



# Effect of surface treatment on thermal stability of the hemp-PLA composites: Correlation of activation energy with thermal degradation



Shubhashini Oza<sup>a</sup>, Haibin Ning<sup>b</sup>, Ian Ferguson<sup>c</sup>, Na Lu<sup>d,\*</sup>

<sup>a</sup> Dept. of Civil and Environmental Engineering, University of North Carolina at Charlotte, Charlotte, NC 28223, USA

<sup>b</sup> Dept. of Materials Science and Engineering, University of Alabama at Birmingham, Birmingham, AL 35294, USA

<sup>c</sup> Dept. of Electrical and Computer Engineering, University of North Carolina at Charlotte, Charlotte, NC 28223, USA

<sup>d</sup> Dept. of Engineering Technology, University of North Carolina at Charlotte, Charlotte, NC 28223, USA

## ARTICLE INFO

### Article history:

Received 8 April 2014

Received in revised form 26 June 2014

Accepted 27 June 2014

Available online 8 July 2014

### Keywords:

A. Polymer–matrix composites (PMCs)

B. Thermal properties

D. Thermal analysis

A. Thermoplastic resin

## ABSTRACT

The thermal behavior of hemp-poly lactic acid composites with both untreated and chemically surface modified hemp fiber was characterized by means of activation energy of thermal degradation. Three chemical surface modification employed were; alkali, silane and acetic anhydride. Model-free isoconversion Flynn–Wall–Ozawa method was chosen to evaluate the activation energy of composites. The results indicated that composites prepared with acetic anhydride modified hemp had 10–13% higher activation energy compared to other composites. Further, among the three surface modifications, acetic anhydride resulted in higher activation energy (159–163 kJ/mol). Fourier transform infrared spectroscopy supported the findings of thermogravimetric analysis results, wherein surface functionalization changes were observed as a result of surface modification of hemp fiber. It was concluded that, higher bond energy results in higher activation energy, which improves thermal stability. The activation energy data can aid in better understanding of the thermal degradation behavior of composites as a function of composite processing.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

An ever increasing drive for new sustainable materials and stringent environmental regulations are creating a demand for greener biocomposites. Therefore, intensified research is being conducted in developing new biodegradable polymers as a replacement to petroleum based polymers [1–5]. Among the available biopolymers, poly lactic acid (PLA) obtained from starch rich resource has been investigated because it can provide an ultimate tensile strength of 53 MPa at the breaking point [6]. On the other hand, natural fibers have been extensively studied as reinforcement in composites due to their low cost, low density, high specific properties, biodegradability, occupational health benefits, and easy availability [7–9]. The most common fibers considered as substitutes for synthetic fibers are bast fibers like flax, hemp, kenaf and jute.

Despite the advantages of natural fibers and biopolymers, when composites are manufactured they perform less effectively with respect to thermal properties due to low thermal stability of the natural fibers. To address this challenge, natural fibers are subjected to different types of surface modifications. The three most commonly used surface modification are chemical [7,10,11], phys-

ical [12,13] and biological [14]. Among them, chemical modification of fibers has been used frequently due to the ease of modification and for the formation of chemical and mechanical bonding between the fiber and matrix. The chemical modification of fibers can be further classified into two groups; chemicals that result in coupling, such as silanes [15,16] and anhydrides [17] and the once that result in mechanical bonding between polymer and fiber, such as sodium hydroxide [1,16,18].

Research related to the effect of fiber chemical treatment on the thermal degradation properties have been studied in depth. Also, research related to kinetics of thermal degradation of natural fibers has also been investigated. However, studies related to the kinetics of thermal degradation of composites are limited. Yao et al. have studied the thermal decomposition processes of ten types of natural fibers including wood, bamboo, agricultural residues and bast fibers. They calculated the activation energy using various degradation models including the Kissinger, Friedman, Flynn–Wall–Ozawa, and modified Coats–Redfern [19]. The results indicated that activation energy of natural fibers ranged between 160 and 170 kJ/mol.

Alvarez et al. studied the kinetic parameters of commercial blends of starch and cellulose derivatives with sisal fibers using a variety of differential or integral kinetic methods [20]. They observed that activation energy remained the same for all the methods and also for these biocomposites, energy values did not

\* Corresponding author. Tel.: +1 704 687 2718.

E-mail address: [nlu2@unc.edu](mailto:nlu2@unc.edu) (N. Lu).

vary with the conversion rate suggesting that the thermal degradation mechanism was similar for all.

