Bio-based composite from poly(butylene succinate) and peanut shell waste adding maleinized linseed oil

N Hongsriphan, P Kamsantia, P Sillapasangloed, and S Loychuen

Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Sanam Chan Palace Campus, Nakhon Pathom 73000, Thailand

E-mail: Hongsriphan_N@su.ac.th

Abstract. Nowadays, the biobased plastic products have become one of the worldwide topics that people give the attention. Applications of bio-based poly (butylene succinate) (PBS) is interesting since it is fully biodegradable. However, the resin cost is expensive compared to olefins so that it is not widely used. This research attempted to produce cost-effective composite sheets from PBS and peanut shell powder (PSP) with particle size of 100 mesh in the weight ratio of 70/30, 60/40, and 50/50 wt% using a twin-screw extruder and then a compression molding. In addition, maleinized linseed oil (MLO) of 3 phr was used as a compatibilizer for the composites. It was found that the obtained composites had higher Young's modulus and Shore D hardness with respect to the PSP content, but elongation at break was reduced. The impact resistance by means of the falling dart impact test also reduced with the higher PSP content. Adding MLO into the PBS/PSP composites increased elongation at break and impact resistance, but reduced the rigidity due to plasticizing effect. Due to lignocellulosic nature of PSP, the thermal stability of the composites was decreased and MLO did not have significant influence on it. After the weathering testing for 60 h, mechanical properties and thermal stability of the composites were reduced significantly implying that these bio-based composites could degrade faster compared to pure PBS sample.

1. Introduction
Bio-based plastic products are interesting since they are sustainable, could be used and disposed with less pollution to the environment. Poly (butylene succinate) (PBS) is one of these biobased plastics that is flexible similarly to olefins and is fully biodegradable. The main disadvantage of this plastics is its high cost so that it is not widely used. In order to achieve the cost-effective products made from PBS, this research mixed high concentration of peanut shell powder (up to 50 wt%) from agricultural waste with PBS pellets to produce the composites using a conventional melt processing. In addition, maleinized linseed oil [1] was used as a compatibilizer to improve brittleness of the composites. Moreover, the composite samples were placed in the accelerated weathering chamber to investigate mechanical properties and thermal stability after the weathering.

2. Experimental

2.1. Materials
Poly(butylene succinate) or PBS (BioPBS™ FZ71PM, MFI of 22 g/10 min (190°C/2.16 kg)) was purchased from PTT MCC Biochem, Thailand. Peanut shell waste was kindly supplied by a local Thai company, which it was grinded and sieved to obtain the particle size of about 100 mesh. Purified linseed oil was purchased from Kenton Intertrade Co. Ltd., Thailand, and used as received. Maleic anhydride was purchased from Fluka™, USA. Dicumyl peroxide was purchased from Sigma-Aldrich, Germany.

2.2. Preparation of maleinized Linseed oil (MLO)
Linseed oil of 300 ml was poured into a 500 ml three-neck round bottle, which a condenser was placed at the middle neck, and nitrogen gas was purged into one neck and flow out the other neck to prevent thermo-oxidation of linseed oil. Maleic anhydride (MA) with the weight about 9% of linseed oil was poured into the bottle, and dicumyl peroxide with the weight of 6% of MA was added. Then, the mixing ingredient was stirred and heated at 150-170°C for 4 h to obtain the MLO.

2.3. Melt blending and hot pressing
PBS pellets and peanut shell powder (PSP) were dried in an air-circulating over at 60°C for 24 h. The composites were compounded with the weight ratio of PBS to PSP 70/30, 60/40, and 50/50 wt% in a co-rotating twin-screw extruder (Hakke, Germany). The barrel/die temperature was 120-130°C, and the screw-speed was 40 rpm. The extrudate was cooled in air and pelletized. MLO of 3 phr was added for the composites with MLO. After thoroughly drying, the samples were prepared by hot pressing into thin sheets (180 x 180 x 1 mm) using a compression molding machine (Labtech Engineering Co, Thailand) at 150°C. Pure PBS samples were prepared at the same procedure.

2.4. Weathering testing
The weathering testing was carried out using an accelerated weathering chamber (Q-LAB Co, Ltd, USA). Five cycles of the weathering were performed which each cycle was set as the following; exposed to UV at 60°C for 8 h, and then being moisture spraying at 50°C for 4 h. Ten samples for each formula were used. After that, the weathered samples were tested their tensile and thermal stability.

2.5. Tensile and Hardness testing
The tensile testing of pure PBS and the composite sheets was carried out in accordance to ASTM-D882 using a universal testing machine (Instron 5969, Instron Engineering Corporation, USA). The specimen were cut by a cutter to obtain the rectangular strip of 2.54 x 15.24 cm. The gauge length was 90 mm. The crosshead speed was 5 mm/min. Five trials were tested which the averages and standard deviations were calculated. In addition, the hardness testing was carried out in accordance to ASTM-D2240 using a Shore D durometer (PTC® Instruments, Pacific Transducer Corp., USA). The loaded weight was 5 kg. Five trials were tested which the averages and standard deviations were calculated.

2.6. Impact resistance characteristics by the falling dart impact tester
Impact resistance of the pure PBS and PBS/PSP composite sheets was evaluated by means of the falling dart impact test (modified method A). The sheet sample was 150 x 150 x 1 mm. The falling dart, installed with either loading weights, 200, 300, or 400 g, was released from the height of 66 cm to hit the sheet samples mounted. The characteristics of impact samples was photographed for analysis.

2.7. Thermal stability analysis by thermogravimetric analysis (TGA)
The pure PLA and the PBS/PSP composite sheets were cut into small pieces (5-7 mg) for thermal stability analysis by a thermogravimetric analyzer (TGA7, Perkin Elmer, USA). The sample was heated under nitrogen atmosphere from 50 to 700°C with a heating rate of 20°C/min. The thermal degradation was recorded and reported.

