Poly(lactic acid)-based Composites Incorporated with Spent Coffee Ground and Tea Leave for Food Packaging Application: A Waste to Wealth

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\textbf{Abstract.} Polymer composites of polylactic acid (PLA) and polybutylene adipate terephthalate (PBAT) incorporated with spent coffee grounds (SCG) and tea leave (TL) were prepared by two-roll mill mixer. 4,4'-methylene diphenyl diisocyanate (MDI), toluene 2,4-diisocyanate (TDI), and bis[3-(triethoxysilyl) propyl] tetrasulfide (TESPT) were used as coupling agents. The influences of coupling agent types, coupling agent content, and weight ratios of polymer to filler on the mechanical properties, melt flow index, and overall migration (OM) of the composites were studied. The results showed that MDI and TDI had better performance compared to TESPT for both tensile and elongation at break. The tensile strength and elongation at break of PLA+PBAT/SCG composites with weight ratio of polymer to filler = 70/30 increased from 19.6 MPa to ~23.0 to 25.0 MPa, and 6.6 to ~10.0%, respectively when using these coupling agents (MDI and TDI) of 3 g/100 g polymers. Moreover, the addition of MDI and TDI greatly increased the viscosity of the melted composites (4-fold), while TESPT made the viscosity decrease. However, the mechanical properties of the composites decreased drastically with increasing SCG proportion. Compared to PLA+PBAT/SCG, interfacial adhesion of PLA+PBAT/TL was higher confirming by tensile strength and SEM images. However, there was no significant difference between PLA+PBAT/TL and PLA+PBAT/SCG composites in terms of elongation at break, impact strength and melt flow index. The OM of PLA+PBAT/SCG and PLA+PBAT/TL composites with coupling agents were in the range of ~0.03–0.28 mg/dm\textsuperscript{2} when using 3% acetic acid and 10% ethanol as food simulants, which not exceed the migration limit (10 mg/dm\textsuperscript{2}) according to Food Contact Materials EU No. 10/2011 legislation. It means that they might be safe for use as food contact materials for packaging and containers.

\textbf{Keywords:} Polylactic acid, Polybutylene adipate terephthalate, Coupling agent, Spent coffee ground, Tea Leave, Migration

1. Introduction

Plastics are used in many types of food packaging and containers in order to protect foods from damage, provide food safety and extend the shelf-life of foods. However, majority of plastics used to pack food
normally dumped as a waste and it leads to serious environmental pollution. In order to reduce the pollution from plastic waste, government has been promoted to implement on the use biodegradable polymers such as polylactic acid, cellulose esters, polyhydric butyl ether polyhydroxyl butyrates and starch etc. to replace the synthetic polymers. This is due to their ability to break down into non-toxic gas, water, biomass and inorganic chemicals after the consumption of food. However, plastics manufactured from petroleum-based derivatives is not a suitable option for the preparation of biodegradable plastics due to its expense. Normally, a reduction of material cost can be achieved by the addition of low-cost extension fillers such as clay, calcium carbonate and talc [6]. These systems normally provide a higher weight of composites compared to natural plant fillers.

Recently the properties of micro- and nanocomposites prepared from several polymers (e.g., polypropylene, polyvinyl alcohol, polypropylene carbonate, polylactic acid, and poly(butylene adipate-co-terephthalate) [1, 4–5, 8–9, 11] and natural fillers (spent coffee grounds (SCG) [1, 4–5, 8–9] and tea leave (TL) [11]) have been reported. From these works, the effect of filler content (filler content is in a range of 5–30 wt%) [1, 4] particle size distribution of coffee particles [8], and hydrophobic treatment on SCG powder [5] on the thermal, rheological, physical and mechanical properties of the composites were investigated. Moreover, some researchers also reported that one possible application of the composite incorporated with SCG is a food container or food packaging [3]. However, the safety of food contact materials has not been evaluated and reported in the examination documents. But in fact, the chemical migration of composite materials should be concerned due to some small size chemicals like coupling agents that have been used to increase the compatibility of immiscible polymer blends such as 4,4-methylene diphenyl diisocyanate (MDI) [1], PP-g-MA [10], silane, and styrene-ethylene-butyne-styrene-graft-maleic anhydride [4] might be migrated from the materials into foods.

