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Biodegradable Poly(butylene succinate) Composites Reinforced by Cotton Fiber with Silane Coupling Agent

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Received: 14 November 2012; in revised form: 8 January 2013 / Accepted: 24 January 2013 / Published: 29 January 2013

Abstract: In this study, the use of cotton fiber (CF) as a filler in poly(butylene succinate) (PBS) and the effect of silane treatment on the mechanical properties, thermal stability, and biodegradability of PBS/CF composites are investigated. The results showed that the tensile strength of PBS was improved (15%–78%) with the incorporation of CF (10–40 wt%) and was further increased (25%–118%) when CF was treated with a silane coupling agent. Scanning electron microscopy (SEM) observation of the fracture surfaces of PBS/CF composites showed that there was slight improvement in fiber-matrix compatibility. Thermogravimetric (TG) analysis showed that the thermal stability of the composites was lower than that of neat PBS and decreased with increasing filler loading. The biobased carbon content of the composites increased with increasing CF content. The incorporation of CF (with and without silane treatment) in PBS significantly increased the biodegradation rate of the composites.

Keywords: cotton fiber; composites; poly(butylene succinate); silane coupling agent

1. Introduction

The waste treatment and accumulation of non-biodegradable polyethylene (PE) mulch films in vegetable fields or soil have become serious problems, mainly in South East Asian countries. Excess amounts of used PE mulch films remaining in the field soil also decrease vegetable yields. To address these environmental issues, biodegradable plastics have been developed. Many aliphatic types of polyester can be degraded in compost and moist soils. Poly(butylene succinate) (PBS) is one of the most promising biodegradable aliphatic polyesters, with desirable properties such as biodegradability, melt processability, and both thermal and chemical resistance. However, its high cost and other properties such as elastic modulus, tensile strength, gas barrier properties, and melt viscosity for further processing, restrict its extensive application [1]. Consequently, numerous studies have been conducted on techniques to modify the properties of PBS-based materials, among which blending with fillers is an efficient, easy, and economic method. Recently, the use of natural biodegradable fibers as alternative reinforcing fillers in composite materials have increasingly been gaining attention owing to their advantages over artificial fibers such as carbon, glass, and aramid [2]. To date, rice straw [3], abaca fiber [4], kenaf fiber [5], jute fiber [6], alkaline lignin [7], bamboo fiber [8], water bamboo husk [9] wood flour [10] and starch [11,12] have been used as natural fillers to enhance the properties of PBS and reduce the cost.

In this study, the use of cotton fiber (CF) as a filler in PBS was investigated. A commercial non-woven paper towel derived from pure cotton was used as the CF. Use of this material as a reinforcing agent for polymeric matrices is favored because CF is strong and durable. Few studies using CF as reinforcement for polymer composites have been reported [13,14]. To our knowledge, no report has been published on PBS composites reinforced with silane-treated CF.

Compared with artificial fibers, natural fibers have many advantageous features as fillers in polymer composites; they are low in cost, environment-friendly, renewable, biodegradable, and available in high quantities [15–17]. However, they also have some drawbacks such as moisture absorption, quality variation, low thermal stability, and poor compatibility with hydrophobic polymer matrices, which lead to composites with undesirable properties. Nevertheless, these undesirable properties can be improved by physical and chemical treatments such as surface modification using coupling agents [18,19]. Silanization is one of the most common chemical coupling methods used for cellulose-filled composites. Silane coupling agents are frequently used as interfacial agents in polymer composites to improve interfacial strength [20,21].

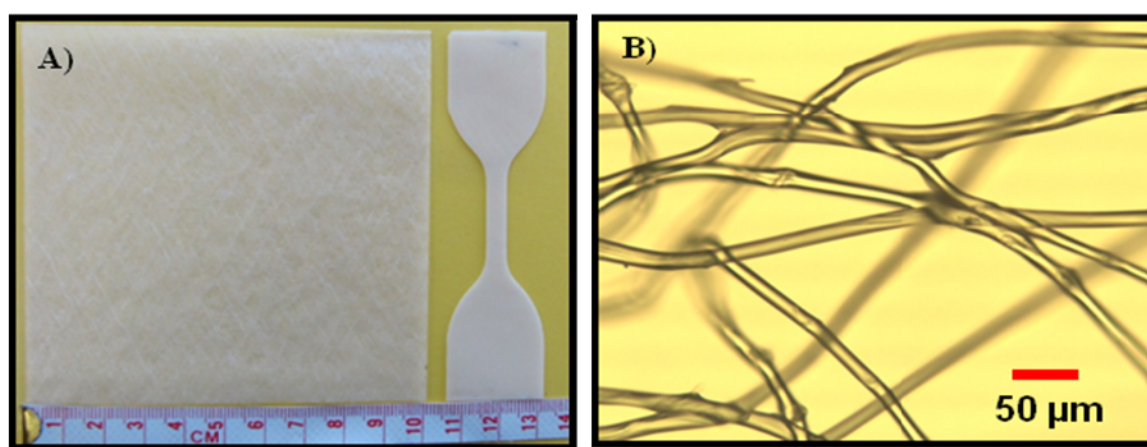
The aim of this work is to investigate the effect of CF concentration on the mechanical properties, thermal stability, and biodegradability of PBS/CF composites, with and without silane treatment. Examinations with differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and thermogravimetric (TG) analysis were conducted to investigate the physical and thermal properties of PBS/CF composites. Biobased carbon content was evaluated by the ratio of ^{14}C to ^{12}C in the samples by using accelerator mass spectrometry (AMS). Biodegradability was monitored under controlled compost conditions at 58 °C based on ISO 14855-2 by using a microbial oxidative degradation analyzer (MODA) apparatus.