Activation energy for a reaction can be calculated by different methods, but isoconversion methods have been used more frequently. There are numerous model-free isoconversion methods that can be adopted for calculating activation energy of thermally activated reactions. The details for few commonly used isoconversion methods are summarized in Table 1. Starink has classified and assessed the accuracy of various isoconversion methods for calculating activation energies [21]. The isoconversion methods were classified into two categories Type A and Type B. Type A method make no mathematical approximations (Eg. Friedman), whereas Type B (Eg. Kissinger) methods apply a range of approximations for the temperature integral to obtain the final equation for activation energy. Based on their investigation, Type B methods were found to be more accurate than Type A. Ozawa in their study also justified that Flynn–Wall–Ozawa (F–W–O) method is a more accurate method and mentioned that the quantities used to estimate the activation energy are simpler in F–W–O method compared to others. Therefore, in this study F–W–O method was chosen to study the activation energy of thermal degradation of composites.

Only a few studies have been conducted on the hemp-PLA composites with respect to their fabrication, mechanical, and thermo-mechanical properties [22–24]. In particular, there are no studies currently reporting the kinetics of thermal degradation of hemp-PLA based biocomposites in correlation to activation energy. Therefore, the main objective of this study was to understand the effect of chemical modification on thermal degradation of hemp-PLA biocomposites by using activation energy approach. Further, Fourier Transform Infrared Spectroscopy (FTIR) was used to understand the surface changes brought about by the chemical modification of hemp fibers.

## 2. Theoretical approach

Thermogravimetric analysis has been used for rapidly assessing the thermal decomposition of the polymeric composites. In the past decade, an increasing number of kinetic studies have been done using TGA for determining rate constants, activation energies, reaction orders and Arrhenius pre-exponential constants [19,20,25].

Kinetics studies generally apply one basic rate equation:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (1)$$

where  $d\alpha/dt$  is the rate of conversion at a constant temperature,  $k$  is the rate constant,  $f(\alpha)$  is the reaction model, and  $\alpha$  is the conversion rate which is determined using Eq. (2)

$$\alpha = \frac{W_o - W_t}{W_o - W_f} \quad (2)$$

$W_t$ ,  $W_o$  and  $W_f$  are the time  $t$ , initial and final weights of the sample. In the case of polymer degradation, it is assumed that the rate of conversion is proportional to the concentration of material that has to react. Extending the assumption to composites, results in Eq. (3)

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

where  $n$  is the apparent order of reaction. One of the ways to conduct a kinetic study in a TGA is to use a heating rate

$$\beta = dT/dt \quad (4)$$

where  $\beta$  is the heating rate and  $dT/dt$  is the change in temperature with respect to time.

The rate constant  $k$  is generally given by the Arrhenius equation:

$$k = A \cdot \exp\{-E_a/RT\} \quad (5)$$

where  $E_a$  is the activation energy,  $A$  is the pre-exponential factor,  $T$  is the temperature, and  $R$  is the gas constant. By combining Eqs. (1)–(5), Eq. (6) is obtained as follows

$$d\alpha/(1 - \alpha)^n = \frac{A}{\beta} \cdot \exp\left\{\frac{-E_a}{RT}\right\} \cdot dT \quad (6)$$

Eq. (6) is the most fundamental equation used for studying kinetic parameters using TGA.

$E_a$ , Activation energy is the minimum energy required to start a chemical reaction and the units are normally given in kilojoules per mole. If the bond dissociation energy for reactants is high then activation energy required for the reaction will also be high.  $E_a$  can be calculated using various models as depicted in Table 1. Flynn–Wall–Ozawa is an integral method which gives  $-E_a/R$  from the slope of the line obtained by plotting  $\log \beta$  against  $1/T$  at any conversion rate. The parameters for activation energy calculation can be calculated from the TGA curves at varying heating rates.

## 3. Experimental study

### 3.1. Materials

Industrial hemp fibers with a length of 25 mm were obtained from Hempline Inc. (Ontario, Canada). The average density of the fiber was 1.24 g/cm<sup>3</sup>. The moisture content of the raw industrial hemp fiber ranged from 6% to 7%. PLA pellets having a density of 1.24 g/cm<sup>3</sup>, a melt mass flow rate (MFR) of 6 g/10 min, and a melting temperature of 210 °C were obtained from Nature Works LLC. (Nebraska, U.S.A). Sodium hydroxide (NaOH) pellets, glacial acetic acid, and acetic anhydride solutions were obtained from Fisher Scientific (New Jersey, U.S.A), and the silane solution (triethoxyvinylsilane) was obtained from Sigma Aldrich Inc. (Missouri, U.S.A).

