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A THESIS FOR THE DEGREE OF MASTER OF SCIENCE

**Improvement of Thermo-mechanical Properties and
Water Absorption Resistance of PLA/Acetylated Kenaf-based
Green Composite**

**폴리유산과 아세틸화 케나프 섬유로 구성된 그린 복합재료의 기계적,
열적 성질 및 수분 흡수 저항성의 향상**

By Taek-Jun Chung

PROGRAM IN ENVIRONMENTAL MATERIALS SCIENCE
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Abstract

Improvement of Thermo-mechanical Properties and Water Absorption Resistance of PLA/Acetylated Kenaf-based Green Composite

Taek-Jun Chung

Program in Environmental Materials Science

The Graduate School

Seoul National University

The objective of this study was to fabricate and improve eco-friendly biocomposites based on poly(lactic acid) and kenaf fibers. First, after measuring the tensile and flexural strength of PLA composites with various kenaf contents as filler, the amounts of PLA and kenaf were fixed at a 70:30 weight percentage blend ratio by considering the economic and processing conditions for a laboratory-scale extruder. Acetylation conducted for 0.5h, 1h, 2h, or 3h was employed to modify kenaf prior to biocomposites fabrication. The acetylated fibers were characterized using fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), acetyl content titration, and thermogravimetric analysis (TGA). The fabricated composites were tested using the universal testing machine, dynamic mechanical thermal analysis (DMTA), FE-SEM (on fractured surfaces), TGA, and water

absorption. Results show that at brief acetylation (18% acetyl content or lower) the mechanical properties of composites were either lower or similar to the untreated-kenaf/PLA composites. This behavior was found to relate to the surface smoothening of briefly acetylated kenaf in addition to insufficient modification of the hydrophilic characters of kenaf. At higher acetylation levels, the hydroxyl availability was effectively reduced, bonding with PLA was improved, mechanical properties and moisture resistance of the composites were enhanced, all evidenced from the material characterization. As the acetyl content of kenaf was increased, the thermal stability of the fibers and the composites that they formed also increased. The optimum acetylation time examined in this study was two hours, with an acetyl content of 28%.

Keywords : Interfacial adhesion, Acetylation, Kenaf fibers, Poly(lactic acid), Biocomposites

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1. Introduction

1.1. Background of this study

In recent years, research attempts are increasingly made to address environmental problems and global warming associated with the increase in CO₂ emission (Avella *et al.*, 2008). Also, due to the increased use of plastic products, the disposal and decomposition of waste plastics and the pollution of soils are becoming crucial problems. The use of biopolymer such as PLA (Polylactic acid), PBS (Polybutylene succinate), PHA (Polyhydroxyalkanoate), and PBAT (Poly(butylene adipate-co-terephthalate)) is one of the approaches to solve these problems. These biopolymers are intended to substitute non-biodegradable polymers based on petroleum-based synthetic materials such as polyethylene, polypropylene, and polystyrene, which are commonly used (Lee *et al.*, 2009).

In this research, biocomposites composed of kenaf and PLA were fabricated by first acetylating the kenaf. This study will focus on the improvement of mechanical properties, thermal properties, water resistance and interfacial adhesion of the biocomposites.

1.2. Biocomposites

There are advantages for using natural fibers, which exist in abundance, to enhance properties of bioplastic materials. For example, the use of such biocomposites reduces carbon dioxide in the atmosphere by increasing the cultivation of fibers and their values. Biocomposites are a generic term of materials composed of biodegradable or non-biodegradable polymer filled or/and reinforced with natural fibers. Commonly, natural fibers have lower mechanical properties and elastic moduli compared to glass fibers but when these properties are normalized with specific gravity, natural fibers are comparable to glass fibers in specific strength and specific moduli. These comparable features imply that biocomposites, with natural fibers incorporated, can compete with conventional glass fiber composites, because of the more favorable price, lightness and environmental performance of the composite (Mohanty *et al.*, 2005; Kim *et al.*, 2009; Mirbagheri *et al.*, 2007).

1.2.1. Kenaf fibers

Kenaf fibers have good thermal properties, low density, and they are cheap, lightweight, abundant, environmentally friendly, and low impact to climate change as a perennial plant. However, if natural fibers are used in combination with plastic polymers, the resulted composites would have low tensile strength values and poor interfacial adhesion because of incompatibility between the kenaf fibers and plastic (Yussuf *et al.*, 2010).

1.2.2. Poly(lactic acid) (PLA)

Among bio-based polymers, poly(lactic acid) (PLA) is a versatile biodegradable polyester produced from starch-rich biomaterials such as corn, beet and wheat. It is eco-friendly, renewable, recyclable, and is one of the most abundantly produced biodegradable polymers. This polymer has received much attention as a good substitution of petroleum products. Though this biodegradable polymer has easy processability, good strength, gloss, transparency and good stiffness, its use is limited due to high price, brittleness, and low thermal properties and so on. To be applied as end products, the composites need to make up for the shortcomings (Sukyai *et al.*, 2012; Oksman *et al.*, 2003).

1.3. Chemical treatment

1.3.1. Acetylation

In order to compensate for the defect of fibers, various chemical treatments had been studied. Among the chemical modifications, acetylation is one of commonly used methods, where -OH groups which show hydrophilic properties of cellulose are modified by hydrophobic acetyl groups (Hu *et al.*, 2010; Ismail *et al.*, 2011). For example, acetylation can be used to control hygroscopic property, dimensional stability, durability, and physical properties. This chemical modification strategy is regarded as an inexpensive, simple method in order to lower the high surface energy characteristics of natural fibers (Ifuku *et al.*, 2010).

2. Literature reviews

2.1. Bio-composites composed of PLA and kenaf fibers

Ochi *et al.* (Ochi, 2008) reported fabrication of PLA/kenaf biodegradable composites using kenaf fiber and PLA resin. The fabrication of plastic materials that has high-strength requires the kenaf fibers as a reinforcement to be obtained from the section of the plants closest to the ground. Biocomposites fabricated of 70 wt % kenaf fibers in an emulsion-type PLA resin were reported to show tensile and flexural strengths of 223 MPa and 254 MPa.

Yussuf *et al.* (Yussuf *et al.*, 2010) reported that rice husk and kenaf fibers were used to prepare PLA composites with cellulose. In addition, mechanical and thermal properties of the composites were evaluated. It was found that the flexural modulus of pure PLA polymer was significantly increased when filled with both kenaf and rice husk fibers; however, the flexural and impact strengths rather decreased than pure PLA polymer. Also, thermal stability of the virgin PLA was decreased by addition of kenaf and rice husk.

2.2. Improvements of interfacial adhesion

2.2.1. Acetylation of reinforcement filler

Jonoobi *et al.* (Jonoobi *et al.*, 2009) reported kenaf fibers was acetylated to produce fibers changed from hydrophilic to hydrophobic more and more. The acetylated nanofibers formed stable suspensions in solvent like ethanol and acetone, but the non-modified nanofibers indicated a slow sedimentation. Microscopic studies revealed that kenaf fibers were swelled via acetylation, and this swelling might expedite isolation of nanofibers. The TEM study showed that diameters of the acetylated nanofibers were slightly smaller (10-20 nm) than non-modified nanofibers (10-30 nm). It can be considered that the smaller size might be a result of lower aggregation of nanofibers during drying because their properties were changed to more hydrophobicity.

Ismail *et al.* (Ismail *et al.*, 2011) reported that kenaf core fibers was modified via acetylation, and it proved that acetylated kenaf core filler improved the mechanical properties of composites composed of HDPE/(soya powder)/(kenaf core).

