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Investigation of the Durability of Sisal Fiber/PLA Biocomposite through Evaluation of Biodegradability by Means of Microbial Growth

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Abstract

The aim of this work was to investigate the microbial biodegradation of 3-(trimethoxysilyl) propyl methacrylate (TPM) modified (silanized) sisal fibres/PLA biocomposites by *Aspergillus niger*. The modification of the sisal fibres performed excellently, improving hydrophobicity as well as mechanical properties. Compared to the unmodified sisal/PLA biocomposite, it produced a better interfacial adhesion between the fibres and the PLA matrix. In addition, silanization also increased the crystal size and crystallinity in the biocomposite, which decreased thermal decomposition to an observed maximal activation energy of 213 kJ/mol. This indicated the stability of silanized sisal biocomposite in resisting. After the microbial growth test, despite the molecular weight of all biocomposites declining due to biodegradation, the silanized sisal PLA still possessed better properties than the unmodified biocomposite, particularly storage modulus, molecular weight and hydrophobicity, which reflected the inhibition of enzymatic degradation. Furthermore, the evidence of less erosion and fewer fungal hyphae on the surface of the modified biocomposite, was authentic confirmation the decrement of fungal growth of the silanized sisal /PLA biocomposite.

Key words: **S**isal fibre; Polylactic acid (PLA); Surface modification; Microbial growth; Biodegradation

Introduction

Nowadays, there is an increasing demand for biodegradable composite materials based on lignocellulosic fibres and polymers, especially polylactic acid. Continuous growth in this demand is seen in both industrial and consumer markets. Concerns about environmental problems and the future depletion of fossil-fuel resources are driving this demand[(1-3)]. The attraction and potential of biocomposite materials depend on their biodegradability, the renewability of their raw materials, and also their functional properties compared to conventional composites already in use in various applications from automobiles, to packaging, household equipment, construction, or furnishings[(4-6)]. The performance of biocomposites[(7)] in these applications must ensure a long product lifetime. In order to maintain the performance of biocomposites, it is essential to restrain enzymatic degradation due to microbial growth. Microorganisms find natural nutrients in the carbon content of biocomposites[(8)], therefore, the antimicrobial activity of the composites is of genuine interest. Among the various microorganisms in nature, *Aspergillus niger* grows anywhere, either indoors or outdoors, under suitable humidity and temperature. It excretes enzymes to degrade and digest substances containing carbon. Its ability to produce many types of enzymes such as cellulase, lipase e.g., enables it to grow and reproduce on many products such as furniture, household equipment or anything containing cellulose. Furthermore, there are evidences to confirm that *Aspergillus niger* can also degrade plastic materials, especially biodegradable polymers such as polylactic acid or polycarpolactone by using the enzyme lipase to hydrolyse ester bonds[(9,10)]. Thus, it has a tendency to shorten the service life of those materials, particularly cellulose fibre/biodegradable polymers such as sisal/PLA biocomposites, which are simply invaded by the fungus.

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There have been many attempts to extend the service life of bioplastics or biocomposites with antimicrobial additives. Although these additives are effective in retarding microbial growth, but some of them might release to environment after product expiration, such as antimicrobial additive type of nano-metal[11] and therefore do not constitute a sustainable solution. Furthermore, those additives possibly migrate from the materials to the environment with negative ecological effects[12]. Modification of the surfaces of the lignocellulosic fibres used as reinforcement fillers in biocomposites is another potential method of improving the antimicrobial behaviour of these materials. The modification of these fibres could significantly inhibit any micro-organism[13]. This inhibiting effect was due to the increased hydrophobicity of the fibres and improved fibre-matrix interfacial adhesion. These changes considerably enhance the performance of biocomposites by reducing water uptake and internal voids[14]. Further important improvements were an increase of crystallinity with the crystal size of the polymer matrix and better loading transfer ability of the fibre. These effects help to control biocomposite performances such as mechanical properties, thermal properties, water uptake, and biological degradation[15-17]. Previous reports on biocomposites point to the remarkable dependence of their biodegradability on their hydrophobic properties and crystallinity, which is able to reduce moisture uptake. These conditions, do not favour microbial growth, and consequently prevent enzymatic degradation from hydrolysis reactions[18,19]. Therefore, in order to improve the inhibition of microbial growth and delay biodegradation, controlling moisture uptake and microbial growth through the improvement of the barrier properties of the biocomposites is essential to sustain their long-term optimal performance in application.

Among the many methods for modifying lignocellulose fibres, such as alkaline treatment, esterification, thiocycanate or silane treatment[14,20,21], silane treatment or silanization has an excellent potential to improve the mechanical and thermal properties and reduce water uptake due to its creation of a glassy barrier in biocomposites[16].