### 3.2. Fiber surface treatment

In this study three different chemical modifications were investigated: alkali (NaOH), silane and acetic anhydride. Alkali treatment of fibers is expected to result in increased surface roughness. This will aid in better mechanical bonding between the fiber and polymer and also, the treatment removes significant amount of wax, pectin, hemicellulose and lignin, exposing more cellulose that result in increased reaction sites for bonding with polymer [26]. Silanization was carried out by using 5 wt.% tri-

**Table 1**  
Kinetic methods used in evaluating various kinetic parameters [7,19,20].

Method	Expressions	Plots
Kissinger	$\ln \left\{ \frac{\beta}{T_p^2} \right\} = \ln \{AR/E_a\} + \{1/T_p\} \left\{ \frac{-E_a}{R} \right\}$	$\ln \{ \beta / T_p^2 \}$ against $1/T_p$
Friedman	$\ln \frac{d\alpha}{dt} = \ln [A f(\alpha)] - \frac{E_a}{RT}$	$\ln \frac{d\alpha}{dt}$ against $1/T$
Horowitz–Metzger	$\ln \left[ \ln \left\{ \frac{1}{1-\alpha} \right\} \right] = \frac{E_a \theta}{RT^2}$	$\ln \left[ \ln \left\{ \frac{1}{1-\alpha} \right\} \right]$ against $\theta$
Flynn and Wall	$\frac{d \log \beta}{d(1/T)} = 0.457 \frac{E_a}{R}$	$-\log \beta$ against $1/T$
Flynn–Wall–Ozawa	$\log F(\alpha) = \log \left\{ \frac{A E_a}{R} \right\} - \log \beta - 2.315 - 0.4567 \frac{E_a}{RT}$	$\log \beta$ against $1/T$ for a fixed degree of conversion

ethoxyvinylsilane to chemically modify hemp fibers. Acetylation treatment results in introduction of acetyl group into the cellulose resulting in plasticization of cellulose. This treatment reduces the hygroscopic nature of the fibers resulting in enhanced dimensional stability. 2.5 wt.% acetic anhydride solutions were used to chemically modify hemp fibers.

### 3.3. Composite processing

A two-step manufacturing process was used in order to improve the surface adhesion of the natural fiber and the matrix. First, PLA was processed separately into thin films using a C.W. Brabender 19.05 mm single-screw extruder. The extruder was operated at a temperature of 175 °C with an extruder rotation speed of 8 rpm. A compression molding technique was used to manufacture composites with different polymeric films using a custom mold. Each composite was manufactured by sandwiching a layer of fiber in between two layers of PLA films. The weights of hemp fiber and PLA layers were controlled to maintain at 20%, 30%, and, 40% fiber volume fraction. Composites were prepared with both, untreated and chemically treated fibers for all above mentioned fiber volume fractions.

### 3.4. Thermogravimetric analysis

Thermal analysis of untreated and treated hemp fibers, pure PLA, and composites were analyzed using a model Q600 simultaneous TGA/DSC system from TA instruments. The analysis were conducted at heating rates in the range of 5–30 °C/min, from room temperature to 550 °C in a nitrogen atmosphere (100 ml/min). The sample amount used was between 10 and 15 mg per specimen, and five specimens were tested for each sample.

### 3.5. Fourier transform infrared spectroscopy

FTIR was used to understand the surface chemical composition changes brought about by the fiber chemical treatments. A Perkin Elmer FTIR spectrometer model Spectra 100 was used. The scans were conducted in the range of 4000–650  $\text{cm}^{-1}$  at a scanning speed of 2 mm/s, with a resolution of 16  $\text{cm}^{-1}$  for 16 scans. Samples were prepared in filament form for the measurement.

## 4. Results and discussion

### 4.1. Thermal decomposition process of hemp-PLA composites

TGA was used to identify the thermal degradation process of the untreated and treated fiber, pure PLA and hemp-PLA composites. Initially, the effect of fiber loading on thermal decomposition was studied and based on these results it was concluded that 30% fiber volume fraction is the optimum loading of hemp fiber. Therefore, activation energy of thermal degradation for the composites was investigated with 30% fiber volume fraction (both with untreated and treated hemp-PLA composites). The heating rate ranged from 5 to 30 °C/min in nitrogen atmosphere.

