suited for large scale commercialization of these composites should be integrated with other processes. In other words, using industry waste, instead of manufacturing chemicals suited for modification was one of the big positives with respect to a green environmental footprint.

Another aspect of great interest has been the development of protocols to produce plastics using renewable feedstocks in an attempt to reduce the dependence on petrochemical-based materials and to aid in the mitigation of possible harmful environmental effects. Researchers have used different proteins such as egg albumin,⁸ soy protein,⁹ and carbohydrate sources such as

corn¹⁰ to produce plastics with properties mimicking those of the conventional polymers. Despite being sourced from a renewable space, most of these systems are limited by high cost and capital investments, large quantities of biological waste as a result of fermentation, as well as poor mechanical, and water resistance properties.¹⁰ The unique feature of most bio-based polymer systems is the availability of large numbers of functional groups that can be exploited to produce plastics via crosslinking or polymerization. Based on a survey of the current literature and the possible technologies of the futures, our research team postulates that in order for a polymer or plastic industry to be commercially viable, it must utilize renewable sources that are part of byproducts from established industries.

Mekonnen *et al.* (2013)¹¹ studied the possibility of thermosetting proteinaceous plastics from hydrolyzed specified risk material (SRM). SRM used in animal feed is one of the main sources of bovine spongiform encephalopathy (BSE). As a result, rendering plants are faced with this abundant and low value material. These researchers produced plastics from thermosetting epoxy resin with the hydrolyzed SRM and these plastics were characterized with good mechanical, water resistance, and thermal properties. As a result, in this research, we aim to study the use of a waste material from the pulping industry as a possible supplementation agent for epoxy plastics.

The use of tall oil rosin acids in novel chemical applications has been a popular area of research over the past decade.¹ It has been used as an additive during the production of diesel, glue, and nylon. Tall oil is a by-product of the paper and pulping industry. After the kraft pulping of coniferous wood, tall oil is recovered from the black liquor. The chemical composition of tall oil depends on the species and age of pine, as well as the processing involved. Tall oil consists of primarily fatty acids, rosin acids, and unsaponifiable matter (e.g., sterols, waxes, and hydrocarbon) in an approximate ratio of 5:4:1.¹

In the present work, tall oil was separated into different fractions using distillation. The heavier fraction, comprising mainly TORAs was used for the subsequent studies. The use of this heavy fraction of polycyclic compounds, primarily abietic acid was used to enhance hemp fibers. In other words, the primary research aim was to improve the surface and thermal properties of the hemp fibers. The reaction chemistry was optimized using abietic acid as a model compound and then the chemistry/knowledge was transferred to the crude system. The reaction time and concentration of tall oil rosin acids were optimized. Second, TORAs were used to supplement epoxy to produce plastics. This was done with two main aims, to firstly reduce the environmental footprints of products made from epoxy by incorporating a waste material, and secondly, to study the effect of the supplementation on the mechanical and thermal properties of the plastics made. In the end, the thermal and mechanical properties were unaffected up to 25% replacement with the TORAs in epoxy blends.

EXPERIMENTAL

Materials

Hemp fibers (Variety X59) were grown and harvested by the Rod Lanier's farm, east of Lethbridge, Alberta. Fibers were

subsequently decorticated at the Alberta Innovates Technology Futures facility at Vegreville, Alberta. The decortication process involved a 2-pass system through a hammer mill type decorticator and cleaning duvex. The product was then passed twice through a finer opener and step cleaner, then re-baled and shipped to the University of Alberta for characterization and utilization. The samples were kept in airtight bags and stored at 4 °C. The hemp fibers used in this study were of dimensions of 2 cm length and approximately 200 microns, width. Also, the chemical composition of these fibers was reported in a previous publication.⁵

Tall oil was obtained from a kraft-pulping mill in Alberta. The tall oil was distilled to produce the different fractions. Tall oil rosin acid (TORA) was the viscous and black liquor remaining after the process. Thionyl chloride (97%, mol. wt. 118.19 g/mol), pyridine (99.8%, mol. wt. 79.10 g/mol), ethyl alcohol (99.8%, mol. wt. 46.07 g/mol), epoxy 506, and 2, 4, 6-Tris (dimethylaminomethyl) phenol (mol. wt. 265.39) were obtained from Sigma-Aldrich (Minnesota, U.S.A.).

Enhancement of Hemp Fibers Using Tall Oil Rosin Acids

Chemical Treatment (Model System). Approximately 1.0 g of hemp fiber was weighed into a 250 mL three-neck round bottom flask. The three-neck flask was fitted with condenser, a separatory funnel, and a gas trap. Approximately 0.15 mol. of abietic acid was dissolved in 100 mL ethanol, and added to the flask. 0.125 mol (~ 9.0 mL) of thionyl chloride was added into the funnel. 1.5 mL (10 mmol. per g dried hemp) pyridine was added to the contents of the flask. The reaction vessel was heated steadily to 80–90 °C for the allotted time periods. After the reaction, the fibers were filtered and washed with ethanol. Treated fibers were originally Soxhlet extracted, but this was discontinued after it was determined that there was no difference in chemistry between the Soxhlet and non-Soxhlet fibers. Fibers were dried at 80 °C for 4 h and stored until analysis. Similarly, to investigate the effect of acylating agent, the reaction was repeated without using thionyl chloride. The treated fibers were washed, and stored as described above.

Chemical Treatment: Tall Oil Rosin Acid System. The conditions selected for this study were based on importance and relevance to industry. Hence, reaction time and the concentration of tall oil rosin acids were studied. Reaction times of 30, 45, 60, 75, and 90 min were studied. Concentrations of 0.010, 0.015, and 0.020 g/L of the rosin acids were used. The procedure outlined in “Chemical treatment (model system)” section was repeated for the TORA system with few exceptions. Instead of abietic acid, the tall oil rosin acid system was used. A control, consisting of everything except the TORAs was also monitored.

Determination of Optimum Reaction Parameters. Percentage weight gain. The percentage weight gain for each system was monitored. After each reaction, the fibers were carefully filtered and washed. The fibers were dried until constant weight and the change in weight was reported as the percentage weight gained. Equation (1) was used for all calculations.

$$\% \text{ Weight gain} = \frac{[(\text{Treated wt.} - \text{initial wt.}) / (\text{initial wt.})] * 100\%}{(1)}$$

Degree of substitution. The volumetric procedure outlined by Freire *et al.* (2005) was used for all analyses. A few modifications were made for this study. 0.1 g of hemp fiber was weighed into a test tube (100 mL). 4 mL of ethanol (70%) was added to each tube. The samples were thoroughly mixed using a vortex. 4 mL of sodium hydroxide (0.5 M) was then added and the tubes were sealed, and kept at 30 °C for 24 h. The contents of each tube were titrated using 0.5 M hydrochloric acid. Phenolphthalein was used as an indicator in all cases. An excess of 0.4 mL acid was added to each tube after the end point was observed. The samples were left to sit for 12 h. Finally, the acid remaining was back titrated using 0.5 M sodium hydroxide (NaOH). The equation provided by Freire *et al.* (2005)¹² was used for all calculations.

It should be noted; the method outlined here was developed for cellulosic material. But, this case, the property was used as a measure of surface change. Hence, the results obtained are a qualitative guide to the degree of substitution and was used only for comparison purposes among these samples and should not be compared to other studies.²

Characterization of Hemp Fibers. Force tensiometry/contact angle measurement. A 700 Sigma One Attension tensiometer (Biolin Scientific-Stockholm, Sweden) was used to measure the contact angles. All samples were pre-conditioned at 80 °C for 3 h prior to analysis. The Washburn capillary rise method was used to characterize the fiber bundles.⁵ For each experiment, triplicate analysis was done for each sample with three cycles of immersion (three measurements taken on a single fiber). An immersion speed of 2 mm/min was used for both advancing and receding measurements. Given the nature of the technique, both advancing (penetration of the fiber into liquid) and receding (recession of the fiber from liquid) contact angles were calculated for each cycle. Equation (2) was used to estimate the contact angle for each sample.⁵

$$\text{Wetting force} = \text{Liquid vapor surface tension} * \text{perimeter of fibres} * \cos \theta \quad (2)$$

Where θ is the unknown contact angle. The contact angle for each sample was calculated using the measured wetting force. No significant difference was found between advancing and receding angles for most samples. Hence, results were reported as mean \pm standard deviation.