Therefore, the aim of this work to evaluate and improve the effect of fibre surface treatment on the long term performance of biocomposites through the comparison of their mechanical, thermal, hydrophobic, and crystalline properties before and after biodegradation. Sisal fibre was modified by 3-(trimethoxysilyl)propyl methacrylate and then compounded into polylactic acid (PLA) for fabrication of the biocomposite. We evaluated the long term service of biocomposite properties and microbial growth by ISO 864-1997 method B test using *Aspergillus niger*[22,23]. To determine the effect of the surface modification on the inhibition of microbial growth and enzymatic degradation, we compared the mechanical and thermal properties, hydrophobicity, and crystallinity, including their surface appearance, both before and after microbial exposure.

Materials and Experimental Procedures

Materials

Polylactic acid pellets (D 1.5%, density 1.25 g/cm^3, MFI 25 g/ 10 min), Ingeo^{TM} Biopolymer 3051D injection moulding grade, were from Nature Works LLC. Sisal fibre was supplied by the Thai Royal Project, the fibre was chopped into length of 5 mm 3-(trimethoxysilyl)propyl methacrylate (Sigma Aldrich, 98%, density 0.971 g/cm^3) was the reagent for the chemical modification. Ethanol (Sigma-Aldrich, purity of 99%) were used as solvents in the chemical modification processes.

Chemical modifications of sisal fibre

Sisal was alkaline treated with 6% NaOH solution for 48 h at ambient temperature. After that, the fibre was neutralized with water and dried in an oven at 80°C for 12 h. The treated sisal was modified with 3-(trimethoxysilyl) propyl methacrylate according to a previous work[14]. After modification, the fibres were dried in order to remove moisture at 80°C for 24 h in an oven. They were then put in a plastic zip bag and kept in a dessicator.

Fabrication of biocomposites

Compounding process

PLA pellets and the sisal fibre (length 4- 6 mm) were dried in an oven at 80°C for 12 h and kept in zip bags to exclude moisture. PLA pellets and 10% by weight of either unmodified or silanized sisal fibres were mixed together at 50 rpm for 5 min in an internal mixer (Brabender) at 185°C.

Compression moulding

The compounded fibre/PLA biocomposites were ground to small granules in a grinding machine.

The granules were dried at 80°C in the oven for at least 12 h before compression moulding in order to avoid degradation by hydrolysis during the thermal process. The biocomposite sheets were fabricated by compression moulding. The granules were put in a mould of 100 × 100 mm and then compressed at the following settings: pressure of 100 kN, temperature of 180°C, and holding time of 2 min, and then allowed to cool down.

Microbial growth test: fungal growth

The test of microbial growth was conducted according to ISO 846-1997 by using method B. A fungus of *Aspergillus niger* was chosen as the active microorganism. In accordance with the procedure, the sample specimens, measuring 20 × 20 mm, were placed in agar Petri dishes. The agar was prepared and separated into no-nutrient agar for method A and nutrient agar for method B (according to ISO 846-1997). A solution of suspended spores of *Aspergillus niger* was prepared following the procedure of ISO 846-1997 and 100 µL of the solution (4.5×10^6 spores/ml) was dropped onto each of the specimens, which were then kept in an incubator. The incubator was conditionally controlled with a temperature of 29 ±1°C and RH humidity of 85-90%. The incubation continued for 28 days.

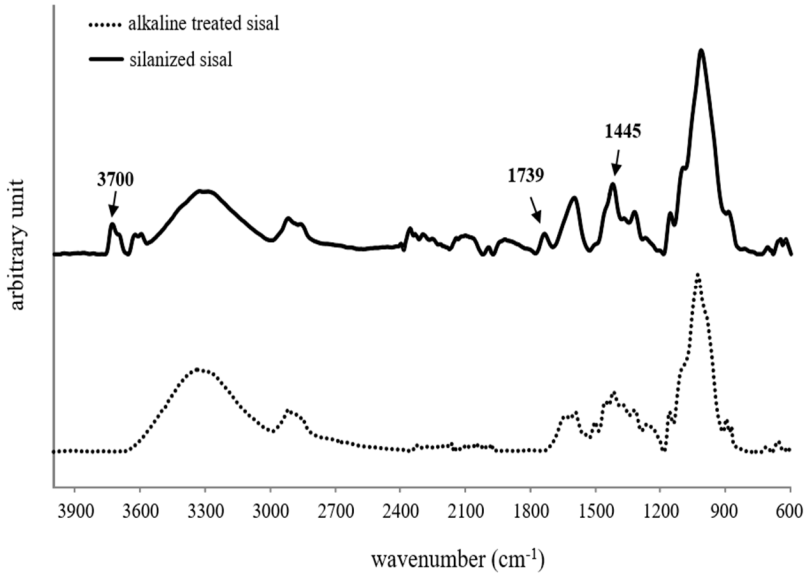

Figure 1. Comparison of FTIR spectrum of alkaline treated and silanized fibre.

