Preparation of Biocomposite from Recycled PET Bottles and Starch Reinforced with Biochar from Durian Peels

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Abstract

This research focuses on the preparation of biodegradable films from recycled polyethylene terephthalate (RPET) and thermoplastic starch (TPS) reinforced with biochar from durian peels. In this study, hexamethylene diisocyanate (HMDI) was used as a compatibilizer and the influences of biochar contents on physical properties, morphology, mechanical properties, thermal properties and water absorption ability of biocomposite films were studied. For biocomposite preparation, all ingredients, i.e. TPS, RPET biochar and HMDI were mixed by internal mixer and fabricated into thin sheets by compression molding. The mixing ratio of TPS/RPET was fixed at 30/70 wt%, while HMDI was added at 5 wt% based on starch content. Biochar contents were varied from 10 to 40 wt%. The results showed that the presence of 5 wt% HMDI led to improvement of mechanical and thermal properties of TPS/RPET compound which resulted in the improvement of interfacial adhesion between RPET and TPS. Moreover, the addition of 20 wt% biochar resulted in the highest flexural strength and flexural modulus of 30 TPS/RPET when compared to other biochar contents because of its better dispersion in RPET matrix. In addition, biochar could improve thermal stability of 30 TPS/RPET biocomposite. Besides, the water absorption ability of TPS/RPET/biochar composite increased with an increase in TPS and biochar. On the other hand, the presence of HMDI led to the diminishing of water absorption ability of TPS/RPET/biochar biocomposite.

Keywords: Polyethylene Terephthalate Bottle; Thermoplastic Starch; Durian Peels; Biochar; Plastic Recycling; Biocomposite

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Introduction

Thailand is one of the well-known cultivated lands. Nowadays, Thailand's farming industry is highly competitive and there is gain of agricultural productivity [1]. Due to an increase in agricultural cultivation, a lot of agricultural plastic wastes such as seed trays, crop coverings, mulch films, pots and fertilizer bags are abandoned in landfills [2]. Most of agricultural plastic wastes are made from petroleum-based polymers because such polymers have good mechanical properties and are inexpensive [3]. However, petroleum-based polymers cause environmental pollution since they take a long time to decompose [3]. Recently, the environmental issue of reducing plastic use has become a serious topic in Thailand. The Thai government has also been driving a policy to avoid using single and non-biodegradable plastics [4]. Thus, the use of biodegradable plastic or recycled plastic for agriculture is a sustainable way to reduce plastic waste from agricultural activities since the reuse and recycling of already acquired non-biodegradable plastics help maintain an environment without waste and reduce demand for new plastic[5] - [7].

Polyethylene terephthalate (PET) bottles is one of the plastic wastes mostly found in landfills and oceans. Many researchers have studied on the utilization of recycled PET bottle by mixing it with biodegradable polymers such as polylactic acid [8], poly (butylene succinate) [9] cellulose [10], and starch [11] to reduce PET bottle waste. From literatures, the addition of biodegradable polymers can improve mechanical properties and the biodegradability of recycled PET for the production of various products, e.g. food packaging, clothes, icluding plastic products for cultivation. However, there are a few research works focusing on the preparation of biocomposite from recycled PET for agricultural application such as trays and films. Thus, this research is aimed at preparing recycled PET biocomposite and its properties to be a guideline for prototype development such as trays and films. Cassava starch and biochar are attractive raw materials because cassava starch is abundant in nature in Thailand. It is cheap and has good biodegradability [12] - [13]. While, Biochar has benefit for crop and soil. It can enhance root yield since it can hold moisture and enrich soil nutrients [14] - [15]. Nevertheless, the main problem of starch and polyester blend is low compatibility because starch is hydrophilic material, while polyester is hydrophobic material. The addition of coupling agent or compatibilizer can improve the compatibility and interfacial adhesion between hydrophilic and hydrophobic materials. Isocyanate compounds, such as methylene diphenyl diisocyanate (MDI) [16], 1,4-phenylene diisocyanate (PDI) [17] and hexamethylene diisocyanate (HMDI) [17] are well-known coupling agents for polyester and starch because they are effective and give rapid reactions. HMDI is one of diisocynate groups which is widely used in bioplastic and food-contact applications [18].