Fourier transform infrared spectroscopy. A Thermo Scientific Nicolet attenuated total reflectance Fourier Transform infrared spectrometer was used for studying the chemical changes associated with surface modification. A zinc selenide crystal was used for all sample analysis. Liquid nitrogen cooling was used to maintain constant temperature within the sample chamber. A resolution of 4 cm^{-1} and 32 scans were used for all samples.

Morphological characterization. Micrographs of the pulp sample surfaces of untreated and chemically treated fibers were taken using a Hitachi S-2700 Scanning Electron Microscope (SEM) equipped with a Princeton Gamma Tech (PGT) IMIX digital

Table I. Relative Percentage of Different Components Used to Produce the Plastics

System	% Epoxy (w/w)	% TORAs (w/w)	% Hardener (w/w)
Control	95	0	5
5%	90	5	5
15%	80	15	5
25%	70	25	5
35%	60	35	5

imaging system and a Prism Intrinsic germanium (IG) detector. A gold sputter coater was used to induce conductivity and a resolution of 4 nm was used for all samples. 0.01 ± 0.001 g of hemp was mounted on conductive adhesive tape, sputtered coated with gold palladium, and observed using a voltage of 15–20 kV.⁵

X-ray photoelectron spectroscopy (XPS). A Kratos Ultra 165 X-ray Photoelectron Spectrometer with energy spectra ranging from 0 to 1000 eV was used for all measurements. The elemental composition and the oxygen to carbon ratio (O/C) of the surface of the different fibers following treatment were the main foci. Both high and low resolution scans were recorded and used for deciphering any changes. Approximately 0.05 ± 0.005 g of pulp sample was pressed into a disc with diameter of about 0.25 mm for analysis. The take-off angle was maintained at 45° in relation to the sample surface. For each sample, three sample locations were scanned at area of 200–400 μm^2 . Raw data was normalized and analyzed using CasaXPS program (Casa Software Ltd., UK). The mole fractions were calculated using normalized peaks based on acquisition parameters after a linear background subtraction and consideration of experimental sensitivity factors. C1s spectra were analyzed with a Gaussian product function, by maintaining the full width at half maximum (FWHM) of all components to within the range of 1.200–1.600.^{5,13}

Thermogravimetric analysis (TGA). The procedure outlined in an earlier study was used for thermal analysis of the treated samples.⁵ Experiments were conducted using a Thermal Analysis Instruments TGA Q50 apparatus under a flow of nitrogen to study the effects of heating on stability of the different treated pulp samples. Platinum pans were used given the high temperatures and the ease of cleaning. The temperature range selected was from room temperature to 600 °C at a rate of 15 °C per min. For each sample, triplicate runs were done. All results were reproduced to 5% error or better.

Supplementation of Epoxy Resin with TORAs: Production of Plastics

TORAs and epoxy resin were heated in a convection oven at 60 °C for 2 h to reduce their viscosity. Mixtures of 5, 15, 25, or 35% (w/w) TORAs, along with 5% (w/w) hardener (2, 4, 6-Tris (dimethylaminomethyl) phenol) were brought up to 100% with epoxy, mixed vigorously for 5 min, and then placed in the molds. The weight ratios were selected based on the possible number of functional groups capable of crosslinking the TORAs fractions. The different formulations are presented in Table I.

High concentrations (25 and 35%) of TORAs when mixed with epoxy, impeded mixing, and tended to cure faster (3 h) when compared to the lower concentrations which took at least 15 h to cure. Curing took place at 165 °C for 5 h followed by post curing at 180 °C for an hour. Plastics were cooled and placed in a desiccator overnight. It should be noted, in the preliminary reactions, the absence of a hardener resulted in uncured samples.

Characterization of Plastics. Infrared spectroscopy. Samples were finely comminuted, mixed with KBr, and compressed into a pellet for analysis. A Shimadzu 8400 S, taking 100 scans for each sample with a resolution of 4 cm⁻¹ was used for all analyses. The spectra were obtained by smoothing with a factor of 10, to improve the sharpness of the peaks. All spectra were reproducible for each sample.

Differential scanning calorimetry. A thermal analyzer (Q₁₀₀ TA Instruments-Minnesota, USA) was used to study the thermal transition temperatures of the plastics under a nitrogen atmosphere. For each test, approximately 5 mg of sample were weighed into an aluminum pan and heated at 10 °C per min from 0 to 175 °C. Triplicate analysis was done for each system.

Thermal gravimetric analysis. The thermal stability of the plastics was determined using a Q₅₀₀ series, TA instruments (Minnesota, USA). Plastics samples (5–10 mg) were placed in platinum pans and heated at 10 °C per min from 20 to 600 °C under a nitrogen atmosphere.

Mechanical properties. Test specimens with dimensions of 4 × 0.5 inches were obtained using silicon molds. Samples thickness was within the range required for the test method used (< 1 mm, between 600 and 800 microns). Specimens were conditioned in a room maintained at a relative humidity of 45 ± 5% and a temperature of 22 ± 2 °C overnight before testing. Mechanical properties, namely tensile strength, modulus, and elongation at break, were determined using an Instron (Norwood, MA) equipped with a 5 kN load cell at a crosshead speed of 10 mm/min. A G229 Series Pneumatic Grip supplied by Instron was used for all tests. ASTM D639-14 was followed for all the mechanical properties measured.

Water resistance properties. Water absorption test for the different plastics were carried out on rectangular specimens, with diameter of 15 mm and length of 20 mm. All specimens were conditioned at 80 °C for 5 h and cooled in a desiccator for an hour prior to measurements. The percentage water absorption, M_t , at any time, t , was calculated by the equation:

$$\frac{(W_t - W_o)}{W_o} * 100 = \text{water absorption, } M_t (\%)$$

Where W_t is the weight of the sample at time t , and W_o is the initial weight of the sample ($t=0$). The percentage water absorption was taken as the average of at least five measurements per sample.

Statistical Analysis

Statistical analyses were done as outlined by George *et al.* (2014).⁵ Treatments were done in triplicates and results reported as mean ± standard deviation. The statistical analyses of the

data were conducted using the statistical software package SAS Version 9.4. The Kruskal Wallis Test was applied to the data populations involved, with a 95% confidence level ($p < 0.05$), in cases where the data was not parametrically distributed. In all other instances, a t test was used.

RESULTS AND DISCUSSION

TORA Enhanced Hemp Fibers

Reaction Mechanism. The reaction mechanism for the proposed chemistry is given in Figures 1 and 2. In Figure 1, the formation of the acylated abietic acid is highlighted. The use of thionyl chloride as an acylating agent was selected based on a previous publication.¹² Pyridine was used as a proton acceptor and to chelate any free chloride ions in reaction mixture.¹⁴

Model Study

A number of concentrations of abietic acid (0.50–0.025 mol.) were investigated. Higher concentrations of abietic acid treated for periods longer than 60 min resulted in brittle hemp fibers. As a result, data from treatments using a concentration of 0.15 mol abietic acid for 90 min will be presented.

Confirmation of Reaction Chemistry. Infrared spectroscopy was used to study the changes in chemical functionality as a result of the reaction. Two controls and a treated sample are presented in Figure 3. The appearance of a peak at approximately 1750 cm⁻¹ corresponds to the ester C=O stretch. This confirmed the successful reaction of the acid and alcohol to produce the ester bond. Also, based on the NIST database used to identify the peaks, the small peak at approximately 1680–1620 cm⁻¹ corresponded to the alkenyl C=C stretch. The presence of C=C double bonds within the structure of abietic acid plausibly resulted in the appearance of the mentioned peak. In summary, infrared spectroscopy highlighted the presence of two important peaks arising from successful reaction.

Contact Angle. The previous section outlined the changes in chemical functionality as a result of the successful reaction. The next obvious question was whether there was any change in the surface properties due to the reaction. Changes in contact angle can be a good tool to determine the influence of chemical reactions on the hydrophobicity of hemp fibers. Table II illustrates the influence of the chemical reaction on the contact angle of the treated samples.