3. Objectives

3.1. Improvements of interfacial adhesion of PLA composites composed of acetylated kenaf

The main purpose of this study is to fabricate the eco-friendly composites that had price reduction, mass production, and high physical properties.

It is difficult to obtain uniform dispersion and interfacial compatibility due to the hydrophobicity of PLA and the hydrophilicity of cellulose. Another shortcoming of natural fiber-filled composites is the possible reduction in mechanical properties when fibers are swollen upon uptake of moisture. In order to make up for fibers' fault and improve interfacial adhesion between the matrix polymer and fibers, pretreatment of reinforcement filler is one way to alter the properties of fiber surfaces. Acetylation as one of chemical treatments is environmental and easy method as well as inexpensiveness. Fibers modified via acetylation is to be hydrophobic, and interfacial adhesion of the PLA composites with acetylated kenaf is to be also improved because of elimination somewhat $-OH$ groups of fibers. In addition, solvent free acetylation used in this experiment is more eco-friendly treatment method than chemical acetylation method as previously used.

Biocomposites containing acetylated kenaf with enhanced interfacial adhesion are anticipated to have higher physical, mechanical and thermal properties compared to PLA composites composed of non-treated fibers. Therefore, this study is to substitute to acetyl groups from $-OH$ groups of fibers and to get the optimum point via different reaction time.

4. Experimental

4.1. Materials

The PLA granules with an average diameter of 81 μm and a density 1.24 g/cm^3 were supplied by NatureWorks LLC, USA. Its melt-flow rate, melt temperature and glass transition temperature were, respectively, 4~8 g/10 min (190 °C /2160 g), 140~152 °C and 56.7~ 57.9 °C (Table 1).

The kenaf fibers used as natural fillers were bast fibers donated by Sutongsang Company, Republic of Korea; it was reduced to a size of 40 mesh through a pulverizer machine before compounding. Acetic anhydride was purchased from Samchun Chemical Company, Republic of Korea and it was used to substitute -OH groups of cellulose. Pyridine used as catalyst was supplied by Daejung Chemical Company, Republic of Korea.

Table 1. The property of PLA polymer

Typical Material & Application Properties (NatureWorks LLC.)	
Physical properties	PLA polymer 2002D
Specific gravity	1.24
Melt index, g/10 min (190 °C/2.16 K)	4-8
Clarity	Transparent
Mechanical properties	
Tensile strength @ break, psi (MPa)	7,700 (53)
Tensile yield strength, psi (MPa)	8,700 (60)
Tensile modulus, kpsi (GPa)	500 (3.5)
Tensile elongation, %	6.0
Notched IZOD impact, ft-lb/in	0.24 (12.81)
Shrinkage is similar to PET	

4.2. Methods

4.2.1. Acetylation

Prior to acetylation, the kenaf fibers were dried for 24 h at 80 °C to remove excess moisture. They were then stored in polyethylene bags in order to avoid penetration of water vapor. To perform the acetylation experiment, a sample of 40 g oven-dried fibers was placed in a 1 L four-neck flask equipped with a condenser and a stirrer. A 400 mL volume of acetic anhydride was transferred into the flask and mixed with kenaf under slow stirring for 30 min. Then, 0.01 mol of pyridine was added as a catalyst to ensure that the fibers react with the chemical reagent. The reaction was carried out for various time durations under reflux condition. Afterward, 300 mL of distilled water was added and the flask was immersed in an ice bath for 15 min in order to change unreacted acetic anhydride to acetic acid and also to avoid reactions among acetic acids. The treated fibers were recovered by filtration using an aspirator. A washing step was then carried out by adding 80 % ethanol solution to the recovered fibers followed by a 30 min mixing, after which the mixture was filtered to remove unreacted acetic anhydride and also newly formed acetic acid. This washing process was repeated twice. The final samples were dried in a vacuum oven at 60 °C overnight.

4.2.2. Compounding PLA/kenaf composites

PLA was dried at 80 °C for 24 h and stored in polyethylene bags. The desired contents of PLA and kenaf (70:30 mass ratio) in the biocomposites were identified from mechanical properties of samples prepared in a preliminary trial. The compounding was performed using a laboratory sized twin-screw extruder (BA-19 in Bautek, Republic of Korea). The barrel temperature (in Celsius) zone of the extruder was as follows: 175/175/185/185/185/175/155/140. The screw speed was maintained at 150 rpm. The extrudate was cooled in a water bath and pelletized using a pelletizer. Extruded pellets were dried for 4 h at 80°C and stored in sealed polyethylene bags to protect moisture penetration. Table 2 shows the blend ratio of biocomposites examined in this research. In addition, Figure 1 shows the manufacturing process of PLA/kenaf composite.

Table 2. Blend ratio of biocomposite specimens

Samples	Based Material (wt %)	Reinforcing Material (wt %)	Time of Acetylation (hrs)
PLA	PLA (100)	-	-
PLA/KFAc-0	PLA (70)	kenaf fibers (30)	-
PLA/KFAc (0.5, 1, 2, 3)	PLA (70)	Acetylated kenaf fibers (30)	0.5, 1, 2, and 3

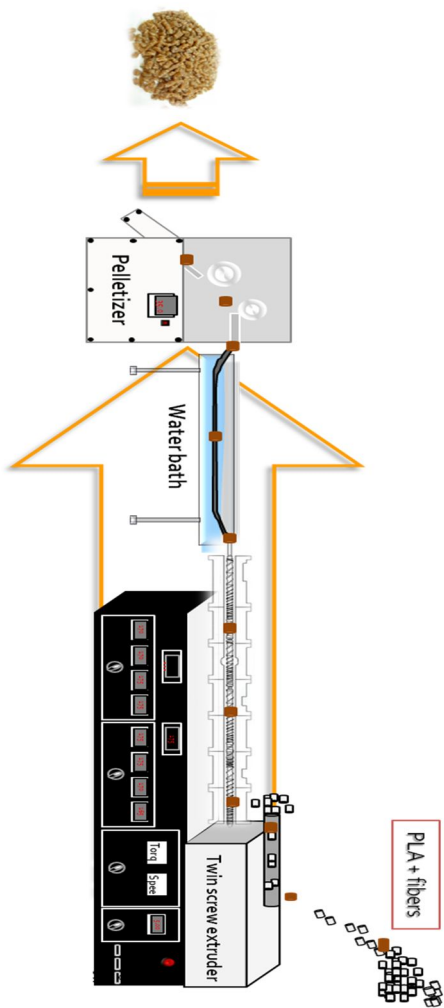


Figure 1. Manufacturing process of PLA/kenaf composite.

4.2.3. Injection molding

The dried extruded pellets are fabricated to samples of tensile, flexural and impact test through injection molding machine (Bautek, Republic of Korea). The conditions of temperature for injection molding are maintained at 190 °C.

4.3. Characterization

4.3.1. Chemical characteristics

4.3.1.1. FT-IR (Fourier Transform Infrared Spectroscopy)

Functional groups of kenaf were examined using a FTIR-ATR spectrophotometer (JASCO 6100; USA) in order to analyze the chemical characteristics of the kenaf samples with and without acetylation. The FTIR spectra were collected over the range of $4000 - 650 \text{ cm}^{-1}$ with a spectrum resolution of 4 cm^{-1} . All spectra were averaged over 30 scans.

