Thermal, mechanical, and physical properties of seaweed/sugar palm fibre reinforced thermoplastic sugar palm Starch/Agar hybrid composites

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A B S T R A C T

The aim of this research is to investigate the effect of sugar palm fibre (SPF) on the mechanical, thermal and physical properties of seaweed/thermoplastic sugar palm starch agar (TPSA) composites. Hybridized seaweed/SPF filler at weight ratio of 25:75, 50:50 and 75:25 were prepared using TPSA as a matrix. Mechanical, thermal and physical properties of hybrid composites were carried out. Obtained results indicated that hybrid composites display improved tensile and flexural properties accompanied with lower impact resistance. The highest tensile (17.74 MPa) and flexural strength (31.24 MPa) was obtained from hybrid composite with 50:50 ratio of seaweed/SPF. Good fibre-matrix bonding was evident in the scanning electron microscopy (SEM) micrograph of the hybrid composites' tensile fracture. Fourier transform infrared spectroscopy (FT-IR) analysis showed increase in intermolecular hydrogen bonding following the addition of SPF. Thermal stability of hybrid composites was enhanced, indicated by a higher onset degradation temperature (259 °C) for 25:75 seaweed/SPF composites than the individual seaweed composites (253 °C). Water absorption, thickness swelling, water solubility, and soil burial tests showed higher water and biodegradation resistance of the hybrid composites. Overall, the hybridization of SPF with seaweed/TPSA composites enhances the properties of the biocomposites for short-life application; that is, disposable tray, plate, etc.

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1. Introduction

Plastic products developed from petroleum-based polymer have caused negative environmental impacts due to the accumulation of non-biodegradable waste. Therefore, interest in utilizing the available natural resources for development of a more environmental friendly polymer has been growing continuously in order to tackle the issue.

Starch has been considered as the most promising resource for development of biopolymer due to several advantages; that is, they are renewable, biodegradable, widely available and low in cost [1]. Apart from the development of thin film, the potential of starch in development of rigid material, namely thermoplastic starch (TPS), was also discovered in previous works [2–5]. In general, TPSs possess similar properties to synthetic thermoplastic which enables the uses of various fabrication machines for its production; that is, extrusion, compression moulding, injection moulding, etc. However, pure TPS also possesses several disadvantages such as poor mechanical strength and water resistance, which limits its potential application. Therefore, modification of TPS is often necessary in order to prepare this material for real application. Blending of TPS with other natural polymer appears to be a promising approach in order to preserve the biodegradable aspect of this biopolymer. Recently, the tensile, thermal and physical properties of modified TPS derived from sugar palm starch and agar has been reported [6].

The results show significant improvement in the tensile properties of thermoplastic sugar palm starch/agar (TPSA) blend following the incorporation of agar.

Moreover, reinforcing TPS with natural fibre is another interesting approach to resolve the drawbacks of TPS. Several results have been reported on the addition of natural fibres such as kenaf [7–9], cotton [10,11], coir [12,13], sugar palm [14], kapok [15] and jute [15] into TPS matrix. Most of these studies were focused on improving the mechanical and thermal properties of TPS. In addition, enhanced water resistance was also obtained with incorporation of natural fibre into TPS material [8].

Eucheuma cottonii seaweed (also known as *Kappaphycus alvarezii*) belongs to the "red seaweed" family and is massively cultivated for the production of its hydrocolloids, namely kappa-carrageenan (k-carrageenan). However, due to the relatively low carrageenan content in the raw seaweed (25–35%), a huge amount of solid waste was produced during processing which is yet to be utilized [16]. Meanwhile, sugar palm (also known as *Arenga pinnata*) is a tropical tree that belongs to the *Palmae* family. Apart from the production of its neera sugar and starch [17], this tree was also known for producing natural fibre from its trunk, namely sugar palm fibre (SPF). Traditionally, SPF was used for various outdoor applications such as broom, ropes and roof materials [18]. This is due to the excellent characteristics of SPF as a natural fibre such as good tensile strength and resistance to water [19].

Even though there are previous studies reported on hybridization of SPF with other fibres, that is, kenaf [20] and glass fibre [21], these studies were using synthetic polymer as a matrix which is not biodegradable. It is clear from the literature review that no study has been carried out on using biodegradable TPSA as a polymer matrix for hybridized SPF/seaweed filler. SPF is known to possess both mechanical strength and water resistance; therefore, the hybridization of SPF with seaweed (Sw) seems to be a good combination to improve the properties of the material. In the present study, the effects of SPF hybridization with Sw/TPSA composites were investigated in terms of the mechanical, thermal and physical properties. Various experimental approaches were used to characterize the properties of the composites including Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), thermogravimetric analysis (TGA), mechanical testing, water absorption, thickness swelling, solubility and soil burial.

2. Materials and methodology

2.1. Materials

Sugar palm starch (SPS) was extracted from the sugar palm tree population location at Jempol, Negeri Sembilan, Malaysia. The interior part of the trunk was crushed in order to obtain the woody fibres which contain the starch. These woody fibres were soaked in fresh water followed by squeezing to dissolve the starch into the water. Water solution that contained starch was filtered to separate the fibres from the solution. This solution was then left for sedimentation of the starch. The supernatant was discarded and the wet starch was kept in the open air for 48 h followed by drying in an air circulating oven at 105 °C for 24 h. Agar powder was procured from R&M Chemicals and glycerol was purchased from Science chem.

Seaweed waste from *Eucheuma cottonii* species was obtained as waste material from seaweed extraction. The solid wastes were obtained after hot alkaline extraction process to obtain carrageenan. This by-product was cleaned with water and dried at 80 °C for 24 h in a drying oven. The dried seaweed wastes were ground and sieved then kept in zip-locked bags until further pro-

Table 1
Relative amount of reinforcing materials in composites.

