Effects of Natural Rubber Compound and Crumb Rubber on Mechanical and Morphological Properties of Biodegradable Poly(butylene succinate)

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Abstract. Natural rubber compound was melt-mixed with biodegradable poly(butylene succinate) (PBS) using an internal mixer. The effect of natural rubber compound (NRC) content on the mechanical properties of PBS was examined. The amount of NRC of 0, 5, 10 and 15 percentage by weight were used. Moreover, crumb rubber (CR) of 5 phr was added into the blend of PBS/NRC (85/15). After mixing, the samples were ground with a grinder and formed to specimen test by hot compression molding. The results of the mechanical tests showed that NRC enhanced the toughness of PBS matrix. As a result, the elongation and impact resistance values increased. However, maximum tensile strength and the modulus of elasticity decreased with an increase in the NRC content. The addition of CR in the PBS/NRC blend resulted in a reduction of all mechanical properties. The morphology of the fractured surface was investigated by scanning electron microscope. It could be seen that the NRC had a good dispersion in the PBS matrix while the CR did not show good interfacial adhesion with the PBS matrix.

1. Introduction

Nowadays, bioplastics are being promoted for research and development due to concerns of environmental problems. Poly(butylene succinate) (PBS) is a biodegradable polymer, which has good mechanical properties and is easy to process. PBS is a polyester polymer polymerized from 1,4-butanediol and succinic acid by condensation reaction. It has a linear structure and thermal stability of up to 200°C and can degrade into carbon dioxide and water after use. However, its cost is still very high. Hence, there have been many attempts to increase the application of PBS i.e. polymer blends [1-4] and/or composites [5-6].

Natural rubber (NR) is a bio-based elastomer with high elasticity. There are many research studies in which the toughness of polymeric matrix has been enhanced by natural rubber [1-4, 7-8]. The examples of some studies have reported bioplastics such as poly(lactic acid) [8] and poly(butylene succinate) [1, 2-3, 7]. For example, Pongtanayut et al. reported the toughness improvement of poly(lactic acid), PLA, with natural rubber and epoxidized natural rubber. They found that the content of NR at 10% weight gave the optimum properties [8]. In addition, the epoxidized natural rubber was also used in PBS matrix. However, the result showed that the tensile properties decreased with the incorporation of epoxidized natural rubber [2].
Waste tire rubber has increased due to the growth of automotive industry. It can be used in civil engineering fields such as geotechnical, hydraulic works, and concretes [9]. Moreover, there are many reports on waste tire rubber/thermoplastics blends such as ethylene-vinyl acetate (EVA) [10], high-density polyethylene (HDPE) [11], and polypropylene (PP) [12].

In this research, natural rubber compound (NRC) was prepared in an efficient vulcanization system on a two-roll mill. The NRC and biodegradable PBS were melt-mixed in an internal mixer. The effect of NRC content on the morphological and mechanical properties was investigated. Moreover, the addition of crumb rubber into the blend was also investigated.

2. Materials and method

2.1. Materials
Natural rubber (NR, STR 5L), stearic acid, zinc oxide (ZnO), tetramethyl thiuram disulphide (TMTD), N-cyclohexyl-2-benzothiazole sulfenamide (CBS), and sulphur (S) were used to prepare natural rubber compound (NRC) in an efficient vulcanization system. All chemicals were purchased from Chareon Tut Co., Ltd., Thailand. Biodegradable PBS (BioPBSTM FZ71PM grade) was supplied by PTT MCC Biochem Co., Ltd. Crumb rubber was purchased from Q2thailand company, Nakhon Pathom, Thailand.

2.2. Natural rubber compound preparation
Natural rubber (NR) and chemicals were blended via a two-roll mill (Chareon Tut co., ltd., ML-D6L12-INV) for 30 min to make a natural rubber compound (NRC). The roller speed ratio between front roll and back roll was 1:1.4. The order of reagents and mixing time are shown in Table 1.

| No. | Raw materials  | Composition, phr | Mixing time, min |
|-----|----------------|------------------|------------------|
| 1.  | Natural rubber | 100              | 5                |
| 2.  | Steric acid    | 2                | 5                |
| 3.  | ZnO            | 6                | 5                |
| 4.  | TMTD           | 3.5              | 5                |
| 5.  | Sulphur        | 0.75             | 5                |
| 6.  | CBS            | 1                | 5                |

2.3. Poly(butylene succinate)/natural rubber compound/crumb rubber blend
Poly(butylene succinate) (PBS) and crumb rubber (CR) were dried in an oven at 50°C for 24 h before use. All blends were melt-mixed by an internal mixer (Chareon Tut co., ltd., MX500-D75L90) at 145°C for 20 min. The rotor speed of 50 rpm was used. The ratio of PBS/NRC consists of 100/0, 95/5, 90/10, 85/15 and the ratio of PBS/NRC/CR was 85/15/5. The CR represented 5 phr of the PBS/NRC (85/15) blend. The order of mixing is illustrated in Table 2. After completely being mixed, the blend was cooled to room temperature and ground by a grinder machine.
Table 2. A sequence of mixing.

| Time sequence, min | Materials                                      |
|-------------------|------------------------------------------------|
| 0                 | Poly(butylene succinate) (PBS)                 |
| 5                 | Natural rubber compound (NRC)                  |
| 10                | Crumb rubber (CR)                              |

2.4. Hot-compression process
The ground PBS/NRC and PBS/NRC/CR blends were dried in an oven at 50°C for 24 h before the hot-compression process. A hot-compression machine (Chareon Tut co., ltd., PR2D-W300L350 PM-WCL-HMI) was used to prepare samples at a temperature of 145°C and pressure of 1500 psi to investigate the mechanical properties. The pre-heat time, pressing and cooling time were 5, 5, and 3 min, respectively. The mechanical testing specimens were prepared according to ASTM D638 for the tensile test and ASTM D256 for the impact test.