4.3.1.2. Acetyl content

After drying for 2 h at 105 °C, 0.3 g of dried acetylated kenaf was placed in an Erlenmeyer flask of 100 mL capacity. A volume of 10 mL 75 % ethanol was then added and the flask was heated to 50 – 60 °C for 30 min while stirring. After that, 10 mL of 0.5 M NaOH solution was added to the mixture, and stirred for 15 min at 50 – 60 °C. The mixture was subsequently placed at room temperature for 72 h under constant stirring. At the end of the reaction, the excess alkali was titrated with 0.5 M HCl using phenolphthalein as an indicator. The trace excess of alkali was titrated again after 1 – 2 h. The process was repeated for solutions not containing fiber samples. Then an acetyl content of acetylated fiber was calculated (Jonoobi *et al.*, 2010; Chen *et al.*, 2006):

$$\%acetyl = \frac{(V_a - V_b) \times N_{HCl} \times M_{acetyl}}{m_s} \times 100$$

V_a = the volume of HCl acid consumed for the blank in liters

V_b = the volume of HCl acid consumed for the sample

N_{HCl} = the molarity of the HCl acid

M_{acetyl} = 43 g/mol

m_s = the weight of the sample in grams

4.3.2. Morphology

4.3.2.1. SEM (Scanning Electron Microscopy)

The surface morphology of the samples was examined using a scanning electron microscopy (SNE-3000M, Dream Corp., Republic of Korea). The SEM specimens were attached to aluminum stubs with a carbon tape and dried at 80 °C for 30 min. The specimen surfaces were then coated with gold to eliminate discharging prior to the image analysis.

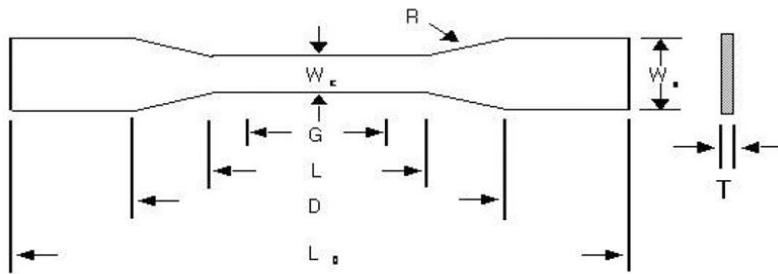
4.3.2.2. FE-SEM (Field Emission – Scanning Electron Microscopy)

Field emission-scanning electron microscopy (FE-SEM, SUPRA 55VP, Carl Zeiss, Germany) at an accelerating voltage of 15 kV is used in order to examine interfacial adhesion between the matrix polymer and filler fibers. Prior to the measurement, all samples are pre-coated with a homogeneous platinum layer (purity, 99.99 %) by ion sputtering to eliminate electron charging.

4.3.3. Mechanical properties

4.3.3.1. Tensile and flexural test

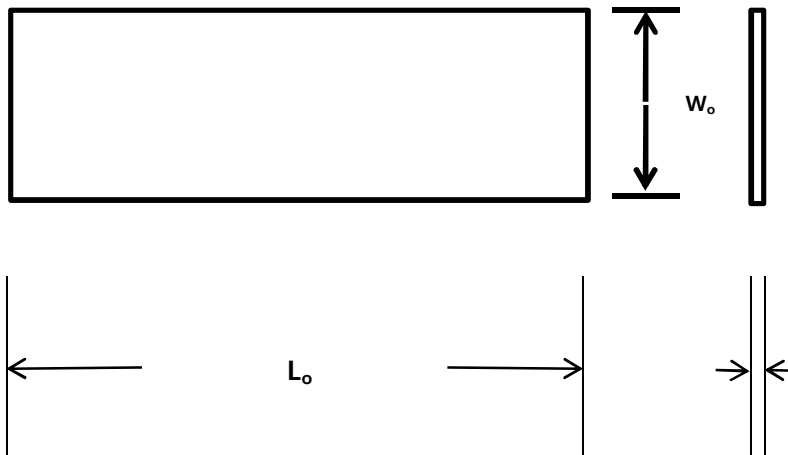
Tensile and flexural analysis is conducted using the universal testing machine (Zwick Co) according to ASTM D 638 – 10 and ASTM D 790 – 10, respectively, at a crosshead speed of 5 mm/min and at room temperature. Five specimens are measured to calculate the margin of error. The size and shape of tensile and flexural samples are indicated in Figure 2.



W_c : 3mm, G : 9mm, L : 12mm, D : 25mm

L_o : 63mm, W_o : 10mm, R : 6mm, T : 3mm

(a) Dimensions of tensile analysis specimen (ASTM D 638 - 10)



L_o : 63.5 $\pm$ 2.0 mm, W_o : 12.7 $\pm$ 0.2 mm T : 3 mm

(b) Dimensions of flexural analysis specimen (ASTM D 790 - 10)

Figure 2. Dimensions of tensile and flexural analysis specimens.

4.3.4. Viscoelastic properties

4.3.4.1. DMA (Dynamic Mechanical Analysis)

The temperature dependence of the dynamic storage modulus (E') and the $\tan \delta$ value of composites was evaluated using a dynamic mechanical analyzer (DMA Q800, TA Instruments) using the dual cantilever mode. Specimens of approximately 60.0 mm in length, 12.0 mm in width, and 3.0 mm in thickness were prepared. The tests were conducted at a strain rate of 0.1 % and a frequency of 1 Hz with a heating rate of 5 °C/min for a temperature range between -20 °C and 140 °C.

4.3.5. Thermal Property

4.3.5.1. TGA (Thermogravimetric Analysis)

TGA measurements were carried out with a thermogravimetric analyzer (TGA 4000, Perkin Elmer Life and Analytical Sciences, USA) on samples from 25 to 600 °C at a heating rate 10 °C /min. The TGA analysis was performed on kenaf/PLA composite specimens placed in a high-quality nitrogen (99.5 % nitrogen, 0.5 °C oxygen) atmosphere with a flow rate of 10 mL/min to avoid oxidation.

4.3.6. Water Absorption

Rectangular specimens (30 mm×12.5 mm×3 mm) were used in the water absorption tests. The specimens were immersed in distilled water at room temperature for up to about 35 days after which they were dried in an oven at 80 °C for 24 h. The percentage of water uptake was calculated according to the following equation (Ichazo *et al.*, 2001):

$$W_{uptake} = \left(\frac{W_t - W_0}{W_0} \right) \times 100$$

- W_0 is the sample's initial weight
- W_t is the sample's weight after immersion time t

5. Results and Discussion

5.1. Mechanical properties

5.1.1. Tensile and flexural test

5.1.1.1. Determination of blend ratio of PLA and kenaf fibers

Figure 3 shows the tensile and flexural strength of PLA composites with various kenaf contents as filler. The tensile strength of pure PLA polymer is about 60 MPa, and tensile strengths of the PLA/kenaf composites are gradually decreased with increasing kenaf content. Because the specific surface area between the hydrophilic kenaf and hydrophobic PLA is increased with kenaf content, poor interface is occurred at higher kenaf content (Yussuf *et al.*, 2010).

The flexural strength of pure PLA polymer is about 114 MPa. However, when only 10 wt% of kenaf was added to the PLA composite, the flexural strength of the PLA/kenaf composite was noticeably increased, unlike the tensile strength. The flexural strength of the PLA/kenaf composite could have been increased because of the stiffness of the fibers in the PLA composite including kenaf, whereas the PLA polymer's flexural strength arises from its viscosity (Agrawal *et al.*, 2000).

The flexural strength did not increase further when more than 10 wt% of kenaf was added; rather, it remained the same or slightly decreased. As previously mentioned, this is due to a decline in the interfacial adhesion resulting from the increase in the specific surface area between the two substances.

The blend ratio of 70:30 was chosen for the composite by considering the economic and processing conditions for a laboratory-scale extruder.