2. Experimental Section

2.1. Materials

Poly(1,4-butylene succinate), extended with 1,6-diisocyanatohexane ($M_n = 5.0 \times 10^5$, $M_w/M_n = 2.7$) was purchased from Aldrich Chemical Co. and used as the matrix polymer. The CF used as the reinforcing filler—a commercial non-woven paper towel derived from pure cotton and measuring $100 \text{ mm} \times 100 \text{ mm} \times 0.05 \text{ mm}$ —was obtained from Asahi Kasei. The average length and diameter of a single CF are about 30 mm and 0.01 mm, respectively (Figure 1).

Figure 1. Photograph (A) and microphotograph (B) of cotton fiber used as the reinforcing filler for poly(butylene succinate)/cotton fiber (PBS/CF) composites.



The silane coupling agents, 3-aminopropyltriethoxysilane (APTES), 3-aminopropyltrimethoxysilane (APTMS), and N1-3-trimethoxysilylpropyldiethylene triamine (TMSPDET), were used as received from Aldrich Chemical Co.

2.2. Treatment of CF with Silane Coupling Agents

The CF samples were pre-dried under vacuum at 80°C for 24 h. The treatment of CF (*ca.* 1.5 g, 10 sheets) with silanes (APTES, APTMS, and TMSPDET) was performed in a 100-mL mixture of ethanol: H_2O (80:20) containing silane. The concentration of the silane coupling agent was varied from 0% to 3.0%. The pH was adjusted to 4.5–5.0 by adding acetic acid; the solution was then stirred for 1 h to ensure complete silane hydrolysis, after which the CF samples were added. The samples were soaked for 2 h, and then removed from the solutions and dried at room temperature (RT) for 24 h. The dried samples were heat-treated at 110°C for 2 h to promote actual coupling. Untreated CF (without the silane coupling agent) samples were prepared in the same way and used as controls.

2.3. Preparation of PBS/CF Composites

The PBS powder was prepared from PBS pellets, which were crushed into powder by using a rotating mechanical mixer with titanium blades (10,000 rpm, 3 L) and cooling with dry ice. Crushing was performed 15 times for 3 min each with a 5-min interval to prevent overheating of the

motor in the mixer. After drying under reduced pressure at RT, the PBS powder was passed through a standard and guaranteed 60-mesh sieve (250 μm). The sieve with crude PBS powder was placed on a sieve vibrator and vibrated for 15 min. The PBS powder obtained was dried under vacuum at 60 $^{\circ}\text{C}$ for 24 h and used in the preparation of PBS/CF composites.

The CF samples were evenly arranged in a stainless mold (100 mm \times 100 mm \times 0.5 mm). The PBS/CF composite sheets were prepared by impregnating the CF with the corresponding concentration of PBS powder on both sides of the CF sheets. The molds were compressed at 150 $^{\circ}\text{C}$ under a 2000 kg load for 5 min.

2.4. Mechanical Property Test

The melt-pressed composite films were cooled at RT and then cut into dumbbell-shaped specimens (100 mm in total length, 25 mm in total width, 5 mm in narrow width, 0.5 mm in thickness, and 25 mm in effective distance between chucks). Tensile tests of these specimens based on ISO 527-type 5 (JIS K7127-3) were performed at RT by using a Shimadzu Autograph AG-1000B. The grip distance was 50 mm and the gage length was 25 mm. The test speed was 10 mm min^{-1} . The results of strength and elongation at break are the average values of four measurements.

2.5. Differential Scanning Calorimetry and Thermogravimetric Analysis

The melting temperature (T_m) and heat of fusion (ΔH_m) were determined using a DSC system (Seiko Instruments Inc., Japan; SSC/520). The samples (*ca.* 10 mg) were heated to 150 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$ and kept for 5 min to remove the thermal history. Then, the samples were cooled to 30 $^{\circ}\text{C}$ and heated again to 150 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$ as the second heating scan. Values of the T_m and ΔH_m were calculated from the first and second heating scan.

