

## Article

# The Improvement of Mechanical Properties, Thermal Stability, and Water Absorption Resistance of an Eco-Friendly PLA/Kenaf Biocomposite Using Acetylation

Taek-Jun Chung <sup>1,†</sup>, Ji-Won Park <sup>2,3,†</sup> , Hyun-Ji Lee <sup>2</sup>, Hueck-Jin Kwon <sup>2</sup>, Hyun-Joong Kim <sup>2,3,\*</sup>, Young-Kyu Lee <sup>4</sup>  and William Tai Yin Tze <sup>5</sup>

<sup>1</sup> LG Chemistry, 188, Munji-ro, Yuseong-gu, Daejeon 34122, Korea; taekjun@lgchem.com

<sup>2</sup> Laboratory of Adhesion & Bio-Composites, Program in Environmental Materials Science, College of Agriculture and Life-Science, Seoul National University Seoul, Seoul 08826, Korea; roorouny@gmail.com (J.-W.P.); hjilee87@snu.ac.kr (H.-J.L.); hjk00153@snu.ac.kr (H.-J.K.)

<sup>3</sup> Research Institute for Agriculture & Life Sciences, Seoul National University, Seoul 08826, Korea

<sup>4</sup> Indoor Air Quality Analysis Center, National Instrumentation Center for Environmental Management, Seoul National University, Seoul 08826, Korea; woodlee9@snu.ac.kr

<sup>5</sup> Department of Bioproducts & Biosystems Engineering, University of Minnesota, Saint Paul, MN 55108-6130, USA; wtze@umn.edu

\* Correspondence: hjkim@snu.ac.kr; Tel.: +82-2-880-4784

† These authors contributed equally to this work.

Received: 30 January 2018; Accepted: 28 February 2018; Published: 5 March 2018

**Abstract:** As a result of industrialization and environmental pollution, increasing importance is being given to eco-friendly materials and technology. In particular, eco-friendly biocomposites using polylactic acid (PLA) have attracted great interest. In this work, fiber-reinforced composites were investigated in order to enhance the mechanical properties and improve the economic efficiency of PLA. Specifically, composite materials using natural fibers, such as kenaf were actively studied. In the utilization of natural fibers, such as kenaf, the treatment method for increasing the bonding force between the fiber and the matrix is very important. In this study, the surface of kenaf was treated using an acetylation technique, and the PLA composite material was prepared using surface-treated kenaf. Changes in fiber properties were observed with acetylation treatment time. The mechanical properties, thermal stability, and water absorption resistance of the acetylated kenaf and PLA composites prepared for each condition were evaluated. Finally, was concluded that acetylation treatment is effective for improving the performance of PLA/kenaf composites. This behavior was found to relate to the surface cleaning of acetylated kenaf, in addition to the efficient modification of the hydrophilic characteristics of kenaf.

**Keywords:** fibers; interface; interfacial strength; surface treatments; extrusion

## 1. Introduction

In recent years, increasing research attempts have been directed towards addressing environmental problems and the global warming associated with increased CO<sub>2</sub> emissions [1]. Also, due to the increased use of plastic products, disposal and decomposition of waste plastics, as well as the pollution of soils are becoming serious issues. The use of biopolymers such as polylactic acid (PLA), polybutylene succinate (PBS), polyhydroxyalkanoate (PHA), and poly (butylene adipate-co-terephthalate) (PBAT) is an approach towards solving 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 [2].

Among the bio-based polymers, PLA is a versatile biodegradable polyester that is produced from starch-rich biomaterials, such as corn, beet, and wheat. PLA is an environmentally friendly material in terms of energy consumption when compared with conventional petroleum polymers through life cycle assessment (LCA) methodology [3,4]. It is renewable, recyclable, and is one of the most abundantly produced biodegradable polymers. This polymer has received much attention as a good substitute for petroleum-based polymers. Though PLA has easy processability and good strength, gloss, transparency, and stiffness, its use is limited due to its high price and brittleness, as well as its low thermal properties. To be applied as end products, the shortcomings of these composites need to be resolved [5–7].

Kenaf (*Hibiscus cannabinus* L.) is an annual warm season fiber crop and a plant in the Malvaceae family. It is also known as Java jute. Kenaf fibers have good thermal properties and low density, and as a perennial plant they are cheap, lightweight, abundant, environmentally friendly, and contribute little to climate change [8]. There are advantages to using natural fibers (which exist in abundance) to enhance the 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 for materials that are composed of biodegradable or non-biodegradable polymers 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 their more favorable price, lightness, and environmental performance [9–11].

However, if natural fibers were to be used in combination with plastic polymers, the resulting composites would have low tensile strength values and poor interfacial adhesion because of incompatibility between the kenaf fibers and plastics [12–15]. In order to compensate for these disadvantages, various chemical treatments have been studied. Among the chemical modifications, acetylation is one of the most commonly used methods, where the –OH groups that are responsible for hydrophilic properties of lignocellulose are modified by hydrophobic acetyl groups [16]. For example, acetylation can be used to control hygroscopic properties, dimensional stability, durability, and the physical properties of plant-based materials and composites. This chemical modification strategy is regarded as an inexpensive, simple method for lowering the surface energy characteristics of natural fibers to make them more compatible with common polymers [11,17].