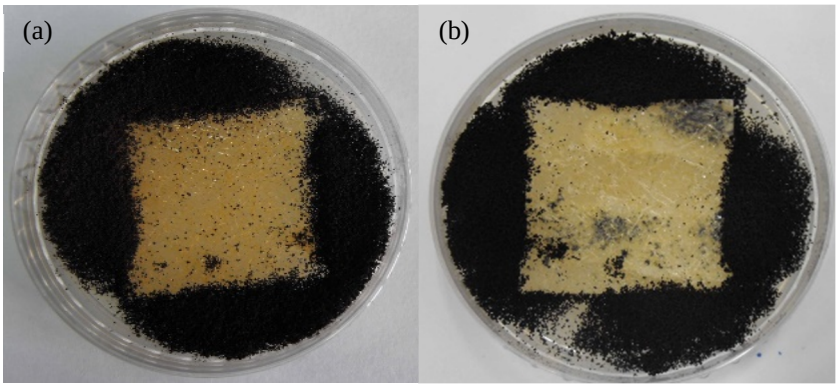

Figure 2. Microbial growth test of biocomposites: (a) unmodified fibre, and (b) silanized fibre.

Characterization

Visible optical images

An ordinary camera captured the images of the specimens.

Fourier-transform infrared spectroscopy (ATR-FTIR)

The functional groups of cellulosic fibre after chemical modifications were monitored with a Bruker Tensor 27 FTIR spectrometer equipped with a gate attenuated total reflection (ATR) holder with a diamond FTIR crystal. Each spectrum was based on 16 scans with a resolution of 4 cm^{-1}.

FTIR quantitative analysis

In order to quantitatively analyse the bio-degradation of the PLA biocomposites, carbonyl intensity index analysis was used as follows:

Carbonyl intensity
C=O (1,745 cm^{-1})/CH_3 (1,450 cm^{-1}) (for PLA)

Size exclusive chromatography (SEC)

The molecular weight of the PLA was analysed by an SEC instrument from Shimadzu (Japan). A PLA solution of concentration 4 mg/mL, was prepared by dissolving in THF (Sigma-Aldrich, purity of 99%). The polymer solution was doubly filtered before being injected into the SEC column. Mn, Mw and MWD data were recorded.

Differential scanning calorimeter (DSC)

The changes in melting temperature (T_m) and polymer crystallinity were determined using a Netzsch DSC 200 F3 Maia (Germany) calibrated with indium standard. Approximately 5 mg of each sample was placed in a standard 40 μL aluminium crucible in N_2 atmosphere at 50 mL/min gas flow. Both the first and the second heating runs were recorded and the heating/ cooling rate used was ±10°C/min. The results were obtained from the first and the second heating run as an average value of three samples.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal behaviour was analysed by a Rheometric Scientific DMTA V in tensile mode. Experiments were carried out with a heating rate of 3°C/min and mode of multiple frequency strain. Storage modulus vs. temperature were recorded and analysed. The results were obtained as an average value from three samples.

SEM analysis

The JEOL model JSM 5800 scanning electron microscope was used. The samples were cut into small pieces and dried at 70°C for 24 h and then kept in a desiccator for 48 h. A cross section surface of the biocomposite samples was analyzed to study the interface between the fibre and matrix. After 28 days of microbial growth test, the samples of biocomposites were cleaned with 70% ethanol to remove all biofilm of *Aspergillus niger* from the surface and were then kept in a desiccator for 48 h. The surfaces of the PLA biocomposites were also imaged by SEM to study biodegradability.

Contact angle

Contact angles on the biocomposite specimens were measured with a Dataphysics OCA 15EC. The measurements were carried out at room temperature using a droplet of distilled water on specimen samples of 1 cm × 1 cm. Sessile drop volume was maintained at 5μL using a microsyringe. The sample measurement was repeated 6–9 times in different positions on the same specimen sample.

Wide angle X-ray diffraction

The crystal structure of specimens of sisal/ PLA biocomposites was determined by wide angle X-ray diffraction (WAXD) using a Phillips model X' Pert MPD (Netherlands). The diffraction scans of the specimens were obtained using a 3kW Rigallu III diffractrometer equipped with Ni-filtered CuKα radiation (λ 0.15418 nm) in diffraction mode. In order to determine the size of crystallites in the specimens, Scherrer's equation was applied to the X-ray diffraction data, which assumed Gaussian profiles.

Results and Discussion

Surface modification of sisal fibre

Figure 1 presents the FTIR spectrum after surface modification of sisal fibres with 3-(trimethoxysilyl) propyl methacrylate. After modification, CH_2 bending increased at 1,445 cm^{-1} and new absorbance peaks appeared at 1,739 cm^{-1} and 3,700 cm^{-1}, which were identified as the functional groups

of C=O of the methacrylate group and Si-O, respectively. This could confirm the successful surface modification of the sisal fibres[24].