TG analysis was carried out under a nitrogen atmosphere by using an Exstar TG/DTA 6200 at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in the temperature range of 30 to 500 $^{\circ}\text{C}$.

2.6. Scanning Electron Microscopy

The morphology of the fracture surface (obtained as a result of tensile testing) in the silane-treated and untreated PBS/CF composites was observed by SEM using a Hitachi Miniscope TM-1000. The samples were viewed perpendicular to the fracture surface.

2.7. Measurement of Biobased Carbon Content

The measurement of the ratio of three carbon isotopes (^{14}C , ^{13}C , and ^{12}C) in the composites by AMS was performed at the Institute of Accelerator Analysis (IAA, Japan). The measurement procedure has already been reported in our previous studies [11,22–28]. Samples prepared for ^{14}C analysis were combusted to CO_2 and then reduced to graphite for use in the AMS ion source. The carbon in the graphite, transferred from the blend samples, was ionized using a cesium cation beam. The ratio of ^{14}C to ^{12}C ($^{14}\text{A}_s$) in the composite samples was calculated from the measured concentrations of ^{14}C and ^{12}C . The measurement of the product's ^{14}Ar ($^{14}\text{C}/^{12}\text{C}$) was determined relative to the modern carbon-based oxalic acid radiocarbon [Standard Reference Material (SRM) 4990c, National Institute of Standards

and Technology (NIST), USA]. The $\Delta^{14}\text{C}$, percent modern carbon (pMC), and biobased carbon ratio were calculated as follows:

$$\Delta^{14}\text{C} = [({}^{14}\text{As} - {}^{14}\text{Ar}) / {}^{14}\text{Ar}] \times 1000 (\text{‰}) \quad (1)$$

$$\text{pMC} = \Delta^{14}\text{C} / 10 + 100 (\%) \quad (2)$$

$$\text{Biobased carbon content} = \text{pMC} \times 0.93 (\%) \quad (3)$$

The abovementioned formulas and the correction factor of 0.93 are specified in ASTM D6866-08. The pMC for an oil-based carbon is 0% because all of the ${}^{14}\text{C}$ in oil has decayed during the action of cosmic rays in the atmosphere and on earth's surface. Moreover, the pMC for a biomass made by the fixation of CO_2 in the modern atmosphere through photosynthesis is 108%–110%.

2.8. Biodegradation Measurement Based on ISO 14855-2

The biodegradation test was carried out using the MODA apparatus based on ISO 14855-2 [29,30]. The MODA is a laboratory-scale apparatus designed to evaluate the aerobic biodegradability of plastic and other materials under controlled composting conditions by analysis of evolved carbon dioxide. The compost used in the biodegradation test was prepared following previously described methods [30,31]. The test materials were cut into sheets (10 mm \times 10 mm \times 0.5 mm) based on ISO 10210 [32], and 10 g of each sample was mixed in the compost (*ca.* 140 g) with sea sand (*ca.* 320 g) and then transferred to the reaction vessel. Compost without the test sample was used as a blank to determine the respiration activity of the compost. The biodegradation tests were performed at 58 °C and an air flow rate of 10 mL min^{−1} (CO_2 -free). The activated compost used in this study produced 50 mg of CO_2 per gram of volatile solids over the first 10 days. Duplicate samples were prepared for each test sample. The amount of produced CO_2 was determined once a day by measuring the weight of the absorption column for CO_2 and that of the absorption column for H_2O . The degree of biodegradation is the percentage of the difference between the total evolved CO_2 and respired CO_2 to the theoretically evolved CO_2 . The theoretical evolved CO_2 (ThCO_2) and percentage of biodegradation are calculated as follows:

$$\text{ThCO}_2 (\text{g}) = \frac{\text{wt of polymer (g)} \times \text{no. of C in monomer unit of polymer} \times \text{MW of CO}_2}{\text{MW monomer unit of polymer}} \quad (4)$$

$$\text{Biodegradation (\%)} = \frac{\text{total evolved CO}_2 (\text{g}) (\text{sample vessel}) - \text{respired CO}_2 (\text{g}) (\text{blank vessel}) \times 100}{\text{theoretical CO}_2 \text{ value (sample material)}} \quad (5)$$

