# ADVANCES IN PROPERTIES AND BIODEGRADABILITY OF CO-CONTINUOUS, IMMICISIBLE, BIODEGRADABLE, POLYMER BLENDS

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**Abstract**

A series of blends consisting of polylactic acid (PLA) and aliphatic succinate polyester (Bionolle#3000) have been prepared. The results of the mechanical property investigation have shown that using more than 20 wt % Bionolle#3000 can significantly increase the toughness of the PLA, increase the elongation at break (more than 200%) and increase the impact strength (more than 70 J/m). These properties were not significantly affected by the aging behavior of PLA for more than two months. DMA results show that Bio#3000 reduces the elastic modulus of the blends between -15°C and 60°C.

Soil degradation rates of the PLA/Bio#3000 blends also increase with increasing Bio#3000 content. However, for the blends with less than 30 wt % of Bio#3000, the degradation rates do not significantly increase. Enzymatic degradation rates of the blends are higher than for those of the two polymers, and these rates increase with increasing PLA content. Composting biodegradation rates increase with increasing Bio#3000 content.

**Materials**

Bionolle #3000 was supplied by Showa Highpolymer Co., LTD, Japan; with a molecular weight (Mn) of 23,300; and a melting point about 91°C.

PLA was supplied by Cargill Inc. (EcoPla Division, Minnesota) in December 1994 with 8% meso content (96% L) and with a molecular weight (Mn) of 70,100.

*Blending and preparing sample*

Blending was performed using a CSI MAX mixing extruder at 150 and 160°C and a screw speed of 50 rpm. Each sample was extruded twice. Each blend composition and code are reported in Table 1. Samples (about 0.3 mm thick for tensile test; 3 mm thick for impact test DMA test) were made by compression molding at 155 °C and cooled in a cooling press machine at 20 °C and 700 psi.

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**Table 1. Sample Code and Composition of PLA/Bionolle #3000 blends**

| Sample Code | PLA % (wt) | Bionolle % (wt) |
|---|---|---|
| A90/B10 | 90 | 10 |
| A80/B20 | 80 | 20 |
| A70/B30 | 70 | 30 |
| A50/B50 | 50 | 50 |
| A30/B70 | 30 | 70 |

***Characterization***

Tensile properties of the blends were obtained respectively after samples were aged at room temperature for 1, 2, 4, 7, 14, 21, 35, 40 and 70 days using an Instron Tensile machine model 1137 at 2.0 in/min of crosshead rate.

The impact strength of PLA/Bio#3000 blends was obtained on the compression molded samples using an Izod Impact Tester, Ceast Model 6545 in Izod mode with a notch of 2.54 mm in accordance with ASTM D256-88.

Dynamic mechanical properties were obtained by using a DuPont 983 Dynamic Mechanical Analyzer. The resonant frequency mode and 3 mm thick samples were used in the test. Oscillation amplitude (p-p) and heating rate are respectively 0.3 mm and 5 °C/min.

Soil biodegradation testing was performed using the respirometric method developed at the NSF Biodegradable Polymer Research Center, University of Massachusetts Lowell and designated UML-7645.

Carbon dioxide production, expressed as a fraction measured of theoretical carbon content of the test materials, is reported as a function of time. 0.3 mm thick films were used in the soil test.

An enzymatic degradation study was carried out by using Proteinase K. The blends samples (10 mm x 10 mm) with an approximate thickness of 0.3 mm were placed in vials containing 5ml of Tris/HCL (PH=8.6) buffer, 1.0 mg of Proteinase K and 1.0 mg of sodium azide. The sample/enzyme incubations were carried out at 37°C in a rotary shaker (200 rpm). The buffer/enzyme system solution was changed every 24 hours to restore the original level of enzyme activity. The samples were periodically removed, washed with distillation water and then dried in high vacuum for 24 hours at room temperature. The control test was carried out in buffer solution without Proteinase K.

The composting test was conducted in a simulated municipal compost mixture consisting of shredded leaves; shredded paper; mixed frozen vegetables; meat waste;

urea; commercial compost seed and water are added to bring the mix to 60% water holding capacity. The C:N ratio of the starting mix is 14:1.

