

Research Article

Properties of Poly(Lactic Acid) Filled with Hydrophobic Cellulose/SiO₂ Composites

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Hydrophobic cellulose/SiO₂ composites were prepared. Resultant hydrophobic cellulose/SiO₂ composites were melt mixed with PLA using a twin-screw extruder to obtain 10 wt% masterbatch. Again, 10 wt% masterbatch was melt mixed with virgin PLA, resulting in PLA containing hydrophobic cellulose/SiO₂ at various contents (1 wt%, 3 wt%, and 5 wt%) using a twin-screw extruder (barrel zone temperature: 150/160/170/180/190 °C (die zone)). Injection-molded samples were prepared for mechanical properties evaluation. Results showed that poor mechanical properties found at low percent loadings were associated with a significant depolymerization of masterbatch composition due to twice thermal treatments. Note that 10 wt% masterbatch was subjected to injection molding straight away in a one-step process. Results showed that 10 wt% hydrophobic cellulose/SiO₂/PLA composites exhibited mechanical properties equivalent to neat PLA. Importantly, the addition of hydrophobic cellulose/SiO₂ at high percent loading could favor landfill degradation of PLA via water absorption ability of cellulose. It was expected that enzymatic hydrolysis of cellulose resulted in the formation of lactic acid and silicic acid which consequently catalyzed the hydrolytic degradation (acid hydrolysis) of PLA. The hydrolytic degradation produced carboxylic acid end group which further accelerated the degradation rate.

1. Introduction

Nowadays, plastic products and packaging are widely used, resulting in nonbiodegradable plastic waste which consequently causes an environment concern. Hence, biodegradable polymers have been developed. Poly(lactic acid) (PLA) is a biodegradable and bioactive thermoplastic aliphatic polyester derived from renewable resources [1, 2]. PLA has several advantages such as transparency, biodegradability (but under composting condition), and hot melt-extrusion processing. However, PLA has disadvantages such as processing difficulty (low melt strength due to poor thermal stability) and slow landfill biodegradability [3–5]. To improve mechanical properties, biocomposites or nanocomposites

approaches have been widely investigated [6]. For packaging, landfill biodegradation is preferable due to low cost of waste treatment. Landfill biodegradation involves hydrolysis and hydrolytic degradation (acid/base hydrolysis). Importantly, water absorptivity plays a key role in hydrolysis process. Unfortunately, PLA is hydrophobic and crystalline polymer when compared to polybutylene succinate, resulting in extremely slow landfill biodegradation. In order to achieve biodegradability under landfill condition, hydrophilic fillers particularly biodegradable materials such as starch or cellulose are preferable since they are consumed by microbes, then generating lactic acid which is an acid donor for acid hydrolysis of PLA. The acid hydrolysis is faster than enzymatic hydrolysis, resulting in accelerating degradation of PLA

under landfill condition [7, 8]. However, the main drawback of PLA/hydrophilic filler biocomposites is the problem of poor filler distribution, leading to agglomeration deriving from poor PLA-filler interaction. Note that the problem of agglomeration is caused by strong cohesive adhesion among filler particles [9, 10]. A resulting problem of filler agglomeration could be solved by surface modification approach to alter the filler-filler interaction [11]. In this study, water absorptivity of PLA was enhanced by the addition of cellulose/SiO₂ composites. Prior to filler loading, the composite requires proper surface modification in order to prevent agglomeration problem during melt-mixing process [12]. Cellulose particle/SiO₂ composite was prepared and followed by surface hydrophobicity modification using hexadecyltrimethoxysilane through surface silanization reaction. PLA composites containing hydrophobic cellulose particle/SiO₂ were prepared using twin-screw extruder [13]. Then, injection-molded samples were prepared for properties evaluation including mechanical properties, water absorptivity, and landfill biodegradation.