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

## 2. Experiment

### 2.1. Materials

PLA granules, with average diameter of 81  $\mu\text{m}$  and density of 1.24  $\text{g}/\text{cm}^3$ , were supplied by NatureWorks LLC (Minnetonka, MN, USA). Their melt flow rate, melt temperature, and glass transition temperature values were, respectively, 4–8 g/10 min (190  $^{\circ}\text{C}$ /2160 g), 140–152  $^{\circ}\text{C}$ , and 56.7–57.9  $^{\circ}\text{C}$ , as per the given data from the manufacturer. The kenaf fibers used as natural fillers were bast fibers donated by the Sutongsang Company (Gyeongju, Korea); they were reduced to a size of 40 mesh through a pulverizer machine before compounding. Acetic anhydride was purchased from the Samchun Chemical Company (Pyeongtaek, Korea), and it was used to substitute –OH groups of cellulose. Pyridine used as catalyst was supplied by the Daejung Chemical Company (Siheung, Korea).

## 2.2. Acetylation of Kenaf Fibers

Prior to acetylation, the kenaf fibers were dried for 24 h at 80 °C in order 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 of 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 at 25 °C. Then, 0.01 mol of pyridine was added as a catalyst to ensure that the fibers reacted with the chemical reagent. The reaction was carried out over various time durations under reflux conditions at 145 °C. 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 the 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 mixing for 30 min, after which the mixture was filtered to remove the unreacted acetic anhydride and also the newly-formed acetic acid. This washing process was repeated twice. The final samples were dried in a vacuum oven at 60 °C overnight.

## 2.3. Fabrication of Composites

### 2.3.1. Compounding of 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 size twin-screw extruder (BA-19 in Bautek, Pocheon, Korea). The barrel temperature zone (in Celsius) 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 was pelletized using a pelletizer. Extruded pellets were dried for 4 h at 80 °C and stored in sealed polyethylene bags to protect moisture penetration. The shape of the fiber has a uniform distribution [18].

### 2.3.2. Preparation of Test Specimens

The dried extruded pellets were fabricated for tensile and flexural test specimens through an injection molding machine (Bautek, Pocheon, Korea). The temperature for injection molding was maintained at 190 °C for 4 min. The main measurement samples were prepared in accordance with American Society for Testing and Materials (ASTM) D 638-10 and ASTM D 790-10, and cut to sizes suitable for each test.

## 2.4. Fiber Characterization

### 2.4.1. Functional Group Analysis

Infrared spectra of a functional group of kenaf fibers were obtained using an fourier-transform infrared spectroscopy (FT-IR) spectrometer (FT/IR-6100, JASCO, Easton, MD, USA) equipped with a Mylar beam splitter and an attenuated total reflectance (ATR) accessory composed of a zinc selenide (ZnSe) crystal (refractive index = 2.4) with a 45° angle of incidence. The spectra were collected from 400 to 4000  $\text{cm}^{-1}$  for 32 scans, with a resolution of 4  $\text{cm}^{-1}$ . All the spectra were corrected through  $\text{CO}_2$  reduction,  $\text{H}_2\text{O}$  reduction, noise elimination, and baseline correction.

### 2.4.2. 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 of 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, the acetyl content of acetylated fiber and degree of substitution (DS) were calculated [19,20]:

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

$V_a$  = 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; and,

$m_s$  = the dried weight of the sample in grams.

$$\text{Degree of substitution (DS)} = \frac{162 \times \%acetyl}{[4300 - (43 \times \%acetyl)]}$$

#### 2.4.3. Scanning Electron Microscopy (SEM)

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

#### 2.4.4. Thermal Stability

Evaluation of pyrolysis characteristics of kenaf fiber were carried out with a thermogravimetric analysis (TGA 4000, PerkinElmer Life and Analytical Sciences, Waltham, MA, USA) on samples from 25 to 600 °C at a heating rate 10 °C/min. The TGA analysis was performed on kenaf–acetylated kenaf specimens/PLA–kenaf composites 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.

### 2.5. Composite Characterization

#### 2.5.1. Field Emission Scanning Electron Microscopy (FESEM)

A field emission scanning electron microscope (FESEM, SUPRA 55VP, Carl Zeiss, Oberkochen, Germany) at an accelerating voltage of 15 kV was used to examine interfacial adhesion between the matrix polymer and filler fibers. Prior to measurement, all of the samples were pre-coated with a homogeneous platinum layer (purity, 99.99%) by ion sputtering to eliminate electron charging. Samples were taken after measuring flexural strength.

#### 2.5.2. Mechanical Properties

Tensile and flexural tests were conducted using the universal testing machine (AllroundLine Z010, 2000N load cell, Zwick, Ulm, Germany) 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 were measured to determine the average and data distribution.

#### 2.5.3. Viscoelastic Properties

The temperature dependence of the dynamic storage modulus ( $E'$ ) and the  $\tan \delta$  value of composites were evaluated using a dynamic mechanical analyzer (DMA Q800, TA instruments) with 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.