Therefore, the objectives of this work are to prepare biocomposite from recycled PET (RPET) and thermoplastic starch (TPS) reinforced with biochar. HMDI was used as a compatibilizer. The effects of TPS and HMDI addition and biochar content on morphology, mechanical properties, thermal properties, and water absorption ability of TPS/RPET biocomposites were studied.

Materials and Method

1. Materials

Commercial cassava starch was used as a raw material for TPS preparation. Recycled PET bottle (RPET) was a raw material used in preparing biocomposites. Analytical grade of HMDI was purchased from Sigma Aldrich. Analytical grade of glycerol was obtained from CT chemical co, Ltd. Durian peel waste was used as raw material for biochar preparation.

2. Biochar (BC) preparation

Durian peel was dried in an oven at 60 ^{o}C overnight to remove absorbed moisture. Later, it was pyrolyzed at 500 - 600 ^{o}C in closed-traditional furnace without oxygen for 24 hrs. After pyrolysis, biochar from durian peel was obtained and then it was ground into fine particles to pass through a 230 sieve mesh.

3. Thermoplastic starch (TPS) preparation

Cassava starch was dried in an oven at 60 ^{o}C overnight for removing absorbed moisture. Next, cassava starch was mixed with glycerol and water. The ratio of starch, glycerol, and water was 70:20:10. All ingredients were stirred and kneaded to prepare homogenous TPS.

4. Preparation of biocomposite from RPET and starch reinforced with biochar

RPET was washed in water and dried in sunlight. After that, it was cut into small sizes (1 - 2 cm). Before mixing, all ingredients, i.e. RPET and biochar were dried at 60 ^{o}C overnight. Afterwards, RPET, TPS, and HMDI were firstly mixed by internal mixer (Enmach Co., Ltd.) at 260 ^{o}C and 60 rpm to prepare TPS/RPET compound. The ratio of TPS and RPET was fixed at 30:70 wt%, while the addition of HMDI was fixed at 5 wt% which depended on TPS content. The mixture was blended until it became homogeneous. After that, biochar was added into the compound and was mixed for 5 minutes to disperse biochar in matrix. Biochar content was 10 wt%, 20 wt%, 30 wt%, and 40 wt% based on the total weight of the compound. After that, TPS/RPET/biochar compound was fabricated into sheet by compression molding machine (CT, Chareon tut Co., Ltd).

5. Characterization

Morphologies of TPS, biochar and biocomposite were studied by scanning electron microscope (SEM) (JEOL, JSM-IT300). Thermal stability of biocomposite films was investigated by Thermogravimetric analysis (TGA) (Tarsus, TGA-209 F3) which was conducted under nitrogen gas with 10 °C/min of scanning rate. Differential calorimetry (DSC) (Phoenix 204 F1) was used to study thermal behavior of RPET and biocomposite under inert gas with 10 °C/min of scanning rate. The degree of crystallinity (χ_c) of biocomposite film was calculated with the following equation (1).

$$\chi_c = \frac{\Delta Hm}{\Delta Hm_0} \times 100, \tag{1}$$

where ΔHm is the melting enthalpy of the crystalline PET and ΔHm_0 is the melting enthalpy of the completely crystalline PET. The values of ΔHm_0 of PET was 140 J g^{-1}.

Universal Testing Machine (UTM DSS-10T) was used for flexural tests according to ASTM standard D790. Water absorption test (water absorption ability) was studied according to ASTM 570. All samples were dried at 60 °C overnight. After that, all samples were weighed and then soaked in excess water for 24 hrs. After 24 hrs, excess water was removed from the samples with tissue paper, and then weighed. Three replicates were tested. The water absorption was calculated on a dry basis with the following equation (2).

$$Water\ Absorption\ Ability\ (\%) = \frac{w_2 - w_1}{w_1} \times 100 \tag{2}$$

where w_2 and w_1 are the wet weight and dried weight of a sample, respectively.