2. Materials and Methods

2.1. Materials. PLA (3052D) was purchased from NatureWorks Company, USA. The specific gravity and the melt flow index of PLA are 1.24 and 14 g/10 min (210°C), respectively. Cellulose gel was prepared according to previous report [14]. Sodium silicate (50 wt%) is of commercial grade. Hexadecyltrimethoxysilane (HDTMS) was kindly supplied by Evonik. Nonylphenoethoxylate EO15 (EO15) under the trade name of TERGITOL™ (DOW Chemical Co., Ltd.) was kindly provided by Star Tech Chemical Co., Ltd. Commercial grade methanol was bought from local supplier.

2.2. Preparation of SiO₂ Nanoparticle [15]. 1000 ml solution containing 55 g of 50 wt% sodium silicate was prepared. The pH value was adjusted to pH 2 with conc. H₂SO₄. The solution was left standing for 2 days to allow the formation of SiO₂ nanoparticles which was observed by laser light scattering. The colloidal solution was employed straight away in preparing cellulose/SiO₂ composite to prevent the formation of SiO₂ gel.

2.3. Preparation and Silanization of Cellulose/SiO₂ Nanocomposite. 2000 g cellulose gel (200 g cellulose based on dry wt) and SiO₂ colloidal solution (5 wt% of cellulose) were stirred together to allow the precipitation of SiO₂ nanoparticles onto cellulose surface. As a result, cellulose (CS)/SiO₂ nanocomposite was obtained. Then, hexadecyltrimethoxysilane emulsion (HDTMS/EO15/CH₃OH/H₂O) was added with vigorous homogenization [16]. To study the effect of degree of surface modification, two ratios of cellulose to HDTMS wt ratio of 1:0.25 and 1:1 were prepared. Resultant mixture paste was left standing freely for 2-3 days to achieve complete silanization reaction. Dry cake was obtained and washed repeatedly until pH value became neutral. The products (1:0.25 CS:HDTMS and 1:1CS:HDTMS composites) were dried in an oven at 65°C. The surface hydrophobicity was confirmed by ATR-FTIR analysis.

TABLE 1: Mixing ratio of poly(lactic acid) to masterbatch.

Sample	Poly(lactic acid) (g)	Masterbatch (g)
neat PLA	—	—
PLA/1:1 CF:HDTMS 1%	1350	150
PLA/1:1 CF:HDTMS 3%	1050	450
PLA/1:1 CF:HDTMS 5%	750	750
PLA/1:1 CF:HDTMS 10%	—	1500
PLA/1:0.25 CF:HDTMS 1%	1350	150
PLA/1:0.25 CF:HDTMS 3%	1050	450
PLA/1:0.25 CF:HDTMS 5%	750	750
PLA/1:0.25 CF:HDTMS 10%	—	1500
PLA/CF1%	1485(CF 15 g)	—

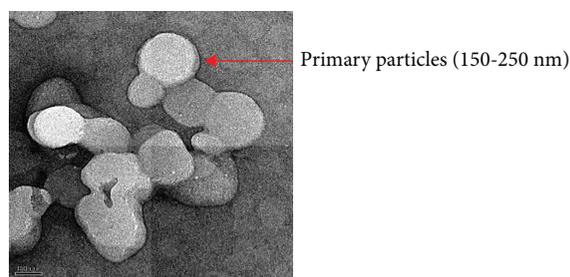


FIGURE 1: TEM image of SiO₂ nanoparticles.

2.4. Preparation of Poly(Lactic Acid) Filled with Cellulose/SiO₂ Nanocomposite. PLA and hydrophobic cellulose/SiO₂ nanocomposite were oven dried at 65°C for 24 h. The masterbatch was prepared by physical mixing PLA with 10 wt% cellulose/SiO₂ nanocomposite in a plastic bag. Then, the mixture was fed into the twin-screw extruder (LTE-26-44, Labtech Scientific, Labtech Engineering, Thailand). The temperature profile of the extruders' barrel zones was 190°(die zone)/190°/180°/165°/150°C, respectively, and the twin-screw speed was maintained at 45 rpm. After that, PLA composites containing cellulose/SiO₂ nanocomposite contents of 1.0, 3.0, and 5.0 wt% were prepared using the same twin-screw extruder. The 10 wt% masterbatch was subject to injection molding in a one-step process. Composite compositions were summarized in Table 1.