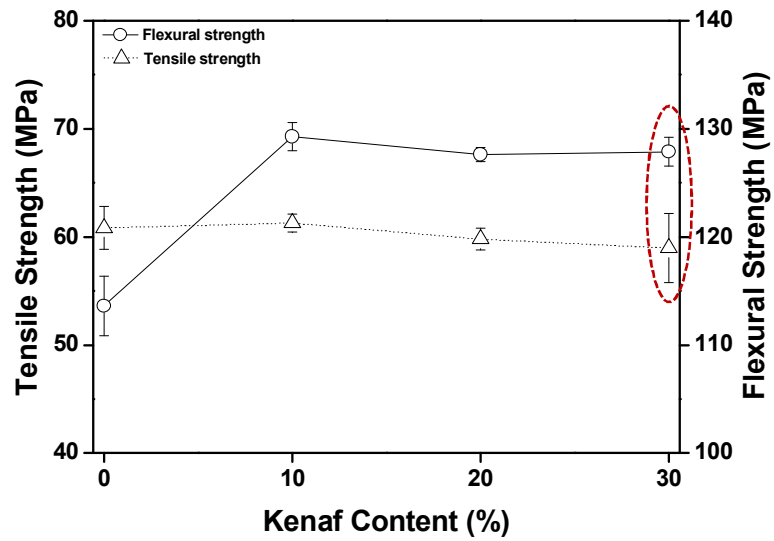


Figure 3. Tensile and flexural strengths of composites with different kenaf content.

5.1.1.2. Tensile and flexural strength of composites via acetylation reaction time

Figure 4 presents the tensile and flexural strength of biocomposites as a function of acetylation reaction time. The non-acetylated kenaf/PLA composite showed tensile and flexural strengths of 58 MPa and 127 MPa, respectively. Upon a brief pre-treatment (0.5 h) of kenaf with acetylation, the composites suffer a loss in strengths. As the kenaf acetylation time was increased, however, the composites were increasingly stronger to eventually, at 2 h acetylation, exceed the strengths of composites containing non-acetylated kenaf.

The reduction in bicomposites strengths as a response to initial acetylation of kenaf is attributable to the partial removal of extractives during the acetylation process. Removal of extractives was commented to be a possible explanation for the weight-percent gain (WPG) being lower than acetyl content of wood at low levels of acetylation (Rowell, 2005); the WPG and acetyl content should be similar if the mass change is merely due to the addition of acetyl groups. Further inferences of extractive removal will be presented later. From the perspective of consequences of extractives removal, the “bleached” fibers could undergo mechanical or/and surface changes to influence their reinforcement effects and/or bonding with PLA.

The enhancement in tensile and flexural strengths of the PLA composites at longer acetylation pre-treatment of kenaf is attributable to the improved kenaf/PLA interaction. Acetylation is known to result in substitution of hydroxyls to make the modified fibers less hydrophilic. If kenaf fibers were made less hydrophilic, their compatibility with PLA would be improved to lead to improvement in adhesion thus also strengths of the resulted composites. No further strength enhancement was observed at acetylation beyond 2 h

probably because the hydroxyl group substitution was increasingly difficult; thus interfacial compatibility was not further improved. To support the aforementioned hypothesis, untreated and acetylated fibers were analyzed using SEM, FT-IR, and titration for acetylation.

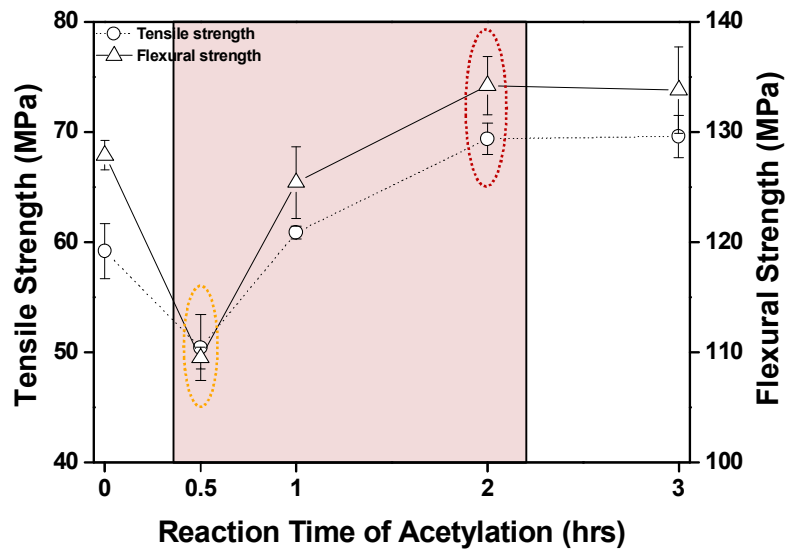


Figure 4. Tensile and flexural strength of composites as a function of acetylation reaction time.

5.2. Morphology

5.2.1. SEM analysis

5.2.1.1. Surface property of kenaf with or without acetylation

Figure 5 shows SEM micrographs of kenaf fibers acetylated for different time durations. As seen for untreated kenaf (Figure 5a), the fiber surface was covered with an unevenly distributed layer similar to the case of olive husk flour reported by Tserki *et al.* (Tserki *et al.*, 2005), who attributed it to the probable presence of waxy substances. After 0.5 h and 1 h acetylation, the fiber surfaces became smoother (Figure 5b and 5c), suggesting the removal of extractive substances, thus supporting the postulation elaborated in the preceding paragraph. Upon longer acetylation (2 h and 3 h; Figure 5d and 5e), the fibers appeared rougher, possibly a result of swelling caused by the pyridine catalysis used for the acetylation reaction. Indeed, pyridine is known to swell and open cell walls of fibers to ease penetration of acetic anhydride (Jonoobi *et al.*, 2009). To summarize the discussion, fiber surface morphology was altered depending on the extent of acetylation; the morphology changes could be related to the chemistry occurring on and in the fibers. In order to support this, results of FT-IR characterization will be discussed next.

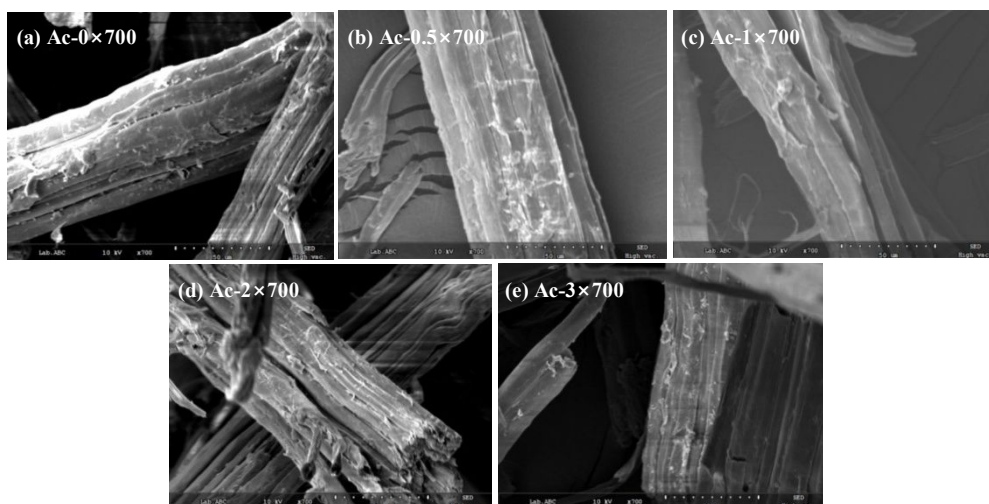


Figure 5. SEM micrographs of kenaf at different acetylation reaction time.