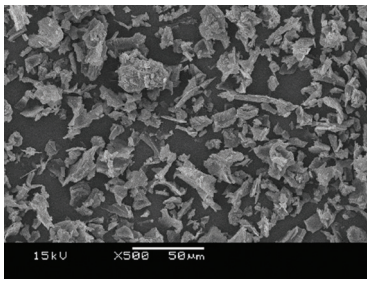
Results and Discussion

1. Physical appearance and morphology of biochar from durian peels

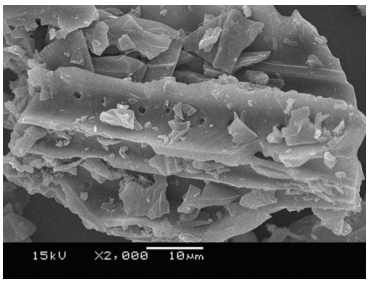
Biochar from durian peels was used as a reinforcement for TPS/RPET biocomposite. Figure 1 shows physical appearances and morphology of durian peels and biochar. Physical appearances of durian peels are shown in Figure 1(a). Durian peels are oblong shape with green and yellow color. The Figure 1(b) shows that obtained biochar exhibited black color with glossy skin after pyrolysis. Then, the biochar was reduced into micron size by a grinder and was sieved by 230 mesh sieve. After grinding, biochar powder was a mixed shape of flake and short fiber with rough surface as seen in Figure 1(c) and (d). Moreover, tiny holes could be found on biochar surface. The average particle size of biochar powder was approximately 33 μm.

(a) Durian peels

(b) Biochar



(c) SEM of Biochar at
x 500 maginification



(d) SEM of Biochar at
x 2,000 maginification

Figure 1 Physical appearances of durian peels and biochar

2. Physical appearance of RPET and RPET biocomposite

Physical appearances of RPET and biocomposites are illustrated in Figure 2. As observed, neat PET sample was of gray color with smooth surface. The presence of 30 wt% TPS resulted in a brownish color in RPET biocomposite. While, the addition of biochar contributed to a black color and rough surface. Moreover, the agglomerations of biochar particles were noticed in samples when biochar content increased from 20 to 40 wt%.

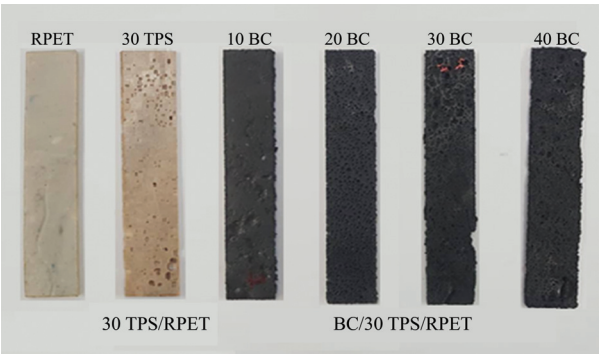


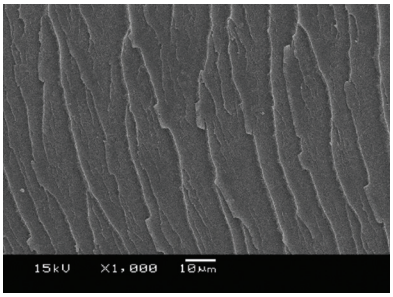
Figure 2 Physical appearances of RPET, 30 TPS/RPET with HMDI, and BC/30 TPS/RPET biocomposites with HMDI