Injection-molded samples were prepared using an injection machine (NEX80, Nissei Injection Molding Machine). The temperature profile was set at 195°(die zone)/190°/180°/180°/165°/30°C.

2.5. Morphology. A JSM-6480LV (JEOL Co., Japan) scanning electron microscope (SEM) was employed to study the morphology of hydrophobic CS/SiO₂/PLA composites. The transmission electron microscope, Hitachi HT-7700, was employed for analysis of SiO₂ nanoparticles.

2.6. Mechanical Properties. The tensile test was carried out using a universal testing machine (Instron 5566, USA) according to ASTM D638. The speed of crosshead and load cell were set at 5 mm/min and 10 KN, respectively.

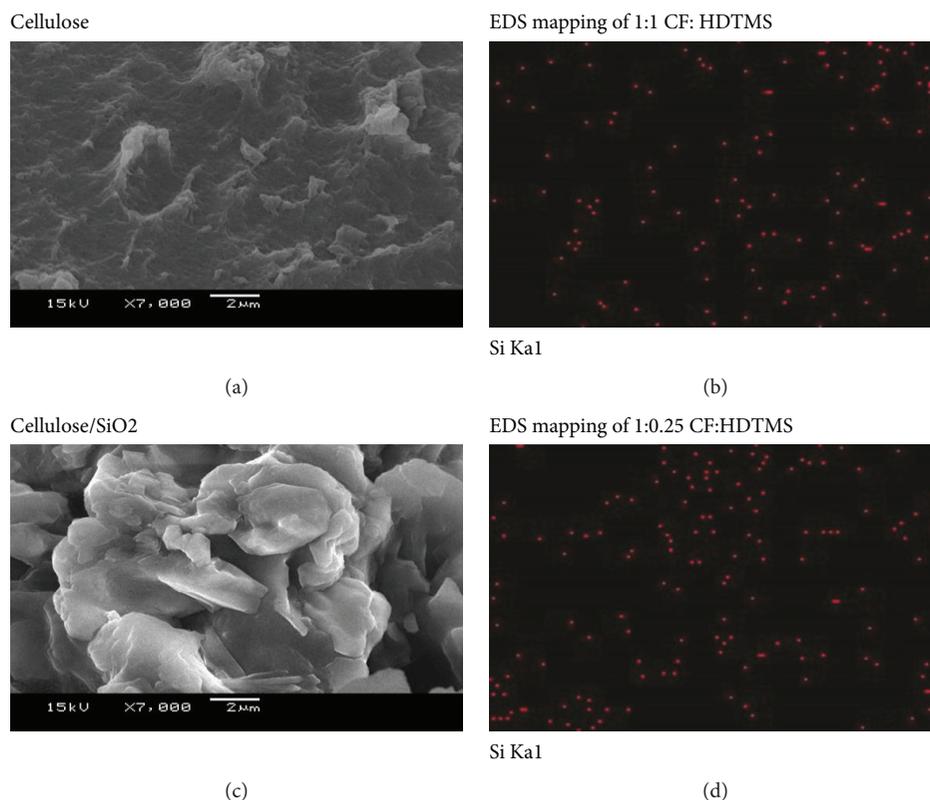


FIGURE 2: SEM images (a, c) of cellulose and cellulose/nanoSiO₂ composite. EDS mapping (b, d) of hydrophobic CF/nanoSiO₂ composites.

Notched izod impact tests of the composites were performed on GT-T045-MD (Gotech testing machines, Taiwan) according to ASTM D256. The angle of the notch and impact energy were 45° and 1 J. The dimension of the test sample was 12.7 × 63.5 × (3.21-3.24) mm³. An average value of 5 samples per formulation was calculated.

2.7. Water Absorption Properties. Samples were dried at 65°C in an oven for at least 24 h according to ASTM D570. The specimens were weighed (W_c) before submerging in distilled water from 0.03 h to 24 h. The samples were taken out at a certain interval time and softly blotted with tissue paper or fabric to remove surface water. The samples were then instantly weighed (W_w), and the percentage of water uptake (W_f) was calculated as follows:

$$\%W_f = \frac{W_w - W_c}{W_c} \times 100\%. \quad (1)$$

2.8. Biodegradation Test. The biodegradation test was carried out by soil burial test in the outdoor condition according to ASTM D338. The samples were accurately weighed and then buried in separate holes with about 15 cm deep for 8 weeks (2 months). The pH value of soil was adjusted to 5-6 by watering with diluted citric acid solution. The percentage of weight loss was calculated for 4 and 8 weeks, respectively. The morphology was observed by SEM.