5.3. Chemical characteristics

5.3.1. FT-IR

5.3.1.1. Analysis of functional groups of kenaf with or without acetylation

To confirm whether chemical modification took place in kenaf, the fibers were analyzed by FTIR-ATR. Figure 6 shows FTIR spectra of the kenaf fibers before and after acetylation. The absorption peaks at about 2950 cm^{-1} and 3350 cm^{-1} observed for all fibers correspond, respectively, to the symmetric C-H vibration and hydroxyl (OH) stretching. These are typical peaks of lignocellulose. On the other hand, acetylated fibers showed peaks of 1740 , 1222 , and 1369 cm^{-1} , all of which were not found in the case of untreated fibers. These were peaks generated by the acetyl group as shown in Figure 7. The peak located around 1740 cm^{-1} are attributed to the carbonyl stretching band (C=O) in ester bonds. The two peaks located around 1222 and 1369 cm^{-1} are attributed to the C-CH₃ and C-O stretching bands of acetyl groups (Sun and Sun, 2002). Overall, these three peaks confirm that kenaf had been acetylated. In addition, the absence of the peak around 1700 cm^{-1} means that no detectable acetic acid by-product remained on the fibers after the acetylation treatment. Also, peaks around $1840\sim 1760\text{ cm}^{-1}$ were not observed, suggesting that the fibers were free from unreacted acetic anhydride (Jonoobi *et al.*, 2009).

Figure 8 shows magnified region between $4000\sim 2600\text{ cm}^{-1}$ of the FTIR spectra depicted in Figure 6. The OH peak ($\sim 3350\text{ cm}^{-1}$) of 0.5 h acetylated kenaf was only slightly lower than that of untreated fibers. On the other hand, kenaf modified for 1-3 h exhibited significantly reduced OH peak intensity.

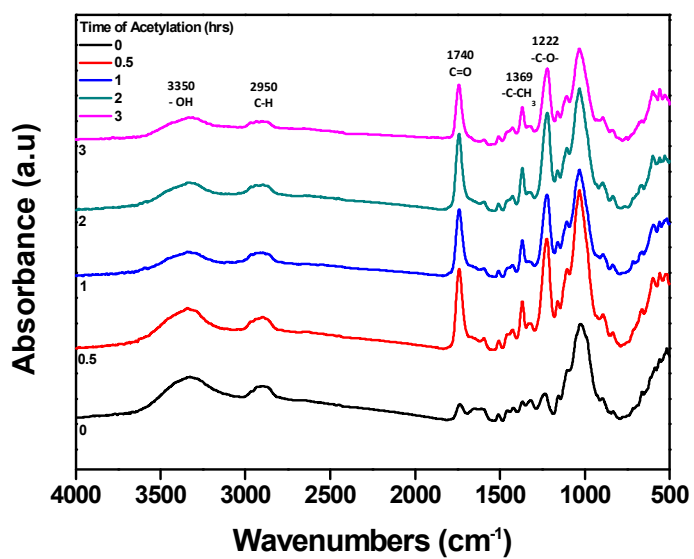


Figure 6. Infrared spectroscopy of untreated and acetylated kenaf fibers.

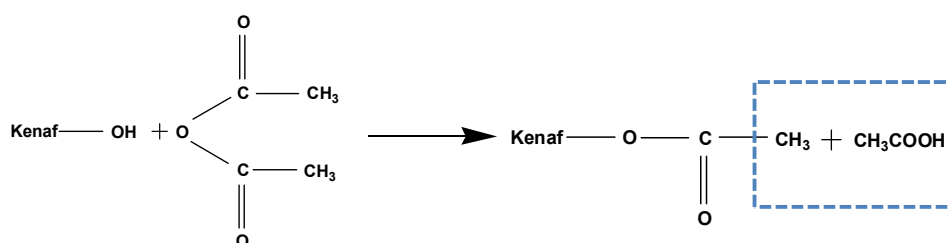


Figure 7. Schematic reaction mechanism of acetylation (Jonoobi *et al.*, 2009).

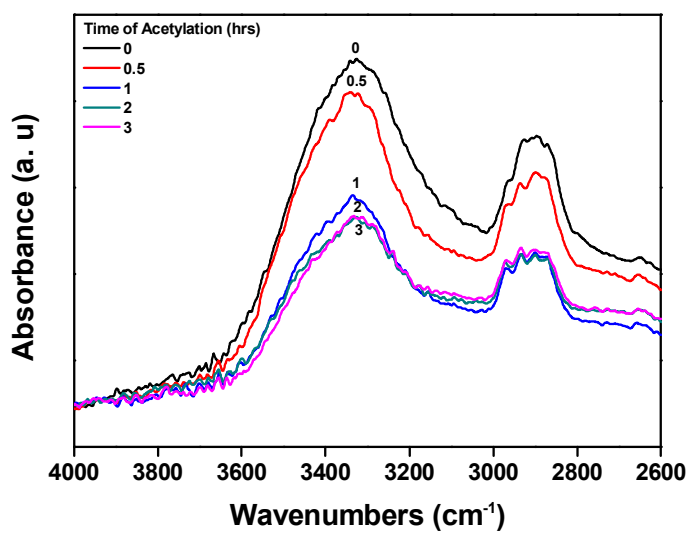


Figure 8. FT-IR analysis of -OH peak between 4000-2600 cm^{-1} for acetylated kenaf fibers.

5.3.2. Acetyl content

Figure 9 shows the degree of acetylation of kenaf fibers. The acetyl content of the fibers for 0.5 h acetylation was the lowest of all (14%), corresponding to the higher hydroxyl availability (lower substitution) of these fibers as revealed from FTIR analysis (Figure 8). These complimentary results, in combination to the surface morphology observation, could explain the reduced strengths of PLA composites containing 0.5 h acetylated kenaf discussed earlier (Figure 4). At the low acetylation level, the benefit of acetylation in improving kenaf/PLA compatibility was not realized, while the accompanying morphology changes (surface smoothening; see Figure 5b) could detrimentally reduce the surface area for bonding and the possibility of mechanical interlocking in adhesion. Figure 9 also shows that as the acetylation time was increased, the acetyl content increased correspondingly until it reached a plateau (28-29%) beyond 2 h treatment. Once again, this result agrees with the behavior of mechanical property changes; (1) compared to 0.5 h acetylated fibers, kenaf modified for 1-3 h contained more acetyl groups, making it more hydrophobic (compatible) for adhesion interaction with PLA, thus improving the strength of PLA composites, and (2) kenaf modified beyond 2 h exhibited no further increase in acetyl content, therefore there was no significant improvement in composite strengths for 3 h acetylation. Overall, it can be concluded that 2 h acetylation time is the optimum when considering the time and energy consumption, and also its mechanical effects on the PLA composites.

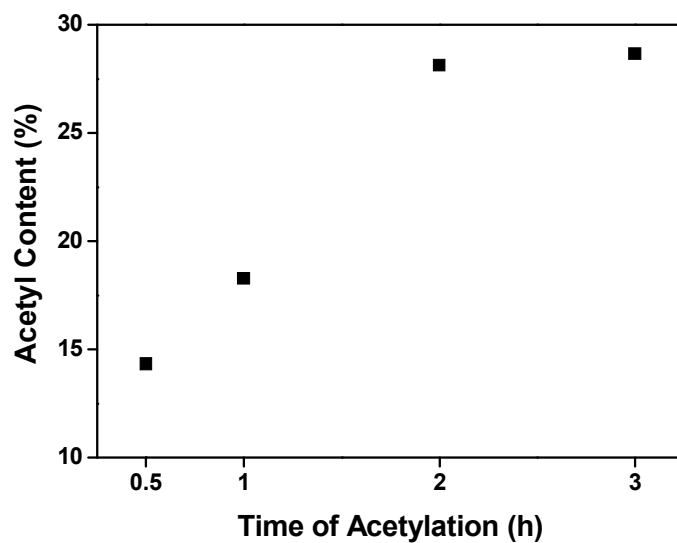


Figure 9. Acetyl content of acetylated kenaf fibers as a function of acetylation reaction time.