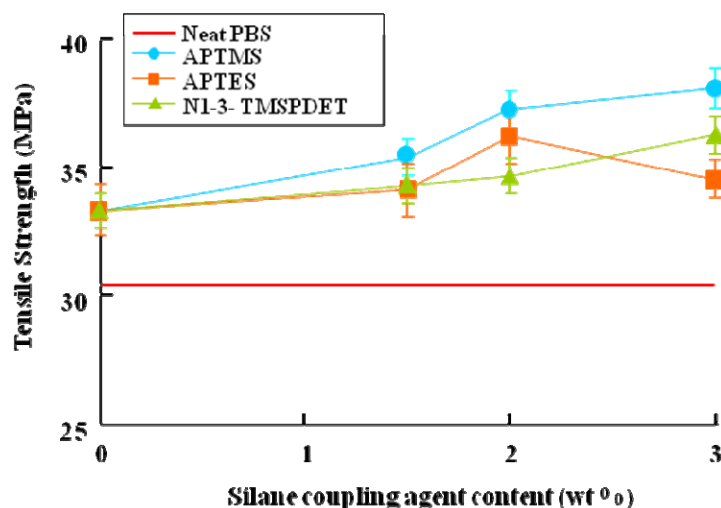
As recommended in ISO 14855-2, the compost mixture was removed from the reaction vessel once a week for mixing. At the same time, the moisture content was adjusted.

3. Results and Discussion

3.1. Mechanical Properties of Composites

The effect of types and concentrations of silane coupling agent on the tensile strength of the PBS/CF composites with 10 wt% CF was investigated. As shown in Figure 2, the tensile strength increased with increasing concentration of silane coupling agent, except in the case of APTES, in which it decreased at 3% concentration. Among the three silane coupling agents, APTMS gave the highest tensile strength, followed by TMSPDET and APTES. The tensile strength of PBS/CF composites with APTMS, TMSPDET, and APTES at 3% concentration is 125, 120, and 114% higher, respectively, than that of neat PBS (30.3 MPa). The tensile strength with 3% APTES decreased, possibly because the amount of ether linkages between the hydroxyl group on CF and APTES was already saturated at 3% [33]. The difference in the tensile strength of the composites with APTMS and APTES was probably caused by the rate of hydrolysis reaction of these two silane coupling agents. The ethoxy functional group is more hydrophobic than the methoxy functional group; therefore, it is more difficult to be hydrolyzed to form a hydroxyl group [34]. This means that the coupling reaction between CF and PBS by APTES was not as complete as that by APTMS.

Figure 2. Tensile strength of PBS (90 wt%)/CF (10 wt%) composites with various concentrations of 3-aminopropyltrimethoxysilane (APTMS), 3-aminopropyltriethoxysilane (APTES), and N1-3-trimethoxysilylpropyldiethylenetriamine (TMSPDET).

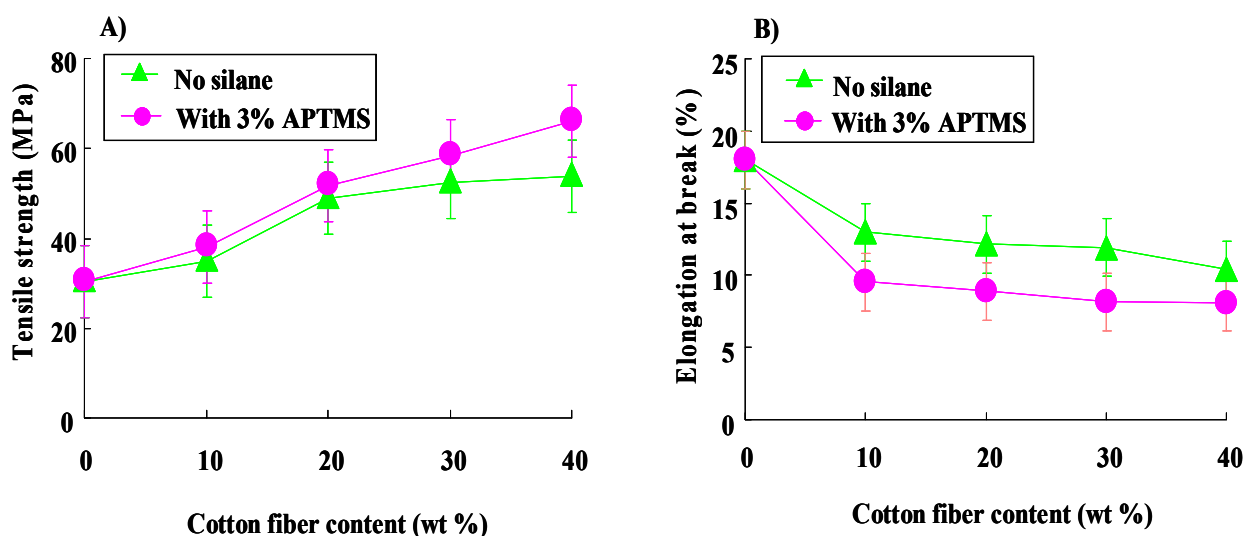


As mentioned earlier, APTMS was found to suitably promote adhesion and result in PBS/CF composites with higher tensile strength. Thus, APTMS at a concentration of 3% was used in the succeeding tests. The effect of CF content on the tensile properties of CF-reinforced composites with and without 3% APTMS was investigated. As shown in Figure 3, the incorporation of CF improved the tensile strength of PBS. Compared with neat PBS, the tensile strength of untreated PBS/CF composites with four different fiber contents (10–40 wt%) was enhanced by 15%, 62%, 73% and 78%, respectively. Moreover, the tensile strength was further increased by 25%, 71%, 92% and 118%,