#### 4.1.1. Effect of hemp fiber treatment on thermal degradation

TGA curves of pure PLA, untreated and treated fibers are represented in Fig. 1. The curves were obtained at 10 °C/min in the range 25–550 °C. In the case of hemp fiber, thermal degradation takes place in two stages for both untreated and treated fiber. The initial 6–8% of weight loss can be attributed to the inherent moisture in the fiber. But after 250 °C, the fiber decomposes rapidly and the complete fiber is degraded by 350–360 °C. This second stage degradation involves the degradation of hemicellulose, lignin and cel-

lulose. These temperatures are in the similar range as analyzed by the U.S. Department of Agriculture for wood, hemicellulose, cellulose and lignin. In their extensive literature review of thermal degradation of various wood and wood components, they found that hemicellulose is the least thermally stable compound which degrades around 300 °C. Lignin degradation begins around 300 °C and completes around 450 °C. Cellulose degradation started at 275 °C and was found to completely degrade at around 550 °C [27].

In case of treated fibers the thermal stability is higher due to the removal of organic impurities such as pectin and wax present on the surface of the hemp fiber. For NaOH treated fibers, the fibers showed higher thermal stability because, the treatment removes most of the impurities and exposes higher amount of cellulose molecules. In case of silane and acetic anhydride treatment, the treatment results in surface coating rather than surface etching as in case of NaOH treatment. This results in reduced thermal stability compared to NaOH, but improved thermal stability in comparison to untreated fibers. A detailed discussion of comparison between the alkali and silane treatment can be found elsewhere [1]. The thermal stability of the treated fibers is better than the thermal stability of the untreated fibers in the order; NaOH treated > acetic anhydride treated > silane treated > untreated. The degradation of pure PLA is a one step process. The degradation process does not start till 300 °C, but after 300 °C it proceeds very rapidly and the polymer completely degrades by 400 °C.

#### 4.1.2. Activation energy of thermal degradation

Activation energy study was conducted using heating rates of 5, 10, 20, 25, and 30 °C/min with 30% fiber volume fraction of hemp-PLA composites. The various heating rates were chosen to avoid compensation effects in determining kinetic constants [20]. Fig. 2 represents the TGA and DTG curves for acetic anhydride treated hemp-PLA composite at different heating rates. A similar trend was observed with untreated, NaOH and silane treated hemp-PLA composites. It can be observed that with increase in heating rate the maximum degradation increased. Similar trend was also reported by Alvarez and Vázquez [20].

The average activation energy of thermal degradation was calculated from the conversion range of 0.1–0.7 through iso-conversional F–W–O method for both untreated and treated hemp-PLA composites (Table 2). Fig. 3 depicts the linear plot for acetic anhydride treated hemp-PLA composites at various conversion rates. The same trend was observed in case of other treated and untreated hemp-PLA composites. From these plots it can be

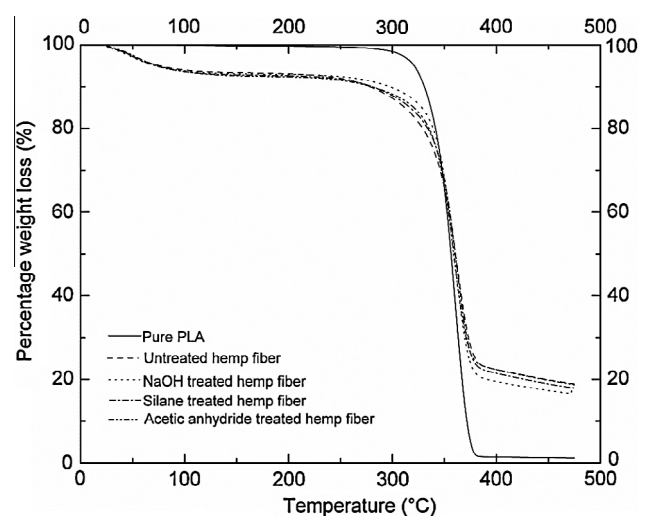


Fig. 1. TGA curves for pure PLA, untreated and treated hemp fibers.