### 2.5.4. Water Uptake

Rectangular specimens ( $30 \times 12.5 \times 3$  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  $80^\circ\text{C}$  for 24 h. The percentage of water uptake was calculated according to the following equation [21]:

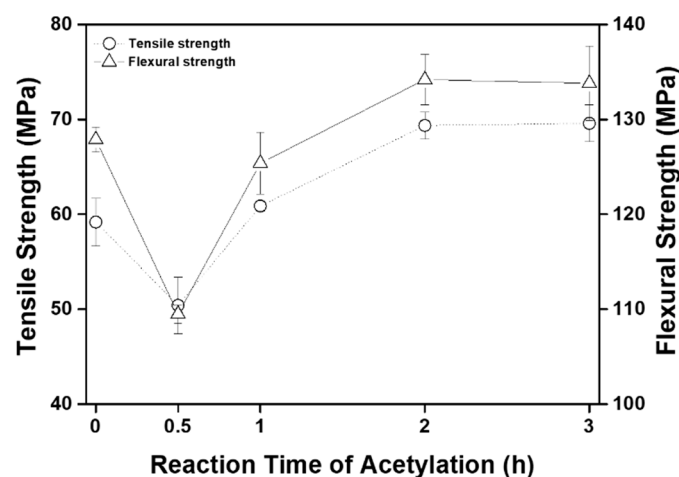
$$W_{\text{uptake}} = \left( \frac{W_t - W_0}{W_0} \right) \times 100$$

– $W_0$  is the sample's initial weight; and,

– $W_t$  is the sample's weight after immersion time  $t$ .

## 3. Results and Discussion

Figure 1 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 suffered a loss in strength. As the kenaf acetylation time was increased, however, the composites were increasingly stronger and eventually, at 2 h acetylation, had strengths exceeding those of composites containing non-acetylated kenaf.



**Figure 1.** Tensile and flexural strength of composites as a function of acetylation reaction time.

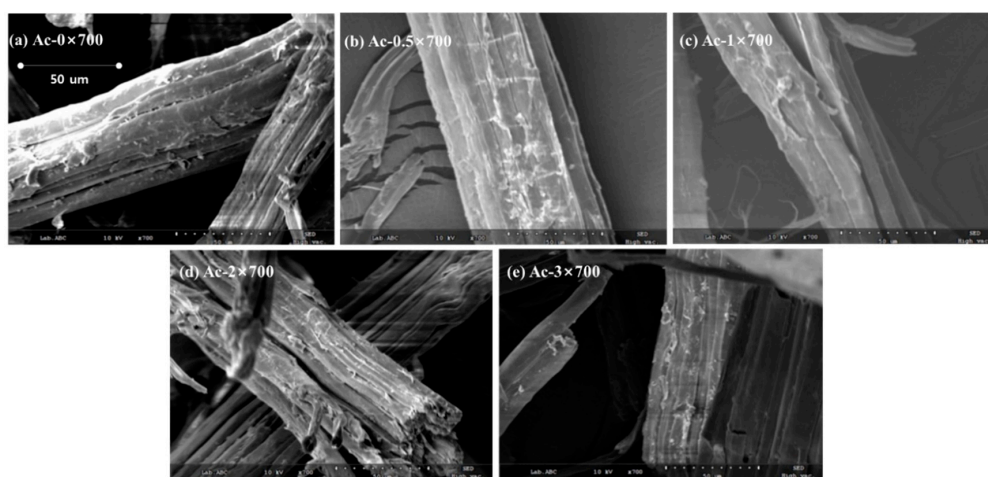
The reduction in biocomposite strength as a response to initial acetylation of kenaf is attributable to the partial removal of extractives during the acetylation process. Removal of extractives was reported to be a possible explanation for the weight percent gain (WPG) being lower than acetyl content of wood at low levels of acetylation [22,23]; the WPG and acetyl content should be similar if the mass change is merely due to the addition of acetyl groups. Further inferences in extractive removal will be presented later. From the perspective of the consequences of extractive 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 with longer acetylation pre-treatment of kenaf is attributable to the improved kenaf–PLA interaction. Acetylation is known to result in the substitution of hydroxyls to make the modified fibers less hydrophilic. If kenaf fibers were made less hydrophilic, their compatibility with PLA would be improved, leading to an enhancement in adhesion, and thus also the strength of the resulting 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 afore-mentioned hypothesis, untreated and acetylated fibers were analyzed using SEM, FTIR, and titration for acetylation.

Figure 2 shows SEM micrographs of kenaf fibers acetylated for different time durations. As seen for untreated kenaf (Figure 2a), the fiber surface was covered with an unevenly distributed layer that is similar to the case of olive husk flour reported by Tserki et al. [24], who attributed it to the probable presence of waxy substances. After 0.5 h and 1 h of acetylation, the fiber surfaces became smoother (Figure 2b,c), suggesting the removal of extractive substances, thus supporting the postulation elaborated in the preceding paragraph. Upon longer acetylation (2 h and 3 h; Figure 2d,e, respectively), the fibers appeared rougher, possibly as a result of swelling that was caused by the pyridine catalysis used for the acetylation reaction. Indeed, pyridine is known to swell and open cell walls in fibers to ease penetration of acetic anhydride [19,25]. In summary, 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 FTIR characterization will be discussed next.