3. Morphology

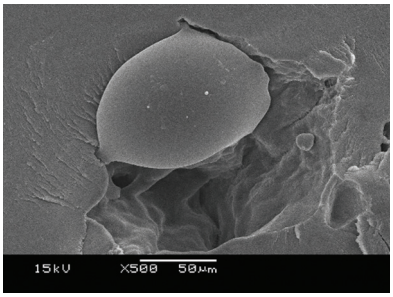
Figure 3(a) - (g) illustrates fracture surface of RPET and all RPET bicomposites. As seen in Figure 3(a) - (c), the gray area with rough surface is RPET matrix, while big particles which embedded in matrix are TPS particles and the large holes in sample surface were imprints of TPS particles. Average particle size of TPS is in range of 30 - 50 μm. Figure 3(b) and (c) exhibit fracture surface of 30 TPS/RPET without and with 5 wt% of HMDI, respectively. As shown in Figure 3(a) and (b), holes in composite surface and large gap between TPS and RPET phases could be found in 30 TPS/RET without HMDI. It indicated that there was poor compatibility between hydrophobic RPET and hydrophilic TPS. After mixing with HMDI, the gaps between RPET and TPS were smaller than those of TPS/RPET without HMDI (Figure 3(c)). Besides, the addition of HMDI contributed to well embedding of TPS in RPET matrix. This phenomenon indicated that the presence of HMDI could increase compatibility between RPET and TPS. Fracture surface images of all BC/30 TPS/RPET biocompoites are shown in Figure 3(d) - (g). These figures illustrate that small white flakes and short fibers are biochar (BC) powder. Small holes in matrix were evidence of biochar imprints. As observed, the degree of agglomeration of biochar increased with an increment of biochar loading since biochar had large surface area which easily tended to agglomerate. Likewise, the addition of 20 wt% biochar had better dispersion in matrix than other biochar contents. These results supported flexural properties of 30 TPS/RPET biocomposite. The optimal 20 wt% biochar content led to the highest flexural strength and flexural modulus.

4. Thermal properties and degree of crystallinity of RPET and all RPET biocomposites

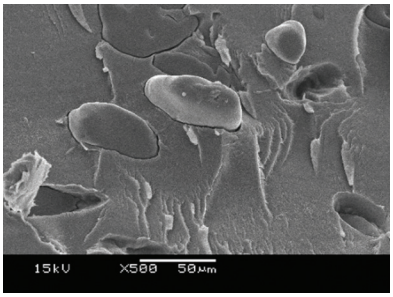
Thermogravimetric curve of RPET and RPET biocomposite is displayed in Figure 4. Data from TGA thermogram are presented in Table 1. The figure shows that neat RPET initially decomposed at around 390.19 ^{o}C which was degradation of PET main chain. While, all RPET biocomposites initially decomposed at nearly 100 ^{o}C which was evaporation of absorbed moisture. After evaporation, all RPET biocomposites showed three step decompositions. First decomposition started at around 250 - 270 ^{o}C which related to decomposition of small molecule i.e., glycerol. Second decomposition was at around 299 - 308 ^{o}C which related to TPS degradation. The decomposition around 390 - 400 ^{o}C was the degradation of RPET component. Obviously, the presence of TPS reduced the thermal stability of RPET because TPS has less thermal stability than RPET. However, the addition of HMDI can improve thermal stability of 30 TPS/RPET biocomposite due to the improvement of compatibility of TPS and RPET. Moreover, thermal stability of 30 TPS/RPET increased with increment of biochar content.



