Impact property enhancement of poly (lactic acid) with different flexible copolymers

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Abstract. The objective of this work was to improve the impact property of Poly (lactic acid) (PLA) by blending with different copolymers. Six flexible copolymers, namely, acrylonitrile butadiene styrene (ABS) powder, Biomax, polybutyrate adipate co-terephthalate (PBAT), polyether block amide (PEBAX), ethylene-vinyl acetate (EVA) and ethylene acrylic elastomer (EAE), with loading less than 20wt% were used and compared. The rheological, mechanical and morphological properties of samples were investigated by melt flow index, tensile testing, impact testing and scanning electron microscope (SEM), respectively. It was found that PLA added 20wt% EAE showed the highest impact strength (59.5 kJ/m²), which was 22 times higher than neat PLA. The elongation at break was also increased by 12 folds compared to neat PLA. The SEM images showed good interface and distribution for PLA containing 20wt% EAE, 15 phr Biomax and 20 wt% PEBAX.

1. Introduction
Poly (lactic acid) (PLA) has emerged as a promising choice for replacing the existing commodity and industrial products. In terms of downstream manufacture of PLA products, the cost of PLA has dropped against the increasing demands. Therefore, many PLA-based products such as film wrap, glass, plate, spoon and fork have readily been marketed. The important features of PLA include high mechanical properties, compostability, transparency, while some weaknesses also exist such as low heat resistance, brittleness due to slow crystallization [1, 2]. To date, many types of polymers regardless of being biodegradable or not, have been reported for increasing impact properties of PLA [3]. The impact improvement was possible through first; the addition of copolymers such as OnCap™ BIO [4], random aliphatic copolyesters [4], ethylene/n-butyl acrylate/glycidyl methacrylate (EBA-GMA) terpolymer with zinc ion-containing ionomer [5], poly (butylene succinate) (PBS) [6], poly-(R-3-hydroxybutyrate) [7], polyurethane elastomer (PU) [8], poly (ethylene glycol) (PEG) [9], and second; using in situ co-polymerization (e.g., c-caprolactone and L-lactide (c-CL/L-LA) [10], poly (β-
hydroxybutyrate-co-β-hydroxyvalerate) [11], ethylene-co-vinyl acetate [12], P[CL-co-LA] random copolymesters [13].

Sin L T et al. [14], used Poly(lactic acid) with Blendex 338 or Ultra High Rubber ABS as an impact modifier. They reported that PLA blended with Blendex 338 (at the amount of 20 wt%) showed the notched impact strength increased from 26.7 J/m to 518 J/m and the elongation at break increased from 10 % to 218 %. Krishnaswamy R et al. [15] demonstrated that blending Biomax strong 120 (other types of ethylene copolymer) at the amount of 10 wt% into PLA could improve the impact strength in a similar fashion. The impact strength increased from 0.2 t.lb/inch to 5.0 t.lb/inch. Afrifah K A et al. [16] used ethylene/acrylate copolymer as an impact modifier for blending with PLA and they found that the blends showed a decrease in tensile strength and modulus with the increasing impact modifier contents. In contrast, the ductility, elongation at break, and energy to break increased significantly. Although a lot of literatures have been reported the use of the above mentioned polymers for impact modifiers, there has not yet been attempt to systematically compare their performance in terms of mechanical properties. Therefore, in this research, six flexible copolymers; namely ABS powder (core shell (rubber core/ABS shell)), ethylene copolymer (Biomax), polybutyrate adipate coterephthalate (PBAT), Polyether block amide (PEBAX), ethylene-vinyl acetate (EVA) and ethylene acrylic elastomer (EAE) were selected to melt-blending with PLA in order to study the effect of their types and compositions on impact properties together with tensile properties and physical appearance. The performance of toughened PLA was discussed and compared.

2. Experimental

2.1. Materials
PLA 2003D was purchased from NatureWorks LLC (USA). ABS Powder (rubber core/ABS shell, AP6200) was kindly supplied by IRPC, (Thailand). Biomax (Ethylene copolymer) and Ethylene Acrylic Elastomer (EAE, Vamac®) were kindly provided by Chemical Innovation Company Limited (Thailand). Ecoflex® (PBAT) was purchased from BASF (Germany). Polyamide elastomer; PEBAX was purchased from Arkema (France). Ethylene vinyl acetate (Escorene™ Ultra EVA copolymer, EVA) was purchased from Exxonmobil Chemical (USA).