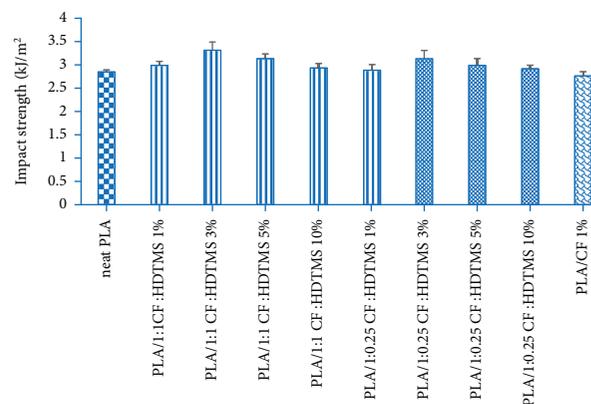


FIGURE 3: Impact strength values of PLA filled with hydrophobic CF/SiO₂ composites at various contents.

3. Results and Discussion

3.1. Morphology of SiO₂ Nanoparticles by TEM Analysis. Figure 1 shows representative TEM image of SiO₂ nanoparticles prepared by precipitation of sodium silicate [17]. The image reveals both primary particle and agglomerate. A primary particle diameter and an agglomerate diameter are found 150-250 nm and 400-600 nm, respectively. The optimum conditions to achieve nanosized ranges of particle sizes with minimum agglomeration are as follows: silicate concentration below 55 g/l, pH values between 1 and 2, room

temperature, and reaction time of 2 days. Longer reaction time than 2 days led to the formation of silica gel.

3.2. Morphology of Cellulose/SiO₂ Composite. Figure 2 shows SEM images (Figures 2(a) and 2(c)) and EDS mapping (Figures 2(b) and 2(d)) of cellulose particle and cellulose/SiO₂ composite, respectively. As seen, there are differences in surface morphology between cellulose and cellulose/SiO₂. Cellulose exhibits irregularly continuous surface. On the other hand, numerous cellulose/SiO₂ particles were observed in the case of cellulose/SiO₂ composite. It is assumed that SiO₂ nanoparticles act as nucleating agent of cellulose. In addition, element mapping by scanning electron microscope-energy dispersive X-ray spectrometry (SEM-EDS) provides Si mapping and its distribution in cellulose matrix. The Si EDX mapping of hydrophobic cellulose/SiO₂ composites is presented in Figure 2 (Figures 2(b) and 2(d)). As seen, SiO₂ nanoparticles are well distributed in cellulose matrix without agglomeration.

3.3. Mechanical Properties. Figure 3 shows the impact strength of neat PLA and hydrophobic CS/SiO₂/PLA composites. The notched impact strength of neat PLA is 2.84 kJ/m². For hydrophobic CS/SiO₂/PLA composites, the results show that the addition of hydrophobic CS/SiO₂/PLA composites up to 10 wt% neither improves nor reduces the impact strength of the composites. The tensile strength values of all samples are shown in Figure 4. Tensile strength values of composites at low percent loadings (1%, 3%, and 5%) decrease slightly. Slightly poor tensile strength found at low percent loadings was associated with a significant decrease in melt strength of PLA masterbatch (observed by a significant decrease in extruder torque) due to twice thermal treatments. For 10 wt% CS/SiO₂/PLA composites, their tensile strength values increase notably when compared to those containing lower hydrophobic CS/SiO₂/PLA contents, indicating that hydrophobic CS/SiO₂ composite acting as a reinforcing agent performed well for PLA. Based on finding results, it can be concluded that PLA containing hydrophobic cellulose/nanosilica composites up to 10 wt% is possible without compensation of mechanical properties [11, 18]; the more the cellulose content, the higher the water absorbency. As a result, the biodegradation rate of PLA could be accelerated.