Hemp fibers exposed to all the required reagents were characterized with a significant increase in contact angle. It is plausible that the grafting of the polycyclic abietic acid onto the surfaces of the fibers resulted in the reduced surface polarity. Given that no previous study using tall oil rosin acids to modify natural fibers has been previously published, it is difficult to foresee how changes in the contact angle can lead to improvements in compatibility with matrices. But, as previously reported by George *et al.* (2015),¹⁵ where they treated hemp fibers with sulfonic acids, there was as a corresponding increase in contact angle. This change was brought on by the aromatic nature of the sulfonic acids used. Similarly, tall oil rosin acids are characterized with these rings, which significantly increased the contact angle of the fibers. This should render the fibers more

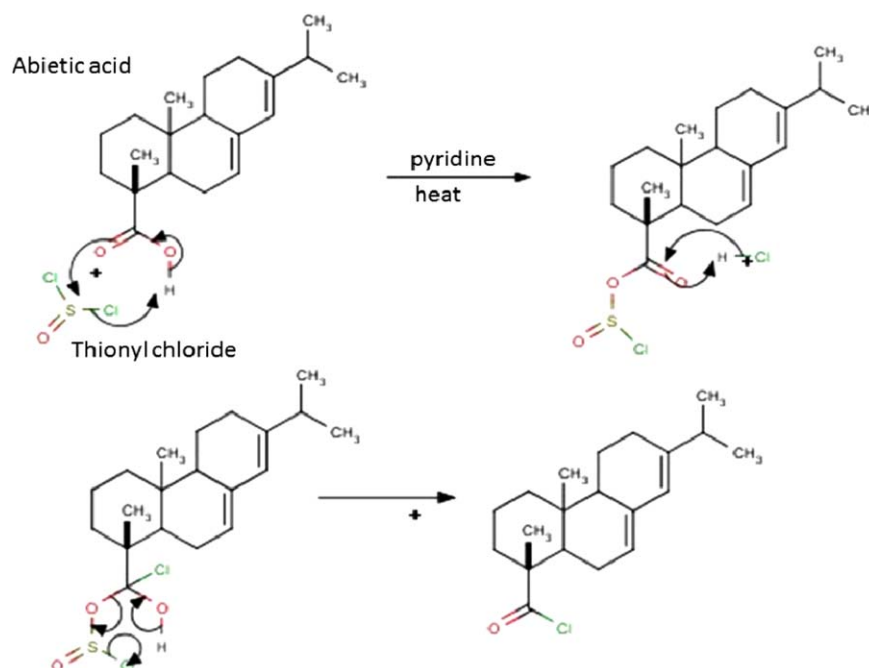


Figure 1. Plausible reaction mechanism for the production of acid chloride from abietic acid. [Color figure can be viewed at wileyonlinelibrary.com.]

compatible with non-polar based resins for composite applications.

X-ray Photoelectron Spectroscopy (XPS). XPS can be used to study the chemical changes on the surfaces of materials up to the 10 nm. In this respect, the effect of treatment on the surface chemical carbon signatures and O/C ratio is presented in Table III. Hemp fibers treated with abietic acid were characterized with a significant increase in the C—C and a decrease in any C—C—O bonding. This is expected because the fiber surface was plausibly coated with the polycyclic abietic acid. Reduction

in O/C corresponds with data generated in the previous section showing a reduction in the surface polarity of the fibers.

Abietic acid was used as a model compound to investigate whether the rosin acids present in tall oil may be an applicable agent for modifying natural fibers. Based on the preliminary results presented, an understanding of the chemistry and behavior of materials were reported, and the next phase focused on studying the tall oil rosin acid system.

Utilization of a Crude Rosin Acid System. The influence of reaction time and the concentration of tall oil rosin acid were

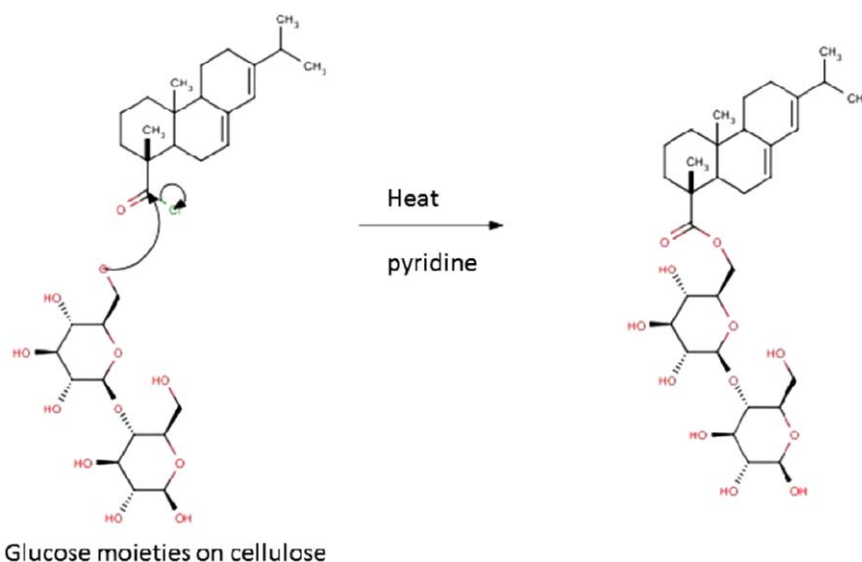


Figure 2. Reaction of the acylated abietic acid moieties and the cellulosic network. [Color figure can be viewed at wileyonlinelibrary.com.]

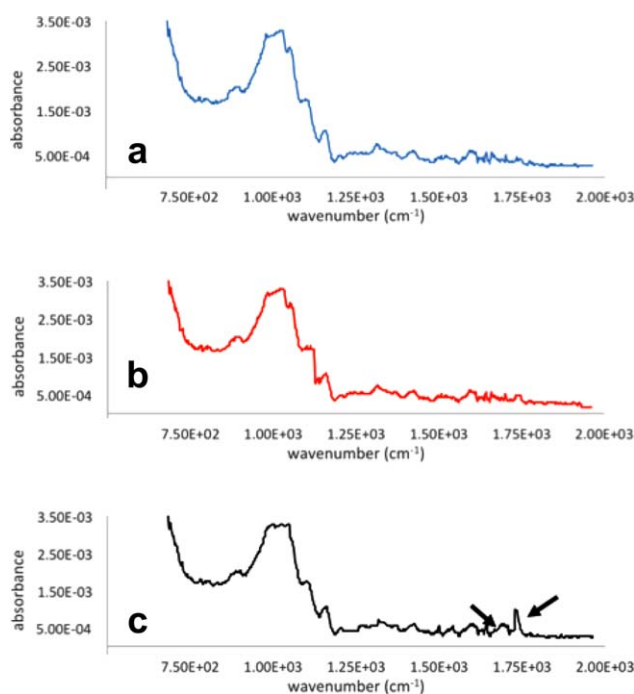


Figure 3. Infrared spectra for (a) untreated hemp fibers, (b) treated hemp fibers in absence of SOCl_2 (un-acylated abietic acid), and (c) hemp fibers treated with acylated abietic acid. [Color figure can be viewed at wileyonlinelibrary.com.]

investigated. Concentrations of 0.01–0.02 g/L and times of 30–90 min were investigated. The reaction chemistry studied for the abietic acid system was used as detailed in the “Experimental” section.

Influence of reaction conditions. The influence of reaction time and concentration of TORAs are shown in Figure 4. It is apparent that the degree of substitution and percentage weight gained were both at a maximum after 75 min. Reacting the fibers with the chemical reagents plausibly resulted in sample degradation of the natural fiber components after 75 min of treatment. In fact, Freire *et al.* (2006)¹⁶ mentioned the effect of fiber degradation after treating cellulosic fibers with fatty acids beyond the optimum time. They cited that the decrease could be explained by possible competition between the esterification reaction and the partial hydrolysis of the ester groups formed as a result of the presence of moisture in the reaction. In the case of this study, possible degradation of the fiber could result because of the accumulation of unreacted species and continued exposure at the reaction temperature.

Hemp fibers treated with 0.02 g/L TORAs were characterized with the maximum degree of substitution and weight gain. In terms of weight percentage gained, after 75 min, there was no significant difference between the 0.015 and 0.020 g/L treated fibers. When compared to a study done by Suryana and Khalil (2011),¹⁷ where succinic and propionic anhydride were used to modify kenaf fibers, it was observed that the percentage weight gain for this study was significantly lower. One possible reason for this may be the steric hindrance due to the bulky nature of the modifying agent used in this study. Freire *et al.* (2006)¹⁶

mentioned that the accessibility of the modifying agent coupled with the surface composition of the fibers significantly influences the extent of modification. Despite this, there was a reduction of contact angle or an increase in wettability with water (increase in polarity) when kenaf was treated with both reagents, while the present study illustrates an increase in contact angle. This represents a decrease in polarity or hydrophilicity, plausible making the treated fibers better suited for composite applications.