2.2. Sample preparation
PLA resin was first dried at 60°C for 12 hr. Copolymers were then weighted according to table 1 and dried mixed before transferring to an internal mixer, Model MX 105-D40L50, Chareon tut CO. LTD., Thailand. Melt blending was performed at the temperature of 190°C and the rotor speed of 60 rpm.

| Table 1. PLA formulations and blend compositions. |
| Sample formulation | PLA (g) | ABS powder (g) | Biomax (g) | PBAT (g) | PEBAX (g) | EVA (g) | EAE (g) |
|---------------------|---------|----------------|------------|----------|-----------|--------|--------|
| neat PLA            | 100     |                |            |          |           |        |        |
| PLA/ABS powder 10 phr | 100   | 10             |            |          |           |        |        |
| PLA/ABS powder 15 phr | 100   | 15             |            |          |           |        |        |
| PLA/Biomax 10 phr   | 100     |                | 10         |          |           |        |        |
| PLA/Biomax 15 phr   | 100     |                | 15         |          |           |        |        |
| PLA90/PBAT10        | 90      |                | 10         |          |           |        |        |
| PLA80/PBAT20        | 80      |                | 20         |          |           |        |        |
| PLA90/PEBAX10       | 90      |                | 10         |          |           |        |        |
| PLA80/PEBAX20       | 80      |                | 20         |          |           |        |        |
| PLA90/EVA10         | 90      |                |          | 10       |           |        |        |
| PLA80/EVA20         | 80      |                |          | 20       |           |        |        |
| PLA90/EAE10         | 90      |                |          |          | 10       |        |        |
| PLA80/EAE20         | 80      |                |          |          | 20       |        |        |
The mixing time was 10 min. The test specimens were prepared using a compression molding machine (Chareon tut CO. LTD., Thailand). Compression molding was carried out at 190°C for 6 min to obtain micro tensile and impact specimen.

2.3. Mechanical properties testing
Tensile and impact tests were carried out according to ASTM D 638 and ASTM D256, respectively. Ten specimens were used for each sample. Tensile testing was measured using a Universal Testing Machine (Instron, Model 5969, Instron Engineering Corporation, USA). Testing speed was 10 mm/min. Impact testing was measured using a Zwick model Pendulum impact tester B5102.202.

2.4. Morphology
The morphology of the PLA/copolymers specimens was observed using SEM (CamScan, MX 2000, UK). The fracture surfaces of impact testing were coated with gold before SEM examinations.

3. Results and discussion

3.1. Torque and melt flow index (MFI)
From table 2, it was found that with the addition of all copolymer showed a decrease in the final torque values compared with neat PLA. PLA containing 20 wt% EVA showed the lowest final torque value at 7.34 Nm, which half of the value of neat PLA. These results were confirmed by the MFI results, and the highest MFI value was observed for the addition of 20 wt% EVA in PLA.

| Sample              | Final torque (Nm) | MFI 190°C (g/10min) |
|---------------------|-------------------|---------------------|
| neat PLA            | 14.77             | 4.7±0.5             |
| PLA/ABS powder 10 phr | 13.37             | 4.8±0.5             |
| PLA/ABS powder 15 phr | 13.35             | 4.8±0.5             |
| PLA/Biomax 10 phr   | 11.29             | 5.5±0.4             |
| PLA/Biomax 15 phr   | 11.43             | 5.6±0.4             |
| PLA90/PBAT10        | 11.41             | 6.4±0.7             |
| PLA80/PBAT20        | 15.03             | 6.9±0.5             |
| PLA90/PEBAX10       | 9.51              | 7.0±0.9             |
| PLA80/PEBAX20       | 8.40              | 9.1±0.5             |
| PLA90/EVA10         | 11.27             | 5.5±0.1             |
| PLA80/EVA20         | 7.34              | 10.9±0.1            |
| PLA90/EAE10         | 11.35             | 8.2±0.1             |
| PLA80/EAE20         | 13.07             | 5.8±0.1             |

Figure 1. Physical appearance of a) neat PLA, b) PLA/ABS powder 10 phr, c) PLA/ABS powder 15 phr, d) PLA/Biomax 10 phr, e) PLA/Biomax 15 phr, f) PLA90/PBAT10, g) PLA80/PBAT20, h)PLA90/PEBAX10, i) PLA80/PEBAX20, j) PLA90/EVA10, k) PLA80/EVA20, l) PLA90/EAE10, m) PLA80/EAE20.
3.2. Physical appearance of blends
Figure 1 showed the physical appearance of polymer blended with copolymers. All added copolymer samples lost their optical property. When ABS powder and PBAT were added into PLA, the specimens became less clear. Samples b) and c) (PLA/ABS powder 10 and 15 phr) were whitened and opaque as well as sample f) and g) (PLA90/PBAT10 and PLA80/PBAT20). In case of samples d) and e) (PLA/Biomax 10 and 15 phr), they were clearer than sample h) and i) (PLA90/PEBAX10 and PLA80/PEBAX20, samples j) and k) (PLA90/EVA10 and PLA80/EVA20), and sample l) and m) (PLA90/EAE10 and PLA80/EAE20).