**Figure 2.** Scanning Electron Microscopy (SEM) micrographs of kenaf with different acetylation reaction times.

To confirm whether chemical modification took place in kenaf, the fibers were analyzed by FTIR-ATR. Figure 3 shows the FTIR spectra of the kenaf fibers before and after acetylation. The absorption peaks at about  $2950\text{ cm}^{-1}$  and  $3350\text{ cm}^{-1}$  observed for all of the fibers correspond, respectively, to symmetric C-H vibration and hydroxyl (OH) stretching. These are typical peaks of lignocellulose. On the other hand, acetylated fibers showed peaks at  $1740\text{ cm}^{-1}$ ,  $1369\text{ cm}^{-1}$ , and  $1222\text{ cm}^{-1}$ , none of which were found in the case of untreated fibers. The peaks located around  $1740\text{ cm}^{-1}$  are attributed to the carbonyl stretching band (C=O) in ester bonds. The two peaks that are located around  $1222\text{ cm}^{-1}$  and  $1369\text{ cm}^{-1}$  are attributed to the C-CH<sub>3</sub> and C-O stretching bands of acetyl groups [17,26]. Overall, these three peaks confirm that kenaf had been acetylated. In addition, the absence of the peak around  $1700\text{ cm}^{-1}$  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 [19]. 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 4 shows the degree of acetylation of kenaf fibers. The acetyl content of the fibers for acetylation of 0.5 h was the lowest of all (14%), corresponding to the higher hydroxyl availability (lower substitution) of these fibers, as revealed from FTIR analysis (Figure 3). These complementary results, in combination to the surface morphology observation, could explain the reduced strengths of the PLA composites containing 0.5 h acetylated kenaf discussed earlier (Figure 1). With low

acetylation levels, there were no benefits with respect to improved kenaf–PLA compatibility, while the accompanying morphology changes (surface smoothening; see Figure 2b) could detrimentally reduce the surface area for bonding and the possibility of mechanical interlocking in adhesion. Figure 4 also shows that, as the acetylation time was increased, the acetyl content increased correspondingly until it reached a plateau (28–29%) beyond 2 h of treatment. Once again, this result is in accordance with the mechanical property changes: (1) when 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, and therefore there was no significant improvement in composite strength with 3 h of acetylation. Overall, it can be concluded that acetylation for 2 h is optimal when considering time and energy consumption, as well as the mechanical effects on the PLA composites. The DS max of cellulose is 3. It was confirmed that the total DS is calculated through the mass change of the acetylation part, and finally, it increases to 1.5. This means that about 50% of the OH group is acetylated. DS can be used as an index for various composite materials [27]. Since there is too much damage to the fiber to increase the DS, an unconditionally high DS is not effective.

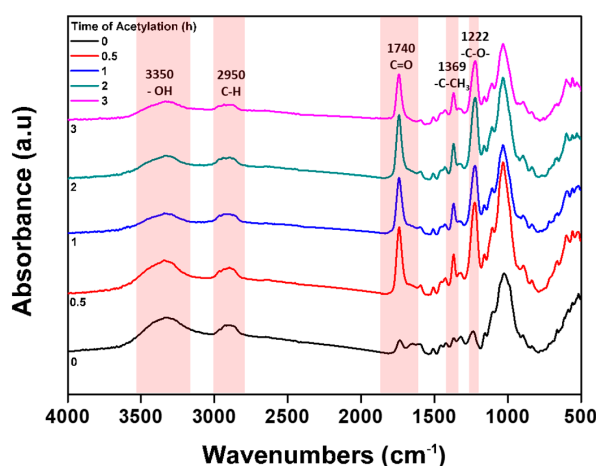


Figure 3. Infrared spectroscopy of untreated and acetylated kenaf fibers.

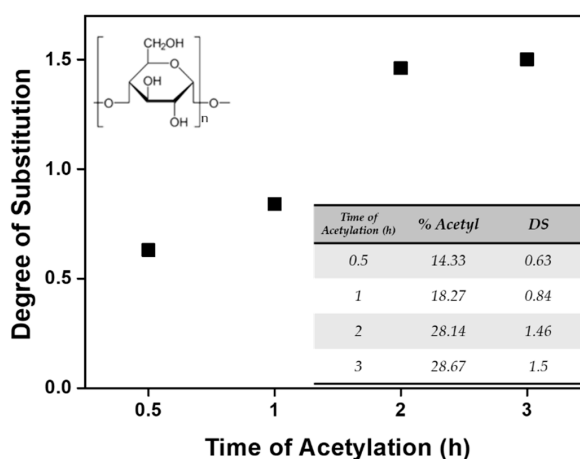
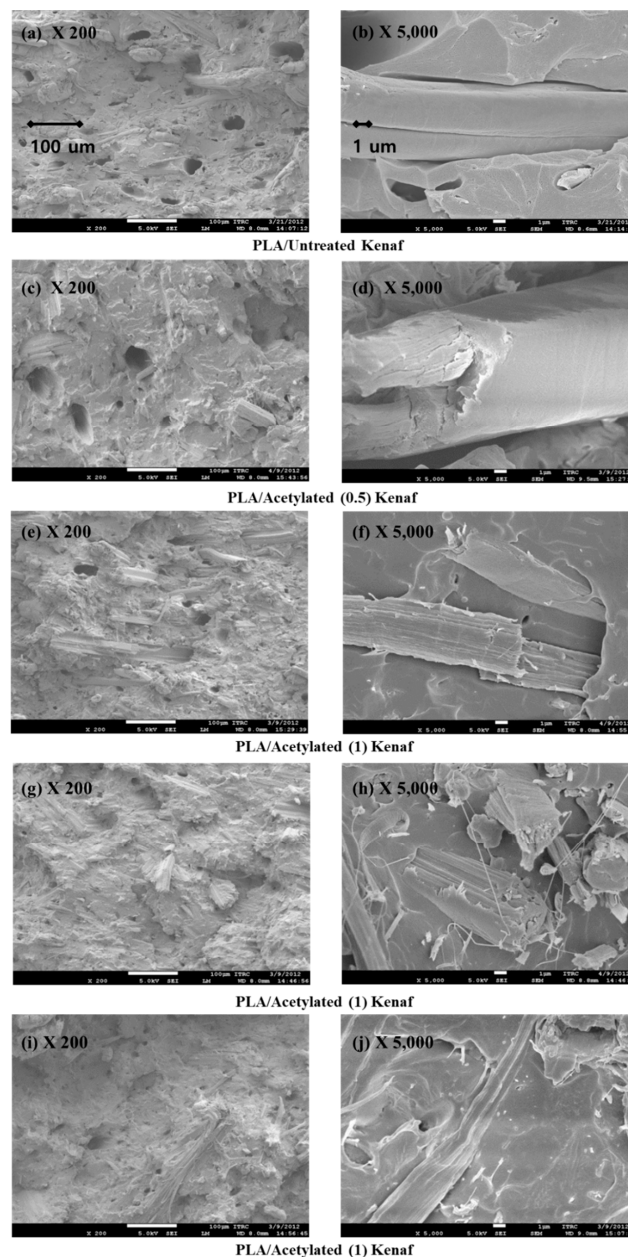