Seaweed (%)	Sugar Palm Fibre (%)	Composites
100	–	Sw
75	25	HC1
50	50	HC2
25	75	HC3
–	100	SPF

cess. The moisture content and average particle size of the ground seaweed are $0.75 \pm 0.2\%$ and 120 μm respectively. Sugar palm fibre (SPF) was obtained from sugar palm trees at Jempol, Negeri Sembilan, Malaysia. The obtained fibres were ground and screened to obtained 2 mm fibre size. The average moisture content of the fibre is $6.55 \pm 0.1\%$.

2.2. Sample preparation

Thermoplastic SPS/agar (TPSA) matrix was prepared according to our previous work [6]. The ratio of starch:agar:glycerol was maintained at 70:30:30 (wt%). After this preliminary step, the resulting blend was melt-mixed using Brabender Plastograph at 140 °C and rotor speed of 20 rpm for 10 min. This mixture was granulated by means of a blade mill equipped with a nominal 2 mm mesh and thermo-pressed in order to obtain laminate plate with 3 mm thickness. For this purpose a Carver hydraulic thermo-press was operated for 10 min at 140 °C under the load of 10 t. The same processes were used for the modification of TPSA with hybridized seaweed/SPF. The weight fraction of the reinforcing materials was shown in Table 1 where the matrix was maintained at 80 wt%. All samples were pre-conditioned at 53% relative humidity (RH) for 48 h prior to testing.

2.3. FT-IR analysis

Fourier transform infrared (FT-IR) spectroscopy was used to detect the presence of functional groups existing in thermoplastic SPS blends. Spectra of the material were obtained using an IR spectrometer (Nicolet 6700 AEM). FT-IR spectra of the sample ($10 \times 10 \times 3$ mm) was collected in the range of 4000–400 cm^{-1}.

2.4. Scanning electron microscope (SEM)

The morphology of tensile fractured surfaces was observed under a scanning electron microscope (SEM), model Hitachi S-3400N, with acceleration voltage of 10 kV.

2.5. Tensile testing

Tensile tests were conducted according to ASTM D-638 at the temperature of 23 ± 1 °C and relative humidity of $50 \pm 5\%$. The tests were carried out on five replications using a Universal Testing Machine (INSTRON 5556) with a 5 kN load cell; the crosshead speed was maintained at 5 mm/min.

2.6. Flexural testing

Flexural tests were conducted according to ASTM D-790 at a temperature of 23 ± 1 °C and relative humidity of $50 \pm 5\%$. The samples were prepared with dimensions of 130 mm (L) x 13 mm (W) x 3 mm (T). The tests were carried out on five replications using a Universal Testing Machine (INSTRON 5556) with a 5 kN load cell; the crosshead speed was maintained at 2 mm/min. The support span length was set at a ratio of 16:1 to the thickness of samples.

2.7. Impact test

Izod impact tests were conducted according to ASTM D256 at a temperature of $23 \pm 1\,^{\circ}C$ and relative humidity of $50 \pm 5\%$. The unnotched samples were prepared with dimensions of 60 mm (L) x 13 mm (W) x 3 mm (T). The tests were performed on five replications using a digital INSTRON CEAST 9050 pendulum impact tester. The impact strength was calculated based on the impact energy and cross section area of the specimen as shown in Eq. (1):

$$\text{Impact strength} = \text{Impact energy (J)/area (mm}^2) \qquad (1)$$

2.8. Thermogravimetric analysis (TGA)

The thermal degradation behaviour of composites was analyzed by TGA with respect to weight loss due to increase in temperature. TGA was performed with a Q series thermal analysis machine from TA Instruments (New Castle, DE, USA). The analysis was carried out in aluminum pans under a dynamic nitrogen atmosphere in temperature range 25–900 °C at a heating rate of 10 °C/min.

2.9. Density

Density determination balance (XS205 Mettler Toledo) was used to measure the density of materials. Five measurements were conducted at 27 °C and the average value was computed.

2.10. Moisture content

Five samples ($10 \times 10 \times 3$ mm) were prepared for the moisture content investigation. All samples were heated in an oven for 24 h at 105 °C. Weight of samples before, M_i and after, M_f the heating were measured in order to calculate the moisture content. Moisture content was determined by using Eq. (2).

$$\text{Moisture content } \% = \frac{M_i - M_f}{M_i} \times 100 \qquad (2)$$

2.11. Water absorption

Five samples ($10 \times 10 \times 3$ mm) were dried in an air circulating oven at $105 \circ C \pm 2$ for 24 h in order to remove existing moisture and then immersed in water at room temperature ($23 \pm 1\,^{\circ}C$) for 0.5 h and 2 h as proposed by previous studies [13,22]. The samples were weighed before, W_i and after immersion, W_f and the water absorption of the laminates was calculated using Eq. (3):

$$\text{Water content } \% = \frac{W_f - W_i}{W_i} \times 100 \qquad (3)$$

2.12. Thickness swelling

To determine the percentage of thickness swelling, similar testing parameter were used as mentioned in Section 2.11. The samples were measured before, T_i and after, T_f immersion using a digital vernier (Model: Mitutoyo) having 0.01 cm accuracy. The thickness swelling ratio of the laminates was calculated using the following equation:

$$\text{Thickness swelling } \% = \frac{T_f - T_i}{T_i} \times 100 \qquad (4)$$

2.13. Moisture absorption

Samples were stored at $75 \pm 2\%$ RH at a temperature of $25 \pm 2\,^{\circ}C$ in order to analyze moisture absorption behaviour of the samples. The 75% RH was obtained by using a saturated solution of sodium chloride (NaCl) in a closed desiccator. Prior to the moisture absorption measurements, five samples (10 mm × 10 mm × 3 mm) were dried at $105 \circ C \pm 2$ for 24 h.

