

# Increased Impact Strength of Biodegradable Poly(lactic acid)/Poly(butylene succinate) Blend Composites by Using Isocyanate as a Reactive Processing Agent

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**ABSTRACT:** Poly(lactic acid) (PLA) blended with poly(butylene succinate) (PBS) was prepared in the presence of lysine triisocyanate (LTI) by using a twin-screw extruder and injection molding machine. The physical properties, rheological behavior, compatibility, and morphology were investigated by using a tensile test, a Charpy impact test, melt mass-flow rate (MFR) measurements, size exclusion chromatography (SEC), and laser scanning confocal microscopy (LSCM). The impact strength of PLA/PBS(90/10 wt %) blend composite was about 18 kJ/m<sup>2</sup> in the absence of LTI, and it increased to 50–70 kJ/m<sup>2</sup> in the presence of LTI at 0.5 wt %. The MFR value of PLA/PBS(90/10 wt %) decreased

from 25 g/10 min at 200°C in the absence of LTI to approximately 3 g/10 min in the presence of LTI. These results imply that isocyanate groups of LTI reacted with both terminal hydroxyl or carboxyl groups of the polymers. Spherical particles at 1 μm were observed by using LSCM in the presence of LTI. These results indicate that the LTI is a useful reactive processing agent to increase the compatibility of PLA/PBS blend composites to increase the impact strength of PLA. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1813–1820, 2007

**Key words:** PLA; biodegradable; biopolymers; reactive processing; compatibility

## INTRODUCTION

Poly(lactic acid) (PLA) is a promising synthetic biopolymer derived from biomass through bioconversion and polymerization.<sup>1</sup> Today PLA is not expensive, as with other engineering plastics, but it used to be expensive because of complex processing procedures. The disadvantage of PLA is that it is too soft above its glass transition temperature (60°C) and has low toughness, which limits its applications. Its brittleness is also a disadvantage for its application in various commercial items. The soft biodegradable plastic poly(caprolactone) (PCL) has been blended to PLA to increase the impact strength to solve the brittleness.<sup>2</sup> However, soft biodegradable plastics decrease the tensile strength of blend composites at high impact strengths (30–50 wt % blend). Copolymerization of PLA/PCL also decreases the brittleness of PLA.<sup>2–4</sup> Various compatibilizers, such as PLA-*co*-PCL, have been studied to increase the miscibility of the blend composites to increase the impact strength.<sup>5,6</sup> PLA-based urethane composites (PEU) have been synthesized by reacting PLA with diisocyanate, such as 1,

6-hexamethylene diisocyanate (HMDI).<sup>7–9</sup> PEU as a compatibilizer or an additive increases the impact strength. Kenaf at 30 wt %<sup>10</sup> or poly(ethyleneglycol) at 10 wt %<sup>11</sup> are also useful to improve the physical properties. The impact strength of PLA/poly(butylene adipate-*co*-terephthalate) (PBAT) is also increased when 20 wt % of PBAT is added.<sup>12</sup>

Miscibility, crystallization behavior, and morphology of the PLA/poly(butylene succinate) (PBS) composites have been reported.<sup>13,14</sup> The average size of the PLA domain is about 30 μm as seen by polarized optical micrographs.<sup>13</sup> Synchrotron small-angle X-ray scattering data shows well-defined double-scattering peaks during crystallization, indicating that this system has dual lamellar stacks.<sup>14</sup> However, we believe the physical properties and characterization of PLA/PBS blend composites using a reactive processing agent have not been reported.

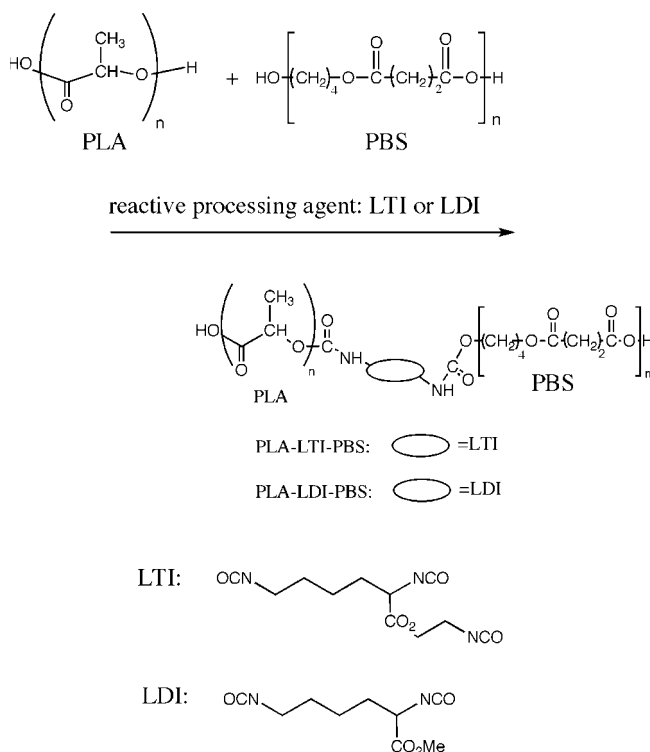
Reactive processing is a frequently used compatibilization strategy for cost-effective production of new multiphase polymeric materials with outstanding physical and chemical properties.<sup>15</sup> Successful application of the principles of reactive processing has produced considerable technological opportunities for compatibilization of immiscible polymer blends. Terminal or graft groups react with the terminal group of the other polymer in the extrusion process during melt reactions. Copolymers of poly(propylene) having poly(maleic anhydride) can react