Figure 4. Acetyl content of acetylated kenaf fibers as a function of acetylation reaction time.

To examine the degree of adhesion between kenaf and PLA, fractured surfaces of the flexural test specimens of composites were imaged using FESEM. As seen in Figure 5a, 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 5c,e). Micrographs of higher magnification (Figure 5b,d,f) show the fracture surfaces of the afore-mentioned composites, including those of untreated kenaf containing cavities and edges, owing to poor interfaces. Poor interfaces are known to impede stress transfer from polymers to fibers. This manifests through compromised strength—when the composites are mechanically tested, the mechanical strength is decreased. This is because the stress does not transfer from the polymer to fiber well [28]. For PLA composites containing kenaf acetylated for 2 h or longer, the fractured surfaces were smoother, with fewer voids (Figure 5g,i). Also, the fibers in these composites appeared to be more evenly dispersed in the PLA matrix (depicted in Figure 5h,j). These observations collectively signify improved compatibility and adhesion, as cell wall hydroxyls were substituted with lower polar acetyl groups [29], leading to improved mechanical strength of the composites.



**Figure 5.** Field Emission Scanning Electron Microscopy (FESEM) micrographs of flexural fractured surfaces of flexural specimens of untreated and acetylated kenaf–polylactic acid (PLA) composites.



Figure 6 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, and 340~400 °C. The first stage of mass loss (below 110 °C) was due to moisture evaporation [11]. At this stage, the mass loss was higher for untreated fibers, followed by fibers that were acetylated for not longer than one hour. Little mass loss was observed for fibers that were acetylated longer (i.e., 2 and 3 h). 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 [30] depicted in Figure 6. At the second stage of mass loss (250~330 °C), the inferred degradation was observed to be higher in untreated kenaf when compared to acetylated kenaf. This degradation is mostly related to the 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. This mass loss is mostly due to cellulose degradation and also the continued decomposition of lignin [24]. 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. Table 1 shows the main pyrolysis temperatures. The temperature at the initial 5% pyrolysis point varies by up to 50 °C depending on the acetylation treatment. This can be interpreted as a result of surface foreign matter decomposition and the removal of moisture mentioned above. The 10% decomposition point also shows a large difference. The stability on the surface increases. However, the 50% decomposition temperature is not significantly different. If the temperature exceeds a certain level, then the main cellulose chain is decomposed.

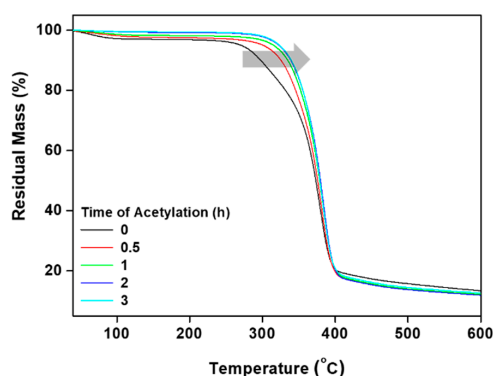


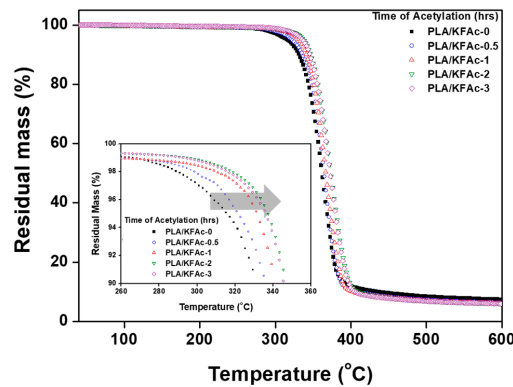
Figure 6. Thermogravimetric curves of kenaf fibers at different acetylation reaction times.

Table 1. Temperature by main pyrol.