The samples were weighed before, W_i and after absorption, W_f for a certain period until a constant weight was obtained. The moisture absorption of the samples was calculated using the following equation:

$$\text{Moisture absorption } \% = \frac{W_f - W_i}{W_i} \times 100 \qquad (5)$$

2.14. Water solubility

Water solubility (WS) of the samples was determined according to the method by Kanmani and Rhim [23] with slight modification. For this, a section of sample ($10 \times 10 \times 3$ mm) was cut and dried at 105 °C ± 2 for 24 h. The initial weight of samples (W_o) was measured before immersion into 30 ml of distilled water with gentle stirring. After 24 h of immersion, the remaining section of sample was taken from the beaker and filter paper was used to remove remaining water on the surface. Then, the samples were dried again at 105 °C ± 2 for 24 h to determine the final weight (W_f). The WS of the sample was calculated as follows:

$$\text{Water solubility } \% = \frac{W_O - W_f}{W_O} \times 100 \qquad (6)$$

2.15. Soil burial

Soil burial degradation test was carried out according to modified method by González and Alvarez Igarzabal [24] and Bootklad and Kaewtatip [25]. Five samples ($15 \times 15 \times 3$ mm) were buried at 10 cm depth in characterized soil which was regularly moistened with distilled water. Iron mesh was used to wrap the samples before burying into the soil to facilitate removal of the degraded samples while maintaining the access of moisture and microorganism. The physico-chemical properties of the soil were pH: 6.52; organic carbon: 1.14%; total nitrogen: 0.07%; phosphorus 96.6 μg/g; and potassium: 45.93 μg/g. Prior to testing, samples were dried at 105 °C for 24 h and weighed to obtain the initial weight, W_i. Two sets of experiments were made for predetermined intervals of 2 and 4 weeks. Samples were taken from the soil at specified intervals and gently cleaned with distilled water to remove impurities. Afterwards, they were dried at 105 °C for 24 h and weighed to obtain the final weight, W_f. The weight loss of samples was determined using the following equation:

$$\text{Weight loss } \% = \frac{W_i - W_f}{W_i} \times 100 \qquad (7)$$

2.16. Statistical analysis

Statistical analysis of the mechanical properties has been carried out by one-way analysis of variance (ANOVA) and the significance of each mean property value was determined ($p < 0.05$) with Duncan's multiple range tests.

3. Results and discussion

3.1. FT-IR analysis

Fig. 1 shows the FT-IR spectra for Sw/SPF hybrid composites, individual Sw and SPF composites, and native SPF. The FT-IR data were examined in order to characterize the chemical bonds between TPSA, Sw and SPF. The band at approximately 2900 cm^{-1} was assigned to C−H stretching vibration from CH$_2$ and/or CH$_3$ [26]. This band also corresponds to the cellulose and hemicellulose components in natural fibre [27]. Meanwhile, the band at
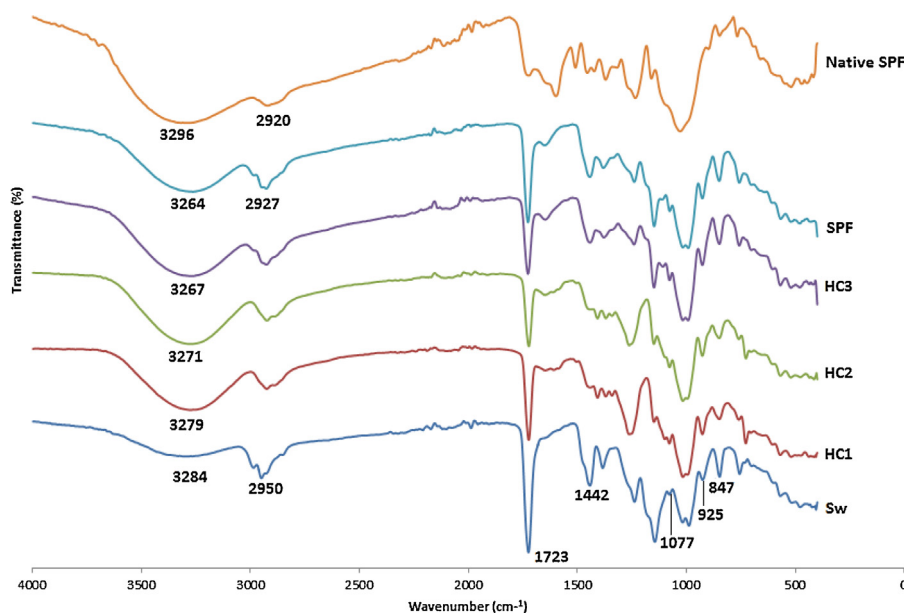
Fig. 1. FT-IR spectra of Sw/SPF hybrid composites.

$3100–3700\,cm^{-1}$ was characteristics of hydrogen bonded hydroxyl group (O—H) from the complex vibrational stretching, associated with free, inter and intra molecular bound hydroxyl groups [28]. The band at approximately $1720\,cm^{-1}$ might be associated with stretching vibrations of carbonyl groups (C=O) [12]. The peaks at approximately $1400–1450\,cm^{-1}$ and $1380\,cm^{-1}$ were assigned to O—H bonding [15] and methyl (CH3) bending [29] respectively. The characteristics of the anhydro-glucose ring C—O stretch were associated to the peaks at approximately $1020–1089\,cm^{-1}$ [28,30]. This band was also associated to the C—O group stretching from lignin of natural fibre [27]. The characteristics of seaweed polysaccharide, namely 3,6-anhydro-D-ans D-galactose-4-sulphate, corresponded to the bands at $925–935\,cm^{-1}$ and $840–850\,cm^{-1}$ respectively [31].