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with polyamide(PA),<sup>6</sup> and with poly(styrene) having an amino group. Because blends of acrylonitrile–butadiene–styrene (ABS) and PA are highly immiscible, compatibilization is achieved by using maleic anhydride-functionalized ABS.<sup>15</sup> In the biodegradable plastics field, maleic anhydride,<sup>16–18</sup> triphenyl phosphite (TPP),<sup>19</sup> and dicumylperoxide (DCP)<sup>20</sup> are added to PLA, PCL, and PBS.

We hoped that isocyanates may be useful for reactive processing of PLA/PBS blend composites in the early stage of this study, because hydroxyl and carboxylic groups that are hydrolyzed in PLA and PBS under heat and high shear stress in an extruding equipment<sup>19</sup> may react with isocyanate groups. Figure 1 shows the predicted reaction of PLA, PBS, and reactive processing agents lysine triisocyanate (LTI, 2-isocyanate ethyl-2,6-diisocyanate ohexanoate, Fig. 1) and lysine diisocyanate (LDI, methyl 2,6-diisocyanatohexanoate, Fig. 1). We searched various isocyanates for biodegradable material, and we found that LTI and LDI may be most suitable due to the main chain of atoms in lysine that is a kind of amino acid residue. PLA-based polyurethanes are synthesized by using HMDI, so we focused on LTI as a reactive processing agent because the LTI molecules have three isocyanate groups in, and we expected that these three isocyanate groups are useful to increase the chance of reaction at the PLA/PBS interface to increase its physical properties.



**Figure 1** Predicted reactions of PLA, PBS, and reactive processing agents.

In this study, PLA was blended with PBS in the presence of LTI and LDI (Fig. 1), and their physical properties, rheological behavior, phase behavior and morphology were investigated by using the tensile test, Charpy impact test, melt mass-flow rate (MFR) measurements, size exclusion chromatography (SEC), and laser scanning confocal microscopy (LSCM). In particular, this study focused on making the impact test more effective by using LTI compared with LDI (Fig. 1) and the observation of morphology in reactive processing to have a better understanding of the reactively compatibilized structure of PLA/PBS.

## MATERIALS AND METHODS

### Materials

PLA (Toyota Motor) (Catalog No. CSL 40529) and PBS (Showa Highpolymer) (Catalog No. 1020) was dried at 80°C for 12 h before use. LTI and LDI (Kyowa Hakko Kogyo) were used as received.

### Blending

The blends were processed in a twin-screw extruder (KZW15-30TGN, L/D= 30, Technovel) at 190°C (die) and 300 rpm. The extrusion rate was 1 kg /60 min and the accumulation time was approximately 2 min. Three hundred and sixty gram PLA and 40 g PBS were mixed in a 1-L beaker and then 2 g LTI or LDI was added. The mixed pellets were extruded and dried for 4 h at 80°C in an oven.

### Injection molding

The test specimens were prepared from the extruded blends by using an injection molding machine (SE 18S Sumitomo Heavy Industry) with a nozzle at 220°C. The temperature of the mold was 30°C and the peak pressure of injection was 40–60 MPa. The cycle time was approximately 50 s.

### Tensile strength

The tensile tests were done by using an Instron 4505 tensile testing machine equipped with a computer adapted to the standard ISO 527-1993. The samples were stored at rest for 48 h at 23°C and 50%RH before the test. The crosshead speed was 5 mm/min.