Weight Loss Point			
Time of Acetylation (h)	T <sub>D5%</sub> (°C)	T <sub>D10%</sub> (°C)	T <sub>D50%</sub> (°C)
0	270.2	297.4	373.3
0.5	300.51	325.4	375.8
1	315.11	334.7	378.5
2	322.43	338.9	379.7
3	323.41	339.5	379

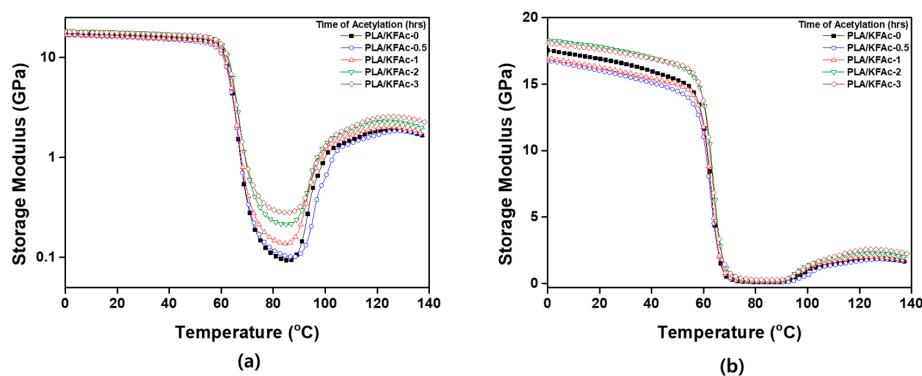
Figure 7 presents the TGA results of PLA composites containing either untreated or acetylated kenaf. The thermal stability of composites was altered depending on the degree of fiber acetylation, and this observation is in accordance with the findings of Liliana et al. [29]. The untreated kenaf–PLA composite 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 polymers when the hydrophilic group (hydroxyl group) of fibers was substituted by the hydrophobic (acetyl) group. The second reason was that the composites contain acetylated kenaf that were more thermally stable, as discussed in the preceding paragraph. These results are directly related to changes in the thermal decomposition properties of the preceding kenaf (Figure 6). Since the initial thermal decomposition temperature of the acetylated kenaf greatly increases, the initial thermal decomposition temperature of the composite material also increases accordingly.



**Figure 7.** Thermogravimetric curves for PLA composites with untreated and acetylated kenaf.

Figure 8 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 by an examination of the fractured surfaces of the composites (Figure 5) and as reported in another study [31]. On the other hand, the storage moduli of PLA composites containing kenaf acetylated for 2 h and 3 h were higher than for the untreated kenaf–PLA composite. This behavior was due to the improvement of interfacial adhesion, as concluded from fractured surface morphology studies of the composites. However, in the high-temperature region (over 60 °C), the lowest modulus is obtained when using kenaf without acetylation treatment. The modulus of PLA rapidly decreases after the glass transition temperature ( $T_g$ ) region, and the modulus of elasticity changes abruptly, according to the degree of interaction with kenaf. As acetylation treatment strengthens the interaction with PLA, the decrease in elastic modulus becomes smaller. Figure 9 indicates damping ratio of the 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 transitions of all the composites were not markedly altered.



**Figure 8.** Storage modulus ( $E'$ ) of untreated and acetylated kenaf-filled PLA composites. (a) Log scale; (b) Linear scale.

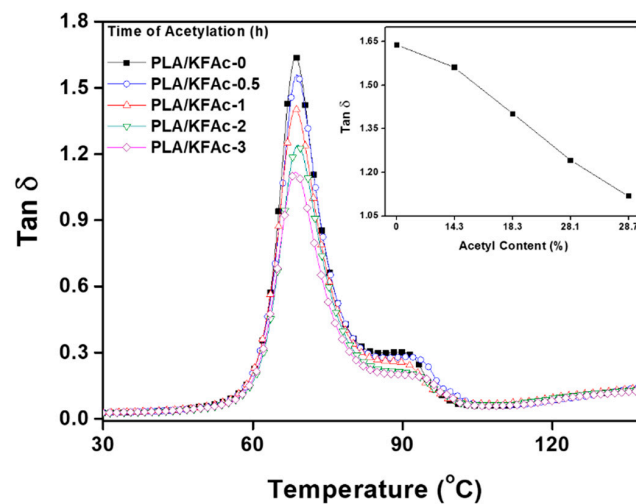


Figure 9. Tan  $\delta$  of untreated and acetylated kenaf-filled PLA composites.

The hygroscopicity of composites was evaluated using a water immersion test conducted at room temperature. Figure 10 shows changes in water uptake for untreated and acetylated kenaf–PLA composites. All of the composites showed rapid water absorption on the first day, but the water uptake eventually reached a plateau state, similar to that observed by Philippe et al. [32,33]. Since the water absorption rate of PLA is less than 1%, the overall result can be interpreted as a result of water absorption of kenaf or water absorption at the interface of PLA/kenaf [34]. PLA composites of acetylated fibers showed a lower rate and extent of water uptake when 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 greater hydroxyl availability of the untreated kenaf fibers, and poor interfaces (affinity) between fibers and PLA.

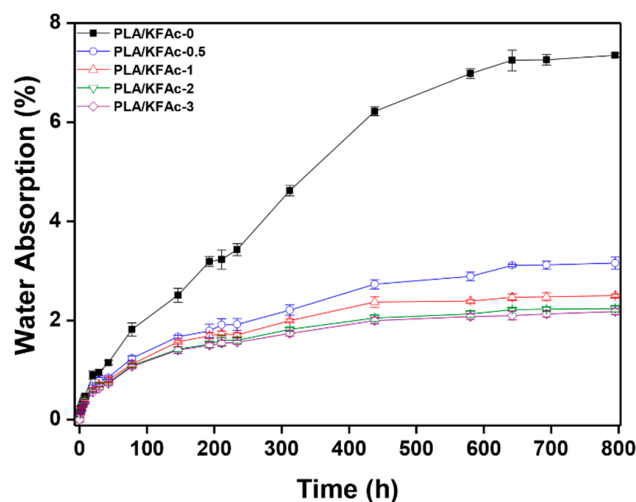


Figure 10. Water uptake of all composites as a function of immersion time.