Blends were compression molded into sheets of about 0.3 mm thickness. The sheets were cut into 20 mm x 20 mm sample. The composting process is carried out for 30 days at 55 °C. Triplicate test specimens were removed from the bioreactors at 5 day intervals. Weight loss was calculated and normalized with respect surface area in $\mu g/mm^2$. A poison compost control was used for comparison of biological vs. abiotic weight loss.

**Results**

*Mechanical properties*

Tensile properties of samples aged for 14 days as a function of Bio#3000 are shown in figures 1-4. Both modulus and stress at yield decrease; elongation at yield and at break increase with increasing Bio#3000 content. This may be attributed to the low modulus, low stress at yield and excellent elongation at break of Bio#3000. Stress at break of the blends (Fig. 2) initially decreases and then increases with Bio#3000 content increasing.

For the PLA sample, no yield phenomenon exists; for the blend A90/B10, the sample breaks rapidly after yield; for the blend A80/B20, necking occurs but the sample broke soon after necking; for the blend A50/B50, after necking, the stress increases with strain until it excesses the yield stress. Stress-Strain curves for PLA, A90/B10, A80/B20 and A50/B50 blends are shown in Figure 3.

The mechanical properties of PLA and its blends usually deteriorates as a function of time due to physical aging. In this study, the change of the tensile properties of PLA/Bio#3000 with aging time was investigated. It was found that the tensile stress and elongation at yield of the blends did not significantly change with time.

The effects of aging time on modulus and elongation at break of PLA, Bio#3000 and their blends are illustrated in Figures 5-7. Modulus of PLA and blend A90/B10 are higher than those of the other blends, and increase steadily with aging time. For blend A80/B20, after the first week the modulus is low and slightly increases; then from the 10th day to the 30th day, the modulus reaching that of blend A90/B10. For blends with 30 wt % and 50 wt % Bionolle#3000, no clear increase is observed with time.

Elongation at break of the pure PLA sample is below 8 % and does not change in the first 30 days of aging, then decreases to 5 % after 40 days of aging. For blend A90/B10, elongation at break of sample reduces rapidly during the first 10 days aging then approaching to that of PLA. For other blends with more than 30 wt % Bio#3000, the elongation at break decreased slightly in the first 10 days then remained at that level.

Impact strength of PLA/Bio#3000 blends (Fig. 5) increased with increasing Bio#3000 content. An improvement of 100-150% (85-120 J/m) in impact strength can be