FTIR analysis of specimens before and after microbial growth test

ATR-FTIR measurement determined the degree of enzymatic degradation in the biocomposites after microbial growth. As the FTIR spectra in Figure 3 the absorbance peaks of C=O and C-O-C of the ester group at 1,745 cm^{-1} and 1,100 cm^{-1} decreased in both biocomposites. This means that *Aspergillus niger* was able to digest and assimilate PLA as nutrition for microbial reproduction. This was in agreement with the appearance of microbial growth after 28 days, as demonstrated in Figure 2. However, the distribution of fungal spores on the unmodified sisal/PLA biocomposite was more regular and noticeable than that on the modified sisal/PLA biocomposite. This could indicate the suitability of unmodified sisal biocomposite as an environment for fungal growth.

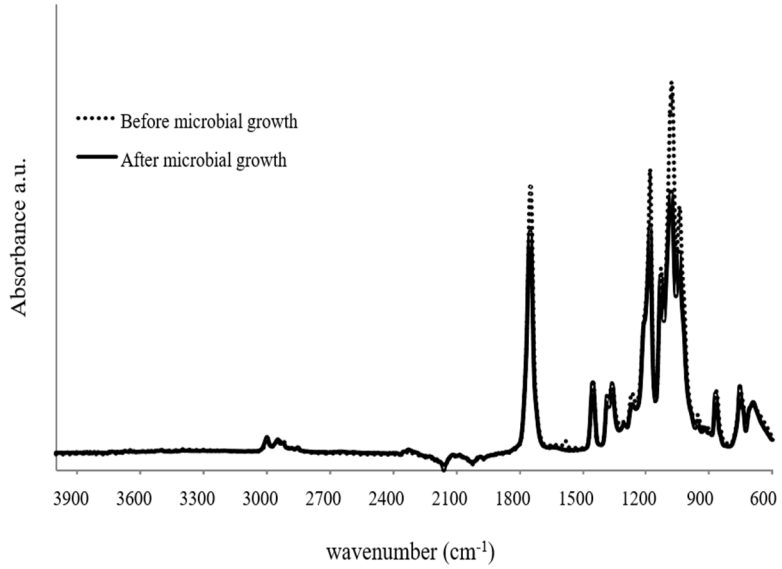

Figure 3. Comparison of FTIR spectrum of unmodified sisal/PLA biocomposite before and after microbial growth test.

The ability of *Aspergillus niger* to degrade PLA biocomposites could be further confirmed by the decline of the absorbance peak of the ester group of carbonyl at 1,745 cm^{-1} and C-O-C at 1,100 cm^{-1} in both sisal biocomposites after 28 days of microbial growth. Normally, *Aspergillus niger* can produce and excrete various types of enzymes, such as cellulase and lipase, to digest nutrient materials for its reproduction and growth. In previous research[17], it was reported that the enzyme lipase produced by *Aspergillus niger* enabled hydrolysis of PLA at ester bonds in the main chains. Therefore, the decrease in ester groups in the biocomposites here could indicate enzymatic degradation by *Aspergillus niger*.

However, comparing silanized sisal with unmodified sisal, the effect of modification on biodegradability was sufficiently effective to retard biodegradation by reducing hydrolysis due to the use of silane as a coupling agent. Biodegradation in the PLA biocomposites was evaluated by the carbonyl index, as expressed by the absorbance intensity ratio between the ester group of 1,745 cm^{-1} and the methyl group of 1,450 cm^{-1} presented in Table 1. The carbonyl index decreased by 1.5% in the silanized sisal/PLA biocomposite, while the reduction of the index in the unmodified sisal/PLA was 3.5%. This indicated that less biodegradation had occurred in the modified fibre composite, probably due to the enhanced compatibility and hydrophobicity produced by the surface modification. This modification built a barrier to biodegradation and, consequently, the microbial growth in the silanized sisal/PLA biocomposite was reduced.

Table 1. Comparison of carbonyl index before and after microbial growth test.

	FTIR peak intensity ratio	
	Before biodegradation	After biodegradation
Unmodification	3.75	3.62
Silanization	3.26	3.21

Molecular weight analysis

Table 2 presents a comparison of the molecular weights of sisal/PLA biocomposites before and after the microbial growth test. The M_w and M_n of the silanized sisal/PLA were significantly higher than those of the unmodified sisal bicomposite, which could be expected due to reduced thermal degradation during the thermal process. A possible reason to explain this effect is resulted by lignin removal out of the fibre after silanization process. Generally, lignin is a substance that is releasable the free radicals when exposed to thermal energy. Therefore, a decrease of lignin in the silanized sisal fibre would sequentially reduce the degradation of PLA due to less free radical attack during compounding the biocomposite. However, after microbial growth, the molecular weights of both biocomposites were noticeably lower, which accorded with the FTIR results. However, the percentage losses of M_n and M_w of unmodified sisal/PLA were 14.3% and 12.2% while TMS-silanized PLA showed losses of 9.7% and 6.9%, respectively. This was significant evidence to confirm that the silanization of sisal had an effective potential to inhibit enzymatic degradation in the PLA biocomposite. As observed in Figure 1, the visual optical images revealed that the *Aspergilus niger* spores grew less on silanized sisal/PLA biocomposite. This could be used as an indicator to explain the low activity of fungal growth. In principle, the silanization of cellulosic fibre results in an enhancement of interfacial adhesion as well as a reduction of moisture uptake[12]. By this condition, it is not probably suitable for colonization of fungus. As considered in term of hygroscopic property, it is known that the fungus preferentially grows up on a humid area and then reproduces as a biofilm on the substrate[25]. Moreover, hyphae of fungus would also slowly penetrate into the substrate for tight support of biofilm growth. Hence, the fibre modification by silane is comparative generating of protective barrier to against the fungal growth. Therefore, the lower reduction in the molecular weight of the silanized sisal biocomposite compared with the unmodified sisal biocomposite could be presented as the proof of fungal inhibition.