From these reasons, in the present work, spent coffee ground (SCG) and tea leaves (TL) have been employed as fillers to prepare the composite of polylactic acid (PLA)+polybutylene adipate terephthalate (PBAT) (PLA/PBAT = 70/30) to make use of large quantities of waste from coffee shops or coffee industries. Overall migration (OM) of the composites with various coupling agents including 4,4-methylene diphenyl diisocyanate (MDI), toluene 2,4-diisocyanate (TDI) and bis[3-(triethoxysilyl) propyl] tetrasulfide (TESPT) and several content (0, 3, 5, and 7 g/100 g polymers) for the weight ratios of polymer to filler (80/20, 70/30, and 60/40) in food simulants have been tested according to Food Contact Materials EU No. 10/2011 legislation in order to determine and compare the quantity of the chemical substances that migrate from the composite samples to the food simulants. Moreover, the effect of blend composition and coupling agent on the mechanical properties and melt flow index have been studied in detail.

2. Experimental methods

2.1 Materials
Polylactic acid (PLA) and Polybutylene adipate terephthalate (PBAT) were purchased from Nature-Works LLC, USA. 4,4-methylene diphenyl diisocyanate (MDI), toluene 2,4-diisocyanate (TDI) and bis[3-(triethoxysilyl) propyl] tetrasulfide (TESPT) were used as coupling agent were supplied by Sigma-Aldrich. Spent coffee ground (SCG) and tea leaves (TL) were obtained from the local coffee shops in Songkhla province, Thailand.

2.2 Methods
The SCG and TL were first sieved through a 35 mesh screen and dried in a hot-air oven at 50 °C for 48 h. Dried fillers were mixed along with PLA/PBAT (70/30 by weight) and coupling agent using a two-roll mill (150 °C for 5 min, nip = 0.5 mm.). The resulting composites were then suddenly compressed by compression molding at 120 °C for 10 sec. The test specimens were stored under room temperature with 50±5 % RH for 5 days before test. The samples were characterized according to the international standards.
2.3 Morphology
The surface morphology of the composites was studied using scanning electron microscope (SEM; Quanta 400, FEI Company, Hillsboro, OR). The samples were first cracked under liquid nitrogen and then coated with gold. The SEM was performed at an accelerating voltage of 20 kV to observe the fractured surface.

2.4 Melt flow index
The melt flow index machine (Charoen TUT, MFR-2, Thailand) was used to measure the melt flow index according to ISO 1133 under the temperature of 160 °C for 10 min. Experiment was performed in triplicate.

2.5 Mechanical properties
Tensile strength was performed using the Hounsfield Tensometer model H 10 KS (Hounsfield Test Equipment Co. UK) at a crosshead speed of 1 mm/min. Impact strength was tested by impact tester (Charoen TUT, IMP-25J, Thailand) according to ISO 8256. Five specimens were exploited and the average value of p<0.05 was considered as significant.

2.6 Overall Migration
The composite sheets (thickness = ~ 1 mm) were cut into small pieces of 1×1 cm for overall migration studies. The experiment was performed with 200 mL of food simulants (3% acetic acid and ethanol) by total immersion method under 70 °C for 2 h according to Regulation (EU) No 10/2011 (surface area of test sample = 100 cm²). After incubation, food simulants were poured into an evaporated dish and evaporated by using water bath at 90 – 95 °C. The evaporated dishes were placed again in a hot air oven at 150 °C for 2 h to ensure the food simulants dry completely. The mass of the residue was determined by subtracting the original weight of the dish from the weight of dish and residue by using Equation 1.

\[
OM \ (mg/dm^2) = \left(\frac{W_b - W_s}{S}\right) \times 1000
\]

Where, OM is the overall migration into the food simulant. W_s is the weight of the residue (g) from the test specimen after evaporation. W_b is the weight of residue (g) from the food simulant (blank). S is the surface area of the test specimen in contact with foodstuffs.