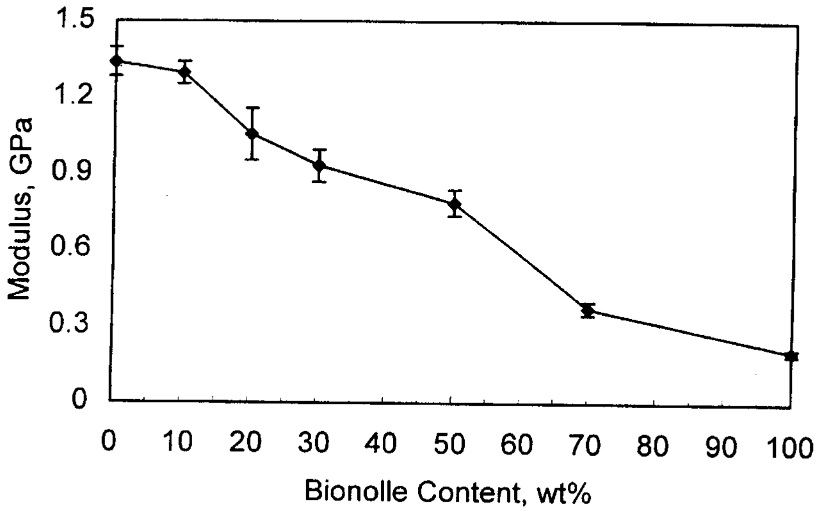


**Figure 1. Modulus of PLA/Bio#3000 blends as a function of Bionolle #3000 content**

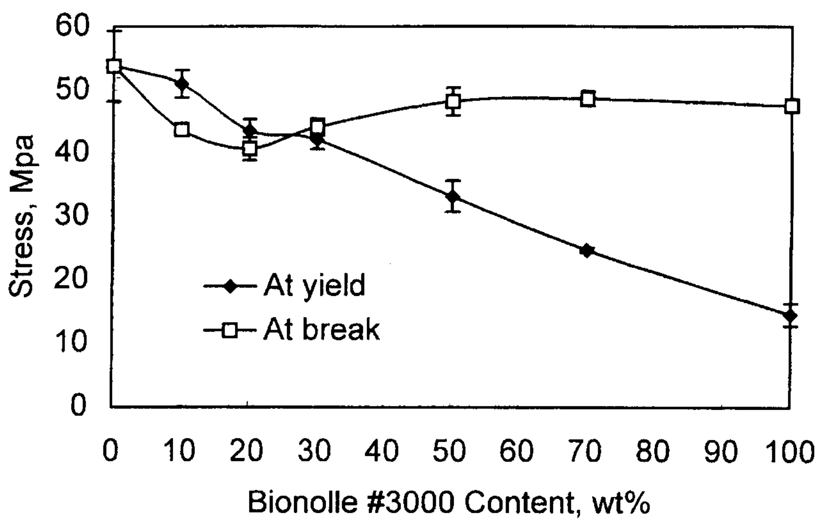


**Figure 2. Stress at yield and at break of PLA/Bionolle #3000 blends as a funtion of Bionolle #3000 content**

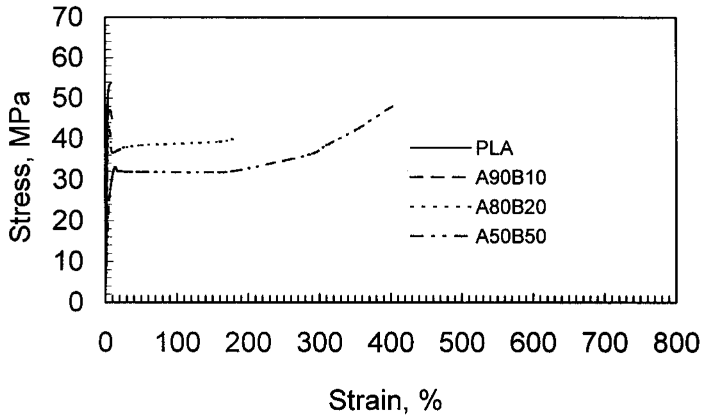


**Figure 3. Stress-strain curves of PLA and blends**

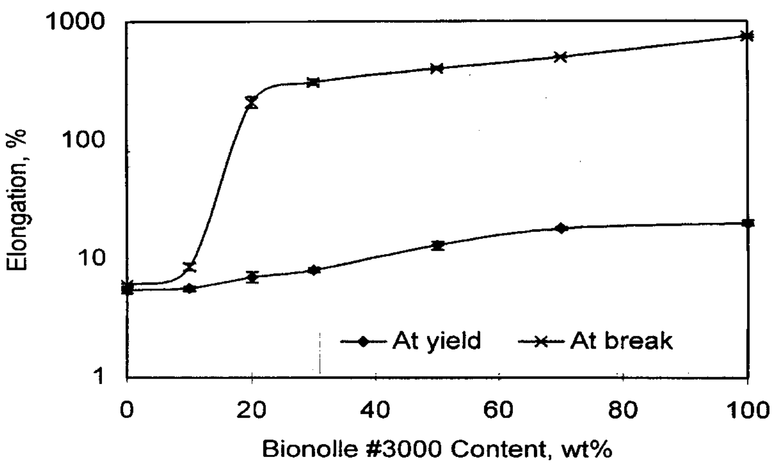


