BIODEGRADATION AND LIFE TIME OF SOY OIL BLENDED PLA AND RAMIE/PLA COMPOSITES

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1. Introduction

Polylactic acid (PLA) is a biodegradable thermoplastic that can be produced from corn starch. It has not only high modulus and strength as well as biocompatibility, but also a brittle nature and a low toughness. The brittleness of PLA limits its general applications in extensive areas because it cannot provide high ductile performance in many cases. Many researchers have tried to improve its brittleness by blending the plasticizers such as citrate ester, oligomeric lactic acid, glycerol, polyethylene glycol, epoxidized soybean oil and etc. [1-5]

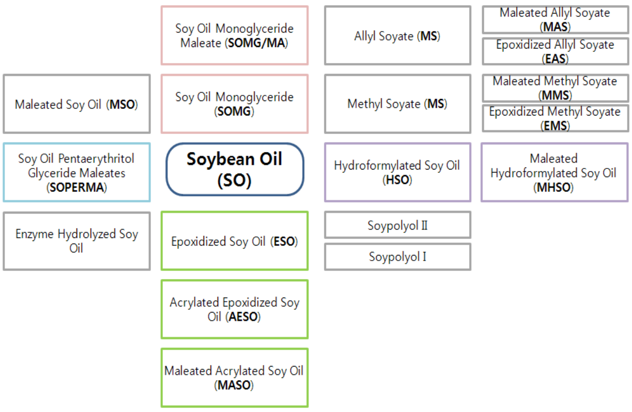
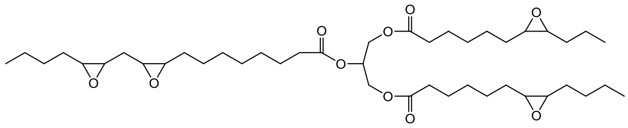
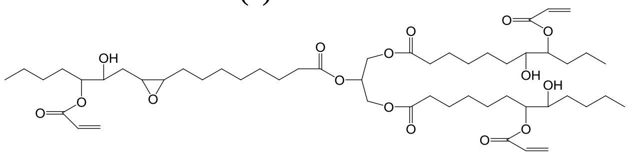


Fig.1. Schematic diagram of various chemical modification ways of the soybean oil(SO).

Soybean oil, extracted from the soy bean residue, can be chemically modified various ways as shown in Figure 1. Among them, epoxidized soybean oil (ESO, Figure 2(a)) is a well known plasticizer for PVC. ESO is modified by the reaction of acrylic acid to form acrylated epoxidized soybean oil (AESO, Figure 2(b)).[6,7] These modified soybean oils give significant improvement of toughness to PLA through grafting or blending.



(a) ESO



(b) AESO

Fig.2. Molecular structure of modified soybean oil, (a)epoxidized soybean oil, (b)acrylated epoxidized soybean oil.

The biodegradation of PLA in a composting environment is consisted of two steps. In first step, the high molecular weight PLA chains are readily hydrolyzed to the low molecular weight oligomer. This step is affected by temperature and moisture. The second step is the conversion of the oligomeric compounds into CO_2, water and humus by means of microorganisms.[8]

The aim of this study is to examine the morphology, biodegradability, mechanical and thermal properties and life-time of plasticized PLA with modified soybean oil (ESO and AESO) and their ramie fiber reinforced composites.

2. Experimental

2.1 Materials

PLA was supplied by HUVIS Co. Ltd. (Korea) having a molecular weight (Mw) of 100,000. ESO was obtained from SHIN WOUN Chemical Co., Ltd. (Korea). AESO was supplied from Sigma-Aldrich

Co. Ramie fiber was supplied from the producers union of Hansan Mosi Co. (Hansan, Korea).

2.2 Ramie fiber treatment

The ramie fiber was chopped to have fiber length of 10mm. The chopped ramie fibers were immersed in 5wt% aqueous sodium hydroxide solution for 1hr at 90^{o}C, and then washed with distilled water. The degummed ramie fibers were beaten using the electrical beater for 5min. Then ramie fibers were washed with distilled water/ethanol and finally air dried.