3. Results and Discussion

3.1 Effect of coupling agent types
The mechanical properties of PLA+PBAT/SCG composites (weight ratios of polymer to filler = 70/30) with different coupling agents (TDI, MDI, and TESPT, 3 g/100 g polymers) are measured and compared the composites without coupling agent as shown in Table 1. It is seen that the composite with MDI and TDI gave better performance in term of tensile strength and elongation at break while TESPT provides lower tensile strength. The addition of MDI and TDI enhances the tensile strength from 18.7 MPa to 23.5 MPa and 25.2 MPa, respectively owing to the addition of coupling agent induced an interaction between isocyanate group of coupling agents and hydroxyl group of the filler which have cellulose, hemicellulose, and lignin as a composition [1]. Therefore, the interaction between polymer and SCG phases are improved and showed smoother surface as shown in SEM image (Figure 1. (a-d)). MFI value of the composite of PLA+PBAT/SCG + MDI is found to be 1.1 g/10 min as same as the composite of PLA+PBAT/SCG+TDI which is lower than the composite of PLA+PBAT/SCG (4.4 g/10 min) as shown Table 1. It means that the viscosity of composites was increased when using MDI and TDI as the coupling agent which is caused by the increase of intermolecular interaction forces and limitation of chain mobility [4]. Whereas, the composite of PLA+PBAT/SCG+TESPT had higher MFI up to 13.4 g/10 min (Table 1.). This might be attributed to the plasticization effect caused by TESPT in the polymer molecules. Interfacial adhesion between the
phase of polymers and hydrophilic fillers cannot be improved by using TESPT. However, the impact strength shows no significant change for all composite samples.

**Table 1.** Mechanical properties and melt flow index of PLA+PBAT/SCG composites using different coupling agents (3 g/100 g polymers) compared to the composites without coupling agents.

| Samples                          | Mechanical Properties | Melt Flow Index (g/10 min) |
|----------------------------------|-----------------------|-----------------------------|
|                                  | Tensile Strength (MPa)| Elongation at break (%)     | Impact Strength (J/m²) |
| PLA+PBAT/SCG                     | 19.6 ± 0.2b           | 6.6 ± 0.8b                  | 81.2 ± 0.2b           |
| PLA+PBAT/SCG + TESPT             | 18.7 ± 0.2b           | 4.6 ± 0.7c                  | 81.7 ± 0.3b           |
| PLA+PBAT/SCG + MDI               | 23.5 ± 0.7a           | 10.9 ± 0.4a                 | 82.7 ± 0.2ab          |
| PLA+PBAT/SCG + TDI               | 25.2 ± 0.5a           | 10.6 ± 0.5a                 | 81.3 ± 0.1b           |

**Figure 1.** SEM micrographs of PLA+PBAT/SCG composites with and without coupling agents: (a) PLA+PBAT/SCG, (b) PLA+PBAT/SCG + TESPT, (c) PLA+PBAT/SCG + MDI, (d) PLA+PBAT/SCG + TDI compared to (e) PLA+PBAT/TL + TDI composite.

OM of PLA+PBAT/SCG composites with and without coupling agents are shown in Figure 2. The results showed that OM values from all composite samples in all food simulants (3% acetic and 10% ethanol) are lower than the maximum limit (10 mg/dm²), which followed according to the EU regulation. OM of PLA+PBAT/SCG + TESPT composites was higher than that of other composites containing TDI and MDI. This confirms that the chemical bonds or chemical interaction has no exist between TESPT and other molecules. On the other hand, the addition of MDI and TDI leads to reduce the OM might be due to the favourable interaction between coupling agent and SCG changes the chemical nature of small molecules in polymer and also filler components. Therefore, the chemicals
cannot be diffused easily through the polymer composites into food simulants. The OM of almost all the composites immersed in ethanol shows significantly higher than water, which can be explained by the affinity of the chemical substances in the SCG and coupling agents [2].