Table 3. Impact properties of PLA and the blends containing different copolymers.

| Sample                  | Izod impact strength (IS) (kJ/m²) |
|-------------------------|-----------------------------------|
| neat PLA                | 2.7±0.3                           |
| PLA/ABS powder 10 phr   | 8.6±0.7                           |
| PLA/ABS powder 15 phr   | 8.5±1.2                           |
| PLA/Biomax 10 phr       | 26.2±3.7                          |
| PLA/Biomax 15 phr       | 38.6±2.3                          |
| PLA90/PBAT10            | 5.6±0.8                           |
| PLA80/PBAT20            | 9.4±0.6                           |
| PLA90/PEBAX10           | 9.0±0.8                           |
| PLA80/PEBAX20           | 35.1±7.5                          |
| PLA90/EVA10             | 14.7±2.8                          |
| PLA80/EVA20             | 11.6±2.5                          |
| PLA90/EAE10             | 13.0±1.8                          |
| PLA80/EAE20             | 59.5±2.1                          |

3.3. Impact properties and SEM of specimens
The izod impact strengths of neat PLA and its blends with copolymer were shown in table 3. With the addition of ABS powder (10 and 15 phr), it showed a slight increase in the impact strengths about 8.6 kJ/m² (3 times) compared with neat PLA. When adding Biomax 10 and 15 phr, the impact strengths of 26.2 and 38.6 kJ/m², respectively, which were higher than those of neat PLA by 9.7 and 14.3 times, respectively. With the incorporation of 10 phr of PBAT or PEBEX, the impact strengths were also 2 and 3 times higher than those of neat PLA, respectively. When increasing the amount of PBAT or PEBAX to 20 phr, the impact strengths were 4 and 13 times higher than neat PLA, respectively. In the case of the addition of EVA (10 to 20 wt%), in the blend, a decrease in impact strengths value was found, which is only 5 and 4 times compared with that of neat PLA, respectively. Surprisingly, when 20 wt% EAE was added, it showed the highest impact strength (59.5 kJ/m²), which was higher than

Figure 2. Photographs of notched Izod impact tested samples showing fracture modes. a) neat PLA, b) PLA/ABS powder 10 phr, c) PLA/ABS powder 15 phr, d) PLA/Biomax 10 phr, e) PLA/Biomax 15 phr, f) PLA90/PBAT10, g) PLA80/PBAT20, h) PLA90/PEBAX10, i) PLA80/PEBAX20, j) PLA90/EVA10, k) PLA80/EVA20, l) PLA90/EAE10, m) PLA80/EAE20.
that of neat PLA by 20 folds. The addition of elastomer EAE showed the dramatic improvement of impact toughness to PLA matrix, hence allowing energy dissipation mechanisms into PLA and retarding crack initiation and propagation.

Figure 3. SEM images of fractured surface of impact specimen a) PLA/ABS powder 10 phr, b) PLA/Biomax 10 phr, c) PLA90/PBAT10, d) PLA90/PEBAX10, e) PLA90/EVA10, f) PLA90/EAE10.