### Impact strength

Charpy impact tests were done by using a Zwick impact tester (JT TOHSI Inc.) and a pendulum of 8 J (hammer weight 1.2 kg) adapted to the standard ISO 179-1993 (E) at 23°C and 50%RH. Testing was done on unnotched specimens of 80 × 10 × 4 mm<sup>3</sup>. The

impact blow was in the edgewise direction. Samples were stored at rest for 88 h at 23°C and 50% RH before test.

### MFR

The MFR was used to characterize the melt viscosity of PLA/PBS blend composites. The MFR was measured by using a Ray-Ran apparatus (Imoto Seisakusho, Kyoto; MB-1) at standard conditions of 200°C and 2.16 kg nominal load adapted to the standard ISO 1133-1997.

### SEC

Molecular weights ( $M_w$  and  $M_n$ ) and molecular weight distributions ( $M_w/M_n$ ) were determined by using a JASCO (PU-2080, CO-2065, and RI-2031) operating with  $\text{CHCl}_3$ . Samples (10 mg) were dissolved in 10 mL  $\text{CHCl}_3$  and were filtered by using a 0.5  $\mu\text{m}$  pore filter (Advantec, DISMIC-13). The molecular weights were calibrated using polystyrene standards (Showa Denko K. K., SM105).

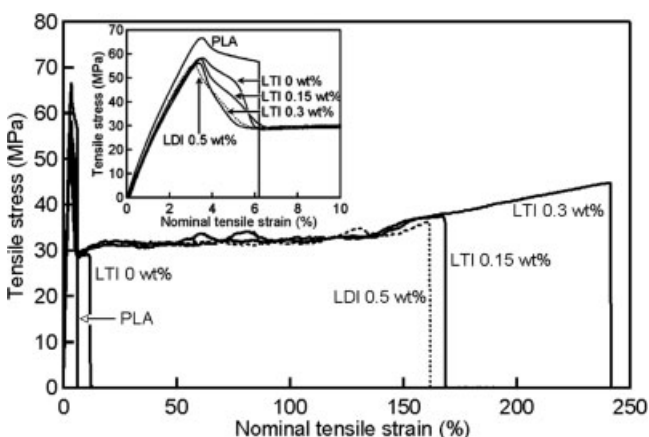
### Observation of morphology

The morphology of the impact tested surface of injection-molded specimens was examined by using a LSCM (Olympus corporation, OLS-1200). The LSCM images were in the reflecting mode.

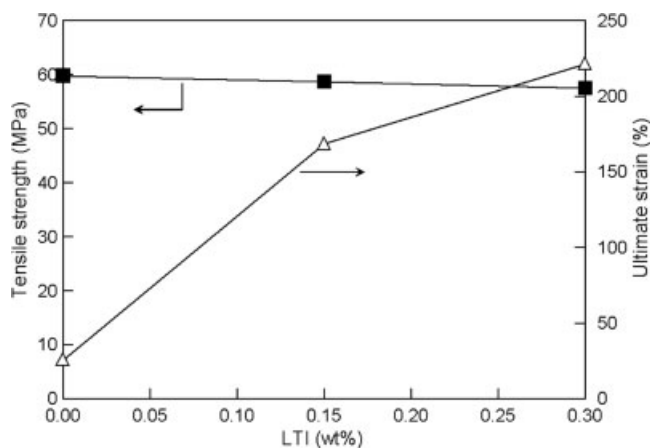
## RESULTS AND DISCUSSION

### Physical properties of PLA/PBS blend composites in the presence of LTI

PLA was blended with viscous PBS with LTI as a reactive agent and the mechanical properties, rheological



**Figure 2** Stress-strain curves of PLA/PBS (90/10 wt %) blend composites in the presence of LTI and LDI, and PLA in the absence of LTI and LDI. The inset gives details of stress-strain of the blends in the neighborhood of yield points.

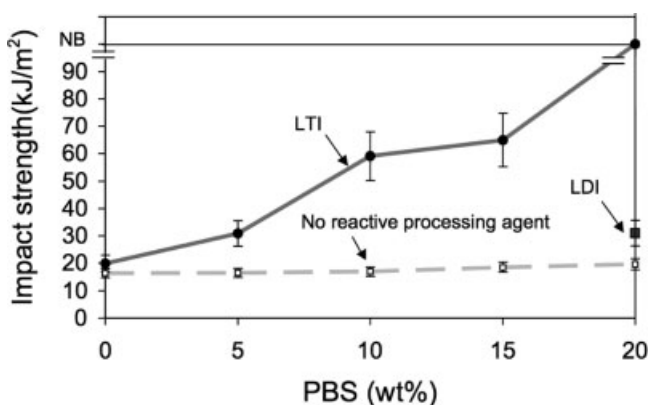


**Figure 3** Tensile strength, ultimate strain and LTI (wt %) in PLA/PBS (90/10 wt %) blend composites. (■) Tensile strength (MPa). (△) Ultimate strain (%).

properties and compatibility of the blend composites were investigated. Blends of PLA with 5, 10, 15, 20 wt % of PBS were prepared. LTI was added at 0.0–1.0 wt % to the PLA/PBS blend composites.