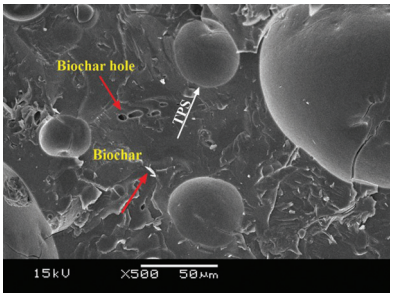
(a) neat RPET



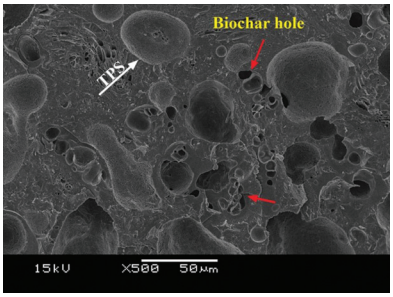
(b) 30 TPS/RPET



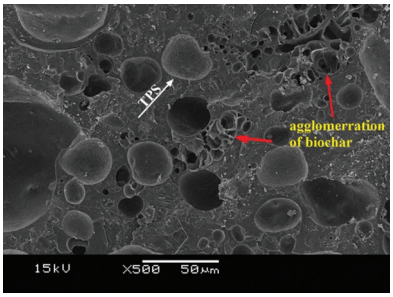
(c) 30 TPS/RPET/ 5 HMDI



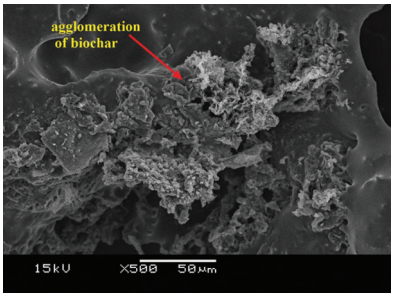
(d)10 BC



(e) 20 BC



(f) 30 BC



(g) 40 BC

Figure 3 SEM images of neat RPET and RPET biocomposites

Table 1 TGA data RPET and RPET biocomposites

Sample	Td_{1onset} [°C]	Td_{2onset} [°C]	Td_{3onset} [°C]	Char yield at 500 °C [%]
RPET	396.10	-	-	16.43
30 TPS/RPET	254.70	303.71	380.00	15.31
30 TPS/RPET + 5 HMDI	268.00	308.00	390.58	14.63
30 TPS/RPET/ 30 BC + 5 HMDI	267.64	273.00	386.39	29.77
30 TPS/RPET/ 40 BC + 5 HMDI	260.78	270.00	406.00	38.90

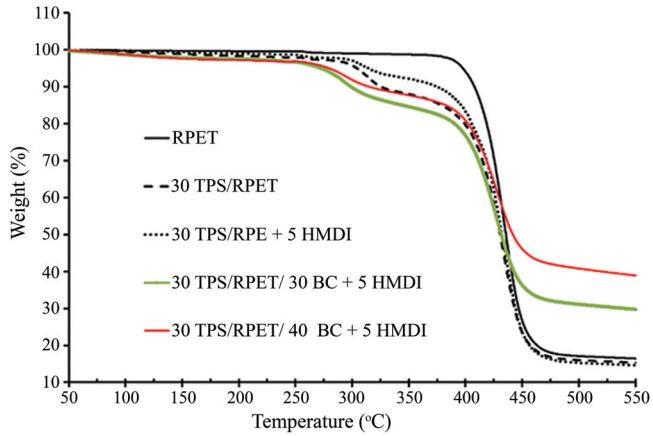
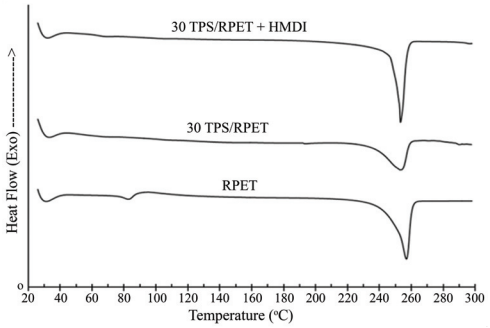


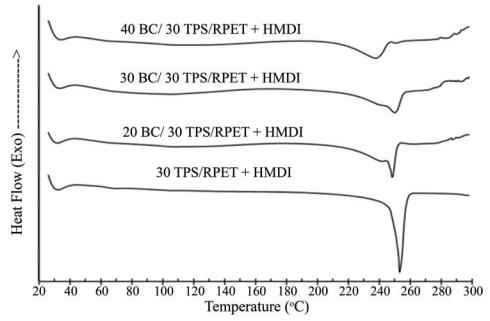
Figure 4 TGA Thermograms of RPET and RPET biocomposites