Table 2. Presents molecular weight of sisal/PLA biocomposites before and after microbial growth test.

	Microbial growth	M_n	M_w	MWD
Unmodified	Before	58,919	103,420	1.76
	After	50,491	90,767	1.80
Silanized	Before	68,964	117,134	1.70
	After	62,241	108,946	1.66

Thermal property analysis

The data of the thermal properties of the PLA biocomposites is presented in Table 3. The glass transition temperature (T_g) of both unmodified and silanized sisal PLA biocomposite increased slightly after biodegradation. Additionally, as considered the value of T_g and % crystallinity either before or after biodegradation, it was found that the silanized sisal PLA biocomposite showed the higher values over than that of the unmodified biocomposite obviously. This was due to facilitating to induce crystallization by the silane groups of sisal fibre. Furthermore, the cold crystallization temperature (T_{cc}) of silanized sisal biocomposite was significantly lower than the T_{cc} of unmodified sisal biocomposite. This meant that after biodegradation, the PLA matrix in silanized sisal biocomposite used less energy to reach the cold crystallization state. On the other hand, the higher T_{cc} of the unmodified sisal biocomposite indicates that it demanded more energy for crystalline rearrangement. Nevertheless, the lower T_{cc} of silanized sisal/PLA biocomposite after the microbial growth test, resulted from the lower M_n of PLA due to enzymatic degradation. Actually, the shorten backbone chains could easier rearrange to recrystallization[26]. Therefore, this meant that the addition of silanized sisal to the PLA matrix not only improved the mechanical and thermal properties but also assisted the promotion of crystallization in the biocomposite, which significantly retarded biodegradation by reducing access to nutrients for *Aspergillus niger*.

Table 3. Information of thermal properties by DSC.

Sisal/PLA biocomposite	Biodegradation	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH heat of fusion (J/g)	% Crystallinity
Unmodified	Before	60.6 ± 0.2	109.4 ± 1.2	153.4 ± 0.8	20.8 ± 0.9	22.6
	After	60.8 ± 0.1	110.4 ± 0.1	153.2 ± 0.8	24.8 ± 0.2	27.6
Silanized	Before	60.5 ± 0.9	108.9 ± 0.0	153.2 ± 0.1	25.3 ± 1.7	27.6
	After	61.3 ± 0.6	107.2 ± 0.2	153.3 ± 0.1	26.9 ± 0.9	29.3

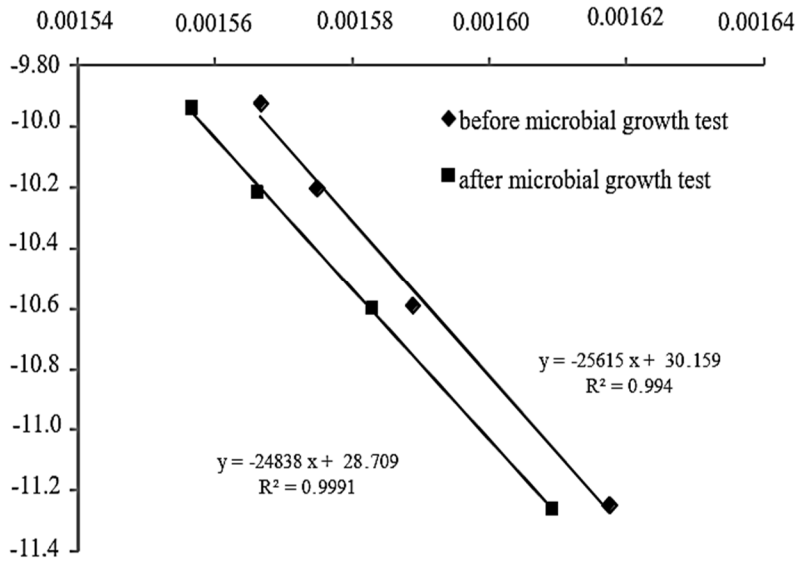

Figure 4. A plot of relationship between $\ln(\beta/Tm^2)$ and $(1/Tm)$ silanized sisal/PLA biocompsite before. and after microbial growth.