The interactions between the individual components in hybrid composites can be determined by identifying the band position shifting of the spectra. It can be noticed from the figure that the bands at approximately $3100–3700\,cm^{-1}$ (O—H stretching) of Sw composites were gradually shifted to a lower wavenumber following the hybridization with SPF. These peak position shifts indicate increase in intermolecular hydrogen in the hybrid composites by addition of hybridized fillers [28]. This might be attributed to similar hydrophilic behaviour of TPSA, Sw, and SPF which led to distinct interaction and compatibility between them. This finding is in agreement with the FT-IR analysis of biocomposites derived from coconut fibre and thermoplastic cassava starch [12]. In addition, hybridization of SPF with Sw results in formation of new peak at approximately $720\,cm^{-1}$, which was associated with CH2 rocking arisen from SPF [26]. A similar finding was reported for incorporation of cotton fibre into thermoplastic waxy rice starch [26].

3.2. Mechanical properties

Fig. 2a demonstrates the tensile properties of Sw/SPF hybrid composites; that is, tensile strength, modulus and elongation at break respectively. Table 2 shows the analysis of variance (ANOVA) of the tensile properties. Statistically significant differences between the mean data from one level of composites to another were evidenced by the P-value ($p < 0.05$). It was observed that both tensile strength and tensile modulus of Sw composites increased following the hybridization with SPF. Increasing SPF content at HC2 composites increased the Sw composites tensile

strength by 17.2% while an increase in tensile modulus by 9.3% was shown by HC3 composites. The elongation at break of HC1 composites shows an increment of 17.2% while a slight decrement was observed with increasing SPF ratio at HC2 and HC3 composites.

A higher tensile strength of the hybrid composites than their individual components might be attributed to a similar hydrophilic character of seaweed and SPF, which led to great compatibility between them. The combination of compatible materials is often associated with improvement in mechanical properties of the resulting materials [32]. In addition, good compatibility between seaweed, SPF and TPSA matrix was also evidenced by FT-IR increasing intermolecular hydrogen bonding in the hybrid composites. This shows that good interfacial adhesion between the components of hybrid composites was achieved, subsequently resulting in higher efficiency of stress-transfer from TPSA matrix to the fillers [33]. This finding is in agreement with previous studies reporting higher tensile strength of hybridized filler composites than the individual filler composites [34–36].

Fig. 2b shows the flexural strength and modulus of Sw/SPF hybrid composites. The analysis of variance (ANOVA) of the flexural properties is shown in Table 2. Since the P-value is less than 0.05, there is statistically significant difference between the mean flexural strength and modulus from one level of composites to another. Overall, a similar trend was observed between tensile and flexural properties of the hybrid composites. Both flexural strength and modulus of Sw composites increased with increasing SPF content in the hybrid composites. Highest flexural strength was shown by HC2 composites while HC3 composites showed the highest flexural modulus. The improvement in the flexural properties of the Sw/SPF hybrid composites might be attributed to similar reasons in the tensile results. Improvement in the flexural properties of hybridized filler composites was also reported in previous studies [34–36].

Fig. 2c shows the impact properties of Sw/SPF hybrid composites. In contrast with the tensile and flexural results, increasing SPF content in the HC1, HC2 and HC3 composites decreased the impact strength of Sw composites by 1.2%, 8.4% and 7.3% respectively. The decrement in the impact strength of the hybrid composites might be attributable to several reasons. Firstly, incorporation of fibre and the presence of void may lead to localised stress concentration point which aids in crack propagation [27]. Secondly, fibre pull-out mechanism absorbed a substantial amount of energy as
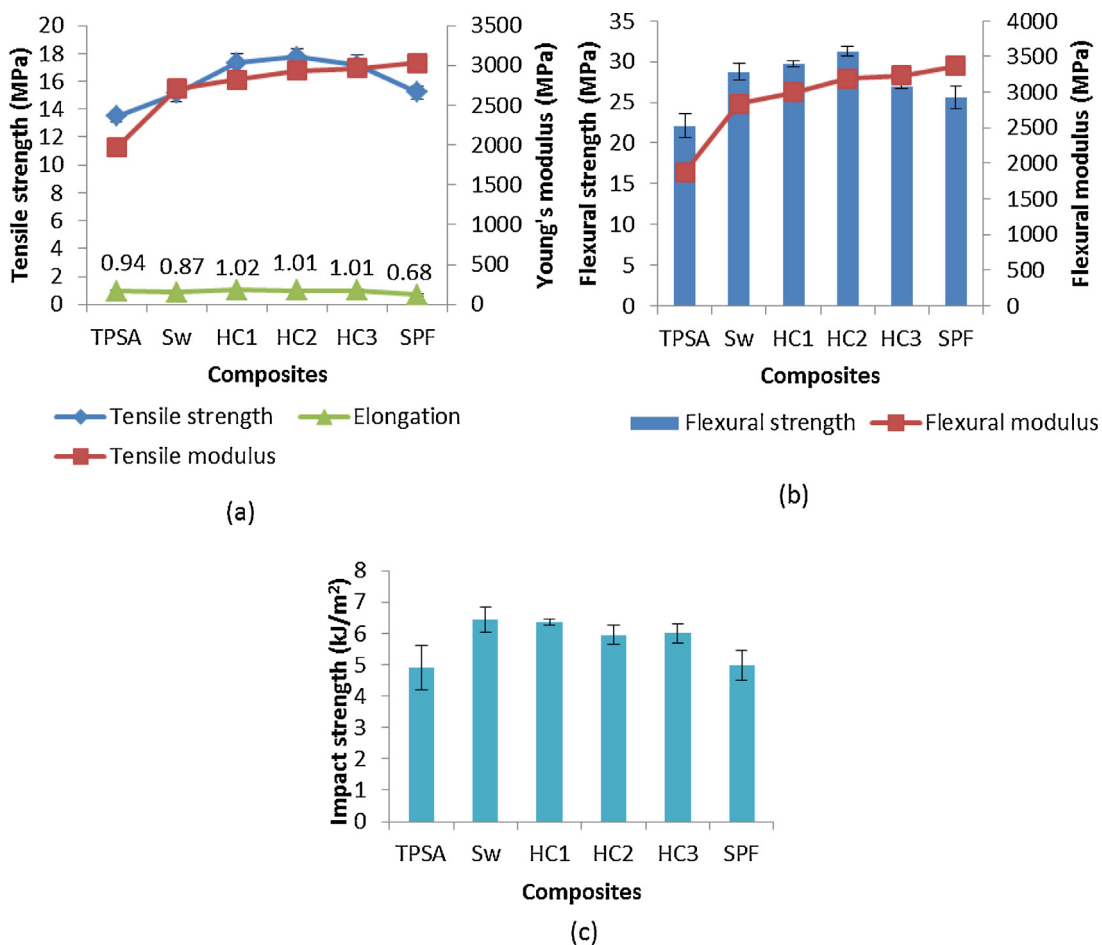
(a)