![Figure 2. OM of PLA+PBAT/SCG composites with and without coupling agents. 3% acetic and 10% ethanol were used as food simulants.](image)

### 3.2 Effect of weight ratios of polymer to filler

The effect of weight ratios of polymer to filler (i.e., 80/20, 70/30, and 60/40) on mechanical properties and MFI are depicted in Table 2. TDI is used as a coupling agent with 3 g/100 g polymers for all formulation of composites because of its better performance. Tensile strength, elongation at break and impact strength values are decreased with increasing filler (SCG) content from 20 to 40 wt%. Reduction in the tensile properties on increasing the percentage of filler can be explained based on the higher phase separation and weak compatibility between the hydrophobic polymer and the hydrophilic SCG particles [11]. This results correspond well with the reported data. Baeck et al. reported decreasing tensile strength with increasing SCG filler loading from 10 to 40 wt% [1]. Essabir et al. also found that tensile strength slightly decreases with increasing SCG from 10 to 20 wt% [4]. Furthermore, flow behavior (MFI) is also decreased on increasing SCG content. This reduction is probably because chain mobility interception of the polymer was occurred by SCG particles during melt state [4] and solid/solid friction between filler particles [7]. The OM of composites in this part has not been investigated due to the TDI content present in the same level of all samples.
Table 2. Mechanical properties and melt flow index of PLA+PBAT/SCG composites with different weight ratio of polymer to filler (80/20, 70/30, and 60/40).

| Samples          | Weight ratio (g) | Mechanical Properties | Melt Flow Index (g/10 min) |
|------------------|------------------|-----------------------|----------------------------|
|                  |                  | Tensile Strength (MPa) | Elongation at break (%)   | Impact Strength (J/m²) |
| PLA+PBAT/SCG +   | 80/20            | 27.6 ± 0.1^a          | 12.2 ± 1.6^c              | 82.8 ± 0.9^a           | 2.3 ± 0.2^a          |
| TDI              | 70/30            | 25.2 ± 0.5^a          | 10.6 ± 0.5^c              | 81.3 ± 0.1^ab          | 1.1 ± 0.1^b          |
|                  | 60/40            | 20.8 ± 1.2^b          | 5.7 ± 0.1^b               | 80.6 ± 0.2^b           | 1.2 ± 0.1^b          |

3.3 Effect of coupling agent content

Table 3 shows the mechanical properties and melt flow index (MFI) of the PLA+PBAT/SCG composites with different TDI contents i.e., 0, 3, 5, and 7 g/100 g polymers. In this part, the composite with weight ratio of polymer/filler of 70/30 has been chosen due to its similarity in mechanical properties with the weight ratio of polymer/filler of 80/20 but a higher cost reduction can be achieved. Based on the tensile strength of the composites, compatibility improvement between phases of polymer and SCG can be confirmed. Increases in tensile strength on increasing the content of TDI up to 5 g/100 g polymers. Upon further addition, there is no significant change in tensile strength. On the other hand, the elongation at break and MFI are slightly decreased due to the higher interaction which lowers mobility of polymer chains. However, there is no significant change in the impact strength of all samples. OM values of the composites in both food simulants slightly increased when increasing TDI content, but they were still lower than the standard (see Figure 3.). This is clearly reflected in the amounts of TDI that not reacted with the filler and polymer.