Force Tensiometry/Contact Angle Measurements. In several cases, hemp fibers treated with TORAs were characterized with a significant ($p < 0.05$) increase in contact angle. In other words, the surface polarities of the hemp fibers were more hydrophobic. Specifically, a reaction time of 75 min resulted in fibers with significantly higher contact angle for all three concentrations of TORAs examined. As mentioned in the previous section, treatment after 75 min likely resulted in degradation; this was supported by the data presented in Table IV, as there were no improvements in contact angle for samples treated beyond 75 min. Interestingly, hemp fibers treated with 0.020 g/L TORAs were characterized with the most significant change in contact angle. One possible reason for this may be the increase in chemical reagents that can react with the surface of the fibers. Also, a higher number of acylated TORAs may have contributed to the number of cases that were significantly improved. Unfortunately, increasing the concentration of TORAs in the reacting flask is not an option because there is aggregation of reagents, instead of surface modification of the fibers.

Fourier Transform Infra-Red Spectroscopy. Infrared spectroscopy was used to study the changes in chemical functionality as a result of the reaction using TORAs. The infrared spectra for a control and each concentration are presented in Figure 5. As in the model study, the appearance of a peak at approximately 1750 cm^{-1} corresponds to the ester $\text{C}=\text{O}$ stretch. This confirmed the successful reaction of the acid and alcohol to produce the ester bond. The reduction of the doublet peaks intensity at approximately 2800 cm^{-1} was as a result of reduction in acid functionality. Finally, the appearance of a peak for 0.015 g/L treated fibers at $2000\text{--}1600 \text{ cm}^{-1}$ in the finger print region corresponds to the phenyl ring substitution. One plausible reason why this peak appeared in this spectrum alone has to do with the resolution of the FTIR equipment, the homogeneity of the sample preparation, and the positioning of the fibers on the crystal for analysis. The possible reaction of abietic acid

Table II. Change in Contact Angle of the Treated Samples

Experiment	Contact angle (°)
Control 1: Raw hemp fibers	88.7 ± 0.35^a
Control 2: Hemp fibers + AB ^a	88.5 ± 0.10^a
Treated: Hemp fibers + AB + SOCl_2	89.6 ± 0.28^b

^a Abietic acid.

Data in this table are presented as means \pm standard deviation with a sample size of at least 3 for each treatment. ^{a-b} Means with the same superscript letters are not significantly different at $p < 0.05$ level.

Table III. Abundance of the Different C1s Signatures and O/C Ratio for the Different System

Experiment	Chemical abundance (%)			O/C
	C—C	C—C—O	O—C—O	
Control 1: Raw hemp fibers	52.5 ± 3.83 ^a	38.8 ± 3.87 ^a	8.77 ± 0.47 ^a	0.44 ± 0.02 ^a
Control 2: Hemp fibers + AB ^a	38.4 ± 3.55 ^b	46.5 ± 2.21 ^a	14.9 ± 1.39 ^b	0.54 ± 0.00 ^a
Treated: Hemp fibers + AB + SOCl ₂	75.1 ± 1.26 ^c	18.5 ± 1.35 ^b	6.42 ± 0.28 ^c	0.34 ± 0.01 ^b

^a Abietic acid.

^{a-b} Means with the same superscript letters are not significantly different at $p < 0.05$ level. Comparisons were made among treatments (1, 2 and treated) for a given category (e.g., C—C) and not between categories.

species with the surface of fibers may have resulted in rearrangement of the stabilization states. These changes in chemical functionality support the successful grafting of the TORAs onto the surface of the hemp fibers.

Morphological Characterization. Scanning electron micrographs of untreated and TORA treated hemp fibers are shown in Figure 6. The micrographs show that the untreated fibers are covered with a layer whose composition as presented in an earlier communication (George *et al.* 2014)⁵ is probably mainly waxy substances and pectic material. It can be seen that the layer is uniformly covering the surface of the fibers and is mostly smooth when compared to the treated samples. Reaction of the fibers with the TORAs resulted in fiber surfaces that are rough,

heterogeneous, and de-fibrillated. As detailed in a previous publication from our group,¹⁸ chemical treatment results in increased surface roughness as measured and confirmed using atomic force microscopy. These are properties that can plausibly result in better mechanical interlock of the natural fibers with the polymeric matrix. Removal of the upper surface possibly occurred during the acylation reaction using thionyl chloride and exposed the cellulosic and pectic hydroxyl groups for reaction. It can also be observed that the reaction resulted in partial surface reaction because some areas are left smooth and untouched. In summary, chemical reaction resulted in partial removal of surface components and increase in surface roughness.

X-ray Photoelectron Spectroscopy. The TORA treated fiber samples exhibited a very simple spectrum containing the two characteristic peaks of carbon (binding energy = 285 eV) and oxygen (binding energy = 533 eV). The O/C ratio and abundance of the different C1s signatures are given in Table V. It can be observed that the O/C ratio for untreated fibers varies between 0.549 and 0.612, values close to the 0.83 of cellulose and hemicellulose. Hemp fibers treated with 0.015 and 0.02 g/L TORAs were characterized with a significant decrease in O/C ratio at all time points examined. This observation correlates to a successful grafting of the polycyclic residues onto the surfaces of the hemp fibers. Also, partial removal of pectic material and exposure of lignin, may have contributed to the changes in O/

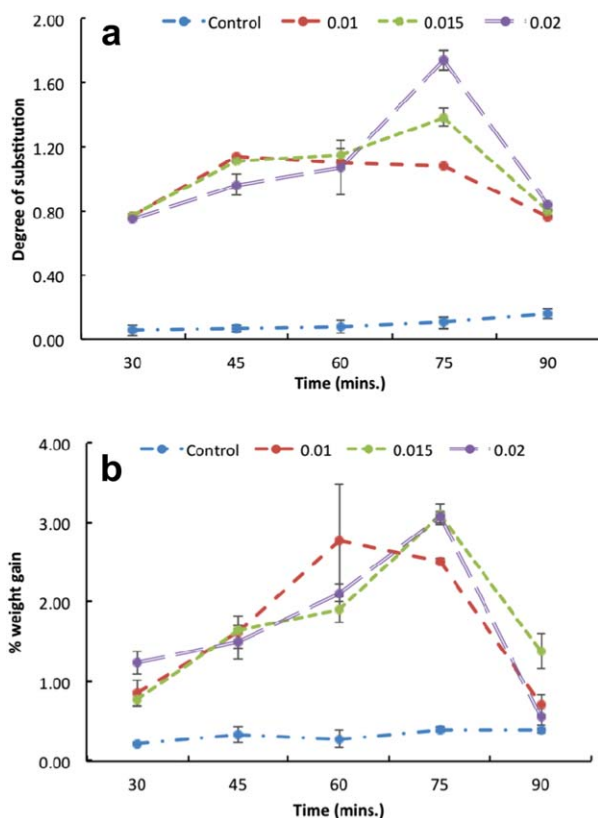


Figure 4. Changes in (A) degree of substitution, and (B) percentage weight gained as a result of the variation in experimental conditions (concentration and reaction time) using TORAs. [Color figure can be viewed at wileyonlinelibrary.com.]

Table IV. Effect of Chemical Treatment on the Contact Angle for Hemp Fibers

Time (minutes)	Influence of concentration of TORAs on contact angle (°)		
	0.010 g/L	0.015 g/L	0.020 g/L
Control	88.6 ± 0.18 ^b	88.5 ± 0.04 ^b	88.5 ± 0.02 ^b
30	89.3 ± 0.08 ^b	88.8 ± 0.42 ^b	88.9 ± 0.74 ^b
45	88.9 ± 0.16 ^b	88.8 ± 0.12 ^b	89.2 ± 0.01 ^a
60	89.4 ± 0.08 ^a	89.0 ± 0.04 ^b	89.5 ± 0.13 ^a
75	89.5 ± 0.14 ^a	89.4 ± 0.17 ^a	89.2 ± 0.05 ^a
90	89.1 ± 0.39 ^{ab}	88.5 ± 0.92 ^b	88.7 ± 0.03 ^b

^{a-b} Means with the same superscript letters are not significantly different at $p < 0.05$ level. For each concentration, the control was compared with each time level. No comparison was made among concentrations.