2.3 Blends and composites preparation

PLA was dried for 12hrs at 65 ^{o}C before processing. Content of ESO and AESO in PLA were controlled at 0, 5, 10 and 15wt%. The blends and composites were compounded using a Brabender mixer (Mixer W 50 EHT), and they are compression-molded using a hot press at 190^{o}C for further characterizations.

2.4 Characterizations

Thermogravimetric analysis(TGA) was carried out using a TA Q500 thermal analyzer in the temperature range of 0-500^{o}C at a heating rate of 10^{o}C/min. Dynamic mechanical tests were performed by using a TA Q800 dynamic mechanical analyzer(DMA) with a heating rate of 5^{o}C/min. Samples were subjected to a single cantilever with the amplitude of 20 at a frequency of 1Hz.

Mechanical properties were measured by using an Instron testing system (model 4467) according to the standard method for tensile and flexural properties of composites (ASTM D3039 and D695). Their fracture surfaces were observed by the SEM.

Biodegradability of plasticized PLA and ramie fiber reinforced composites was investigated with a homemade compost instrument at 58±2^{o}C as shown in Figure 3. The used compost was prepared from garden and food waste. The size of composting specimens have same dimension of flexural test samples. Changes of weight and flexural strength of samples were measured for 50days.

3. Results and Discussion

3.1 Thermal properties of blends

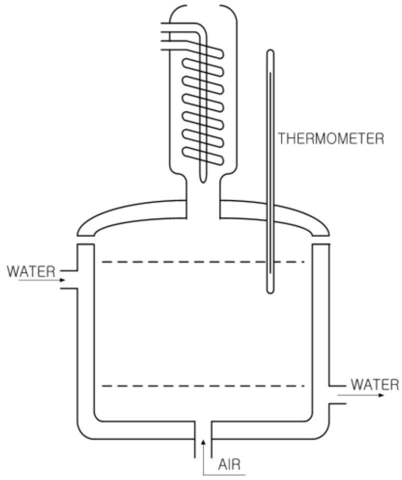


Fig.3 Schematics of a test chamber for the compost test

Figure 4 shows TGA results of PLA/ESO and PLA/AESO blends. Thermal stability of PLA was almost not changed by plasticizing with ESO and AESO. Results of DMA(Figure 5 and 6) show that a single glass transition (T_g) appeared at the plasticized PLA in lower temperature region than at the neat PLA. In this study, T_g gradually decreased with increasing ESO (Figure 5) and AESO (Figure 6) content. From the results, the T_g decreased from 70.1^{o}C of neat PLA to 64.6 and 65.2^{o}C for PLA/ESO(85:15) and PLA/AESO(85:15), respectively.

3.2 Mechanical properties of blends

Neat PLA showed a brittle fracture behavior and thus, no yield point was observed, whereas the blended PLA exhibited a ductile behavior with yielding and a subsequent plastic deformation. In this study, ESO and AESO blended PLA showed a stress-whitening phenomenon during tensile deformation. The elongation at break of the blended PLA increased to 120% with 15% addition of the ESO and to 80% with 15% addition of the AESO, respectively. From the viewpoint of elongation, addition of ESO and AESO gives more flexible nature to the PLA matrix. Therefore, plasticized PLA showed an increase of the toughness although sacrificing strength and yield stress to some extent.

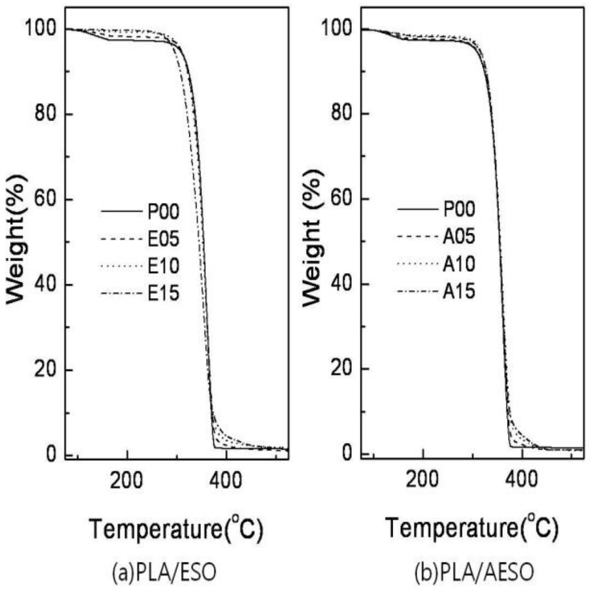


Fig.4. TGA analysis of blended PLA with various content of (a)ESO and (b)AESO.