respectively, when CF was treated with APTMS. The increase in the tensile ~~increase~~ strength of PBS/CF composites was due to the strong interfacial bonding between PBS and CF.

The elongation at break of PBS/CF composites decreased with increasing CF content because the addition of CF reduced the mobility and increased the brittleness of the composites. Increasing the amount of CF decreases the amount of PBS available for elongation (Figure 3B).

Figure 3. Effect of silane treatment (with 3% APTMS) on the (A) tensile strength and (B) elongation at break of PBS/CF composites.



3.2. DSC Analysis

The thermal properties of the composites such as T_m , ΔH_m , and percent crystallinity (X_c) were investigated using DSC. The obtained results are summarized in Table 1. The X_c was calculated from $\Delta H_m / \Delta H_m^\circ$, where ΔH_m° is the melting enthalpy of 100% crystalline PBS. The ΔH_m° of PBS was reported to be 110.3 J/g [35]. The T_m of the obtained PBS/CF composites with and without silane treatment was relatively the same as that of neat PBS as shown in Table 1. The ΔH_m , however, of neat PBS was increased by the addition of CF because of the nucleating effect of the fiber. Moreover, a slight increase was observed in silane treated PBS/CF composites probably because the compatibility between PBS and CF was improved when CF was treated with APTMS. Liang *et al.* [5] reported that the ΔH_m of PBS/kenaf (KF) composites increased with the addition of KF but when the KF is more than 20% the ΔH_m decreased implying that KF also hinder the migration and diffusion of PBS molecular chain to the surface of the nucleus in the composites, besides the nucleation effect. SEM photographs revealed that the interfacial adhesion between PBS and KF (no treatment) needs further improvement. However, this was not the case for the CF used in this study, the ΔH_m of PBS/CF composites increased with the addition of CF up to 40%.

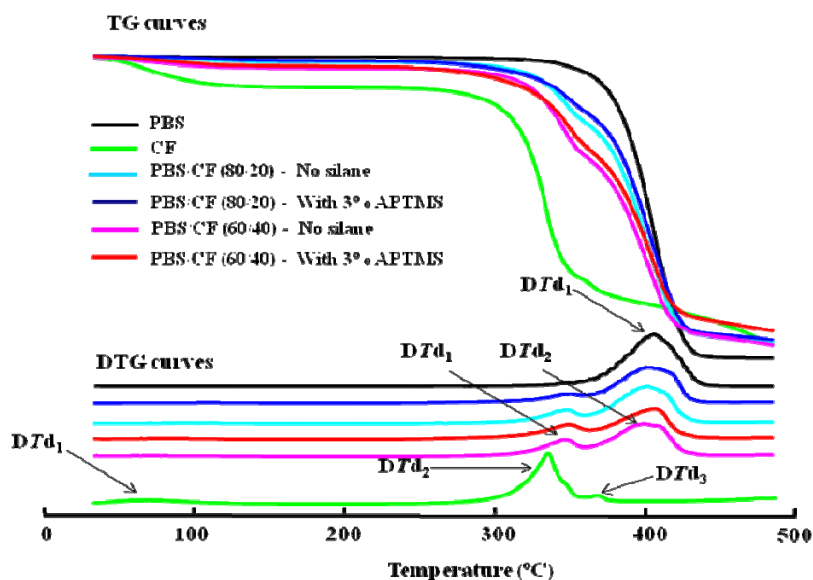
In general, 2 factors control the crystallization of polymeric composite systems: (1) the nucleation effect of fillers, which enhances crystallization; and (2) the hindering effect of fillers on the movement of polymer molecular chains to the surface of the growing polymer crystal, which inhibits crystallization [5,36]. The first factor applies in this study.

Table 1. Thermal properties of poly(butylene succinate)/cotton fiber (PBS/CF) composites with different concentrations of CF.