DSC Thermograms of RPET and all RPET biocomosites are shown Figure 5, while DSC data of all RPET biocomposites are displayed in Table 2. As seen in Figure 5, glass transition temperature (T_g) and melting temperature (T_m) of RPET are exhibited at around 82.60 °C and 256.93 °C, respectively. The DSC thermograms and Table 2 exhibit that the glass transition temperature of RPET dramatically shifted toward a lower temperature (53.40 °C) with the addition of 30 wt% TPS. Besides, the presence of 30 wt% TPS decreased the degree of crystallinity of RPET owing to the low miscibility between RPET and TPS. However, the glass transition temperature of 30 TPS/RPET slightly shifted to a higher temperature (59.60 °C) when HMDI was added. This phenomenon indicated that the addition of HMDI can improve interfacial adhesion between TPS and RPET. On the other hand, there was no significant change in T_m when 30 TPS and HMDI were added. The results are similar to Ferri and co-workers [18], they studied poly(lactic acid) blends with thermoplastic starch by physical blending without compatibilizer. They found that the slight decrement in T_g is representative for poor miscibility between PLA and TPS.

The effects of biochar loading, glass transition temperature, melting temperature and degree of crystallinity of 30 TPS/RPET decreased when biochar loading increased because biochar cannot act as a nucleating agent due to its poor dispersion in RPET matrix. In addition, agglomeration of biochar can be noticed in matrix as seen in Figure 5. The degree of crystallinity results are related to flexural properties of RPET biocomposite film.



(a) 30 TPS/RPET with and without HMDI



(b) BC/ 30 TPS/RPET biocomposites

Figure 5 DSC thermograms of RPET and RPET biocomposites

5. Flexural test

Flexural properties, i.e. flexural strength, flexural modulus, and extension of RPET and biocomposite are shown in Table 3. The table shows that the addition of TPS and biochar contributed to a decrease in flexural properties of RPET. This may be due to the low interfacial adhesion between RPET, TPS, and biochar. Effects of HMDI, 30 TPS/PET biocomposite with HMDI were higher flexural strength, flexural modulus, and extension value than biocomposite without HMDI because HMDI can improve interfacial adhesion between RPET and TPS. In addition, flexural strength, flexural modulus, and extension of 30 TPS/RPET bicomposite decreased when biochar content increased since biochar could not be well dispersed in the RPET matrix. However, it was found that the addition of 20 wt% biochar gave the highest flexural modulus and flexural strength with reasonable extension

value when compared to other concentrations of biochar. The morphological results of fracture surface of 30 TPS/RPET/BC biocomposite were used as supporting evidence.

Table 2 DSC data of RPET and BC/ 30 TPS/RPET biocomposites

Samples	T_g onset [˚C]	T_m [˚C]	Δ*Hm*	% Crystallinity
RPET	82.60	256.90	55.42	39.58
30 TPS/RPET	53.40	252.60	48.56	34.28
30 TPS/RPET + 5 HMDI	59.60	250.00	60.14	42.96
30 TPS/RPET/ 20 BC + 5 HMDI	57.60	250.10	45.15	32.22
30 TPS/RPET/ 30 BC + 5 HMDI	57.00	248.80	43.81	30.84
30 TPS/RPET/ 40 BC + 5 HMDI	55.80	237.80	27.6	19.71

Table 3 Flexural properties of RPET and RPET biocomposite

Sample	Flexural Strength [MPa]	Flexural Modulus [MPa]	Extension [mm]
RPET	17.30±3.60	4063±338	2.53±0.55
30 TPS/RPET	8.87±1.48	3482±919	1.30±0.48
30 TPS/RPET + 5 HMDI	9.78±0.90	3822±960	1.73±0.28
30 TPS/RPET/ 10 BC + 5 HMDI	2.74±1.05	702±419	1.00±0.35
30 TPS/RPET/ 20 BC + 5 HMDI	3.27±0.69	1822±504	0.85±0.08
30 TPS/RPET/ 30 BC + 5 HMDI	2.25±1.06	677±373	0.80±0.03
30 TPS/RPET/ 40 BC + 5 HMDI	1.73±0.47	702±444	0.61±0.18