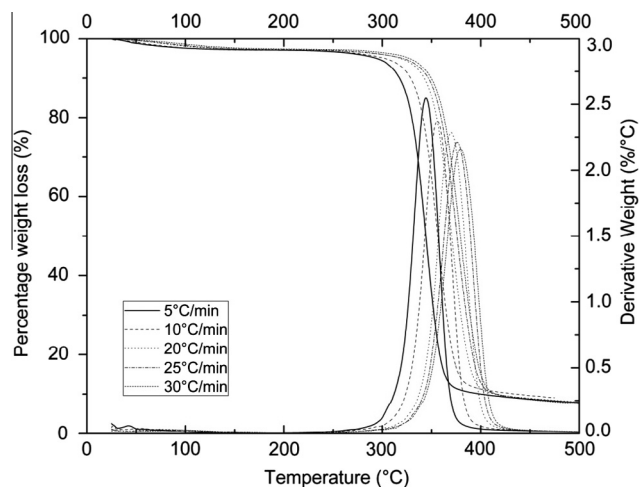


Fig. 2. TGA and DTG curves of acetic anhydride treated hemp-PLA composites at various heating rates.

observed that the reaction mechanism of thermal degradation for both treated and untreated hemp-PLA composite is similar. Activation energies at varying conversion rate were calculated from the slope of these curves. Table 3, gives the summary of the activation energy values with the  $R^2$  values for these lines.

The plots of activation energy as a function of conversion rate for  $\alpha = 0.1$ – $0.7$  for all the four composites are given in Fig. 4. Activation energy changed drastically from low conversion (10%) to high conversion rate (40%) and was quite stable at higher conversion, which indicated that the degradation mechanism at low conversion was different than at higher conversion. This could be explained by the thermal degradation temperatures of the TGA curves. The thermal degradation temperature range for 10% conversion is around  $\sim 310$  °C and for 40% conversion is around  $\sim 350$  °C. This is the part of the TGA curve where in the slope is maximum, suggesting that this is the region where in highest thermal degradation takes place. As discussed previously, maximum degradation of hemicellulose, cellulose and lignin take place in this temperature range [27]. Therefore, activation energy changes drastically below 40% conversion since the mechanism involving the decomposition of these ligno-cellulosic matter is different and once most of these materials are degraded, that is, the decomposition mechanism after 40% is different resulting in quite stable activation energy values. A similar trend was observed by other groups who studied activation energy for fibers [7,19,20]. Both untreated and treated hemp fiber composites showed similar trend. Although the composites showed similar trend, the activation energy values with acetic anhydride treated hemp-PLA composite was 10–13% higher than untreated hemp-PLA composites. The value of activation energy can be ranked as acetic anhydride treated hemp-PLA

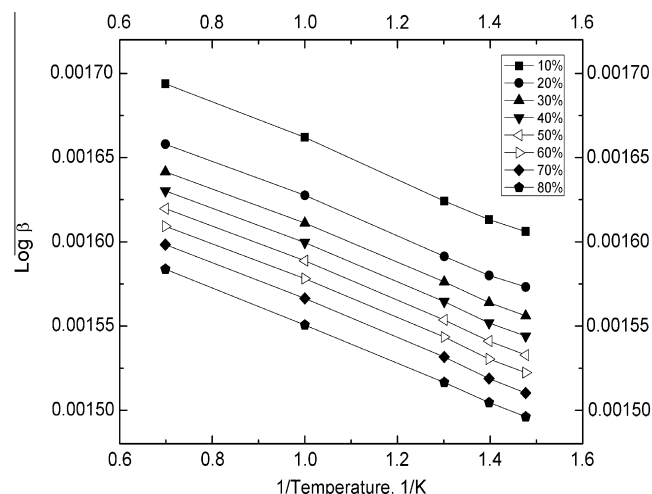


Fig. 3. F-W-O model for conversion rate 0.1–0.7, of 30% acetic anhydride treated hemp-PLA composites.

composite (157–163 kJ/mole) > silane treated hemp-PLA composite (148–153 kJ/mole) > NaOH treated hemp-PLA composite (138–150 kJ/mole) > untreated hemp-PLA composite (136–141 kJ/mole). The higher activation energy of the acetic anhydride treated hemp-PLA composite can be explained as the result of higher bond energy that results from the acetic anhydride treatment which consecutively results in higher thermal stability of these composites in comparison to other composites.

#### 4.2. Fiber surface functionalization

FTIR aids in understanding the surface chemical changes brought about by the chemical treatment of hemp fibers. Fig. 5 presents the FTIR spectrum of untreated and treated hemp. From this figure it can be observed that, the percentage of –OH group increased after the chemical treatment for all the treatments, and can be observed by increase in intensity of the peak at  $1000\text{ cm}^{-1}$ . As a result, the reaction of hydroxyl bonds with the carboxyl group also increased as revealed in the range  $3200$ – $3600\text{ cm}^{-1}$ . In comparison to untreated fiber, the peaks at  $1250\text{ cm}^{-1}$  for treated hemp fibers were not observed. This peak is due to C–O stretching of acetyl groups of lignin, suggesting removal of lignin from the hemp fiber surface treatment. The hemicelluloses group is partially removed from the fiber surface after the treatment, as evident of decreased carbonyl peak at  $1600$ – $1650\text{ cm}^{-1}$ . In addition, the peak at  $1740$ – $1750\text{ cm}^{-1}$  in untreated hemp is also not observed after chemical treatments. This is due to the removal of pectin and wax present on the hemp fibers. Mwaikambo also found similar results when he treated fibers with alkali [10]. For silane treated fibers, the peak at