Figure 2 shows stress-strain curves of PLA/PBS (90/10 wt %) blend composites in the presence of LDI and LTI, and the PLA in the absence of a reactive processing agent. Figure 3 shows the tensile strength and ultimate strain of PLA/PBS (90/10 wt %) blend composites in the presence of LTI. Adding LTI by 0.3 wt % did not improve the tensile strength, but gradually decreased it (Fig. 3). This result agreed with that of Hiljanen-Vainio et al.<sup>2</sup> who reported that the tensile strength of PLA/PCL blend composites, with PLA-PCL copolymer as a compatibilizer, gradually decreased. However, the ultimate strain was higher in the presence of LTI than its absence and increased with increasing LTI to 0.3 wt % LTI. The effect of 0.5 wt % LDI was as same as that of 0.15 wt % LTI (Fig. 2). These results imply that LTI is effective for PLA/PBS blending, and agrees with the results of Semba et al.,<sup>20</sup> who reported that the tensile strength of PLA/PCL blend composites with 0.1–0.2 wt % DCP as a compatibilizer gradually decreases and the ultimate strain increases.

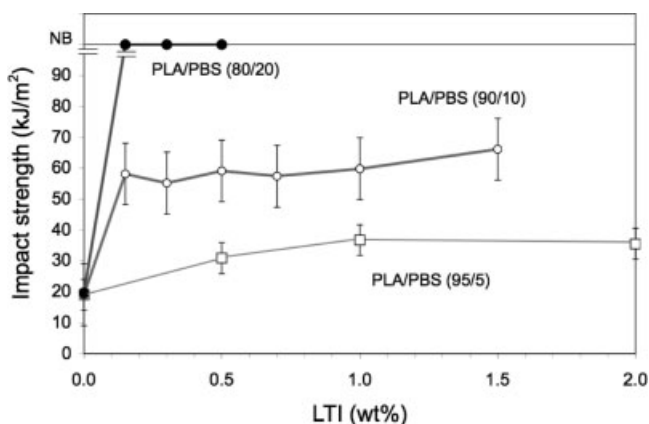
Figure 4 shows the dependence of the impact strength on the PBS content (5–20 wt %) in both the presence and absence of LTI. The impact strength increased with increasing PBS content in the presence of LTI (0.5 wt %). The impact strength of 10–15 wt % PBS content was more or less saturated at 50–70  $\text{kJ}/\text{m}^2$ . The impact strength of over 20 wt % PBS content could not be measured in the presence of LTI because the test specimens were not breakable. Although 30 wt % PBS was added to PLA in the absence of LTI, the impact strength did not increase (18  $\text{kJ}/\text{m}^2$ ). In the presence of LTI, the impact strength of 10 wt % PBS increased 2–3 times and



**Figure 4** Impact strength and PBS (wt %) in PLA. Absence of reactive processing agent ( $\square$ ), presence of LTI (0.5 wt %,  $\bullet$ ), and presence of LDI (0.5 wt %,  $\blacksquare$ ). NB: not breakable.

was the same as for normal ABS (Technopolymer, Catalog No. 350) (unnotched, 60–80 kJ/m<sup>2</sup>). Adding LDI to PLA with 20 wt % PBS was not as effective for influencing the impact strength (31 kJ/m<sup>2</sup>, Fig. 4), indicating that LTI is the more useful reactive processing agent for impact strength. In the case of blending of PCL as viscous biodegradable polymer in the absence of LTI to PLA, the impact strength of PLA clearly increases with 20 wt % of PCL.<sup>2</sup> In this study, using PBS with LTI as a reactive agent, the impact strength clearly increased with the lower amount of the viscous polymer PBS. Preliminary results showed that the impact strength of PLA/PCL blend composites in the presence of LTI also increases.<sup>21,22</sup>

Figure 5 shows the effect of LTI on the impact strength at PBS 5, 10, and 20 wt % in PLA. At 5 wt % PBS, the impact strength increased gradually with increasing LTI and was saturated at 1.0 wt % LTI. At 10 and 20 wt % PBS, the impact strength suddenly increased and was saturated at 0.15 wt % LTI.