6. Water absorption test

Water absorption ability of neat RPET and all RPET biocomposites is shown in Figure 6. As seen in this figure, neat RPET showed the lowest water absorption value which was less than 1% owing to its hydrophobic characteristic. While, water absorption of 30 TPS/RPET without HMDI was around 6%, higher than that of neat RPET due to the hydrophilic characteristic of TPS. Moreover, the presence of large gaps between RPET and TPS led to the increment of water absorption because water can easily diffuse into samples via the defects such as gaps and voids. On the other hand, the addition of 5 wt% HMDI decreased the water absorption of 30 TPS/RPET since the presence of HMDI resulted in the improvement of compatibility between RPET and TPS, contributing to the reduced gap between RPET and TPS. Considering effect of biochar content, water absorption of 30 TPS/RPET with 5 wt% HMDI increased when biochar content increased. This is because the biochar is a porous material which has a high capacity for absorbing water.

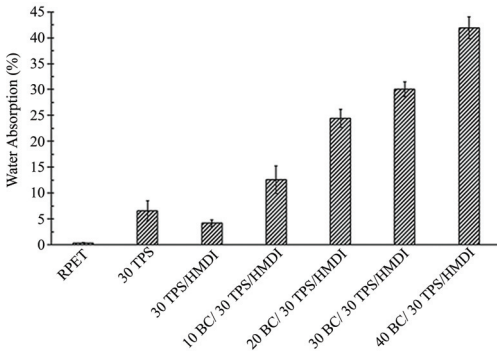


Figure 6 Water absorption of neat RPET and RPET biocomosites

Conclusions

Biocomposites from RPET and TPS reinforced with biochar from durian peels were prepared by internal mixer and compression moulding. HMDI was used as a compatibilizer for TPS and RPET. The addition of starch and HMDI to RPET was fixed at 30 wt% and 5 wt% (based on starch content), respectively. While, biochar content in TPS/RPET was varied from 10 to 40 wt%. The effects of TPS, HMDI, and biochar content on morphology, thermal properties, flexural properties, and water absorption ability of RPET biocomposites were studied. Considering the effects of TPS addition, the presence of 30 wt%TPS decreased mechanical properties and thermal properties of RPET due to low compatibility between TPS and RPET. However, flexural properties and thermal stability of 30 TPS/RPET with 5 wt% HMDI were higher than those of 30 TPS/RPET without HMDI. It may be because there was an improvement of compatibility between TPS and RPET. Moreover, the addition of 30 wt% TPS led to the decrease of glass transition temperature and degree of crystallinity of RPET. While, the addition of 30 wt% TPS did not have a significant effect on melting temperature of RPET. However, it was noticed that the presence of HMDI increased the degree of crystalinity of RPET owing to the improvement of interfacial adhesion between RPET and TPS. SEM image confirmed that the HMDI can improve the interfacial adhesion between RPET and TPS because of the reduction of gap between TPS and RPET. Considering biochar content, the addition of biochar decreased the flexural properties of 30 TPS/RPET. However, the optimal content of biochar was 20 wt% because this content gave the highest flexural strength and flexural modulus with reasonable extension value when compared to other biochar contents. Besides, the degree of crystallinity of 30 TPS/RPET decreased with an increment of biochar content. This because biochar did not act like a nucleating agent due to its poor dispersion in matrix. Likewise, the addition of TPS and biochar led to the increment of water absorption ability of RPET due to hydrophilic

properties of TPS and porosity of biochar. However, the presence of HMDI contributed to the decrease of water absorption ability of 30 TPS/RPET due to the improvement interfacial adhesion between TPS and RPET.

Acknowledgement

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