3.4. Water Uptake. Figure 5 shows percent water absorption values for all samples taken after 24 h or 2 days. It can be seen that neat PLA hardly absorbs water after submerging in water for 1 h and then marginally increases due to the hydrophobic characteristic of PLA. In the case of hydrophobic CS/SiO₂/PLA composites, a significant increase in percent water uptake is observed when compared to neat PLA. It can be understood that cellulose and SiO₂ are responsible for water absorptivity of the composites. Percent water absorption increases with an increase in filler content. Note that PLA containing 1.0:0.25 CS:HDTMS tends to have more water than those containing 1.0:1.0 CS:HDTMS due to their less hydrophobicity associated with less HDTMS ratio. As a result of water absorption performance, it is expected that

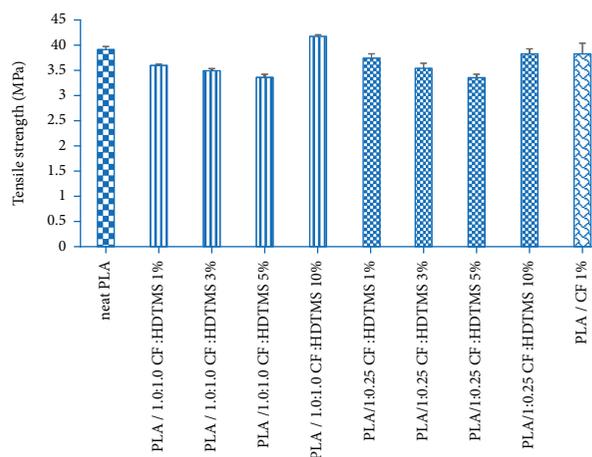


FIGURE 4: Tensile strength values of neat PLA and PLA/hydrophobic CF/SiO₂ composites.

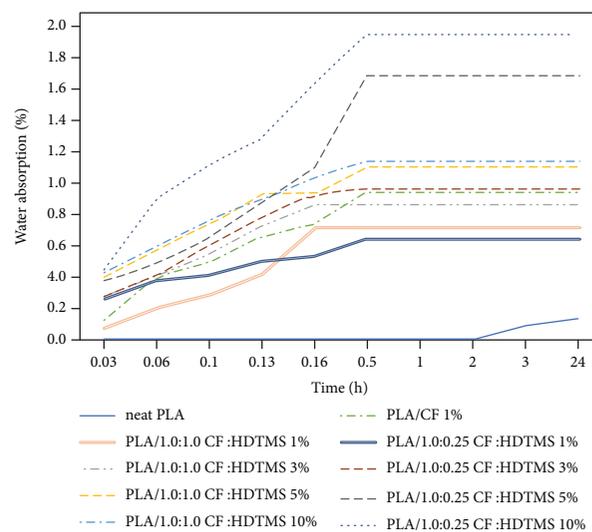


FIGURE 5: Percent water absorption of neat PLA and PLA/hydrophobic CF/SiO₂ composites.

TABLE 2: Percent weight loss after soil burial test.

Sample	% weight loss		
	1 month	2 months	3 months
neat PLA	0.07	0.16	0.73
PLA/1.0:1.0 CF:HDTMS 1%	0.23	0.38	1.13
PLA/1.0:1.0 CF:HDTMS 3%	0.28	0.59	1.74
PLA/1.0:1.0 CF:HDTMS 5%	0.76	1.98	4.32
PLA/1.0:1.0 CF:HDTMS 10%	0.45	2.67	6.14
PLA/CF 1%	0.28	1.23	1.59
PLA/1.0:0.25 CF:HDTMS 1%	0.14	0.45	1.33
PLA/1.0:0.25 CF:HDTMS 3%	0.66	1.35	2.70
PLA/1.0:0.25 CF:HDTMS 5%	1.45	3.23	7.75
PLA/1.0:0.25 CF:HDTMS 10%	1.73	7.21	11.3

TABLE 3: Physical appearance after soil burial test.