**Figure 4. Elongation at yield and at break of PLA/Bionolle #3000 blends as a function of Bionolle content**

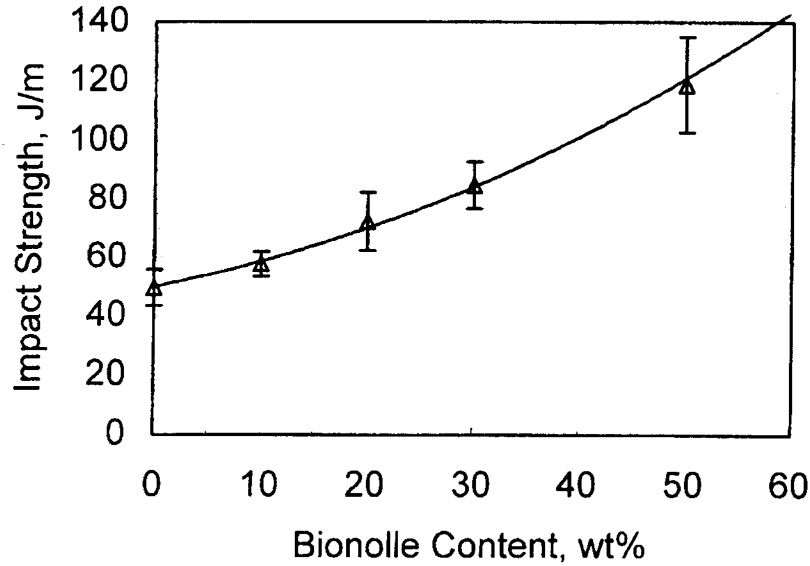


**Figure 5. Impact strength versus Bionolle #3000 content for PLA and PLA/Bionolle #3000 blends**

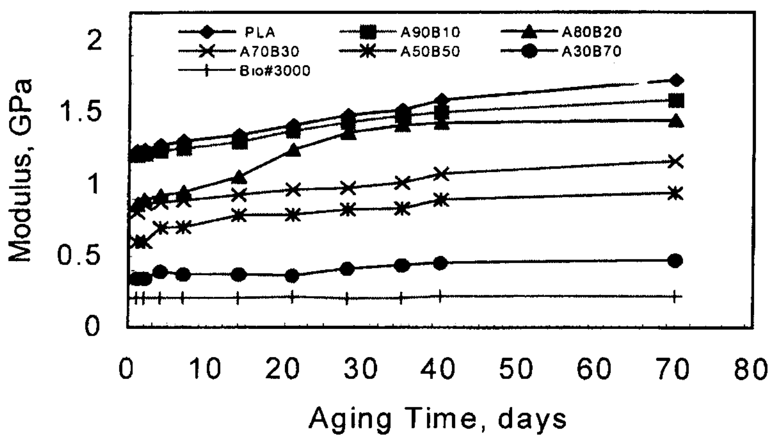


**Figure 6. Change of Modulus Values with Aging Time**

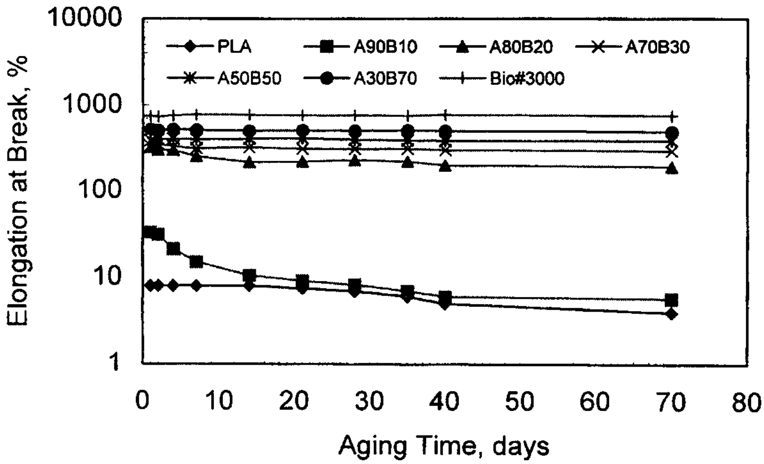