CF content Wt%	$T_m(^{\circ}\text{C})$		$\Delta H_m (\text{J/g PBS})$		$X_c (\%)$							
	First heating		Second heating		First heating		Second heating		First heating		Second heating	
	Without treatment	With 3% APTMS	Without treatment	With 3% APTMS	Without Treatment	With 3% APTMS	Without treatment	With 3% APTMS	Without treatment	With 3% APTMS	Without treatment	With 3% APTMS
0	114.2	-	112.6	-	65.38	-	64.55	-	59.27	-	58.52	-
10	112.8	113.4	112.6	112.9	65.20	67.51	64.10	66.01	59.11	61.21	58.11	59.85
20	112.7	113.3	112.5	112.7	67.18	71.06	65.65	68.84	60.91	64.42	59.52	62.41
30	112.5	112.9	112.3	112.5	73.07	76.80	69.37	72.48	66.25	69.63	62.89	65.71
40	112.3	112.7	112.2	112.4	75.85	78.65	73.96	75.51	68.77	71.31	67.05	68.46

3.3. Thermogravimetry (TG) Analysis

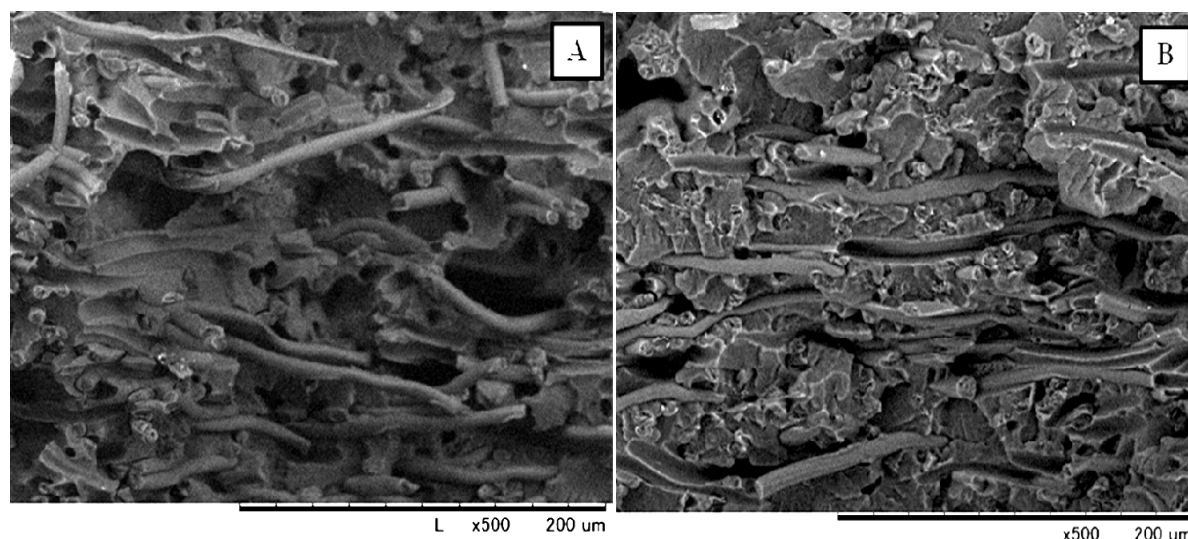
Figure 4 shows the TG curves and derivative thermograms (DTG) for PBS, CF and PBS/CF composites (treated and untreated). The major peak of the DTG curve of neat PBS is observed at about 402 °C. The thermal degradation of CF occurs in three stages. An initial DTG peak at around 50 to 150 °C corresponds to the heat of vaporization of water from the fiber. The second stage at 150 to 350 °C is the degradation of cellulosic and non-cellulosic materials. The third stage (350 to 450 °C) is due to the final decomposition of CF materials. Similar patterns were observed in other natural fibers such as those of kenaf [5], bamboo [8], and recycled newspaper [37]. In PBS/CF composites, two peaks were observed: the first at 345 °C, which corresponds to the degradation of cellulose, and a second at around 400 °C, which corresponds to decomposition of the PBS matrix. At 400 °C, the weight losses of treated and untreated PBS/CF composites were 60 and 66%, respectively. The silane treated composite has slightly lower weight loss than the treated composite.

Figure 4. Thermogravimetry (TG) and derivative thermograms (DTG) curves of PBS, CF, PBS/CF (80/20 wt%), and PBS/CF (60/40 wt%) composites with and without 3%-APTMS treatment.