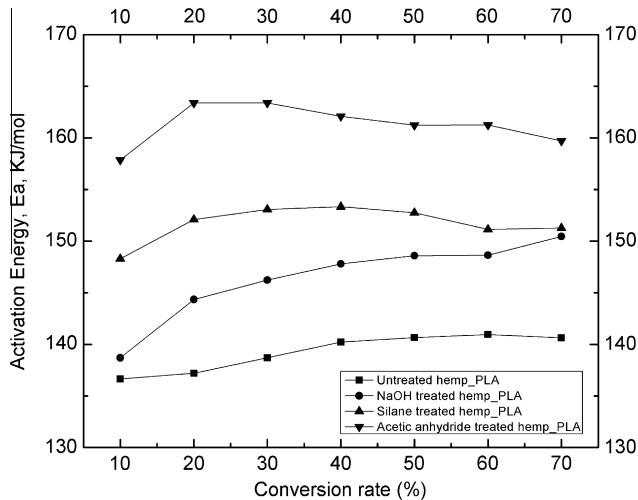
Table 2

Activation energy and  $R^2$  values for untreated and treated hemp-PLA composites for conversion rate 0.1–0.8 (for 30% fiber volume fraction).

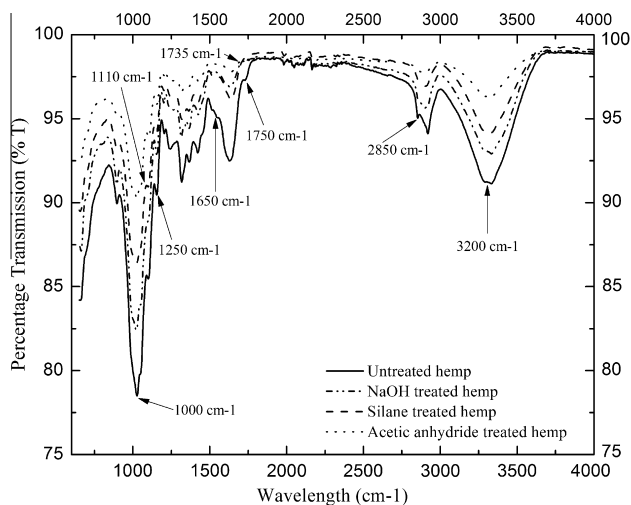
Conversion rate ( $\alpha$ ), %	Untreated hemp_PLA		NaOH treated hemp_PLA		Silane treated hemp_PLA		Acetic anhydride treated hemp_PLA	
	Activation energy, $E_a$ , kJ/mol	$R^2$	Activation energy, $E_a$ , kJ/mol	$R^2$	Activation energy, $E_a$ , kJ/mol	$R^2$	Activation energy, $E_a$ , kJ/mol	$R^2$
10	136.64	0.9989	138.68	0.9954	148.28	0.9423	157.853	0.9985
20	137.20	0.9983	144.35	0.9981	152.08	0.9893	163.391	0.9984
30	138.70	0.9985	146.23	0.9984	153.06	0.9955	163.398	0.9988
40	140.22	0.9985	147.79	0.9986	153.33	0.9976	162.091	0.9986
50	140.66	0.9979	148.59	0.9987	152.75	0.9989	161.226	0.9988
60	140.95	0.998	148.64	0.9989	151.14	0.9983	161.246	0.9988
70	140.63	0.9975	150.45	0.9993	151.27	0.9966	159.705	0.9991

**Table 3**  
FTIR peaks and bond details for untreated and treated hemp fiber [1].

Wave length	Associated chemical group	Untreated hemp	NaOH treated hemp	Silane treated hemp	Acetic anhydride treated hemp
1000	–OH intensity	Low	High	High	High
1110	Si–O–Si	Not observed	Not observed	Observed	Not observed
1250	Lignin	Predominant	Reduced	Reduced	Reduced
1600–1650	Hemicellulose	Predominant	Reduced	Reduced	Reduced
1735	Esterification of –OH due to acetyl group	–	–	–	Observed peak
1750	Pectin–Wax	Present	Removed	Removed	Removed
2850	Methylene group	Present	Removed	Removed	Removed
3200–3600	–OH stretching	Low	High	High	High



**Fig. 4.** Activation energy at various conversion rates (0.1–0.8) for 30% fiber volume fraction of untreated and treated hemp-PLA composites.