(b)

(c)

Fig. 2. Mechanical properties of Sw/SPF hybrid composites.

Table 2
Summary of the analysis of variance (ANOVA) of mechanical properties.

Variables	df	Tensile strength	Tensile modulus	Elongation	Flexural strength	Flexural modulus	Impact strength
Mixture	4	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*

*Note: Significantly difference at $p \leq 0.05$.

friction during impact; hence, a good interlocking surface between fibre and matrix (as can be seen in Fig. 2) is likely to show lower impact resistance due to the tendency to avoid fibre pull-out [27]. In this condition, fibre breakage is more likely to occur with a slight change in the cracking plane, instead of fibre pull-out [37]. Furthermore, lower impact strength of the hybrid composites might be associated with increase in the rigidity of the material following the incorporation of SPF, which leads to weak impact resistance of the material [8]. This finding is in agreement with that of Nadlene et al. [27] which attributed the decrease in the impact strength of roselle/vinyl ester composites to the great fibre-matrix adhesion between roselle fibre and the polymer matrix.

3.3. Morphological properties

Fig. 3 shows the scanning electron micrographs of the tensile fracture of Sw/SPF hybrid composites and their individual components. Sw composites show homogenous structure with no apparent phase separation (Fig. 3a) which can be attributed to good miscibility of seaweed in TPSA during the processing. Meanwhile, incorporation of SPF in the hybrid composites results in smooth structure with the presence of SPF in its surface. It can be seen

that SPF and TPSA/Sw are highly compatible, which is indicated through the good fibre wetting by the matrix (Fig. 3d). Again, this might be attributed to similar hydrophilic character between SPF and TPSA/seaweed which led to good adhesion between them. As a result of tensile fracture, the fibre breakage of SPF was observed on all composites. This finding suggests effective stress-transfer from matrix to fibre which gives reinforcement effect to the composites [13]. This finding is in good agreement with the tensile results. This reinforcement effect is highly dependent on fibre–matrix interface and the individual mechanical properties of fibres and the matrix [7]. Similar fibre breakage structure was reported on kenaf/TPS composites [9]. Moreover, incorporation of SPF was also leading to formation of void, which is more visible at the individual SPF composites (Fig. 3e).