3.4. Fracture Morphologies of PBS/CF Composites

The microstructure of the fracture surface of the composites tested for tensile strength was examined using SEM. SEM images of PBS/CF composites at a filler loading of 40 wt% are shown in Figure 5. The composite without silane treatment has numerous voids and free long fibers on the surface. This indicates that the interaction between the CF and PBS matrix is weak, resulting in less interfacial adhesion (Figure 5A). On the other hand, the gaps are reduced and densely knitted texture is observed in the silane-treated composites (Figure 5B). This implies that the compatibility between the CF and PBS is improved when CF is treated with the silane coupling agent APTMS. Similar observations of silane-treated composites have been published showing that silane coupling agents improved the compatibility between the polymer matrix and fiber. For instance, Shih *et al.* [9] observed that the compatibility between the bamboo husk fiber and Bionolle was improved when the fiber was treated by silane coupling agent which is shown by the densely knitted texture similar to the SEM photograph of PBS/CF shown in this paper. Zhao *et al.* [3] reported that aminosilane was observed to be a suitable adhesion promoter for PBS/rice straw fiber (RSF) composites which improved the tensile strength of the composites and the interaction between RSF and PBS matrix. The FTIR results showed that aminosilane could form hydrogen bonds with the ester carbonyl of the PBS matrix, thus improving the tensile strength.

Figure 5. SEM micrographs of fracture surface of PBS/CF (60/40 wt%) composites (A) without silane treatment and (B) with 3% APTMS.



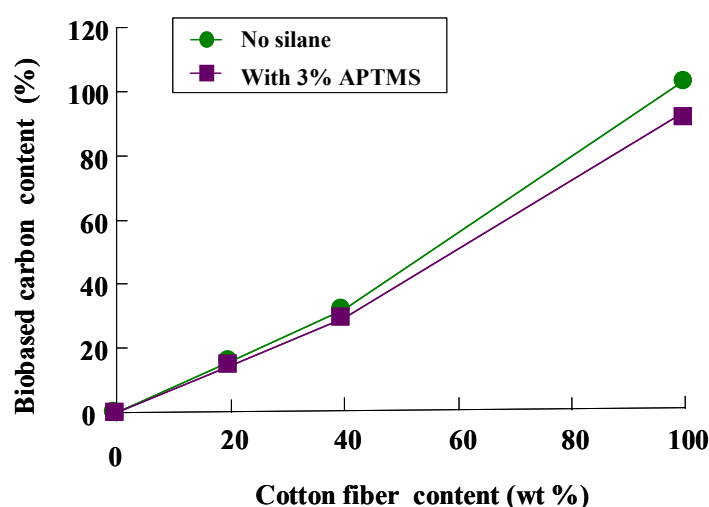
3.5. Biobased Carbon Content of PBS/CF Composites

The measurement of biobased carbon content is important in promoting polymer composite products developed from biomass [29]. The biobased carbon content of PBS/CF composites (treated and untreated) is shown in Figure 6. The biobased carbon contents of PBS and APTMS are almost 0% because these materials are petroleum-based compounds. CF has a biobased carbon content of $103.8\% \pm 0.32\%$, which is slightly higher than 100%. This may be explained by the use of cotton several years old to produce the CF. For PBS/CF composites (treated and untreated), the biomass carbon ratios

increased with increasing CF content. Silane-treated PBS/CF composites gave a lower biomass carbon ratio than untreated composites. This can be explained by the fact that APTMS is a petroleum-based compound and its biomass carbon ratio is nearly 0.

The pMC value of silane-treated CF was reduced from 103.8 to 94.15 owing to the dilution of fossil-based C3 units in APTMS relative to CF. The ratio of the silane units (C3) inside the CF to the cellobiose units (C6) was calculated as 0.205. From this calculation, it was found that one molecule of APTMS silane coupling agent per 5 cellulose unit of CF (18.11 wt%) was inserted in the case of 3% APTMS treatment. However, the extent to which APTMS was bonded to CF was unclear because CF was simply mixed with free APTMS.

Figure 6. Biobased carbon content of PBS/CF composites as a function of CF content.



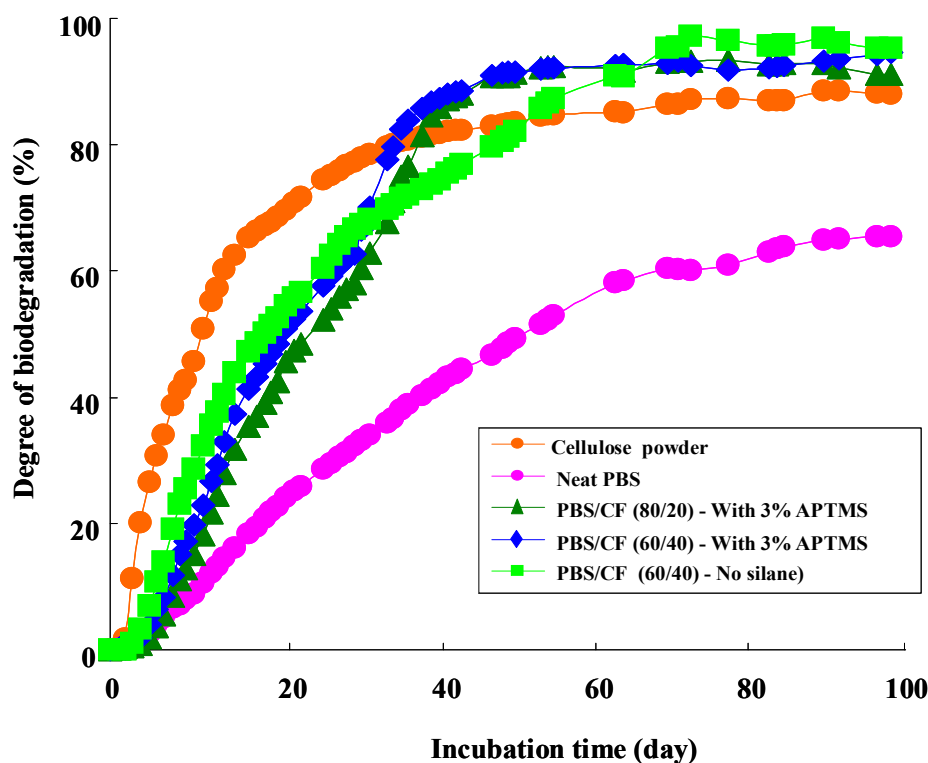
3.6. Biodegradability of PBS/CF Composites in Accordance with ISO 14855-2