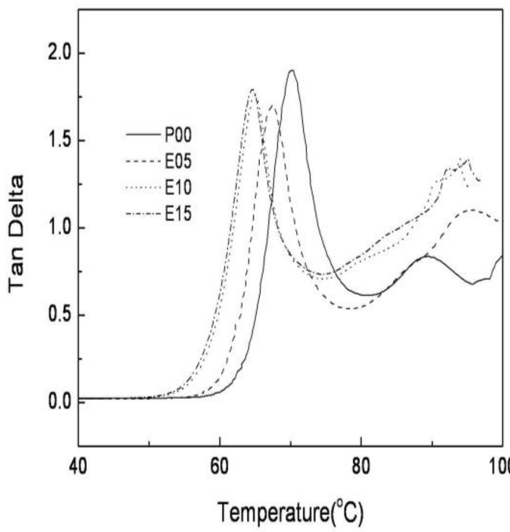


Fig.5. DMA overlaid tan delta of neat PLA and blended PLA with various content of ESO.

3.3 Biodegradability of blends and ramie fiber reinforced composites

Figure 7 showed weight loss of PLA blends in the compost environments. In this study, the order of biodegradation rate is shown as following: PLA > PLA/AESO > PLA/ESO/AESO > PLA/ESO.

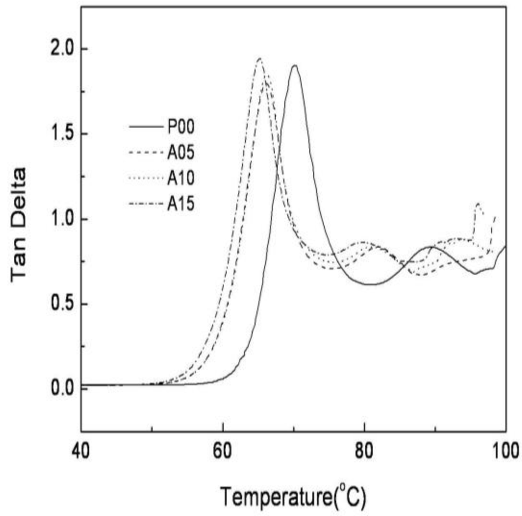


Fig.6. DMA overlaid tan delta of neat PLA and blended PLA with various content of AESO

About 4% of weight loss was recorded for 50days in a neat PLA. For plasticized PLA with ESO, biodegradation is about 1.5%. Ramie/PLA composite showed about 5% of weight loss in 50days (Figure 8). The weight loss of the Ramie/PLA/ESO and the Ramie/PLA/AESO composites were about 2.5 and 3.5%, respectively.

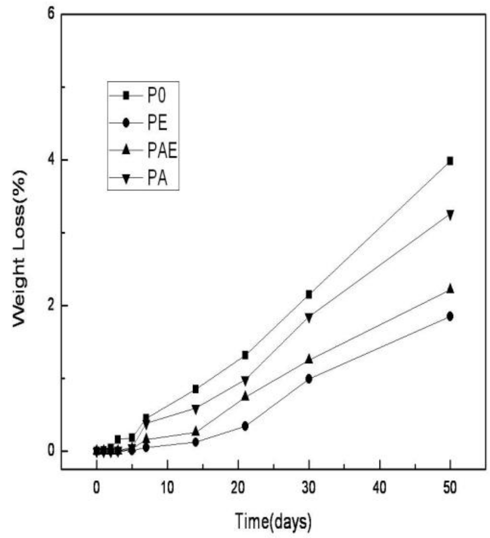


Fig.7. Weight loss of neat PLA and blended PLA (PE=PLA/ESO, PAE=PLA/AESO/ ESO, PA=PLA/AESO) in the compost.