3.4. Thermal properties

The decomposition and thermal stability of Sw/SPF hybrid composites were presented in the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves (Fig. 4). Overall, multistep degradation was observed for all hybrid composites and their individual components. The initial step of degradation that occurs
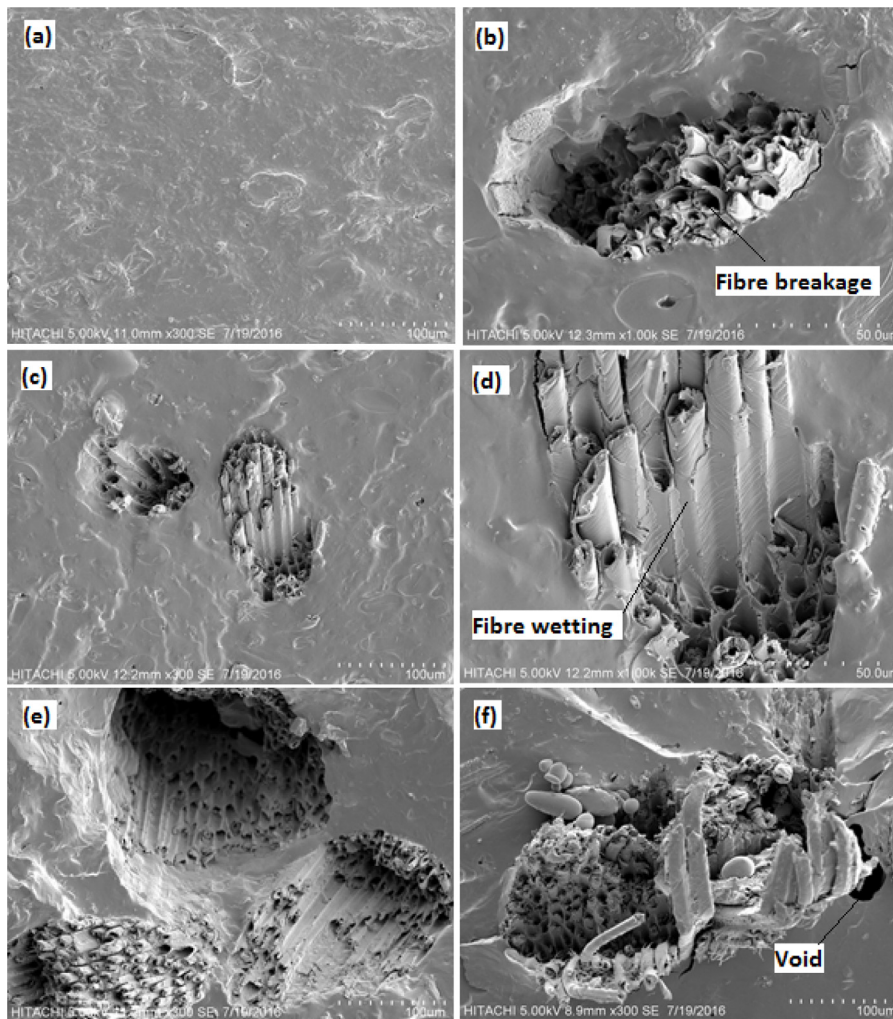
Fig. 3. Scanning electron micrograph of (a) Sw composites (b) HC1 composites (c) HC2 composites (d) magnified image of HC2 composites (e) HC3 composites and (f) SPF composites.
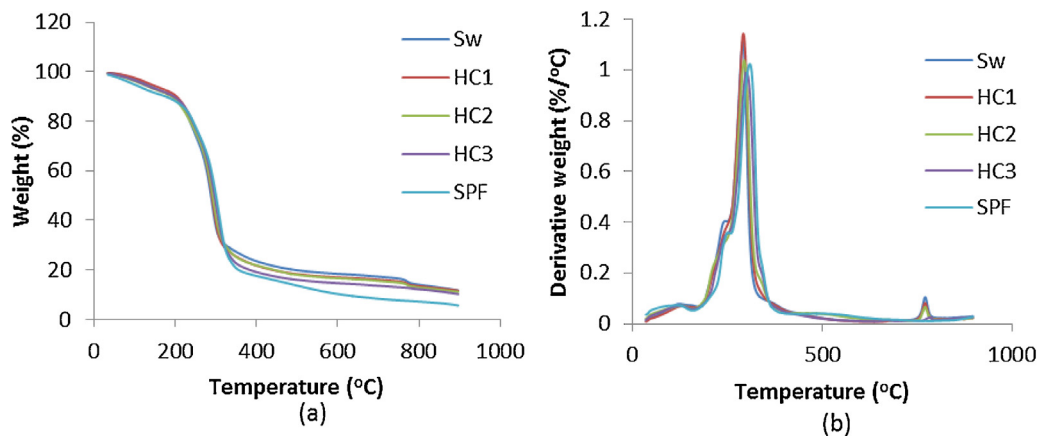

Fig. 4. TGA results of Sw/SPF hybrid composite.

below 100 °C can be associated with the dehydration of loosely bound water and low molecular weight compound [38]. The degradation steps that occured between 100 °C to 200 °C were assigned to the evaporation of water and glycerol [15]. The degradation of agar was reported to take place at a temperature above 270 °C [26]. Meanwhile, the decomposition and depolymerization of starch carbon chains were assigned to the maximum degradation step

which occured at approximately 300 °C [15,39]. In addition, the decomposition of carbohydrate and protein from seaweed was assigned to degradation at temperature range of 180–450 °C [40]. The decomposition of the main component in SPF, namely cellulose and hemicellulose, was assigned to the degradation step at temperature range of 200–270 °C [41]. The decomposition of lignin and final decomposition of cellulose occurred at 270–370 °C [41].

Table 3
Summary of TGA results for Sw/SPF reinforced TPSA composites.

Samples	T_{on} (°C)	T_{max} (°C)	Weight loss (wt%)	Char at 900 °C (wt%)
Sw	253	291	88.32	11.68
HC1	256	292	88.38	11.62
HC2	256	294	88.88	11.12
HC3	259	300	89.77	10.23
SPF	265	309	94.38	5.62

The decomposition beyond 500 °C can be attributed to carbonate degradation in seaweed which led to the formation of char Ross et al. [41]. The oxidation of the remaining char was assigned to the final decomposition stage of the composites [40].

Hybridization of SPF with Sw composites led to several alterations in the thermal degradation behaviour of the hybrid composites. Increase of SPF loading in HC1, HC2 and HC3 composites was observed to increase their onset and maximum degradation temperature (Table 2). This might be attributed to higher lignocellulose components in SPF than seaweed which led to an increase in thermal stability of the composites. It appears that degradation temperatures of these hybrid composites are between the values of each individual component (Sw and SPF). Increase in onset and maximum degradation temperature of composites were also reported for incorporation of jute [15], leafwood [42] and pulp fibre [42] into thermoplastic starch.

Moreover, the DTG peak shows obvious changes in the degradation behaviour of Sw composites following the hybridization with SPF. The observed peak beyond 500 °C, which was associated with the carbonate decomposition in seaweed, was gradually diminished in HC1, HC2 and HC3 composites and totally disappeared in SPF composites. This finding suggests that seaweed is mainly responsible for this degradation peak.

At the final stage of decomposition, it can be seen that the hybrid composites show slightly lower char residue (higher weight loss) than Sw composites (Table 2). This finding can be assigned to larger carbonate composition in seaweed than SPF which is mainly responsible for char formation upon thermal decomposition [43]. In previous works, seaweed has been identified as the main factor for increasing the char residue of seaweed/polymer composites [43,44]. The weight of char residues of the hybrid composites seems to be in between the individual Sw and SPF composites. Overall, hybridization of seaweed with SPF in TPSA matrix has resulted in increase in the onset and maximum degradation temperature of the composites. Table 3 summarize the TGA results.