5.4. Morphology

5.4.1. FE-SEM analysis

5.4.1.1. Analysis of flexural fractured surfaces of untreated and acetylated kenaf/PLA composites

To examine the degree of adhesion between kenaf and PLA, fractured surfaces of the flexural test specimens of composites were imaged using FE-SEM. As seen in Figure 10a, the untreated kenaf/PLA composite showed rugged surfaces containing numerous voids, indicating that fibers were pulled out from the PLA matrix during flexural tests due to weak interfacial adhesion. PLA composites containing kenaf pre-acetylated for one hour or shorter also indicated similar morphologies (Figure 10c and 10e). Micrographs of higher magnification (Figure 10b, 10d, and 10f) show that the fracture surfaces of the afore-mentioned composites including those of untreated kenaf contained cavities and edges owing to poor interfaces. Poor interfaces are known to impede stress transfer from the polymer to fibers, manifested by compromised strength as the composites are mechanically tested the mechanical strength was decreased because the stress did not transfer from polymer to fiber well (Kim *et al.*, 2011). For PLA composites containing kenaf acetylated for 2 hours or longer, the fractured surfaces were smoother with fewer voids (Figure 10g and 10i). Also, the fibers in these composites appear to be more evenly dispersed in the PLA matrix (depicted in Figure 10h and 10j). These observations collectively signify improved compatibility and adhesion as cell wall hydroxyls were substituted with lower polar acetyl groups (Tomé *et al.*, 2011), leading to improved mechanical strength of the composites.

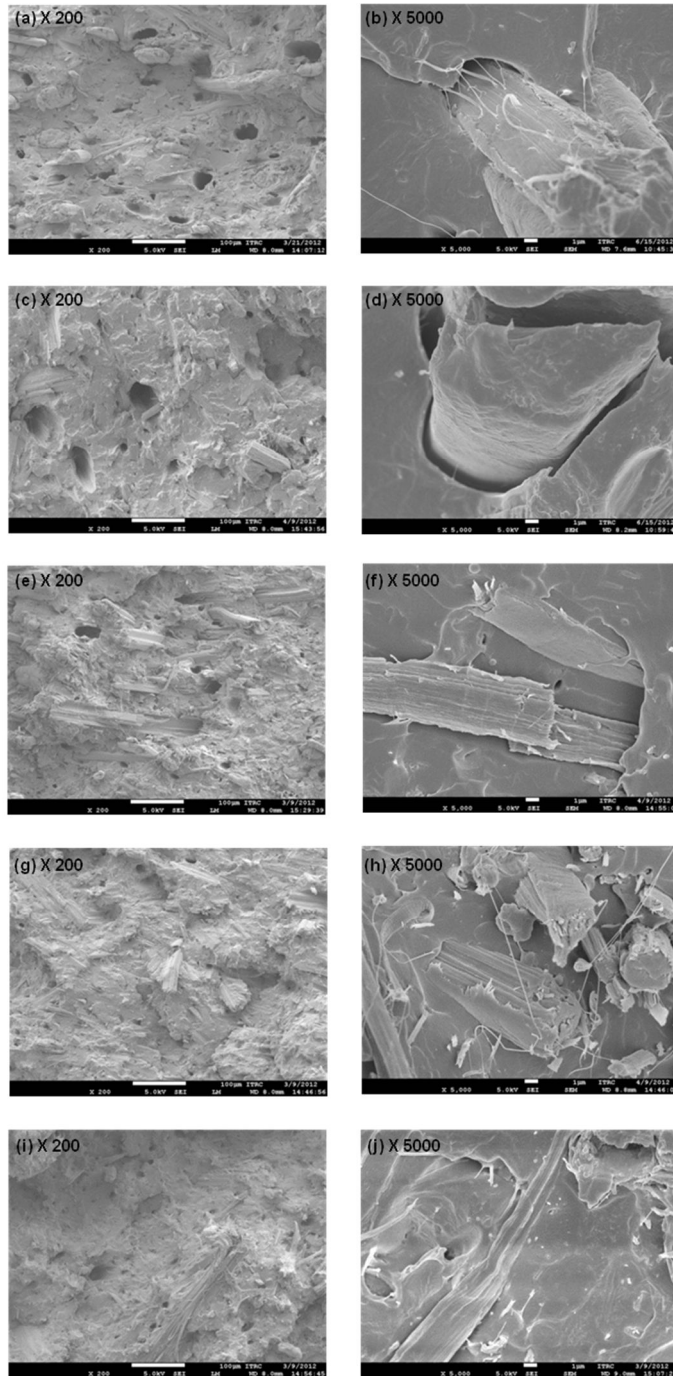


Figure 10. FE-SEM micrographs of flexural fractured surfaces of flexural specimens of untreated and acetylated kenaf/PLA composites.

5.5. Thermal property

5.5.1. TGA analysis

5.5.1.1. TGA analysis of kenaf fibers via acetylation reaction time

Figure 11 shows results of TGA analysis for observing thermal stability of kenaf before and after acetylation. From the residual mass curves, thermal degradation of these fibers could be divided into three stages: 50~110, 250~330, 340~400 °C. The first stage of mass loss (below 110 °C) was due to moisture evaporation (Ismail *et al.*, 2011). At this stage, the mass loss was higher for untreated fibers, followed by fibers acetylated not longer than one hour (see magnified TGA curve in Figure 12a). Little mass loss was observed for fibers that were acetylated longer (i.e., 2 and 3 hours). This observation is related to moisture effects owing to the considerable amounts of available hydroxyls (at zero or low acetylation levels), and is consistent with the trend of fiber acetyl content depicted in Figure 9. At the second stage of mass loss (250~330 °C), the inferred degradation was observed to be higher in untreated kenaf compared to acetylated kenaf (Figure 12a). This degradation is mostly related to decomposition of hemicelluloses and lignin. At the third and most prominent stage of mass loss (at 340~400 °C), untreated fibers were the most severely affected (Figure 12b). This mass loss is mostly due to cellulose degradation and also the continued decomposition of lignin (Tserki *et al.*, 2005; Kabir *et al.*, 2012). The consistently lower mass loss for acetylated fibers compared to untreated fibers is an indication of improved thermal stability imparted by acetylation. The increased thermal stability could also be due to the pre-removal of impurities (during acetylation, as discussed earlier), which are presumably smaller and thermally unstable.

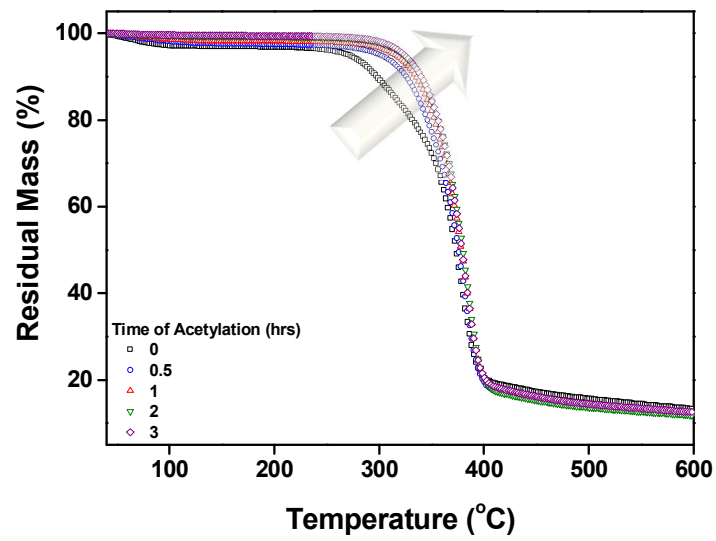


Figure 11. Thermogravimetric curves of kenaf fibers at different acetylation reaction time.