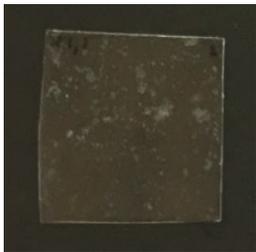
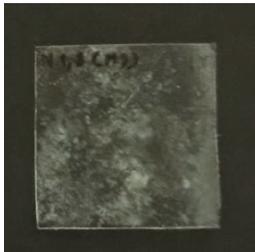
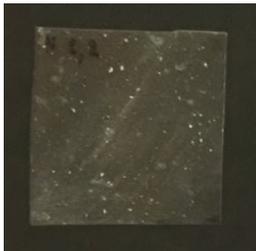
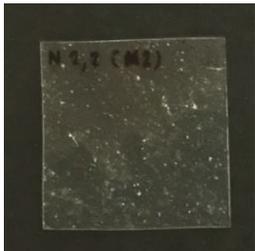
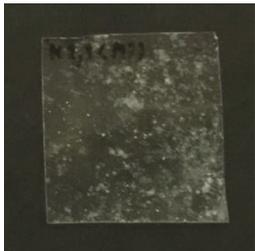
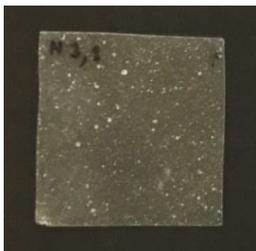
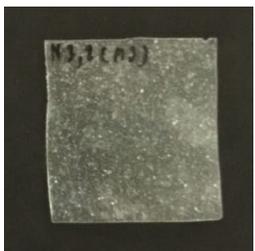
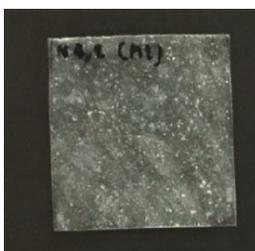
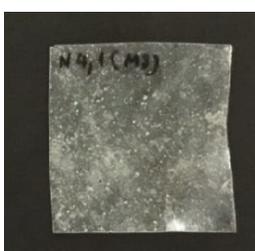
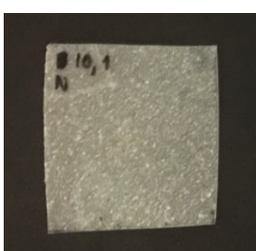
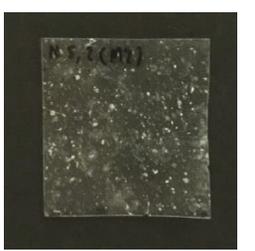
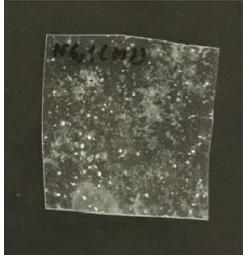
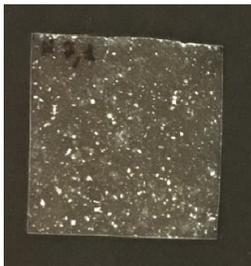
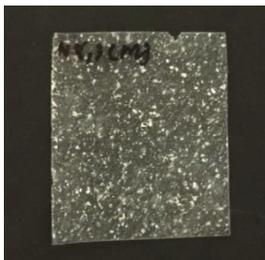
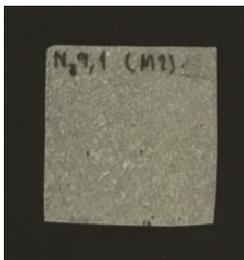
Sample	Physical appearance after soil burial test		
	1 month	2 months	3 months
neat PLA			
PLA/1.0:1.0 CF:HDTMS 1%			
PLA/1.0:1.0 CF:HDTMS 3%			
PLA/1.0:1.0 CF:HDTMS 5%			
PLA/1.0:1.0 CF:HDTMS 10%			
PLA/CF 1%			

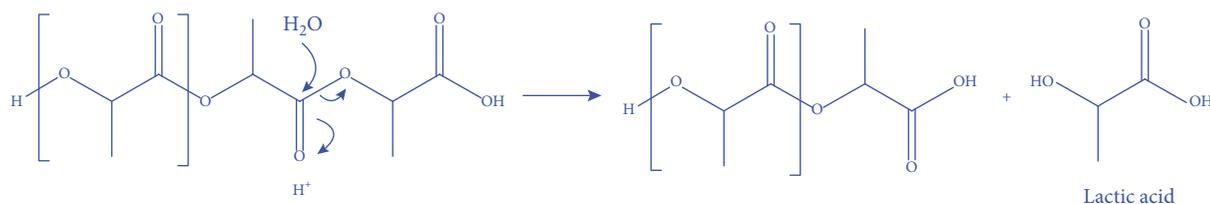
TABLE 3: Continued.