**Fig. 5.** FTIR spectra of untreated and treated hemp fiber.

$1110\text{ cm}^{-1}$  could be observed due to the formation of Si–O–Si bonds, which indicate the occurrence of chemical reaction between hydrolyzed silane and the hemp, and the existence of polysiloxane network. This is consistent with Sgriccia et al. work [28]. In case of acetic anhydride treatment, the presence of a peak around  $1735\text{ cm}^{-1}$  is due to the esterification of hydroxyl group. Tserki et al. found similar changes in their study of acetylation on various natural fibers and wood fibers [29].

In summary, alkali, silane and acetic anhydride chemical modifications removed the pectin, wax, and partially removed the

hemicelluloses and lignin from hemp fiber resulting in increased percentage of cellulose structure. The silane treatment result in the formation of Si–O–Si bonds and for acetic anhydride esterification of hydroxyl group was noticed. The formation of peaks in relation to chemical bonds changes are tabulated in Table 3.

## 5. Conclusions

In this work, we have investigated the effect of chemical surface modification on the thermal degradation characteristics of the hemp-PLA composites by using activation energy approach. From the results it can be concluded that NaOH treated hemp fiber composites have the lowest thermal stability compared to that of the other two treated ones. NaOH treatment of hemp can be suggested as an etching mechanism resulting in removal of organic impurities and exposing higher amount of cellulose. On the other hand, the treatment with silane and acetic anhydride is more of a surface coating mechanism (coupling), where in the reaction would be complete once the fibers are embedded in the matrix. In the case of composite with the treated fibers, acetic anhydride and silane treated hemp composites resulted in the higher thermal stability because the coupling reactions are complete once the fibers are brought in contact with the matrix. These coupling reaction result in strong covalent bonds, such as the Si–O–Si. In case of untreated and NaOH treated fibers, thermal stability is lower in comparison to acetic anhydride and silane treated hemp fiber-PLA composites. NaOH treated fibers result in only hydrogen bonding with the matrix and these bonds are not as strong as the covalent bonds created by the silane or acetic anhydride. These bonds could be attributed to the higher bond energies with these treatments. This was further justified by the activation energy calculation, where in it was observed that acetic anhydride treated hemp composite resulted in higher activation energy in the range of 158–163 kJ/mole. Which indicated that higher energy is required to break these bonds, resulting in enhancement fiber–matrix adhesion after silane and acetic anhydride treatments, compared to NaOH surface modification. Therefore, it can be concluded that activation energy of thermal degradation can be used as an effective tool to understand the thermal stability and the resulting bond energies before and after surface modification.

## Acknowledgements

The authors are grateful for the support of the US National Science Foundation I-CORPS program, and Dr. Katherine Weaver, manager of the Materials Characterization Laboratory at the University of North Carolina at Charlotte, Charlotte, NC, USA for assisting with testing.

## References

- [1] Lu N, Oza S. Thermal stability and thermo-mechanical properties of hemp-high density polyethylene composites: effect of two different chemical modifications. *Compos B Eng* 2013;44(1):484–90.