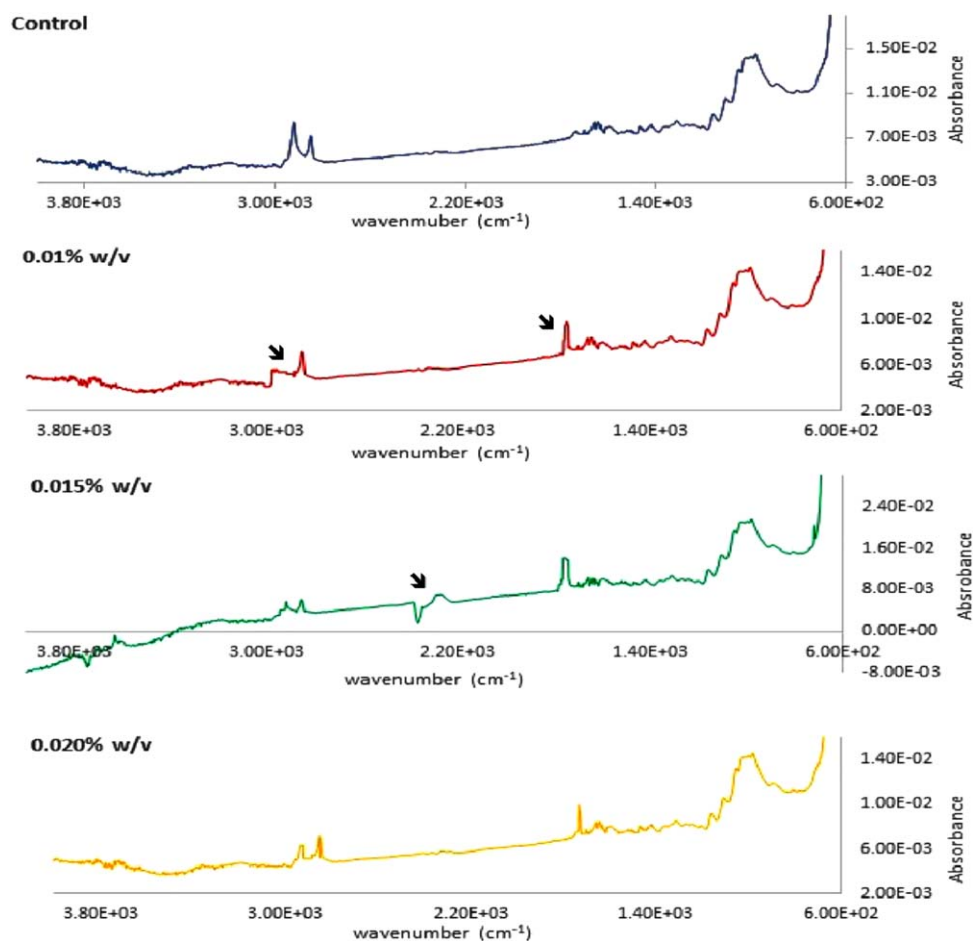


Figure 5. Infrared spectra for each system compared to control. [Color figure can be viewed at wileyonlinelibrary.com.]

C. The O/C ratio resulting from primarily lignin was quoted as 0.35 by Tserki *et al.* (2005).¹³ Both of these scenarios are advantageous because the exposure of non-polar lignin and/or grafting of TORAs onto the fiber surface will improve its mixing with non-polar matrices such as polypropylene.

Additionally, there was significant ($p < 0.05$) increase in the carbon fraction (C—C) for treated fibers at all concentration levels, especially for 75 and 90 min of treatment. The changes in carbon-oxygen signatures did not follow a defined pattern but when hemp fibers were treated with 0.02 g/L TORAs, there were significant changes in O—C—O, characteristic of the main bonds formed during the reaction. Also, increases in the C—O—O signatures compliment this result for the 0.02 g/L system.

Thermogravimetric Analysis. Thermal gravimetric analysis was used to study the thermal changes resulting from chemical modification of the hemp fibers. Given the number of different treatments, for each concentration level, samples treated at the time with the highest (HCA) and lowest contact angle (LCA) were presented. This was done to illustrate the overall trend and to determine whether the chemical change results in thermal improvement of the fibers.

In Table VI, the percentage degradation and initial degradation temperature are presented. The percentage degradation was calculated by estimating the amount of fiber (%) degraded between 200 and 300 °C. This is of importance because when natural fibers are processed into composites, they are heated with the matrix at temperatures around 200 °C. Hence, improving the degradation around this range would make natural fibers more attractive for composite applications. In Table VI, it is shown that treatment of hemp fibers using any of the concentration level resulted in improved percentage degradation.

On the other hand, treated samples generally exhibited improvement in the initial temperature of degradation, that is, the temperature where 10% of the samples degraded. One possible reason for this may have been increased rigidity brought on by successful chemical grafting. Also, removal of thermal labile pectic and hemicellulose material as a result of chemical treatment, may have resulted in a more thermally stable material. Hemp fibers treated with 0.015 g/L TORAs after 90 min were characterized with the lowest contact angle for that batch. As a result, the onset or initial degradation was very inferior when compared to the other systems. Plausible reasons for this may be the partial degradation of the cellulosic network as a result of long treatment time and or competition between the

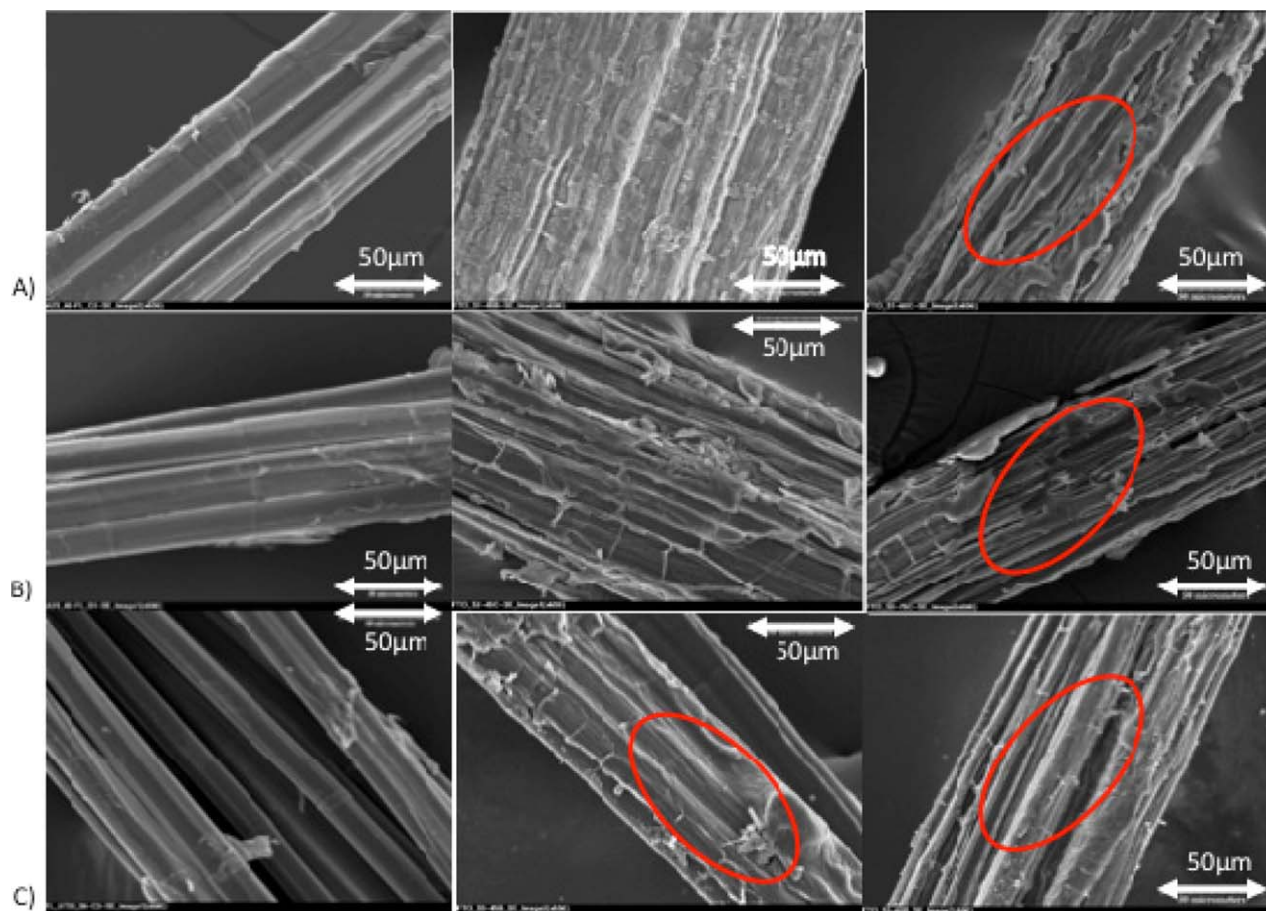


Figure 6. SEM micrographs of (A) 0.010, (B) 0.015 and (C) 0.020 g/L TORA treated hemp fibers (First column = the control micrographs). Red circles indicate areas partially covered/modified with the reagent used. [Color figure can be viewed at wileyonlinelibrary.com.]

esterification and degradation reaction. Importantly, all systems treated with TORAs showed improved maximum degradation temperature. One plausible reason for this may have been the selectively removal of components and the increased rigidity of the fibers as a result of chemical reaction.