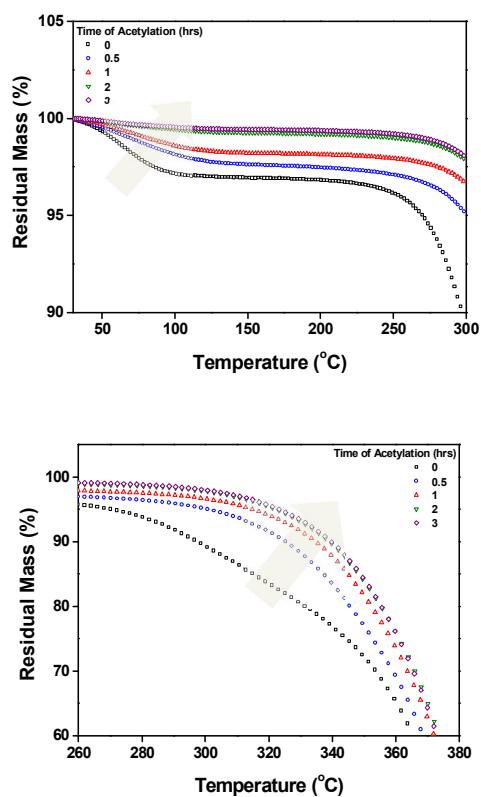


Figure 12. Magnified thermogravimetric curves of untreated and acetylated kenaf (12a top, 12b bottom).

5.5.1.2. TGA analysis of PLA/kenaf composites with or without acetylation

Figure 13 presents TGA results of PLA composites containing either untreated or acetylated kenaf. The thermal stability of composites was altered depending on the degree of fiber acetylation, and this observation agrees with the finding of Tomé *et al.* (Tomé *et al.*, 2011). The untreated-kenaf/PLA composite degraded earlier than composites of acetylated kenaf. As the degree of kenaf acetylation increased, the thermal stability of composites was further enhanced. There are two possible reasons for the increased thermal stability. The first reason is the favorable improvement of interfacial adhesion between fibers and polymer when the hydrophilic group (hydroxyl group) of fibers was substituted by hydrophobic group (acetyl group). The second reason was that the composites contain acetylated kenaf that were more thermally stable, as discussed in the preceding paragraph.

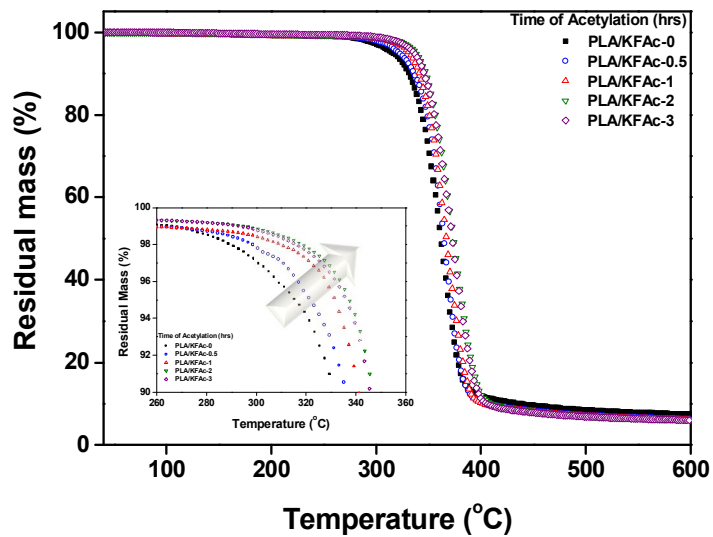


Figure 13. Thermogravimetric curves for PLA composites with untreated and acetylated kenaf.

5.6. Viscoelastic property

5.6.1. DMA analysis

Figure 14 shows the storage moduli of kenaf/PLA composite as a function of temperature based on dynamic mechanical analysis (DMA). The storage moduli of the untreated-kenaf/PLA composite was higher than PLA composites containing briefly (0.5 h and 1 h) acetylated kenaf. The reason was due to poor interfacial bonding as suggested from fractured surface examination of the composites and as reported in another study (Zhou *et al.*, 2009). On the other hand, the storage moduli of PLA composites containing 2 h and 3 h acetylated kenaf were higher than untreated-kenaf/PLA composite. This behavior was due to the improvement of interfacial adhesion as concluded from fractured surface morphology studies of the composites. Figure 15 indicates damping ratio of loss modulus/storage modulus. The damping ratio was lower for PLA composites containing kenaf acetylated for 2 h or longer. This observation can be interpreted as lower mobility of polymer chains attributable to the improved interfacial adhesion. However, glass transition of all composites was not markedly altered.

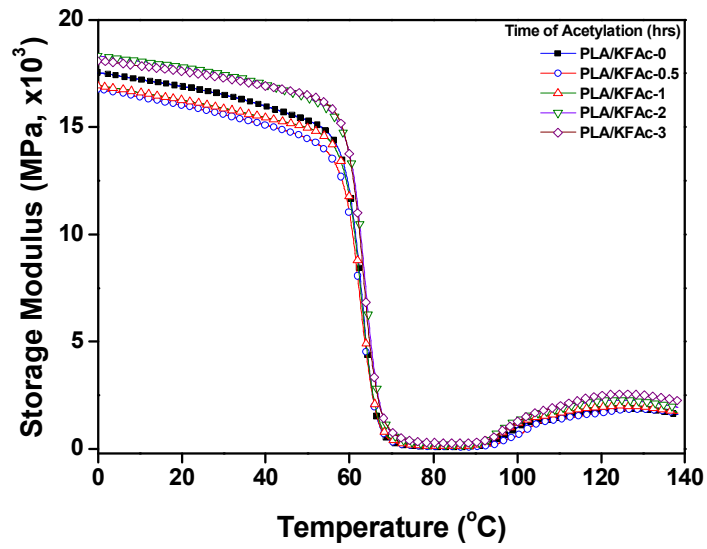


Figure 14. Storage modulus (E') of untreated and acetylated kenaf filled PLA composites.

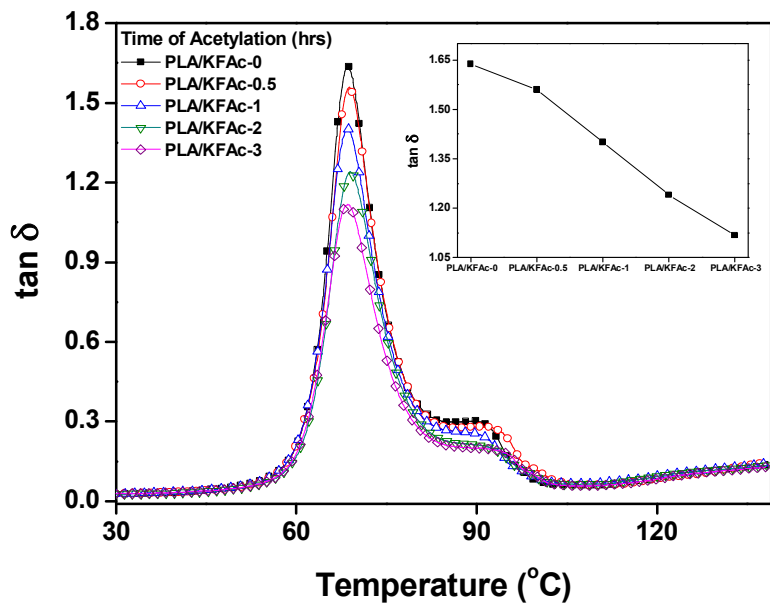


Figure 15. $\tan \delta$ of untreated and acetylated kenaf filled PLA composites.