2.5. Testing and characterization
2.5.1. Mechanical testing.
For the impact test, the notched Izod impact type was conducted according to ASTM D256 at room temperature by impact tester machine (INSTRON, Ceast 9050). At least ten samples were tested and evaluated. For the tensile test, the universal testing machine (UTM, LLOYD INSTRUMENT, LR10K plus) was used at a crosshead speed of 50 mm/min at room temperature.

2.5.2. Morphological study. The fractured surface from the tested impact sample was investigated by using a scanning electron microscope (JEOL, JSM-6510).

3. Results and discussions
3.1. Effect of natural rubber compound
In this research, the mechanical properties of poly(butylene succinate)/natural rubber compound (PBS/NRC) blends and poly(butylene succinate)/natural rubber compound/crumb rubber (PBS/NRC/CR) blends were investigated in terms of impact and tensile tests.

Figure 1 shows the impact strength of PBS/NRC blends. The results showed that the impact strength of 100/0, 95/5, 90/10, 85/15 was 5.24 ± 0.10, 6.81 ± 0.42, 8.70 ± 0.95, 11.51 ± 0.78 kJ/m², respectively. The highest impact strength was exhibited at 85/15 of PBS/NRC blends. It was enhanced 2 times when compared with the pure PBS. This might be attributed to the fact that the NRC acted as a stress absorber in the polymeric matrix; a toughened polymer matrix similar to a previous report [4].

Figure 2 illustrates the elongation at break, tensile strength, and Young’s modulus of PBS/NRC blends. The elongation at break of the blends tended to increase with an increase in the NRC content (Figure 2a). This result implied that NRC contributed to improving the elongation at break in the polymer blends. The ratio of 85/15 has the highest elongation at break of 20.7 ± 3.1 percentage. The elongation at break was improved to 1.2 times as compared with pure PBS due to the elastic property of NRC, similar to the polymer-rubber system [4]. On the other hand, the incorporation of NRC significantly decreased the tensile strength and Young’s modulus of PBS (Figure 2b and 2c, respectively). As expected, tensile strength and Young’s modulus decreased with an increase in the amount of NRC due to rubber having lower of the said properties.
**Figure 1.** Impact strength of poly(butylene succinate)/natural rubber compound (PBS/NRC) blends

**Figure 2.** Tensile properties of poly(butylene succinate)/natural rubber compound (PBS/NRC) blends; (a) elongation at break and (b) tensile strength and (c) Young’s modulus
3.2. Effect of crumb rubber
Table 3 exhibits the mechanical properties of pure PBS, PBS/NRC, and PBS/NRC/CR blends. It could be seen that all properties of PBS/NRC/CR blends were slightly lower than that of PBS/NRC blends. This might be due to the low interfacial adhesion between crumb rubber and polymer matrix. However, the impact strength and elongation at break of the PBS/NRC/CR blends were still higher than that of pure PBS.

Table 3. Mechanical properties of pure PBS, PBS/NRC, and PBS/NRC/CR blends

| Properties                  | PBS       | PBS/NRC:85/15 | PBS/NRC/CR:85/15/5 |
|-----------------------------|-----------|---------------|---------------------|
| Impact strength (kJ/m²)     | 5.24 ± 0.10 | 11.51 ± 0.78 | 9.61 ± 0.58         |
| Tensile strength (MPa)      | 33.80 ± 4.67 | 23.95 ± 1.06 | 21.12 ± 0.75        |
| Young’s Modulus (MPa)       | 356.06 ± 2.09 | 244.44 ± 6.67 | 235.25 ± 4.89       |
| Elongation at Break (%)     | 17.30 ± 4.59 | 31.88 ± 6.35 | 20.69 ± 3.08        |

3.3 Morphological study.
Figure 3 illustrates the SEM micrographs of the fractured surfaces of pure PBS, PBS/NRC blends with various blend ratios and PBS/NRC/CR. The result showed that a slightly coarse surface could be observed in the pure PBS (Figure 3a). All PBS/NRC blends illustrated dispersed NRC particles in the PBS matrix (Figure 3b-e). The particle size of NRC was around 2-5 µm. Figure 3f shows the void of CR in the blend that demonstrated a poor interfacial adhesion between CR and PBS matrix. Subsequently, this reason brings about the low mechanical properties of the PBS/NRC/CR as mentioned above.

Figure 3. Morphology of pure PBS, PBS/NRC blends and PBS/NRC/CR with a weight ratio of; (a) 100/0, (b) 95/5, (c) 90/10, (d) 85/15, (e) 85/15/5, and (f) 85/15/5 (higher magnification). The black arrows indicate the dispersed NRC.
4. Conclusions
The amount of NRC affected the mechanical and morphological properties of the blends. NRC could increase the impact strength and percentage elongation at break of PBS, while it decreased the tensile strength and Young’s modulus of PBS. Toughness properties of PBS/NRC blend were decreased by the incorporation of CR. However, blending PBS with small amounts of CR still showed higher toughness properties than that of the pure PBS. The surface modification of CR could improve the interfacial adhesion between CR and PBS in future work.

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