Table 3. Mechanical properties and melt flow index of PLA+PBAT/SCG composites (weight ratios of polymer to filler = 70/30) with different TDI content (3, 5, and 7 g/100 g polymers).

| Samples          | Coupling agent amounts (g/100 g polymers) | Mechanical Properties | Melt Flow Index (g/10 min) |
|------------------|------------------------------------------|-----------------------|----------------------------|
|                  |                                          | Tensile Strength (MPa) | Elongation at break (%)   | Impact Strength (J/m²) |
| PLA+PBAT/SCG +   | 0                                        | 19.6 ± 0.2^c          | 6.6 ± 0.8^b               | 81.2 ± 0.2^a           | 4.4 ± 0.3^a          |
| TDI              | 3                                        | 25.2 ± 0.5^a          | 10.6 ± 0.5^c              | 81.3 ± 0.1^a           | 1.1 ± 0.1^b          |
|                  | 5                                        | 25.3 ± 0.3^ab         | 7.5 ± 1.0^b               | 81.2 ± 0.1^a           | 0.6 ± 0.0^c          |
|                  | 7                                        | 26.8 ±0.6^a           | 5.8 ± 0.5^c               | 81.1 ± 0.1^a           | 0.4 ± 0.1^c          |
3.4 Comparison of the composites based on SCG and TL

Table 4. shows the mechanical properties and melt flow index (MFI) of the PLA+PBAT/SCG and PLA+PBAT/TL composites with the weight ratios of polymer to filler of 70/30 and TDI content of 3 g/100 g polymers. It was found that the composite based on TL provided better tensile strength than that of the composite of SCG. The result gave good agreement with SEM image as shown in Figure 1(e). This might be attributed by the differences in shape and chemical structure of both materials. TL may consists of higher polyphenol group, which develops the interaction and improvement in the properties of the composites can be observed. The composite of PLA+PBAT/TL shows smoother cracked surface, implying that the better compatibility of TL compared to the composite of SCG. However, elongation at break, impact strength and melt flow index (MFI) showed no significant changes. The OM values of both composites are lower than the migration limit. Higher OM values observed in the composite of PLA+PBAT/TL indicates the chemical substances present in the TL have more affinity with food simulants compared to SCG as shown in Figure 4.

Table 4. Mechanical properties and melt flow index of PLA+PBAT/SCG composite compared to PLA+PBAT/TL composite with constant TDC content (3 g/100 g polymers).

| Samples                  | Mechanical Properties | Melt Flow Index (g/10 min) |
|--------------------------|-----------------------|----------------------------|
|                          | Tensile Strength (MPa)| Elongation at break (%)    |
|                          |                       | Impact Strength (J/m²)     |
| PLA+PBAT/SCG + TDI       | 25.2 ± 0.5<sup>a</sup> | 10.6 ± 0.5<sup>a</sup>    |
|                          |                       | 81.3 ± 0.1<sup>a</sup>    | 1.1 ± 0.1<sup>a</sup>   |
| PLA+PBAT/TL + TDI        | 37.4 ±1.7<sup>b</sup> | 10.5 ± 1.7<sup>a</sup>    | 82.1 ± 0.4<sup>a</sup>  |
|                          |                       |                            | 1.1 ± 0.1<sup>a</sup>   |
4. Conclusions
Phase compatibility of poly (lactic acid)-based composites incorporated with the spent coffee ground (SCG) and tea leave (TL) have been improved using coupling agents. Among the three different coupling agents, TDI exhibited the highest mechanical properties followed by MDI, without coupling agent and TESPT, respectively. The properties of the composites increased with increasing TDI content. However, adding TDI 3 g/100 g polymers exhibited lowest migration value. Furthermore, the composite based on TL showed better tensile strength, while elongation at break, impact strength and melt flow index (MFI) showed no significant change. The results gained from this study exhibited the beneficial advantages (i.e., cost and waste reduction) for applying as a food contact material. However, specific migration of coupling agent should be studied in the future. Finally, it can be concluded that the method involved in this investigation is a waste to wealth approach.

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