3.5. Density

Table 4 shows the density of Sw/SPF hybrid composites. In general, slight decrease in the density was evidenced by increasing SPF content in the composites. The hybrid composites of HC3 show 0.7% lower density than the Sw composites. Moreover, SPF composites also show 1.5% lower density than Sw composites. This finding can be associated with the fibrous structure of SPF which has lower density than the seaweed. Reduction in density of composites following the incorporation of natural fibre was also reported in previous work [45]. Ramanaiah et al. [45] conducted a study on the effect of Borassus seed shoot fibre on the properties of polyester composites where increasing fibre content was shown to decrease the density of the composites. The decrease in density of hybrid composites in this study is an attractive attribute to these green composites since lightweight material is often associated with easy handling and low transportation costs [46].

3.6. Moisture content

The moisture content of the hybrid composites is shown in Table 4. In general, slight increment in moisture content was evidenced by incorporation of SPF in HC1 composites. However, further incorporation of SPF in HC2, HC3 and SPF composites shows no apparent trend on the moisture content compared to HC1. Slight increase in the moisture content of the hybrid composites might be associated with the relatively higher moisture content of SPF than seaweed.

3.7. Water absorption

Bio-based material is known to be sensitive to water; thus, it is important to investigate the water absorption characteristics of the fully bio-based material prepared in this study. Table 4 shows the water absorption capacity of the hybrid composites after immersion for 0.5 h and 2 h. It is obvious that longer immersion time led to higher water absorption of all composites due to a larger amount of water allowed to be absorbed by the materials. After 0.5 h of immersion, it can be seen that the hybridization of SPF with seaweed in HC1 composites decreased the water uptake of the material. Further incorporation of SPF in HC2 and HC3 composites were continued to show lower water uptake than Sw composites. The lowest water uptake was shown by SPF composites. The difference in water uptake between Sw and the hybrid composites was more evident after 2 h of immersion. The decline in water uptake can be attributed to the presence of SPF in the composites. According to Ramirez et al. [13] lower water uptake of fully bio-based composites following the addition of natural fibre can be attributed to several reasons: (a) better interfacial bonding between fibres, (b) greater water affinity of the matrix compared to the fibres and (c) hindering of water diffusion through the matrix due to the network formed by higher fibre content. In addition, the presence of lignin and wax on the surface of fibre promotes the water hindrance by the composites [13]. Sahari et al. [47] also reported significant drop in the water uptake of thermoplastic starch with addition of SPF. According to Ishak et al. [18] SPF has good resistance to water, which makes it a promising material for development of products such as brushes, brooms and ropes for ship cordages.

3.8. Thickness swelling

The swelling ratio of the hybrid composites was studied in order to determine the changes in dimensional stability of the composites following the hybridization of the reinforcing materials. Table 4 shows the percentage of swelling ratio for the hybrid composites as well as individual Sw and SPF composites. The thickness of all hybrid composites was increased following longer immersion duration from 0.5 h to 2 h. Similar findings were also reported in previous work on wood flour/recycled newspaper fibre reinforced polypropylene hybrid composites [48]. This effect can be associated with more water molecules being allowed to engage with the hydrogen bonding sites of the composites, which expedites swelling. In general, hybridization of SPF with seaweed in HC1, HC2 and HC3 led to a lower swelling ratio than Sw composite. The decline in swelling ratio of the hybrid composites can be seen after 0.5 h of immersion. However, more significant effects were evident after 2 h of immersion where Sw composite shows 63.8% swelling while HC1, HC2 and HC3 composites show 48.5, 45.8, 43.0, and 43.0% swelling respectively. This finding can be ascribed to the presence of SPF in the composites which has more rigid structure and less hydrophilic character than Sw, thus, providing better resistance to swelling when exposed to water. Improvement in dimensional stability of fully bio-based composite following the addition of natural fibre was reported in previous work [13]. In their

Table 4
Physical properties of Sw/SPF hybrid composites.

Composites	Density (g/cm³)	Moisture content (%)	Water absorption (%)		Thickness swelling (%)		Water solubility (%)
			0.5 h	2 h	0.5 h	2 h	
Sw	1.36 ± 0.01	3.39 ± 0.06	40.30 ± 6.14	71.35 ± 0.66	29.92 ± 1.76	63.81 ± 0.94	60.49 ± 0.03
HC1	1.36 ± 0.01	3.93 ± 0.03	34.69 ± 0.84	66.98 ± 0.49	26.96 ± 0.10	48.50 ± 2.50	53.87 ± 0.34
HC2	1.35 ± 0.01	3.68 ± 0.19	32.86 ± 0.94	67.41 ± 0.62	26.88 ± 0.56	45.82 ± 1.84	44.71 ± 4.37
HC3	1.35 ± 0.01	3.97 ± 0.18	31.90 ± 1.01	60.99 ± 0.07	25.81 ± 1.14	43.04 ± 2.14	39.79 ± 2.15
SPF	1.34 ± 0.01	3.87 ± 0.06	30.21 ± 5.77	58.09 ± 1.52	25.61 ± 1.61	43.03 ± 1.90	32.56 ± 2.49

study, incorporation of coir fibre significantly reduced the swelling ratio of thermoplastic cassava starch, which was attributed to better water resistance of coir fibre than the matrix [13].

It is known that the swelling of composite materials is mainly caused by the water uptake. In the present study, incorporation of SPF reduced the water uptake of the composites. This explains the improvement in dimensional stability of the hybrid composites in this study. The correlation between water uptake and thickness swelling of composites were also reported in previous studies [49,50].

3.9. Moisture absorption

Thermoplastic starch is known to be sensitive to moisture; therefore, controlling the material moisture uptake is vastly important. Fig. 5 shows the moisture absorption curve of Sw/SPF hybrid composites during storage at $75 \pm 2\%$ RH at a temperature of $25 \pm 2 °C$. Overall, all composites show a similar trend for moisture uptake with increased storage time. It can be seen from the curve that more rapid moisture absorption was taking place at the initial stages and became slower as the storage time increased. This result is in agreement with previous studies on moisture absorption behaviour of starch-based material [17,51,52]. After 15 days of storage, a more stable moisture absorption was observed suggesting equilibrium moisture content of composites with the surroundings (it reaches a plateau).