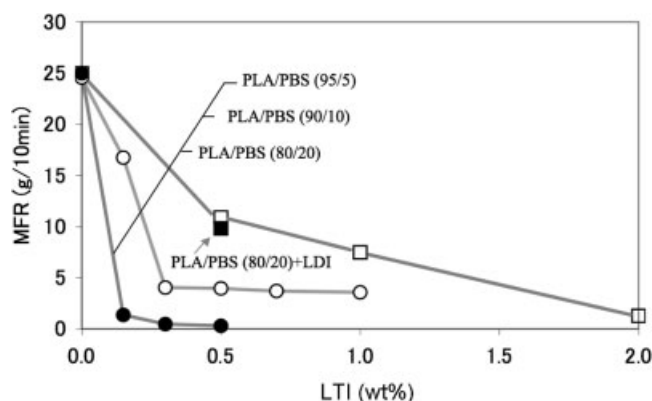


**Figure 5** Impact strength and LTI (wt %) of PLA/PBS blend composites (PLA/PBS = 95/5, 90/10, 80/20 wt %).

Blending of high molecular weight PBS (Catalog No. 1001;  $M_w = 128,000$ ) in the absence of LTI did not increase the impact strength in PLA blend composites (data not shown). Thus an increase in impact strength does not depend on the molecular weight of PBS but depends on the presence of LTI. The reaction might occur between isocyanate groups of LTI and hydroxyl or carboxyl groups at the terminals of the polymer (Fig. 1) so that the interfacial adhesion between PLA and PBS might increase the impact strength.

### Rheological properties of PLA/PBS blend composites in the presence of LTI

Adding LTI was effective to increase the ultimate strain and impact strength of PLA/PBS blend composites, but was not effective to increase the tensile strength. The addition level of LTI required to optimize physical properties of PLA/PBS (90/10 wt %) is approximately 0.15 wt %, as well as for the impact strength of ABS. To investigate the rheological properties of reactive processing, the MFR was measured. Figure 6 shows the dependence of adding LTI at 5, 10, and 20 wt % PBS with PLA on the MFR, which decreased with increasing LTI, implying that the viscosity increased, indicating that LTI has a crucial role in the rheology of PLA/PBS blending. The total trend of MFR level decreased with increase in PBS amount, implying that PBS might also be important for reactive blending. LDI, which has two isocyanate groups, was not effective to decrease MFR of PLA/PBS (80/20 wt %) (Fig. 6), implying that three, not two, isocyanate groups in the reactive processing agent decrease MFR. The viscosity of PLA and PCL cross-linked blend composites by TPP<sup>19</sup> and DCP,<sup>20</sup> respectively, increases when the torque data is measured by using an internal mixer. In this study, the sudden decrease in MFR by adding LTI at 3 g/10 min



**Figure 6** MFR and LTI (wt %) in PLA/PBS blend composites (PLA/PBS = 95/5, 90/10, 80/20 wt %).

**TABLE I**  
Molecular Weight Determination of PLA/PBS Blend Composites by Using SEC

Blend composition (wt %)		$M_n$ ( $10^4$ )	$M_w$ ( $10^4$ )	$M_w/M_n$
PLA/PBS	LTI			
100/0	0	9.2	16.3	1.77
100/0	0.5	9.7	16.3	1.68
90/10	0	7.0	14.4	2.06
90/10	0.5	7.1	15.7	2.21
80/20	0	6.8	14.2	2.09
80/20	0.5	6.9	17.9	2.59
0/100	0	4.9	10.5	2.14

suggests cross-linking as in the cases of TPP or DCP. Although the impact strength was more or less saturated for 10 wt % PBS with 0.15 wt % LTI (Fig. 5), the MFR was not too low (17 g/10 min), indicating that 10 wt % PBS with 0.15 wt % LTI in PLA is suitable for required properties and productivity of blends by injection molding.