The kinetic study of non-isothermal degradation used a maximum rate model to calculate the activation energy of decomposition (Ea) via the equation: $\ln \beta/Tm^2 = \ln AR/Ea - Ea/R.Tm$, where β and T_m were, respectively, heating rate and temperature at the maximum rate of decomposition. Meanwhile, *Ea* was calculated from the linear relationship of slope.

A comparison of the activation energy (Ea) of thermal decomposition of the biocomposites is presented in Table 4. The silanization of sisal fiber significantly increased the resistance of the biocomposite to thermal degradation. The better interfacial adhesion of silanized sisal with the PLA matrix, observed in Figure 7(c) of SEM section, could act as a heat barrier in the biocomposite, confirming the benefit of silanized sisal in the PLA matrix. This meant that silanization could not only improve thermal properties but also inhibit the fungal growth of *Aspergillus niger* on the biocomposite. Obviously, the images of the cross-section and surface of the biocomposites in Figure 7, indicated the preference of *Aspergilus niger* for the unmodified sisal biocomposite. The strong interfacial adhesion between fiber and matrix in the modified biocomposite restrained moisture absorption and therefore the permeation of *Aspergillus niger* into the biocomposite. Furthermore, the inherent hydrophobicity of silanized sisal also reduced water uptake in the biocomposite and this was confirmed by contact angle measurements.

Table 4. Activation energy of thermal decomposition.

Sisal/PLA biocomposites	Activation energy (*Ea*) (kJ/mol)	
	Before microbial growth	After microbial growth
Unmodified	205	198
Silanized	213	207

Evaluation of hydroscopic property of biocomposites.

As previously explained, the use of 3-(trimethoxysilyl) propyl methacrylate as a coupling agent to modify sisal fibres could increase hydrophobicity, reducing water uptake in the biocomposite. Consequently, it could also restrain microbial invasion. The contact angle on silanized sisal/PLA biocomposite was significantly higher than on the unmodified biocomposite as presented in Table 5. This crucial evidence indicated that the silanized sisal/PLA biocomposite repelled moisture better than the unmodified biocomposite. Although the contact angle on silanized sisal biocomposite declined after the microbial growth test, it still remained greater than 90° which indicated the inherent hydrophobicity of the biocomposite.

Table 5. Comparison of degree of contact angle of before and after microbial growth test.

Biocomposite	Microbial growth test (degree of contact angle)	
	Before	After
Unmodified sisal/PLA	97.3 ± 1.8	89.4 ± 1.2
Silanized sisal/PLA	109.9 ± 0.5	102.4 ± 0.8

However, after the microbial growth test, the decrease in molecular weight in the biocomposites included surface damage which could significantly facilitate moisture diffusion. Therefore, the contact angle of all biocomposites declined noticeably after the microbial growth test as shown in Figure 5.

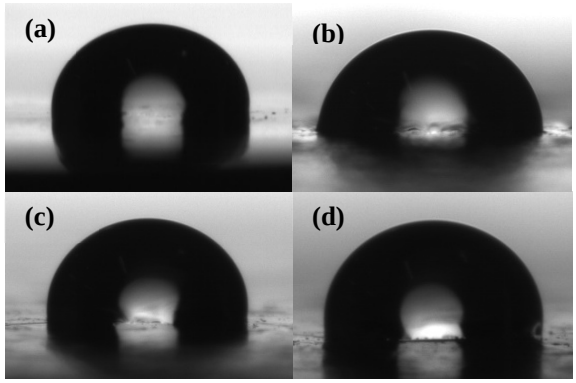

Figure 5. Contact angle measurement of bio-composite – microbial growth test: (a) unmodified – before, (b) unmodified – after, (c) silanized-before, and (d) silanized – after.

Dynamic thermal mechanical analysis (DMTA)

The mechanical properties of the PLA bio-composites were analysed by dynamic thermal mechanical analysis (DMTA). The results are presented in Figure 6. The greater storage modulus (E') of silanized sisal/PLA biocomposite, indicated a better interfacial adhesion between the two phases, as described previously. The TPM silane on the sisal tightly bound the PLA and fiber phases, substantially increasing the reinforcing efficiency of the sisal fibre in the biocomposite. Furthermore, between 125°C and 135°C, the appearance of a small peak in the DMTA spectrum of silanized sisal/PLA biocomposite was identified as cold crystallization which was induced by the silane group of sisal. However, after the microbial growth test, the storage modulus of both biocomposites decreased as a result of enzymatic degradation by *Aspergillus niger*.