**Figure 7. Change of elongation at break with aging time**

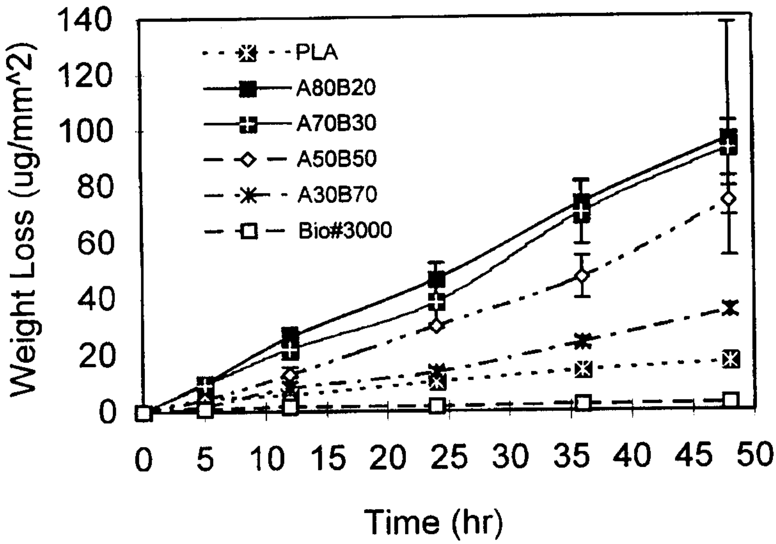


**Figure 8. Enzymatic degradation testing results of PLA/Bio#3000 blends**

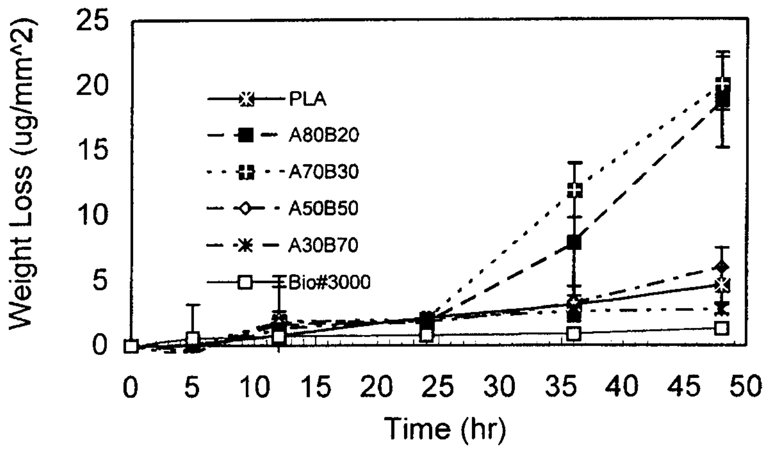


**Figure 9. Control Degradation Testing (without enzyme) Results**

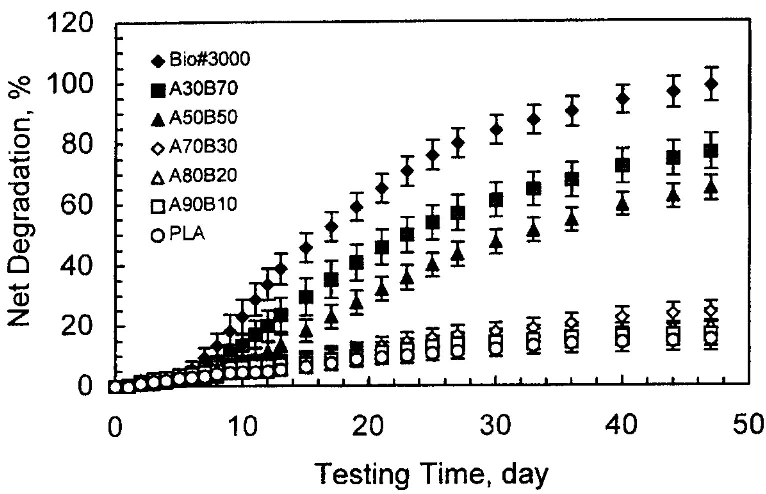


**Figure 10. Degradation percentage of PLA, Bionolle #3000 and their blends versus test time in soil testing conditions**