Supplementation of Epoxy Using TORAs

Reaction Chemistry and Possible Crosslinking. TORAs are comprised of primarily abietic acid. A possible reaction scheme for reacting epoxy with abietic acid is shown in Figure 7.

It is possible that the carboxylic or hydroxyl groups in the rosin acids can react with epoxy as shown in Figure 7. Epoxy resins are one of the most widely used base polymer for coatings, laminates, and matrices for composite materials. The epoxide functional group can react with a variety groups, including carboxylic and alcohol groups. In this study, the hydroxyl and carboxyl groups of TORAs were used to crosslink the epoxy resin. The final product went through a number of transitions, from liquid to viscous rubbery and finally solid state. Because of the chemical reaction that takes place upon addition of the hardener [2, 4, 6-Tris (dimethylaminomethyl) phenol], and the TORAs, the solid state is irreversible.

Infrared Spectroscopy. IR spectra for epoxy, the hardener, TORAs and the plastics are given in Figure 8. It can be observed that the epoxide peak at around 915 cm^{-1} reduces in intensity when compared to the plastic spectrum. Also, the peak at approximately 1400 cm^{-1} in the plastics is as a result of aromatic stretches from the TORA bonds, confirming the reaction of the epoxide groups with the rosin acids. The —OH groups present at $3215\text{—}3400\text{ cm}^{-1}$ in the TORAs significantly diminished in the plastic samples. This also confirms the reaction of the acid with the epoxy groups. Finally, the peak at approximately 2820 cm^{-1} corresponds to the C=H stretch of aldehydes. It is not clear as to how carbonyl compounds may be introduced or produced, but one plausible reason may be from the TORAs, since traces of lignin fragments (rich in aldehyde groups) can be found in the complex mix. The peaks reported here were in agreement with the those published by Mekennon *et al.* (2013)¹¹ when they investigated the thermosetting properties of specified risk material-based plastics.

Thermal Properties. The thermal properties of the plastics were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TGA was used to determine the thermal stability of the plastics at different temperatures. The onset decomposition temperature is reported in Table VII.

Table V. Effect of Chemical Treatment on the Abundance of C1s Signatures and O/C Ratio of Hemp Fibers

[TORA]	Time (min)	Relative abundance of carbon signatures (%)				O/C
		CH ₂ -CH ₂	C-O	C-C-O	O-C-O	
0.010 M	CNT	43.7 ± 1.02	39.8 ± 3.61	12.0 ± 2.19	4.52 ± 0.92	0.59 ± 0.05 ^a
	30	50.1 ± 1.82	36.6 ± 2.11	7.24 ± 0.33	6.11 ± 0.04	0.52 ± 0.06 ^b
	45	52.3 ± 0.98	34.1 ± 0.45	10.0 ± 2.24	3.56 ± 0.81	0.51 ± 0.02 ^b
	60	42.9 ± 3.93	40.9 ± 2.50	12.2 ± 1.60	4.07 ± 0.16	0.54 ± 0.02 ^b
	75	37.4 ± 8.01	43.7 ± 2.50	13.5 ± 1.02	5.39 ± 2.21	0.62 ± 0.12 ^a
	90	58.6 ± 3.59	30.6 ± 3.51	5.93 ± 1.05	4.92 ± 0.98	0.39 ± 0.03 ^c
0.015 M	CNT	41.7 ± 4.09	45.8 ± 6.61	11.2 ± 0.49	1.32 ± 0.19	0.61 ± 0.04 ^a
	30	43.2 ± 13.0	26.8 ± 1.31	25.7 ± 1.23	4.40 ± 0.62	0.41 ± 0.06 ^b
	45	26.5 ± 3.82	48.0 ± 10.1	19.2 ± 3.54	6.13 ± 1.42	0.47 ± 0.09 ^c
	60	39.7 ± 4.18	42.9 ± 1.15	13.1 ± 3.16	4.38 ± 0.16	0.47 ± 0.00 ^c
	75	60.5 ± 6.39	22.1 ± 1.15	10.9 ± 0.71	6.54 ± 1.12	0.40 ± 0.03 ^b
	90	48.3 ± 4.20	32.0 ± 8.20	14.2 ± 3.51	4.05 ± 1.46	0.38 ± 0.02 ^b
0.020 M	CNT	45.7 ± 3.69	39.4 ± 4.08	12.3 ± 0.18	2.62 ± 0.24	0.55 ± 0.10 ^a
	30	56.5 ± 0.64	10.7 ± 3.01	23.4 ± 3.47	8.74 ± 5.85	0.31 ± 0.02 ^c
	45	54.0 ± 5.45	11.7 ± 3.33	23.0 ± 2.92	14.3 ± 5.51	0.37 ± 0.07 ^b
	60	50.1 ± 3.03	22.8 ± 6.54	16.9 ± 0.64	6.52 ± 4.12	0.34 ± 0.07 ^b
	75	57.0 ± 0.21	13.7 ± 4.17	17.7 ± 0.82	8.62 ± 2.73	0.30 ± 0.05 ^c
	90	64.2 ± 2.56	19.8 ± 2.04	11.4 ± 0.71	4.68 ± 0.17	0.37 ± 0.05 ^b

^{a-b}Means with the same superscript letters are not significantly different at $p < 0.05$ level. For each concentration, the control was compared with each time level. No comparison was made among concentrations.

When compared to the virgin epoxy blend, replacement up to 15% (w/w) with TORAs can be used without altering the thermal stability of the produced plastics. On the other hand, as the concentration of TORAs increases in the plastics, there was a corresponding decrease in the temperature needed for degradation of 10% of the samples. It was observed that the thermal stability of the plastic gradually decreased with increasing TORAs concentration in the formulation. Plausible reasons for this may be the variation in the crosslinking/reaction of the different formulations, the superior thermal behavior of virgin epoxy, and the heterogeneous nature of the TORAs.

Table VI. Thermal Properties for Hemp Fibers Treated with TORAs

System	Maximum degradation temperature (°C)	Percentage degradation (%)	Initial degradation (°C)
CNT	324 ± 1.44 ^b	9.21 ± 0.31 ^a	230 ± 3.19 ^b
0.010 (HCA)	346 ± 3.82 ^a	6.40 ± 0.22 ^b	237 ± 4.34 ^b
0.010 (LCA)	345 ± 0.48 ^a	6.90 ± 0.09 ^b	252 ± 3.82 ^a
0.015 (HCA)	339 ± 5.32 ^a	4.60 ± 0.05 ^b	261 ± 7.55 ^a
0.015 (LCA)	335 ± 0.48 ^a	4.60 ± 0.21 ^b	200 ± 1.43 ^a
0.020 (HCA)	344 ± 0.48 ^a	5.40 ± 0.37 ^b	245 ± 1.43 ^a
0.020 (LCA)	342 ± 1.20 ^a	5.30 ± 0.07 ^b	238 ± 1.63 ^b

For each concentration, the treatment times that produced fibers with the highest (HCA) and lowest contact angle (LCA) were investigated.

^{a-b}Means with the same superscript letters are not significantly different at $p < 0.05$ level. For each concentration, the control was compared with each time level. No comparison was made among concentrations.