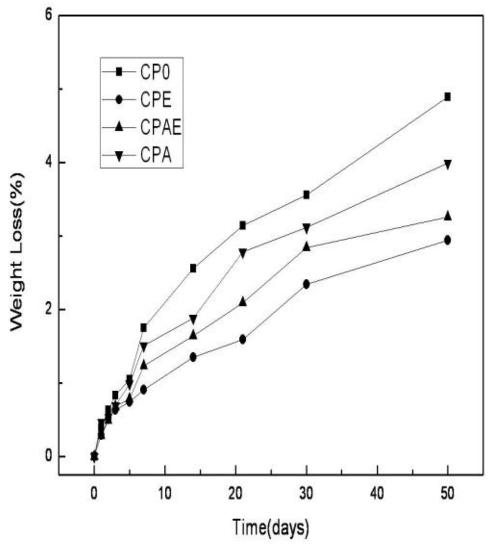


Fig.6. Comparison of weight loss of ramie fiber reinforced composites with various matrix resin (neat PLA and blended PLA) in the compost.

3.4 Life-time of blends and ramie fiber reinforced composites

Generally, flexural strength of neat PLA, plasticized PLA and their ramie fiber composites showed a decreasing tendency in compost. A logistic equation was used to assess the strength of plasticized PLA, and Kamal equation was used to evaluate the ramie fiber composites, respectively. From the normalized flexural strength curves of the PLA blends, the life-time of PLA/ESO and PLA/AESO blend increased of 1.6 times and 1.1 times, respectively, compared to neat PLA. It is clear that the addition of ESO and AESO to PLA retards the rate of biodegradation, also increases life-time of PLA. But the addition of ramie fiber for composite promotes the rate of biodegradation, also decreases its life-time.

4. Conclusions

Plasticized PLA and ramie fiber composites with ESO and AESO were prepared and their biodegradability was examined. Addition of ESO and AESO was effective for improving the thermal and toughness properties of the PLA. The biodegradation rate and life time were significantly affected by the inclusion of the modified soybean oils and ramie fibers.

Acknowledgement

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References

[1] L. V. Labrecque, R. A. Kumar, V. Dave, R. A. Gross and S. P. Mccarthy "Critrate esters as plasticizers for poly(lactic acid)". *Journal of Applied Polymer Science*, Vol. 66, pp 1507-1513, 1997.

[2] O. Martin and L. Averous "Poly(lactic acid): plasticization and properties of biodegradable multiphase systems". *Polymer*, Vol. 42, No. 14, pp 6209-6219, 2001.

[3] S. Jacobsen and H. G. Fritz "Plasticizing polylactide – the effect of different plasticizers on the mechanical properties", *Polymer Engineering & Science*, Vol. 39, No. 7, pp 1303-1310, 1999.

[4] N. Ljungberg and B. Wesslen "The effects of plasticizers on the dynamic mechanical and thermal properties of poly(lactic acid)", *Journal of Applied Polymer Science*, Vol 86, No. 5, pp 1227-1234, 2002.

[5] Y-Q. Xu and J-P Qu "Mechanical and rheological properties of epoxidized soybean oil plasticized poly(lactic acid)", *Journal of Applied Polymer Science*, Vol. 112, pp 3185-3191, 2009.

[6] J. L. Scala and R. P. Wool "Property analysis of triglyceride-based thermosets", *Polymer*, Vol. 46, No. 1, pp 61-69, 2005.

[7] C. K. Hong and R. P. Wool "Development of a bio-based composite material from soybean oil and keratin fibers", *Journal of Applied Polymer Science*, Vol. 95, No. 6, pp 1524-1538, 2005.

[8] S. S. Ray and M. Okamoto "Biodegradable polylactide and its nanocomposites: Opening a new dimesion for plastics and composites", *Macromolecular Rapid Communications*, Vol. 24, No. 14, pp 815-840, 2003.