The biodegradation of neat PBS and PBS/CF composite sheets (treated and untreated) in controlled compost at 58 °C was measured using a MODA apparatus on the basis of ISO 14855-2. The results are shown in Figure 7. During the first stage of biodegradation (0–30 days), the degradation of neat PBS was slower than that of the PBS/CF composites indicating that CF improved the degradation of PBS. As compared between the composites with and without silane treatment, the untreated composite showed a slightly higher degradation rate (*ca.* 65%) than the treated composite (*ca.* 60%). The improved interfacial adhesion between PBS matrix and CF caused by the silane coupling agent reduces the possibility of water and microorganisms or enzymes (*i.e.*, cellulase and lipase) to penetrate the samples, thus the lower degradation rate. However, during the second stage of biodegradation (30–50 days), the silane-treated composite showed a higher level of biodegradation than the untreated composite. A possible explanation is that the surface of the composite was already disintegrated at the end of 30 days due to the prolong exposure to the composting environment; therefore the composites had become susceptible to microbial access. Meanwhile, the biodegradation rate of the untreated composite slowed down and it should be related to the preferential decomposition of CF at an early stage and slower biodegradability of the PBS at the next stage. After 60 days, the levels of biodegradation for neat PBS and PBS/CF composite sheets were *ca.* 60% and 90%, respectively. In the last 90–100 days, the biodegradation rate of both treated and untreated PBS/CF (60/40) was *ca.* 95%,

showing that silane treatment of CF had not affect the biodegradation rate of the composites. Liu *et al.* [8] reported that the weight loss after 180 days of PBS and PBS/jute fiber composites with fiber content of 10, 20, 30% after 180 days is 31.4%, 62.5%, 54.8, 47.3%, respectively. Moreover, soil burial test of PBS/abaca composite with fiber content of 10% was degraded by 40% after 90 days [4]. These results suggest that the presence of natural fibers in the composites promotes the biodegradation of PBS.

The biodegradation of neat PBS sheet was observed to saturate at *ca.* 65%. This could be attributed to the activity of the compost, which cannot be maintained for more than 3 months without reinoculation. However, if the compost in this system is refreshed or reinoculated, the biodegradation of neat PBS will be re-started and may reach 100%.

Figure 7. Biodegradation of cellulose powder (microcrystalline), neat PBS, and PBS/CF composites sheets (10 mm × 10 mm × 0.5 mm) with and without silane treatment in controlled compost at 58 °C based on ISO 14855-2.



4. Conclusions

In this study, CF was demonstrated as effective filler for PBS, as shown by the increase in tensile strength and higher degradation rate (as evidenced by higher ΔH_m and X_c values, higher biobased carbon content and degree of biodegradation) of PBS/CF composites. Addition of silane coupling agent APTMS improved the tensile strength and crystallinities of the composites. Although the thermal stability of the composites decreased with the addition of CF, the addition of silane led to a slight increase in the thermal stability of the composites relative to that of untreated composites. The interfacial adhesion between the CF and PBS is slightly improved when CF is treated with the silane coupling agent APTMS. PBS/CF composites showed a higher level of biodegradation than did

neat PBS in controlled compost at 58 °C. Therefore, the addition of both CF and APTMS to PBS gives better results.

Acknowledgements

The authors are thankful for the financial support of the New Energy and Industrial Technology Development Organization (NEDO) for the Research Project entitled “Development of Preparatory Basic Bioenergy Technologies: Accelerated Technology Development for Biofuel: R&D of Method to Measure Biomass Carbon Ratio of Biopolyolefin”.

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