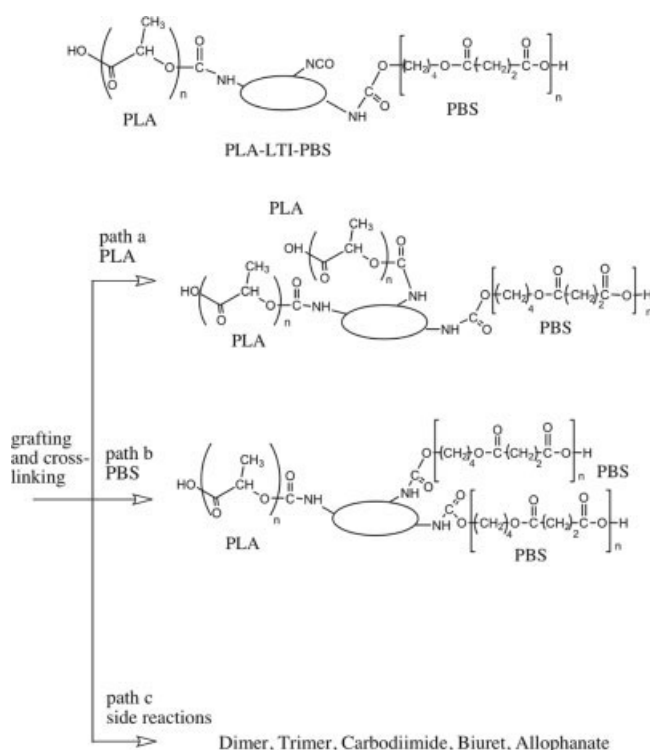
In this study using SEC, the absence of LTI, the  $\text{CHCl}_3$  solution of blend composites of PLA/PBS were easily filtered by using a 0.5  $\mu\text{m}$  pore filter before the SEC measurements. However, in the presence of LTI, the filter was gradually plugged up, indicating that the blend composites of PLA/PBS in the presence of LTI might also produce cross-linking parts. So, SEC was used to measure only the soluble parts. Table I shows molecular weights of PLA/PBS blend composites by using SEC. The molecular weight of PLA in the presence of LTI was almost same for PLA without LTI. However, the molecular weight of the blend composites of PLA/PBS in the presence of LTI slightly increased to compare in the absence of LTI, suggesting that LTI might react in the presence of both PLA and PBS. These results imply that LTI may produce both high molecular weight parts and insoluble cross-linking parts (Fig. 7) in PLA/PBS blend composites. In the synthesis of PLA-based polyurethanes, the molecular weight of telechelic prepolymers that have low molecular weight increases by reaction with HMDI.<sup>7-9</sup> In this study, the molecular weight also increased during reactive processing.

#### Morphology of PLA/PBS blend composites in the presence of LTI by LSCM

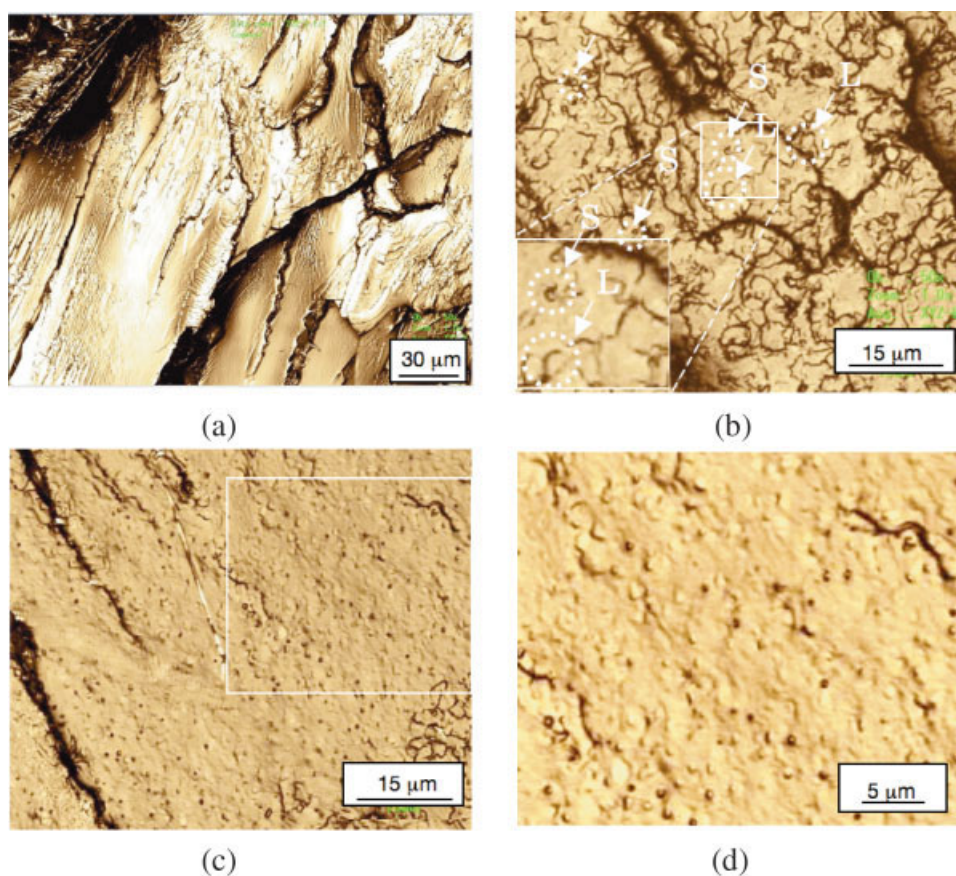
To investigate the reactive compatibility of PLA/PBS blend composites, the fracture surface of impact tested specimens was observed by using an LSCM. The LSCM image of the fracture of PLA with 0.5 wt % LTI showed that the fracture surface was brittle [Fig. 8(a)] and that it was similar in the absence of LTI. Figure 8(b-d) show LSCM images of PLA/PBS (90/10 wt %) blend composites in the presence of 0 and 0.15 wt % LTI. Spherical particles of 0.9–1.4  $\mu\text{m}$