5.7. Water uptake

The hygroscopicity of composites was evaluated using a water immersion test conducted at room temperature. Figure 16 shows changes of water uptake for untreated- and acetylated-kenaf/PLA composites. All composites showed rapid water absorption on the first day, but the water uptake eventually reached a plateau state, similar to the observation of Philippe *et al.* (Tingaut *et al.*, 2010). PLA composites of acetylated fibers showed a lower rate and extent of water uptake compared to composites of untreated fibers. The reduced affinity of the composites to water was due to the replacement of sorption sites (hydroxyl groups) of the constituting kenaf with acetyl groups. On the other hand, untreated-kenaf/PLA composites showed faster and more absorption of water, and this was due to relatively more hydroxyl availability of the untreated kenaf fibers and poor interfaces (affinity) between fibers and PLA.

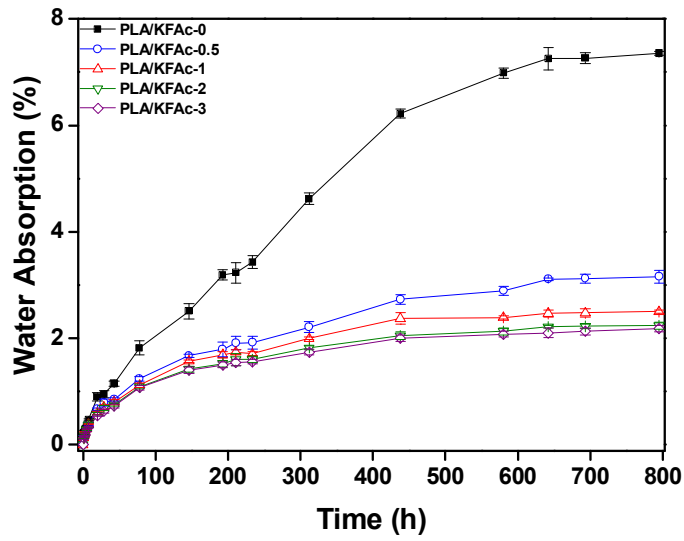


Figure 16. Water uptake of all composites as a function of immersion time.

6. Conclusions

In this study, eco-friendly materials or green composites composed of kenaf and PLA were prepared. Kenaf fibers were made less hydrophilic through acetylation. The flexural and tensile strengths of the kenaf/PLA composites were enhanced when the introduced acetyl constituted around 28% of the mass of fibers. At lower acetylation levels examined in this study, the mechanical properties of composites were either lower or similar to the untreated-kenaf/PLA composites. The detrimental surface smoothening of kenaf upon brief acetylation, as evidenced from morphology studies, was a possible explanation for such mechanical performance. Other contributing factors were the relatively higher hydroxyl availability of the briefly acetylated kenaf (revealed by FT-IR analysis) and the resulted poorer bonding with the more hydrophobic PLA (confirmed by fractured surface analysis of composites). Likewise, the FT-IR and fractured composite surface analyses indicated that sufficient acetylation would effectively reduce hydroxyls thus hydrophilicity of the kenaf to improve its bonding with PLA. The result was therefore an improved mechanical performance (strengths and storage moduli) and also water resistance. As the acetyl content of kenaf was increased, the thermal stability of the fibers and the composites that they formed also increased. The optimum acetylation time examined in this study was two hours, with an acetyl content of 28%.

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초 록

최근 불안정한 원유가격과 이산화탄소 배출 증가에 따른 지구온난화 및 자연환경에서 분해되지 않는 폐플라스틱 처리 등의 문제를 개선하기 위한 연구가 활발히 진행 중에 있다. 이러한 해결책 중 하나로 바이오매스 기반인 바이오소재(바이오플라스틱, 바이오복합재료 등)의 활용은 지속적으로 사용되고 있는 폴리에틸렌, 폴리프로필렌, 폴리스티렌 등과 같은 비분해성 고분자를 대체하기 위함이다.

본 연구에서는 친환경 소재인 바이오복합재료의 제조를 위하여 기질 고분자로 생분해성 고분자인 폴리유산과 그리고 충전제로는 케나프 섬유를 사용하였다. 먼저, 폴리유산/아세틸화 케나프 섬유 복합재료의 인장 및 굴곡 강도를 측정하기 전에 실험실용 압출기의 공정조건과 경제성을 고려하여 폴리유산과 케나프 섬유의 혼합비율은 70 : 30 으로 정하게 되었다.

폴리유산과 케나프 섬유의 상호적합성을 개선하기 위해 케나프 섬유의 표면을 아세틸기로 치환하고 이를 기반으로 폴리유산/아세틸화 케나프 섬유 복합재료를 제작하였다. 아세틸화 반응은 아세틸화 반응의 조건 중 아세트산 안하이드라이드와 피리딘의 양을 동일 조건으로 하였으며 변수로는 반응시간을 다음과 같이 0.5 시간, 1 시간, 2 시간, 3 시간으로 각각 나누어 최적의 시간과 이를 통한 아세틸 함유량에 따른 복합재료의 성능은 평가되었다.

아세틸화된 섬유의 특성을 알기 위하여 FTIR, SEM, 산적정, TGA 측정은 수행되었으며, 이를 통하여 섬유의 화학적 관능기, 표면 변화, 아세틸 함유량, 열적 안정성은 평가되었다. 또한 폴리유산과 아세틸화 케나프

섬유로 구성된 복합재료의 특성을 알아보기 위하여 DMTA, FE-SEM, TGA, 수분 흡수 저항성 실험을 수행하였다.

아세틸 함유량이 18 %이하(반응시간 1 시간 이하)로 구성된 폴리유산/아세틸화 케나프 섬유 복합재료는 기존의 폴리유산/무처리 케나프 섬유 복합재료와 유사하거나 낮은 물성 값을 보였다. 이는 섬유의 하이드록시기는 아세틸기로 적게 치환 되었으며, 이를 통해 추출물 중 하나인 왁스 층은 거의 제거가 되었기 때문이다. 반면에 28 % 이상(반응시간 2 시간 이상) 아세틸 함유량을 가진 폴리유산/아세틸화 케나프 섬유 복합재료의 경우, 섬유의 하이드록시기는 효과적으로 감소되었기 때문에 인장 및 굴곡 강도, 열적 안정성, 수분 흡수율 저항성은 향상되었다. 케나프 섬유의 아세틸화는, 이와 같은 조건을 갖추었을 때 최적 반응시간은 2 시간이며 그때의 아세틸 함유량은 28 % 이었다.

이상과 같이 본 연구는 섬유의 아세틸화 처리를 통해 PLA 고분자와의 상호적합성의 향상을 주었으며 이외에 반응시간의 조건 변수를 주어 그에 따른 최적 점을 구명한 점으로 볼 때 석사학위 논문으로 충분한 가치가 있다고 판단된다.

키워드 : 계면결합, 아세틸화, 케나프 섬유, 폴리유산, 바이오복합재료

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