Sample	Physical appearance after soil burial test		
	1 month	2 months	3 months
PLA/1.0:0.25 CF:HDTMS 1%			
PLA/1.0:0.25 CF:HDTMS 3%			
PLA/1.0:0.25 CF:HDTMS 5%			
PLA/1.0:0.25 CF:HDTMS 10%			

composites are prone to hydrolysis degradation at a faster rate than neat PLA [19].

3.5. Biodegradation Test. Soil burial test up to 3 months was conducted to study the biodegradation behavior. In every one month, the sample was taken out, weighed, and morphologically observed. Results are presented in Table 2 and Table 3. As seen, neat PLA is little change in terms of physical appearance and weight loss after soil burial test for 3 months due to its hydrophobic nature similar to conventional plastics. For composites, cracks and holes which increase by time are found. In a similar manner, percent weight loss is found to increase by time. In the case of PLA/1.0:0.25 CS:HDTMS 10 wt%, up to 11 percent weight loss is recorded. In contrast, PLA/1.0:1.0 CS:HDTMS

10 wt% loses by 6 percent weight loss due to its more hydrophobicity than PLA/1.0:0.25 CS:HDTMS 10 wt%. The addition of untreated cellulose (as in the case of PLA/CF 1 wt%) results in changes in both physical appearance and percent weight loss. However, attempt to adding untreated cellulose above 1 wt% was unsuccessful due to agglomeration problem. Therefore, it is important that water plays a key role in initiating the biodegradation process. Firstly, water acts as a carrier for microbes to get in touch with cellulose. Then, enzymatic hydrolysis of cellulose occurs to produce lactic acid. In acidic condition, silicic acid is generated from silica nanoparticles. In following degradation process, PLA undergoes hydrolytic degradation catalyzed by lactic acid combined with silicic acid. This process is more severe and faster than enzymatic hydrolysis of cellulose. As a result,



SCHEME 1: Proposed hydrolytic hydrolysis of PLA in acidic condition.

composites containing hydrophobic cellulose/nanosilica degrade at a faster rate when compared to neat PLA. The hydrolytic hydrolysis mechanism is proposed as shown in Scheme 1 [7, 8].

4. Conclusions

Cellulose/SiO₂ composites were prepared and followed by surface hydrophobicity modification using hexadecyltrimethoxysilane (HDTMS) through surface silanization reaction. Resultant hydrophobic cellulose/SiO₂ composite was melt mixed with PLA using a twin-screw extruder to obtain composites containing hydrophobic cellulose/SiO₂ at various contents (1 wt%, 3 wt%, and 5 wt%). Injection-molded samples were prepared for mechanical properties evaluation. Note that 10 wt% masterbatch was subjected to injection molding straight away in a one-step process. Results showed that 10 wt% hydrophobic cellulose/SiO₂/PLA composites exhibited mechanical properties equivalent to neat PLA without a compromise of PLA mechanical properties. Importantly, the addition of hydrophobic cellulose/SiO₂ could favor landfill degradation of PLA via water absorption ability of cellulose. It was expected that enzymatic hydrolysis of cellulose resulted in the formation of lactic acid and silicic acid which consequently catalyzed the hydrolytic degradation (acid hydrolysis) of PLA. The hydrolytic degradation produced carboxylic acid end group which further accelerated the degradation rate.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request. Also, previous report of cellulose gel preparation to support this study is cited at a relevant place within the text [14]. Previous report of hydrophobicity modification to support this study are available at <https://doi.org/10.1155/2015/741242>.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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