diameter were in the presence of LTI [Fig. 8(c,d)]. In this case, PBS was a smaller amount (10–20 wt %), and so PLA and PBS might form a matrix and islands, respectively, in the blend composites. In the absence of LTI [Fig. 8(b)], the morphology was unstable and irregularly shaped. Spherical particles of 1  $\mu\text{m}$  diameter were fewer [Fig. 8(b), white arrows S] and domains of 2–5  $\mu\text{m}$  [Fig. 8(b), white arrows L] were many, agreeing with the observation by using transmission electron microscopy.<sup>23</sup> Table II shows the size and number of spherical particles in a 15  $\times$  15  $\text{mm}^2$  area of the composites. The standard deviation of size of particles in the absence of LTI was wider than in the presence of LTI, indicating that LTI stabilizes the morphology of PLA/PBS blend composites. Clearly the number of the particles was smaller at LTI 0.15 wt % and their size did not depend on the LTI and PBS concentrations.

The impact tested specimens of PLA/PBS (80/20 wt %) in the presence of 0.15 wt % LTI were not completely broken. The fracture surface was smooth (brittle) and white (ductile). The brittle surface [Fig. 9(a,b)] was far from the stress point and 1  $\mu\text{m}$  diameter spherical particles were also in the flat surface [Fig. 9(b)]. The fracture surface of ductile surface had many spherical cavities [Fig. 9(c,d)]. Thus the PBS-rich domain might form spherical particles in the presence of LTI by phase separation and adsorb the impact strength. Our results suggest that LTI



**Figure 7** Predicted reaction pathways of PLA-LTI-PBS, PLA, and PBS.



**Figure 8** LSCM images of Charpy-fractured brittle surface of the blend composites. (a) PLA in the presence of LTI (0.5 wt %). (b) PLA/PBS (90/10 wt %) blend composite in the absence of LTI. (c) PLA/PBS (90/10 wt %) blend composite in the presence of LTI (0.15 wt %). (d) Inset of (c). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

changed the PBS domain size from 1.4–4.0  $\mu\text{m}$  to 0.8–1.4  $\mu\text{m}$  under shear stress in the extruder. The morphology development during dissipative mixing in these reactive blends may occur by a sheeting mechanism as described by Scott and Macosko.<sup>24</sup>