#### 4. 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 over

25% of the mass of fibers. With respect to the lower acetylation levels that were examined in this study, there was no improvement in the mechanical properties as compared with 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 FTIR analysis) and the resulting poorer bonding with the more hydrophobic PLA (confirmed by fractured surface analysis of composites). The FTIR and fractured composite surface analyses indicated that sufficient acetylation would effectively reduce the number of hydroxyls (and thus the hydrophilicity of the kenaf) in order to improve bonding with PLA. The result was therefore an improved mechanical performance (strengths and storage moduli), and also water resistance. As the acetylation time 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. In these conditions, the acetylation DS is 1.5.

**Acknowledgments:** This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0009390).

**Author Contributions:** Taek-Jun Chung and Hyun-Joong Kim conceived and designed the experiments; Hyun-Ji Lee, Hueck-Jin Kwon and Young-Kyu Lee performed the experiments; Taek-Jun Chung and Ji-Won Park analyzed the data; William Tai Yin Tze contributed reagents/materials/analysis tools; Taek-Jun Chung and Ji-Won Park wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Avella, M.; Bogoeva-Gaceva, G.; Bužarovska, A.; Errico, M.E.; Gentile, G.; Grozdanov, A. Poly(lactic acid)-based biocomposites reinforced with kenaf fibers. *J. Appl. Polym. Sci.* **2008**, *108*, 3542–3551. [\[CrossRef\]](#)
2. Lee, B.-H.; Kim, H.-S.; Lee, S.; Kim, H.-J.; Dorgan, J.R. Bio-composites of kenaf fibers in polylactide: Role of improved interfacial adhesion in the carding process. *Compos. Sci. Technol.* **2009**, *69*, 2573–2579. [\[CrossRef\]](#)
3. Madival, S.; Auras, R.; Singh, S.P.; Narayan, R. Assessment of the environmental profile of PLA, PET and PS clamshell containers using LCA methodology. *J. Clean. Prod.* **2009**, *17*, 1183–1194. [\[CrossRef\]](#)
4. Vink, E.T.; Rabago, K.R.; Glassner, D.A.; Gruber, P.R. Applications of life cycle assessment to Natureworks™ polylactide (PLA) production. *Polym. Degrad. Stab.* **2003**, *80*, 403–419. [\[CrossRef\]](#)
5. Sukyai, P.; Sriroth, K.R.; Lee, B.H.; Hyun, J.K. The effect of bacterial cellulose on the mechanical and thermal expansion properties of kenaf/polylactic acid composites. *Appl. Mech. Mater.* **2012**, *117–119*, 1343–1351. [\[CrossRef\]](#)
6. Oksman, K.; Skrifvars, M.; Selin, J.-F. Natural fibres as reinforcement in polylactic acid (PLA) composites. *Compos. Sci. Technol.* **2003**, *63*, 1317–1324. [\[CrossRef\]](#)
7. Chung, T.; Lee, B.; Lee, H.; Kwon, H.; Jang, W.; Kim, H.; Eom, Y. Performance evaluation of bio-composites composed of acetylated kenaf fibers and poly(lactic acid) (PLA). *Elastom. Compos.* **2011**, *46*, 195–203.
8. Webber, C.L., III; Bhardwaj, H.L.; Bledsoe, V.K. Kenaf production: Fiber, feed, and seed. In *Trends in New Crops and New Uses*; ASHS Press: Alexandria, VA, USA, 2002; pp. 327–339.
9. Mohanty, A.K.; Misra, M.; Drzal, L.T. *Natural Fibers, Biopolymers, and Biocomposites*; CRC Press: Boca Raton, FL, USA, 2005.
10. Kim, H.-S.; Kim, H.-J.; Cho, D. Thermal analysis of hydrolysis and degradation of biodegradable polymer and bio-composites. *J. Therm. Anal. Calorim.* **2009**, *96*, 211–218. [\[CrossRef\]](#)
11. Ismail, H.; Abdullah, A.H.; Bakar, A.A. Influence of acetylation on the tensile properties, water absorption, and thermal stability of (high-density polyethylene)/(soya powder)/(kenaf core) composites. *J. Vinyl Addit. Technol.* **2011**, *17*, 132–137. [\[CrossRef\]](#)
12. Yussuf, A.; Massoumi, I.; Hassan, A. Comparison of polylactic acid/kenaf and polylactic acid/rise husk composites: The influence of the natural fibers on the mechanical, thermal and biodegradability properties. *J. Polym. Environ.* **2010**, *18*, 422–429. [\[CrossRef\]](#)
13. Nishino, T.; Hirao, K.; Kotera, M.; Nakamae, K.; Inagaki, H. Kenaf reinforced biodegradable composite. *Compos. Sci. Technol.* **2003**, *63*, 1281–1286. [\[CrossRef\]](#)