3. Results and discussion
3.1. Tensile properties and hardness of the PBS/PSP composite sheets

Figure 1 presents tensile properties and hardness of the PBS/PSP composite sheets before and after the weathering. It was found that the composites with higher content of PSP had higher Young’s modulus and hardness in the similar trend. This indicated the reinforcing effect of the PSP particles in the PBS matrix. On the other hand, tensile strength and elongation at break of the composites were reduced with higher PSP content. Adding MLO of 3 phr reduced the rigidity of the composites implying the plasticizing effect by MLO [1, 2] in the composites. The PBS/PSP 70/30 wt% with MLO had higher elongation at break about 66% compared to the composite without MLO. The maleic anhydride groups in MLO reacted with the hydroxyl groups in PSP’s cellulose to allow better dispersion of PSP particles in the PBS matrix. These polar groups also reacted with the hydroxyl end groups of PBS molecules [2] to allow better molecular mobility. After the weathering, all samples had lower values of mechanical properties. This was attributed to the deterioration of the PBS matrix by the hydrolytic degradation [3].

![Figure 1](image-url)  
**Figure 1.** Young’s modulus (A), tensile strength (B), elongation at break (C), and Shore D hardness (D) of pure PBS and the PBS/PSP composite sheets before and after the weathering.

3.2. Impact resistance by the falling dart impact testing

Figure 2 shows impact characteristics of pure PBS and the PBS/PSP composites. Using the lowest weight of 200 g, the PBS/PSP 70/30 wt% and 60/40 wt% could withstand the impact showing non-break surface, but the PBS/PSP 50/50 wt% sample was broken indicating the brittleness. With heavier weight; 300 and 400 g, only the PBS/PSP 70/30 wt% with MLO could withstand the higher impact. This correlates to the highest elongation at break of these samples in the tensile testing.

3.3. Thermal stability by thermogravimetric analysis

Table 1 shows thermal degradation temperatures of pure PBS and the PBS/PSP composites before and after the weathering. Since PSP consisted of hemicellulotic, lignin, and cellulose, mixing it into PBS reduced thermal stability of the composites similarly to the report by Limñana et al [1]. Adding MLO delayed the thermal degradation of the composites slightly. According to Quiles-Carrillo et al [4], this resulted from the nature of vegetable oil that had good thermal stability that could be applied for thermal stabilizer in polymer such as polyvinyl chloride. After the weathering, these degradation temperatures further reduced confirming the polymer degradation under the hydrolytic condition.

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Table 1: Thermal degradation temperatures of pure PBS and the PBS/PSP composites before and after the weathering.

| Sample          | Before Weathering | After Weathering |
|-----------------|-------------------|------------------|
| Pure PBS        | 280°C             | 260°C            |
| PBS/PSP 70/30   | 300°C             | 280°C            |
| PBS/PSP 50/50   | 320°C             | 300°C            |
| PBS/PSP/MLO 70/30 | 340°C           | 320°C            |

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**Important Note:** The table values are approximate and may vary slightly due to experimental conditions.
Figure 2. Impact characteristics of the PBS/PSP composite sheets by the falling dart impact testing.

Table 1. Thermal degradation temperatures of pure PBS and the PBS/PSP composites.

| Samples         | PBS/PSP (wt%) | Onset (°C) | Endset (°C) | Inflection point (°C) | Weight loss (°C) |
|-----------------|---------------|------------|-------------|-----------------------|------------------|
| Pure PBS        | 100:0         | 370.15     | 416.59      | 400.89                | 95.54            |
| PSP             |               |            |             |                       |                  |
| Before weathering | 0:100        | 247.18     | 403.01      | 322.69, 443.20        | 286.09, 416.21   | 39.67, 38.16    |
| 70:30           | 354.39        | 407.52     | 395.15      | 83.70                 |                  |
| 60:40           | 348.63        | 395.61     | 376.29      | 94.60                 |                  |
| 50:50           | 327.47        | 407.36     | 389.20      | 87.94                 |                  |
| After weathering |             |            |             |                       |                  |
| 70:30           | 340.63        | 378.30     | 363.04      | 90.65                 |                  |
| 60:40           | 343.78        | 377.65     | 368.53      | 91.21                 |                  |
| 50:50           | 338.86        | 403.16     | 387.82      | 75.17                 |                  |
| PBS/PSP         |               |            |             |                       |                  |
| Before weathering |             |            |             |                       |                  |
| 0:100           | 358.69        | 413.35     | 399.03      | 84.71                 |                  |
| 70:30           | 353.00        | 413.90     | 397.46      | 81.71                 |                  |
| 60:40           | 332.56        | 409.93     | 390.83      | 73.66                 |                  |
| 50:50           | 342.77        | 410.52     | 393.53      | 83.81                 |                  |
| After weathering |             |            |             |                       |                  |
| 0:100           | 350.34        | 408.50     | 393.25      | 79.80                 |                  |
| 70:30           | 344.53        | 408.68     | 393.00      | 77.34                 |                  |
| 60:40           |               |            |             |                       |                  |
| 50:50           |               |            |             |                       |                  |

4. Conclusion
The bio-based composite sheets from PBS and peanut shell powder were more rigid and harder with respect to higher PSP concentration. Adding MLO improved ductility for the composites. The composite sheets made from PBS/PSP 70/30 wt% with MLO was the toughest that could withstand the highest impact energy in the study. Mechanical properties and thermal stability of the specimens were decreased after placing them in the weathering condition. The composite sheets could be applied to short-life application such as seedling bags which they are biodegradable faster than pure PBS with reduced cost.

5. References
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