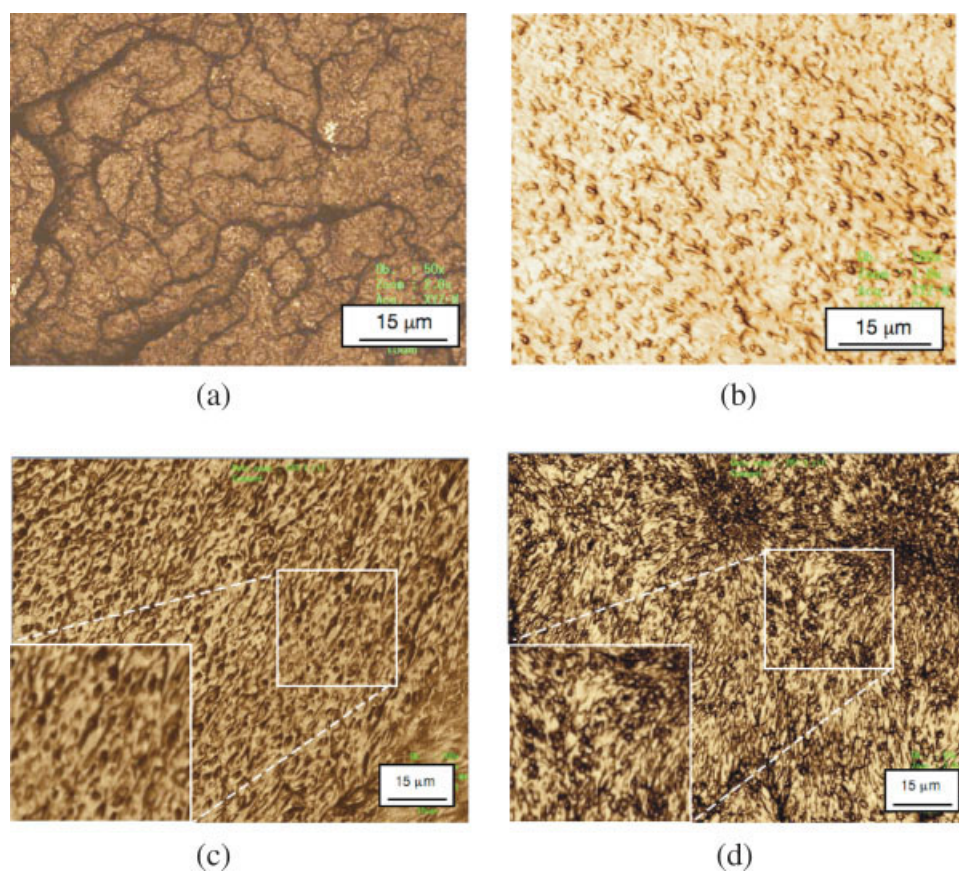
Figures 1 and 7 show proposed chemical reactions between LTI and biodegradable polymers. First, hydroxyl or carboxyl groups of PLA and PBS, respectively, might react with two isocyanate groups of the LTI or LDI molecule (Fig. 1) to form grafting PLA. However, the impact strength did not effectively increase, and the MFR did not decrease in the presence of LDI. These results suggest that a third isocyanate group might have an important role in the formation of physical properties.

Second, the third isocyanate group of LTI might react with PLA (Fig. 7, path a) or with PBS (Fig. 7, path b) for grafting and cross-linking. Increasing molecular weight and decreasing MFR with increasing PBS suggest that path b might react with these composites. Further reactions of the terminals of paths a and b induce cross-linking of the PLA/PBS blend

system. Several other reactions occur during the synthesis of polyurethane between diisocyanates and a polyol.<sup>25–29</sup> The major side reactions are dimerization, trimerization, and carbodiimide, biuret and allophanate formation. The dimerization, trimerization, and biuret and allophanate reactions might induce cross-linking in PLA/PBS blend composites. In this study, insoluble parts of over 500 nm pore filtration were in the  $\text{CHCl}_3$  organic solvent and a spherical structure of about 1  $\mu\text{m}$  was found by using LSCM.

**TABLE II**  
Number and Size of Particles in  $15 \times 15 \text{ mm}^2$  of Brittle Surface Imaging Area

Blend composition (wt %)		Number	Size ( $\mu\text{m}$ )	Standard deviation ( $\mu\text{m}$ )
PLA/PBS	LTI			
90/10	0.0	8	2.60	1.2
90/10	0.15	11	1.10	0.20
90/10	0.3	26	1.26	0.19
90/10	0.5	26	1.29	0.13
80/20	0.5	20	0.92	0.17



**Figure 9** LSCM images of Charpy-fractured brittle and ductile surface of the PLA/PBS (80/20 wt %) blend composites. (a) Brittle surface in the absence of LTI. (b) Brittle surface in the presence of LTI (0.5 wt %). (c) Ductile surface in the presence of LTI (0.15 wt %). (d) Ductile surface in the presence of LTI (0.5 wt %). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Unfortunately, direct evidence of chemical reaction by using spectroscopic methods, such as infrared spectroscopy or nuclear magnetic resonance spectroscopy could not be observed (data not shown). Our results suggest that control of the biodegradable polymer interfaces by chemical reaction may have a crucial role in the structure of isocyanates. The systematic relationship of structure and properties of biodegradable polymers should be further studied in the presence of other isocyanates as reactive processing agents.

In conclusion, LTI was found to be a reactive processing agent in the PLA/PBS blend composites that were processed by using a twin-screw extruder, and the impact strength of sample specimens increased to 2–4 times that of PLA. The impact strength much increased at 10 wt % PBS content. The LTI concentration was sufficient at 0.15 wt % to increase the impact strength. The decrease in MFR implies that LTI reacts with polymers. The morphology study showed that spherical structures induced by a reactive process contribute to an increase in impact strength.

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