14. Akil, H.; Omar, M.; Mazuki, A.; Safiee, S.; Ishak, Z.M.; Bakar, A.A. Kenaf fiber reinforced composites: A review. *Mater. Des.* **2011**, *32*, 4107–4121. [[CrossRef](#)]
15. Alavudeen, A.; Rajini, N.; Karthikeyan, S.; Thiruchitrabalam, M.; Venkateshwaren, N. Mechanical properties of banana/kenaf fiber-reinforced hybrid polyester composites: Effect of woven fabric and random orientation. *Mater. Des. (1980–2015)* **2015**, *66*, 246–257. [[CrossRef](#)]
16. Hu, W.; Chen, S.; Xu, Q.; Wang, H. Solvent-free acetylation of bacterial cellulose under moderate conditions. *Carbohydr. Polym.* **2011**, *83*, 1575–1581. [[CrossRef](#)]
17. Ifuku, S.; Morooka, S.; Morimoto, M.; Saimoto, H. Acetylation of chitin nanofibers and their transparent nanocomposite films. *Biomacromolecules* **2010**, *11*, 1326–1330. [[CrossRef](#)] [[PubMed](#)]
18. Kwon, H.-J.; Sunthornvarabhas, J.; Park, J.-W.; Lee, J.-H.; Kim, H.-J.; Piyachomkwan, K.; Sriroth, K.; Cho, D. Tensile properties of kenaf fiber and corn husk flour reinforced poly(lactic acid) hybrid bio-composites: Role of aspect ratio of natural fibers. *Compos. B Eng.* **2014**, *56*, 232–237. [[CrossRef](#)]
19. Jonoobi, M.; Harun, J.; Mathew, A.P.; Hussein, M.Z.B.; Oksman, K. Preparation of cellulose nanofibers with hydrophobic surface characteristics. *Cellulose* **2010**, *17*, 299–307. [[CrossRef](#)]
20. Chen, Z.G.; Zong, M.H.; Li, G.J. Lipase-catalyzed modification of konjac glucomannan. *J. Appl. Polym. Sci.* **2006**, *102*, 1335–1340. [[CrossRef](#)]
21. Ichazo, M.; Albano, C.; Gonzalez, J.; Perera, R.; Candal, M. Polypropylene/wood flour composites: Treatments and properties. *Compos. Struct.* **2001**, *54*, 207–214. [[CrossRef](#)]
22. Kumar, S. Chemical modification of wood. *Wood Fiber Sci.* **2007**, *26*, 270–280.
23. Hassouna, F.; Raquez, J.-M.; Addiego, F.; Dubois, P.; Toniazio, V.; Ruch, D. New approach on the development of plasticized polylactide (PLA): Grafting of poly(ethylene glycol) (PEG) via reactive extrusion. *Eur. Polym. J.* **2011**, *47*, 2134–2144. [[CrossRef](#)]
24. Tserki, V.; Matzinos, P.; Panayiotou, C. Novel biodegradable composites based on treated lignocellulosic waste flour as filler. Part II. Development of biodegradable composites using treated and compatibilized waste flour. *Compos. A Appl. Sci. Manuf.* **2006**, *37*, 1231–1238. [[CrossRef](#)]
25. Li, Z.Q.; Zhou, X.D.; Pei, C.H. Preparation and characterization of bacterial cellulose/polylactide nanocomposites. *Polym. Plast. Technol. Eng.* **2010**, *49*, 141–146. [[CrossRef](#)]
26. Sun, X.F.; Sun, R. Comparative study of acetylation of rice straw fiber with or without catalysts. *Wood Fiber Sci.* **2007**, *34*, 306–317.
27. Vaca-Garcia, C.; Borredon, M.; Gaseta, A. Determination of the degree of substitution (DS) of mixed cellulose esters by elemental analysis. *Cellulose* **2001**, *8*, 225–231. [[CrossRef](#)]
28. Kim, H.-S.; Lee, B.-H.; Lee, S.; Kim, H.-J.; Dorgan, J.R. Enhanced interfacial adhesion, mechanical, and thermal properties of natural flour-filled biodegradable polymer bio-composites. *J. Therm. Anal. Calorim.* **2010**, *104*, 331–338. [[CrossRef](#)]
29. Tomé, L.C.; Pinto, R.J.; Trovatti, E.; Freire, C.S.; Silvestre, A.J.; Neto, C.P.; Gandini, A. Transparent bionanocomposites with improved properties prepared from acetylated bacterial cellulose and poly(lactic acid) through a simple approach. *Green Chem.* **2011**, *13*, 419–427. [[CrossRef](#)]
30. Kabir, M.; Wang, H.; Lau, K.; Cardona, F.; Aravinthan, T. Mechanical properties of chemically-treated hemp fibre reinforced sandwich composites. *Compos. B Eng.* **2012**, *43*, 159–169. [[CrossRef](#)]
31. Zhou, Q.; Cho, D.; Song, B.K.; Kim, H.-J. Novel jute/polycardanol biocomposites: Effect of fiber surface treatment on their properties. *Compos. Interfaces* **2009**, *16*, 781–795. [[CrossRef](#)]
32. Tingaut, P.; Zimmermann, T.; Lopez-Suevos, F. Synthesis and characterization of bionanocomposites with tunable properties from poly(lactic acid) and acetylated microfibrillated cellulose. *Biomacromolecules* **2009**, *11*, 454–464. [[CrossRef](#)] [[PubMed](#)]
33. Bher, A.; Uysal Unalan, I.; Auras, R.; Rubino, M.; Schvezov, C.E. Toughening of poly(lactic acid) and thermoplastic cassava starch reactive blends using graphene nanoplatelets. *Polymers* **2018**, *10*, 95. [[CrossRef](#)]
34. Wahit, M.U.; Hassan, A.; Ibrahim, A.N.; Zawawi, N.A.; Kunasegeran, K. Mechanical, thermal and chemical resistance of epoxidized natural rubber toughened polylactic acid blends. *Sains Malays.* **2015**, *44*, 1615–1623.