Differential scanning calorimetry (DSC) was used to determine the peak of curing and glass transition temperature of the plastic samples. Curing was observed for all TORAs/epoxy formulations between 125 and 145 °C. The different curing temperatures for epoxy with varying ratios of TORAs are shown in Figure 9. Curing involves the exothermic reaction when the epoxide group of the epoxy resin and the reactive functional group in the TORAs react. As observed in Table VII, there is a gradual decrease in the peak of curing, plausibly as a result of

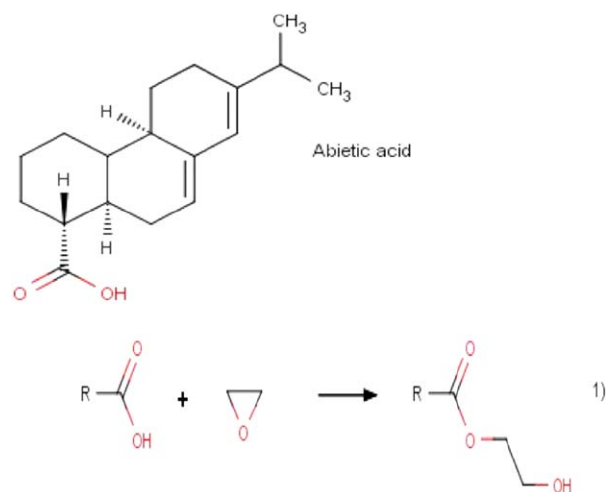


Figure 7. Plausible reaction between epoxy and the hydroxyl group of abietic acids found in tall oil rosin acids. [Color figure can be viewed at wileyonlinelibrary.com.]

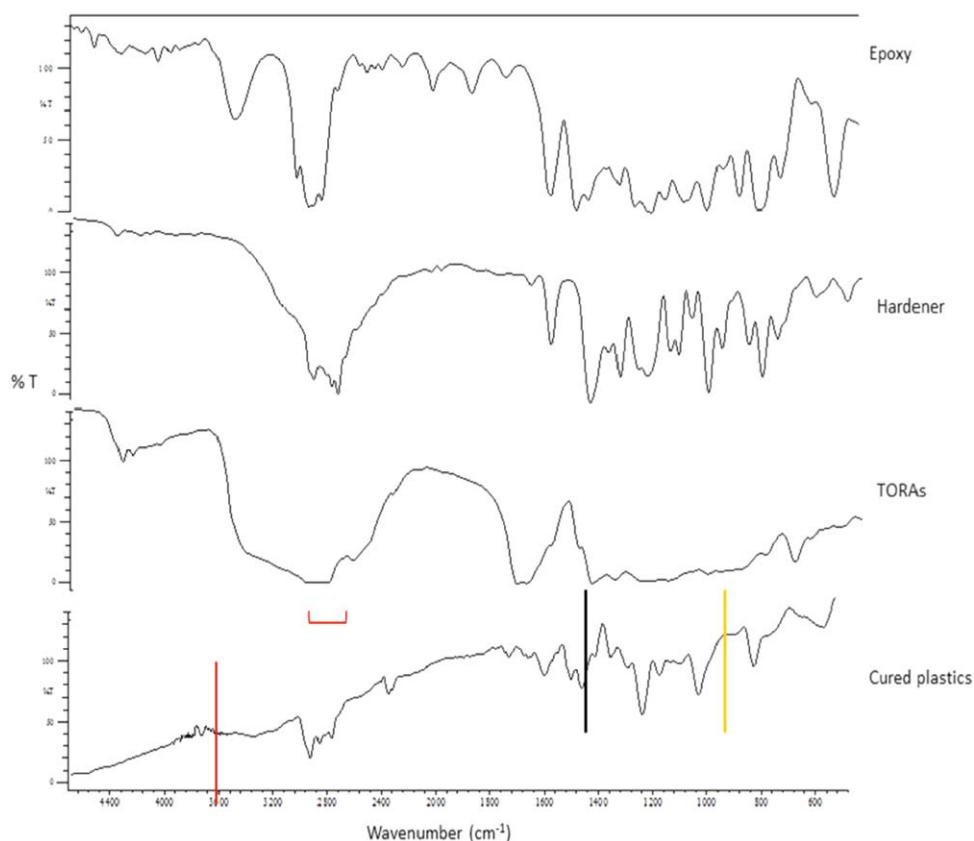


Figure 8. IR spectra for epoxy, hardener, TORAs, and plastics. [Color figure can be viewed at wileyonlinelibrary.com.]

relative availability of functional groups in TORAs. Mekonnen *et al.* (2013)¹¹ and Wang *et al.* (2005)¹⁹ reported similar pattern of results. Wang *et al.* (2005)¹⁹ studied the effect of varying amounts of curing agents in epoxy blends and reported on the thermal properties. They reported similar curing as reported here, that is, as the agent concentration increases, the curing temperature decreases.

Another very important parameter for characterization of plastics is the glass-transition temperature (T_g). This is the temperature where polymers goes from a hard glass like state to a rubbery state, and can provide useful insight into the structure and properties of polymeric materials. As reported in Table VII, there is a reduction in T_g with increasing TORAs concentration in the formulations. This difference can be explained by the

variability in chemical reaction, because of the heterogeneous nature of TORAs. Also, TORAs are characterized with having the polycyclic structures, which when introduced into the epoxy crystalline region may have caused kinks, resulting in voids. As a result, less energy or heat is needed to transform the material from the brittle to rubbery state, via bonding disruption.

Mechanical Properties. An insight into the polymer integrity under stress conditions can be obtained by evaluating the mechanical properties of the plastics manufactured. The data for the tensile strength, tensile modulus, and elongation at break are presented in Table VIII. According to Mekonnen *et al.* (2013),¹¹ mechanical properties of plastics depend on the cross-linking density and network structure of the resulting thermoset. Supplementation of 15 and 25% of epoxy with TORAs did

Table VII. Thermal Properties for the Different Plastic Blends

System	Onset decomposition temperature (°C)	Temperature for 10% degradation (°C) - T_{10}	T_g	Peak of curing
Control	316 ± 6.23 ^a	385 ± 7.21 ^a	95.1 ± 3.85 ^a	141 ± 1.09 ^a
5%	314 ± 7.57 ^a	385 ± 6.56 ^a	92.7 ± 2.30 ^a	138 ± 0.72 ^a
15%	316 ± 8.22 ^a	367 ± 4.93 ^b	90.4 ± 3.28 ^a	136 ± 2.87 ^b
25%	292 ± 3.61 ^b	369 ± 1.15 ^b	79.8 ± 3.22 ^b	122 ± 3.62 ^b
35%	275 ± 6.03 ^c	355 ± 4.36 ^c	67.6 ± 1.94 ^b	126 ± 2.71 ^b

Systems with different letters are significantly different from each other at $p < 0.05$.

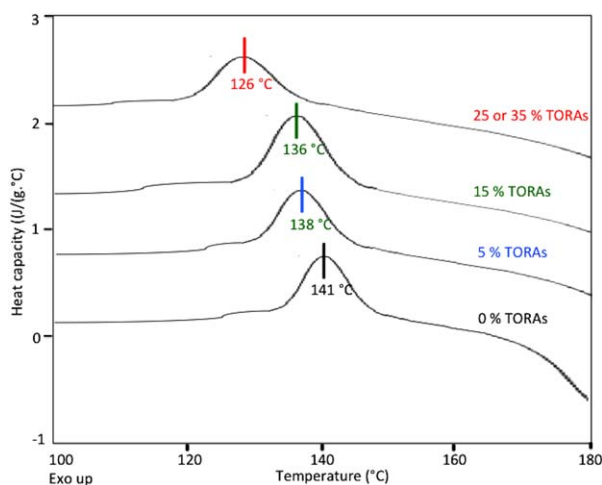


Figure 9. DSC scans of epoxy with varying ratios of TORAs. [Color figure can be viewed at wileyonlinelibrary.com.]

not adversely affect the tensile strength of the plastics. Good dispersion and crosslinking between the epoxy resin and TORAs plausibly contributed to this. On the other hand, replacement of epoxy with TORAs resulted in decrease in stiffness or tensile modulus of the plastics. As mentioned above, one plausible reason for this may be the introduction of kinks in the polymer chains of the plastics as a result of the structure of the TORAs, resulting in flaws. Wang *et al.* (2005)¹⁹ investigated the mechanical properties of epoxy nanocomposites with exfoliated clay and reported a significant decrease in tensile strength with increasing clay content. They mentioned that flaws in the existing nanocomposites, as a result of clay particles getting trapped within bubbles during sample preparation, might have resulted in the decrease in tensile properties observed. Hence, as the volume of clay filler increases, so does this flaw within the structure. On the other hand, as similarly reported in this present study, they also noticed an increase in tensile/Young's modulus with increasing filler content (binder - clay volume). Manzione *et al.* (1981)²⁰ reported one of the earlier studies looking at reducing cost and amount of epoxy used in plastics. They utilized dissolved rubber to produce rubber-modified epoxies via careful control of compatibility and curing. The range of tensile modulus reported in that study (0.935–1.256 GPa) was lower than those observed in the present communication. As a result, it may be possible to substitute epoxy with