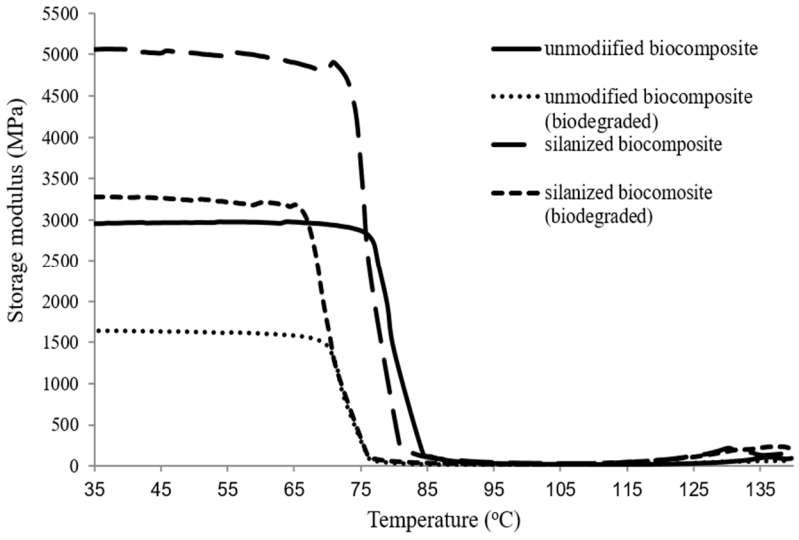

Figure 6. Comparison DMTA spectrum of the biocomposites before and after microbial growth test.

The decline of storage modulus of both PLA biocomposites after the microbial growth test indicated the damage of the biocomposite caused by biodegradation. However, inspection of the SEM image in Figure 7 reveals that very few *Aspergillus niger* spores appeared in the silanized sisal/PLA biocomposite, confirming the ability of silanization to inhibit microbial growth in the biocomposite. However, the decline of the storage modulus in silanized sisal biocomposite possibly resulted from gaps at the interface which might result from during the incubation stage of the experimental procedure. Since swelling caused by water uptake in the biocomposite could compromise its microstructure[16], it could then provoke internal stress cracking and degrade the mechanical properties of the composites

Surface morphology analysis

After the microbial growth test, *Aspergillus niger* spores were widely distributed in the unmodified sisal biocomposite, especially, at the fibre-PLA matrix interface, as observed in Figure 7(b). This could indicate the better growth of *Aspergillus niger* in unmodified sisal biocomosite. On the other hand, the presence of few fungal spores growing in the silanized sisal biocomposite, as presented in Figure 7(d), could reflect unsuitable conditions for fungal growth. As previously explained, the surface modification of sisal by 3-(trimethoxysilyl)propyl methacrylate could improve hydrophobicity which promotes the retardation of biodegradation from microbial growth. Similarly, Figure 7(e) and 7(f) demonstrated surfaces of biodegraded unmodified and silanized sisal PLA, respectively. Notably, *Aspergillus niger* preferred to attack and grow on the unmodified sisal biocomposite rather than the silanized sisal biocomposite. The existence of hyphae penetrating into the surface of the unmodified biocomposite can be observed in Figure 7(e) but not in the modified composite, which could confirm that *Aspergillus niger* preferred to grow on the unmodified rather than the modified composite. Furthermore, a clearer surface of silanized sisal biocomposite, as presented in Figure 7(f), could indicate the ability of silanization to inhibit the fungal invasion of sisal and thus retard enzymatic degradation.