- [2] Cheung H-Y et al. Biodegradation of a silkworm silk/PLA composite. *Compos B Eng* 2010;41(3):223–8.
- [3] Christian SJ, Billington SL. Mechanical response of PHB- and cellulose acetate natural fiber-reinforced composites for construction applications. *Compos B Eng* 2011;42(7):1920–8.
- [4] Porras A, Maranon A. Development and characterization of a laminate composite material from polylactic acid (PLA) and woven bamboo fabric. *Compos B Eng* 2012;43(7):2782–8.
- [5] Jia W, Gong RH, Hogg PJ. Poly (lactic acid) fibre reinforced biodegradable composites. *Compos B Eng* 2014;62:104–12.
- [6] Technical Data Sheet. <[http://www.natureworksllc.com/~media/Technical\\_Resources/Technical\\_Data\\_Sheets/TechnicalDataSheet\\_2003D\\_FFP-FSW\\_pdf.pdf](http://www.natureworksllc.com/~media/Technical_Resources/Technical_Data_Sheets/TechnicalDataSheet_2003D_FFP-FSW_pdf.pdf)> [cited 01.11.12].
- [7] Ouajai S, Shanks RA. Composition, structure and thermal degradation of hemp cellulose after chemical treatments. *Polym Degrad Stab* 2005;89(2):327–35.
- [8] Thielemans W et al. Novel applications of lignin in composite materials. *J Appl Polym Sci* 2002;83(2):323–31.
- [9] Lu N, Oza S. A comparative study of the mechanical properties of hemp fiber with virgin and recycled high density polyethylene matrix. *Compos B Eng* 2013;45(1):1651–6.
- [10] Mwaikambo LY, Ansell MP. Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization. *J Appl Polym Sci* 2002;84(12):2222–34.
- [11] Huda MS et al. The effect of silane treated- and untreated-talc on the mechanical and physico-mechanical properties of poly(lactic acid)/newspaper fibers/talc hybrid composites. *Compos B Eng* 2007;38(3):367–79.
- [12] Ferreira L et al. Improving the adhesion of poly(ethylene terephthalate) fibers to poly(hydroxyethyl methacrylate) hydrogels by ozone treatment: surface characterization and pull-out tests. *Polymer* 2005;46(23):9840–50.
- [13] Sinha E, Panigrahi S. Effect of plasma treatment on structure, wettability of jute fiber and flexural strength of its composite. *J Compos Mater* 2009;43(17):1791–802.
- [14] Li Y, Pickering KL. Hemp fibre reinforced composites using chelator and enzyme treatments. *Compos Sci Technol* 2008;68(15–16):3293–8.
- [15] Arbelaiz A et al. Thermal and crystallization studies of short flax fibre reinforced polypropylene matrix composites: effect of treatments. *Thermochim Acta* 2006;440(2):111–21.
- [16] Kabir MM et al. Mechanical properties of chemically-treated hemp fibre reinforced sandwich composites. *Compos B Eng* 2012;43(2):159–69.
- [17] Park J-M et al. Interfacial evaluation of modified Jute and Hemp fibers/polypropylene (PP)-maleic anhydride polypropylene copolymers (PP-MAPP) composites using micromechanical technique and nondestructive acoustic emission. *Compos Sci Technol* 2006;66(15):2686–99.
- [18] Lu T et al. Effects of modifications of bamboo cellulose fibers on the improved mechanical properties of cellulose reinforced poly(lactic acid) composites. *Compos B Eng* 2014;62:191–7.
- [19] Yao F et al. Thermal decomposition kinetics of natural fibers: activation energy with dynamic thermogravimetric analysis. *Polym Degrad Stab* 2008;93(1):90–8.
- [20] Alvarez VA, Vázquez A. Thermal degradation of cellulose derivatives/starch blends and sisal fibre biocomposites. *Polym Degrad Stab* 2004;84(1):13–21.
- [21] Starink MJ. The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods. *Thermochim Acta* 2003;404(1–2):163–76.
- [22] Hu R, Lim J-K. Fabrication and mechanical properties of completely biodegradable hemp fiber reinforced polylactic acid composites. *J Compos Mater* 2007;41(13):1655–69.
- [23] Graupner N. Improvement of the mechanical properties of biodegradable hemp fiber reinforced poly(lactic acid) (PLA) composites by the admixture of man-made cellulose fibers. *J Compos Mater* 2009;43(6):689–702.
- [24] Mukherjee T, Kao N. PLA based biopolymer reinforced with natural fibre: a review. *J Polym Environ* 2011;19(3):714–25.
- [25] Yao F et al. Rice straw fiber-reinforced high-density polyethylene composite: effect of fiber type and loading. *Ind Crops Prod* 2008;28(1):63–72.
- [26] Valadez-Gonzalez A et al. Effect of fiber surface treatment on the fiber-matrix bond strength of natural fiber reinforced composites. *Compos B Eng* 1999;30(3):309–20.
- [27] U.S.D.A, F.S. Thermal degradation of wood components: a review of the literature. <<http://www.fpl.fs.fed.us/documnts/fplrp/fplrp130.pdf>>; 1970. [cited 02.02.13].
- [28] Sgriccia N, Hawley MC, Misra M. Characterization of natural fiber surfaces and natural fiber composites. *Compos A Appl Sci Manuf* 2008;39(10):1632–7.
- [29] Tserki V et al. A study of the effect of acetylation and propionylation surface treatments on natural fibres. *Compos Part A-Appl Sci Manuf* 2005;36(8):1110–8.