From figure 2, it was demonstrated that complete breakage could be obtained with samples a), b), c), d), e), f), g), j) and l), whereas the partial breakage of specimens was found in samples h), i), k) and m). Stress whitening near the notched tip was observed due to crazing or micro cracks, and it showed that the matrix could bear most of the stress [17]. It is common that the continuous transfer of energy is an important factor for impact resistance. In adding dispersed phases into the polymer matrix, the good distribution of the dispersed phase, smaller particle sizes and good interfacial adhesion are key factors to determining the optimum performance of materials. Fractured surface of impact specimens corresponding to the same concentration of copolymers are shown in figures 3a)-3f). At the same amounts of copolymer (10 wt%), the SEM image of PLA added 10 phr ABS powder samples showed good dispersion of ABS powder throughout PLA matrix. In addition, separated particles of ABS powder phase could still be observed. The dispersion phases did not retain the spherical shapes, but partially adhered to PLA matrix. This might provide the positive impact property as seen in figure 3(a).
In figure 3(b), the particle phases in the matrix could retain the spherical shapes, copolymers particle elongation and had good interphase between modifier and the matrix. In figure 3(c), impact modifier particle sizes were regularly dispersed in PLA matrix. The particle sizes of dispersed phase were 3 µm. In this case, it showed the partial interfacial adhesion between PLA and PBAT matrix. In the case of PLA added PEBAX (in figure 3(d)), it was found that the adhesion between PEBAX and PLA was prominent and the distribution of tiny particle sizes in the matrix could be seen as the same as that in the case of Biomax. In figure 3(e), the addition of EVA demonstrated the superior distribution of particles in the matrix, but the particles of EVA were not adhered to PLA matrix. In addition, dispersed phase particles were not spherical and do not change shape when applied force. In figure 3(f), broken fibrils from polymer blend between PLA with 10 wt% of EAE could still be observed. Particles of EAE were well dispersed in PLA matrix. There were many fibrils on fractured surface of the specimen. This indicated the toughening mechanism of polymer matrix. When force was applied to the samples by impact testing, EAE would adsorb force and the extension of particle took place. These results were attributed to the higher elongation at break which will be discussed later.

3.4. Tensile properties
The modulus, tensile strength and elongation at break were displayed in table 4. For all added copolymers, the increase in their contents led to the decrease in the modulus and tensile strengths, because copolymer was flexible than PLA. The decreased tensile strength probably resulted from the presence copolymers inserted in PLA matrix [18, 19]. The increase in elongation at break probably resulted from the samples were more ductile. For the addition of 20 wt% of PBAT, PEBAX and EVA, the elongation at break increased to over 35% (from 8.7% of neat PLA), whereas the tensile strength decreased by 30% when compared to neat PLA. PLA added 20 wt% PBAT showed the highest elongation at break value. It also appeared necking phenomenon which demonstrated the ductile behaviour of the polymer blends.

| Sample                  | Modulus [MPa] | Tensile Strength [MPa] | Elongation at break [%] |
|-------------------------|---------------|------------------------|-------------------------|
| neat PLA                | 1619.2±115.1  | 91.6±8.3               | 8.7±1.4                 |
| PL/A ABS powder 10 phr | 1517.8±59.2   | 76.0±2.8               | 39.4±10.5               |
| PL/A ABS powder 15 phr | 1231.8±11.2   | 57.0±4.3               | 41.1±7.6                |
| PL/A Biomax 10 phr     | 1247.8±67.6   | 63.0±3.2               | 19.6±3.4                |
| PL/A Biomax 15 phr     | 1179.6±48.3   | 57.5±3.2               | 44.1±23.6               |
| PLA90/PBAT10           | 1287.1±70.5   | 85.4±2.2               | 96.7±40.6               |
| PLA80/PBAT20           | 1117.3±96.5   | 65.2±4.9               | 185.9±34.0              |
| PLA90/PEBAX10          | 1294.4±46.9   | 83.1±6.3               | 52.1±22.0               |
| PLA80/PEBAX20          | 1042.8±49.5   | 66.0±2.4               | 110.1±10.1              |
| PLA90/EVA10            | 1082.1±51.2   | 52.6±3.7               | 33.5±7.1                |
| PLA80/EVA20            | 934.5±53.3    | 39.7±1.7               | 96.5±32.4               |
| PLA90/EAE10            | 1293.3±134.1  | 74.8±5.6               | 32.4±3.5                |
| PLA80/EAE20            | 1030.8±105.6  | 57.8±2.9               | 104.1±53.2              |

4. Conclusion
This work aimed to study and compare the effect of six flexible copolymers on the impact property. The impact results show that the impact strength is significantly improved in all PLA added copolymer samples when compared to neat PLA. Especially, PLA with the addition of 20 wt% EAE, shows superior performance on impact strength improvement which its impact strength was 22 times higher than neat PLA and this is confirmed by SEM images of fractured surfaces from impact testing, which show good interface and distribution between PLA matrix and copolymer for PLA containing 20 wt% EAE, 15 phr Biomax and 20 wt% PEBAX. In addition, the elongation at break of all samples
was greatly increased compared to neat PLA. Therefore, in summary, it indicates that the addition of 20 wt% EAE is the most effective thermoplastic elastomer for improving impact resistance of PLA.

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