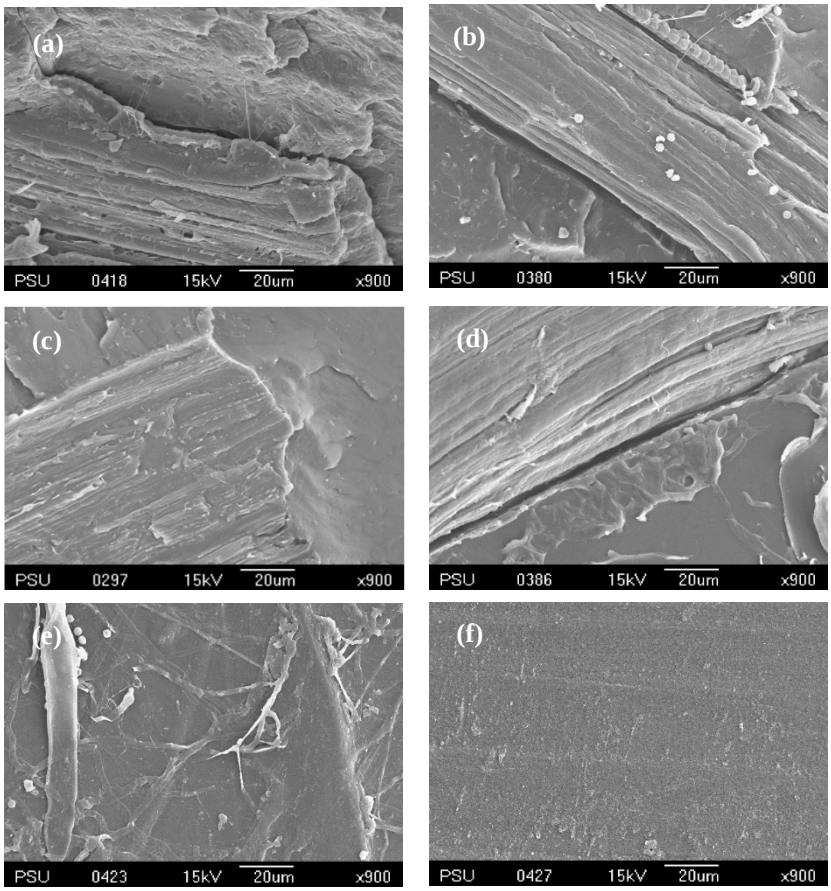

Figure 7. Cross-section images of (a) unmodified – before, (b) unmodified – after, (c) silanized – before, and (d) silanized – after and surface images of (e) unmodified – after, and (f) silanized – after.

X-ray diffraction

Figure 8 presents the WAXD spectra of PLA biocomposite after the microbial growth test. Considering the biocomposite XRD spectra before microbial growth, the broad spectrum between 10° and 25°, and also the sharp peak of the crystalline phase at 16.8°, were indications that the PLA in the biocomposites was mostly an amorphous phase. However, after the microbial growth test, the XRD peak intensity at 2θ of 16.5° in the unmodified sisal biocomposite was substantially increased, which could result from increased numbers of the short chains of biodegraded PLA. This factor could facilitate the crystallization process to reach equilibrium state as previously confirmed by DSC.

Also, the size of the crystal structure was larger after biodegradation. More short chains in the PLA might decrease the barrier energy of crystallization and, therefore, the crystals could be formed completely without any hindrance from long chains of PLA.

However, comparison of both biocomposites before and after biodegradation, reveals that the crystal size of the silanized sisal biocomposite was significantly larger than that of the unmodified sisal biocomposite: perhaps because the 3-(trimethoxysilyl) propyl methacrylate present on the sisal induced the crystallization of the PLA matrix which assisted the inhibition of fungal growth in the composite[27].

The radar chart presented in Figure 9 shows a comparison of properties in all aspects of both biocomposites after biodegradation. From this information, it is clear that the properties of the silanized sisal biocomposite were superior to the properties of the unmodified sisal biocomposite. The contact angle and the crystal size, especially, of the silanized sisal biocomposite showed significantly higher values than the unmodified biocomposite. This could indicate that the silanization of sisal effectively improved hydrophobicity as well as crystallinity to resist moisture uptake and microbial growth in the biocomposite.

Table 6. Comparison of crystal size of PLA biocomposite before and after microbial growth test.

Biocomposite	Microbial growth test	Crystal size D (nm) at 2θ = 16.5°
Unmodified sisal/PLA	Before	11.2
	After	21.7
Silanized sisal/PLA	Before	20.6
	After	24.4

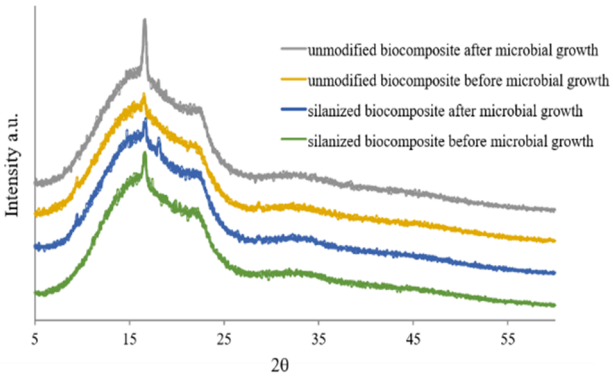

Figure 8. X-ray diffraction spectrum of the PLA biocomposites.

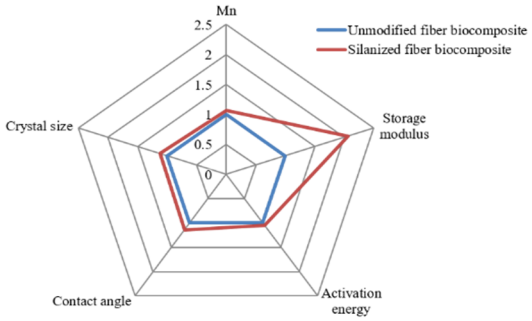

Figure 9. Comparison performance aspects of PLA biocomposites before and after microbial growth test.

Conclusions

The silanization of sisal fibre with 3-(trimethoxysilyl) propyl methacrylate enhanced interfacial adhesion between the fibres and the PLA matrix in the biocomposite. It also possessed superior properties of microbial resistance over the unmodified sisal biocomposite, as confirmed by the microbial growth test due to a product of the combination of excellent interfacial adhesion, hydrophobicity and crystallinity which formed a preventive barrier to protect the composite from microbial attack. The assessment of the performance of the silanized sisal biocomposite after biodegradation suggests that silanization could improve the durability and service lifetime of this biocomposite.

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