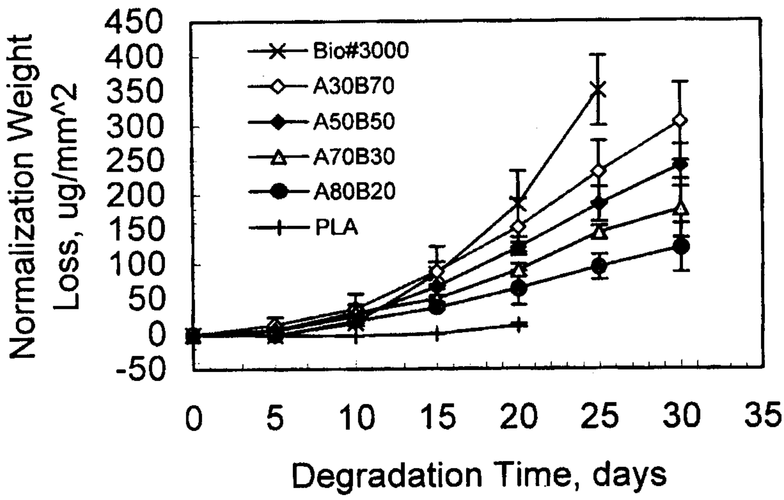


**Figure 11. Normalization weight loss of PLA/Bio#3000 Blends in composting conditions**

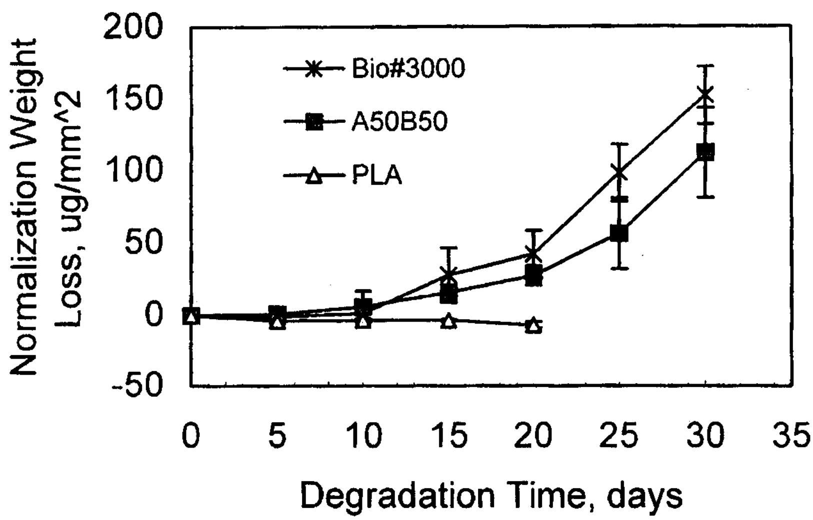


**Figure 12. Normalization weight loss of PLA/Bio#3000 blends in poison composting conditions**

realized by using 30 to 50 wt % Bio#3000 in PLA. The samples of neat Bio#3000 and the blend A30/B70 did not break on impact at room temperature.

***Dynamic Mechanical Properties***

The glass transition temperature of PLA and Bio#3000 are respectively about 60°C and -40°C. Below 60°C, the storage modulus of PLA is very high (about 3.5 GPa) and does not significantly change with decreasing. For Bio#3000, the storage modulus is relatively high below -40°C, then decreases markedly from -40°C to -15°C and keep a relatively low value above - 15°C, hence it is flexible at room temperature.

The PLA/Bio#3000 blends have two glass transition points that correspond to that of the two components and these do not change with varying composition. As Bio#3000 content increases, the storage modulus of the blends decreases significantly above -15°C.

***Biodegradability***

PLA is enzymatically degraded by Proteinase K, as shown in Figures 8 and 9. In this study, the PLA sample was found to exhibit a weight loss of about 20 μg/MM2 after 48 days at 37°C. Bio#3000 did not degrade in the Proteinase K solution. However, all of the blends of PLA and Bio#3000 exhibited higher weight loss rate than predicted from the parent polymers and these rates increased with increasing PLA content; even though in the control testing condition, buffer solution without enzyme, the blends with 20 and 30 wt % Bio#3000 have relative high weight loss. This might be due to the phase morphology of the blends so that enzyme accessed the PLA domain and more weigh loss was obtained.

The biodegradation testing in soil, Figure 10, showed the biodegradation rate of Bio#3000 was extremely fast, while the rate of PLA was relatively slow. After degrading for 45 days, Bio#3000 degraded almost 100 %, while PLA only degraded about 14 %. For the blends with 70 and 50 wt % Bio#3000, the degradation rate is relatively fast. After 45 days, the A30/B70 blend degraded about 77%; the A50/B50 blend degraded about 65 %. These values are equal to those expected on the basis of additivity rule. However, for blends with less than 30 wt % Bio#3000, the degradation percentage values are less than those expected on the basis of additivity rule.

The composting degradation testing results at 55°C are shown in Figures 11 and 12. Bio#3000 had a very high weight loss rate, while PLA showed a slight weight loss after being tested for 20 days. For PLA/Bio#3000 blends, the weight loss rates are between the rates of two parent polymers and increases with increasing Bio#3000 content. Even though in poison composting condition (without bacteria), Bio#3000 and PLA/Bio#3000 50/50 blend still have relatively high degradation rates.