As shown in Fig. 5, hybridization of SPF with seaweed within TPSA was observed to induce a notable improvement of the composites' water resistance comparatively to the composites containing no SPF. After 19 days of storage, a gradual reduction of moisture uptake with increasing SPF content in Sw/SPF hybrid composites can be noted for HC1, HC2 and HC3 composites respectively. It seems that the equilibrium moisture content of the hybrid composites is between the values of each individual component (Sw and SPF composites). This result is in agreement with the water absorption behaviour of the hybrid composites.
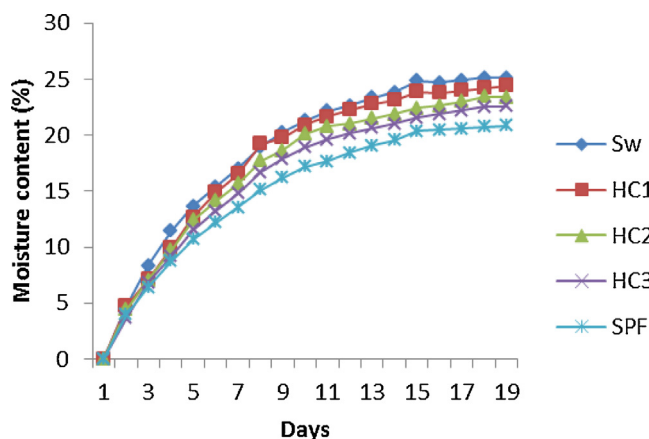
3.10. Water solubility

Table 4 shows the water solubility of the hybrid composites, which indicates the water resistance of the materials when subjected to immersion and continuous stirring in water. It was observed that hybridization of Sw with SPF in HC1, HC2 and HC3 composites results in lower water solubility. The Sw composites show 60.48% solubility whereas HC1, HC2 and HC3 composites show 53.9, 44.7 and 39.8% solubility respectively. Lower water solubility of the hybrid composites compared to Sw composites might be ascribed to greater water resistance of SPF, which aids in hindering water absorption that can lead to disintegration and dissolving of the materials. Furthermore, incorporation of fibre also contributes in preventing disintegration of materials by formation of fibre network in the composites. On the other hand, decreased content of seaweed in HC1, HC2 and HC3 composites means a lower amount of residual carrageenan in the composites. Since carrageenan is a highly soluble material that is known to exist in seaweed, a decreasing amount of carrageenan might well be associated with less solubility of composites in water [53]. This finding is in good agreement with the results for water absorption and thickness swelling in this study.

3.11. Soil burial

The biodegradation characteristics of materials can be measured by the weight loss due to the moisture and microorganism activity during the soil burial period [25,54]. Fig. 6 shows the weight loss of Sw/SPF hybrid composites after soil burial for 2 and 4 weeks respectively. It is obvious that a longer period of burial leads to higher weight loss for all composites, suggesting higher number of microorganism activities in the materials.

Overall, lower weight loss was observed following the increasing amount of SPF in the hybrid composites where HC3 shows the lowest at 53.7% and 73.2% after 2 and 4 weeks of burial respectively. According to Maran et al. [54], increase in hygroscopic characteristics of material will promote the growth of microorganisms during degradation and increases the weight loss of material. Therefore, lower weight loss of the hybrid composites can be associated with higher biodegradation resistance of SPF due to a less hydrophilic
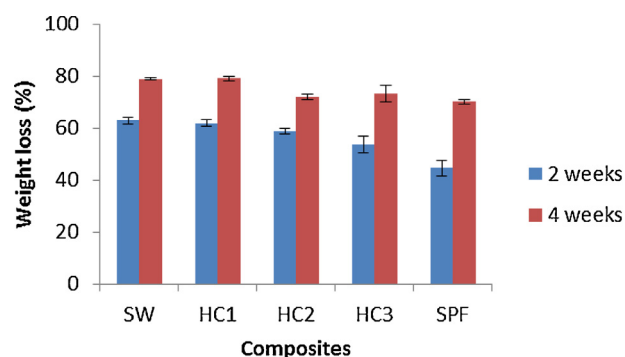
Fig. 5. Moisture absorption behaviour of Sw/SPF hybrid composites.

Fig. 6. Weight loss of Sw/SPF hybrid composites after soil burial for 2 and 4 weeks.

characteristic than seaweed. This finding is in good agreement with the incorporation of silk protein fibre [55], cotton fibre [11] and eggshell [25] onto thermoplastic starch matrix.

4. Conclusions

Fully bio-based hybrid composites derived from Sw, SPF and TPSA matrix were successfully prepared via melt mixing and hot pressing in this study. The experimental results revealed that Sw and SPF were compatible and increase in intermolecular hydrogen bonding was evident following their hybridization in the composites. Mechanical testing of the hybrid composites showed that the tensile and flexural properties were improved, and the impact resistance was reduced with the addition of SPF. Scanning electron micrograph study of tensile fracture showed good fibre-matrix adhesion and efficient stress-transfer from matrix to fibre (fibre breakage). Improvement in water resistance of the hybrid composites was evident in all tests, namely water absorption, thickness swelling, water solubility and moisture absorption. Soil burial results manifested that hybridization of Sw composites with SPF led to a slower biodegradation process due to higher hydrophobicity of the fibre. Overall, hybridization of seaweed with SPF in TPSA improves the mechanical, thermal and physical properties of the composites, which widened the potential application of this biodegradable material.

Acknowledgements

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