Table VIII. Mechanical Properties for formulated Plastics

System	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
Control	24.5 ± 1.90 ^a	2.46 ± 0.07 _a	6.77 ± 0.54 _a
5%	22.5 ± 1.07 _a	1.99 ± 0.11 _b	5.78 ± 0.78 _a
15%	24.4 ± 0.93 _a	1.91 ± 0.22 _b	5.54 ± 0.98 _a
25%	14.7 ± 1.92 _b	1.66 ± 0.04 _c	9.02 ± 0.71 _b
35%	13.6 ± 0.24 _b	1.91 ± 0.10 _b	8.86 ± 0.62 _b

^{a,b,c}Systems with different letters are significantly different from each other at $p < 0.05$.

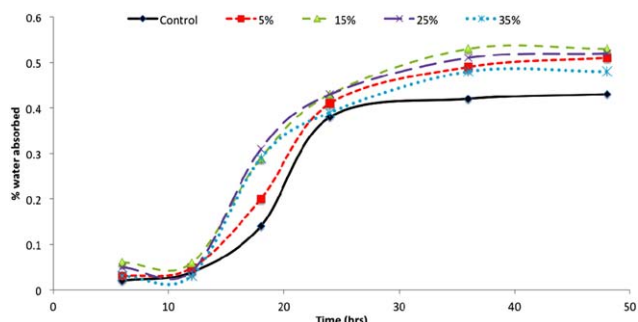


Figure 10. Water uptake of the different plastic formulations (percentage indicates % of TORAs in each system). [Color figure can be viewed at wileyonlinelibrary.com.]

TORAs up to 35% and still produce plastics with comparable mechanical properties, depending on the properties of the end products that are desired.

Finally, as the percentage of TORAs increased in the plastics, the elongation at break (%) increased. This is in agreement with the decrease in T_g observed earlier. As the concentration of TORAs increased, there is a greater possibility of a larger number of chain disruptions (polycyclic rings), hence allowing the macrostructure of the polymer to stretch further without failing. In summary, the supplementation of epoxy resin with TORAs has the potential to reduce cost and produce plastics with mechanical strengths that are comparable up to 15% replacement or up to 35% replacement, depending on the application.

In summary, depending on the application, the increased elongation at break can be tailored for specific applications where reduced stiffness and strength are desired properties. For example, one key application can be the manufacturing of epoxy protective layer for the housing industry, and so forth.

Water Resistance Properties. The water resistance properties of the different plastic systems are presented in Figure 10. The plastics were submerged in water and removed periodically (wiped clean) and the weight measured on a calibrated balance. The plastics reached equilibrium water absorption in most cases after 48 h. When compared to the control sample (100% epoxy), the plastics supplemented with TORAs were characterized with higher water uptake.

As previously reported by Bisanda and Ansell (1991),²¹ addition of any other component to pure epoxy tends to increase the moisture absorption. Several plausible reasons can account for these observations. First, with our system, the addition of TORAs can induce micro gaps and micro cracks that are more susceptible to the penetration of water molecules over time. Nevertheless, the values reported ($\leq 0.6\%$ over 48 h) are significantly lower than those previously reported for epoxy based systems, where other agents were added. Hence, these numbers point to the polymer system as a potentially good system where water absorption over time is a concern.

CONCLUSIONS

The proposed chemical system outlines a method for grafting a bio-product stream, TORAs onto the surface of hemp fibers.

The reaction system was studied using industrially important factors of time and concentration of the acids. A reaction time of 75 min and a TORAs concentration of 0.02 g/L resulted in hemp fibers with superior chemical and surface properties. Also, comprehensive surface analysis using infrared and X-ray photoelectron spectroscopy confirmed changes in chemical functionality and O/C, respectively. Treated fibers were characterized with improved thermal properties and increased contact angles.

TORAs can be used as a filler or supplementary agent for epoxy based plastics. In fact, supplementation up to 15% of the epoxy resin can be done without affecting the properties of the plastics generated. Also, addition of TORAs to epoxy does not significantly inflate the water absorption of the plastics, despite, observed micro gaps and cracks. In summary, this study outlined two successful paths for utilizing an abundant and possibly hazardous material from the pulping industry to produce fibers suitable for composites and partial supplementation of epoxy base plastics.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of Alberta Livestock and Meat Agency (ALMA), Alberta Innovates Bio Solutions (AI BIO) and the Natural Sciences and Engineering Research Council of Canada (NSERC). The authors are grateful to Alberta Innovates Technology Futures (AITF) for kindly supplying the pulp samples needed for this study. The experimental support provided by Drs. Shihong Xu and Dimitre Karpuzov from the Alberta Centre for Surface Engineering and Science (ACSES) at the University of Alberta is much appreciated. The help with SEM imaging provided by Gayle Hatchard at the Department of Chemical and Materials Engineering at the University of Alberta is appreciated. The guidance provided by Dr. Michael Chae is greatly appreciated.

REFERENCES

1. Pietrzak, K.; Kirpluks, M.; Cabulis, U.; Ryszkowska, J. *Polym. Degrad. Stab.* **2014**, *108*, 201.
2. George, M.; Mussone, P.; Bressler, D. *Carbohydr. Polym.* **2016**, *142*, 300.
3. Mohanty, A. K.; Misra, M.; Hinrichsen, G. *Macromol. Mater. Eng.* **2000**, *276*, 1.
4. Mwaikambo, L. Y.; Ansell, M. P. *Angew Makromol Chem* **1999**, *272*, 108.
5. George, M.; Mussone, P.; Bressler, D. *Ind Crops and Prod* **2014**, *53*, 365.
6. Tajvidi, M.; Takemura, A. *Polym. Composite* **2009**, *30*, 1226.
7. George, M.; Chae, M.; Bressler, D. *Prog. Mater. Sci.* **2016**, *83*, 1.
8. Gennadios, A.; Weller, C. L.; Hanna, M. A.; Froning, G. W. *J. Food Sci.* **1996**, *61*, 585.
9. Tian, H.; Wang, Y.; Zhang, L.; Quan, C.; Zhang, X. *Ind. Crops Prod.* **2010**, *32*, 13.
10. Chun, K. S.; Husseinsyah, S. J. *Thermoplast. Compos. Mater.* **2014**, *27*, 1667.
11. Mekonnen, T.; Mussone, P.; El-Thaher, N.; Choi, P. Y. K.; Bressler, D. C. *Macromol. Mater. Eng.* **2013**, *298*, 1294.
12. Freire, C. S. R.; Silvestre, A. J. D.; Neto, C. P.; Rocha, R. M. A. *Cellulose* **2005**, *12*, 449.
13. Tserki, V.; Panayiotou, C.; Zafeiropoulos, N. E. *Adv. Compos. Lett.* **2005**, *14*, 65.
14. Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew Chem. Int. Edit.* **2001**, *40*, 200.
15. George, M.; Mussone, P.; Bressler, D. *Carbohydr. Polym.* **2015**, *134*, 230.
16. Freire, C. S. R.; Silvestre, A. J. D.; Neto, C. P.; Belgacem, M. N.; Gandini, A. *J. Appl. Polym. Sci.* **2006**, *100*, 1093.
17. Khalil, H. P. S. A.; Suraya, N. L. *Bioresources* **2011**, *6*, 1122.
18. George, M.; Mussone, P.; Abboud, Z.; Bressler, D. *Carbohydr. Polym.* **2014**, *142*, 300.
19. Wang, K.; Chen, L.; Wu, J. S.; Toh, M. L.; He, C. B.; Yee, A. F. *Macromolecules* **2005**, *38*, 788.
20. Manzione, L. T.; Gillham, J. K.; Mcpherson, C. A. *J. Appl. Polym. Sci.* **1981**, *26*, 907.
21. Bisanda, E.; Ansell, M. *Composites Composites Sci. Technol.* **1991**, *41*, 165.