Plasticized Poly(lactic acid) with Low Molecular Weight Poly(ethylene glycol): Mechanical, Thermal, and Morphology Properties

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ABSTRACT: Poly(lactic acid) PLA was plasticized with low molecular weight poly(ethylene glycol) PEG-200 to improve the ductility of PLA, while maintaining the plasticizer content at maximum 10 wt%. Low molecular weight of PEG enables increased miscibility with PLA and more efficient reduction of glass transition temperature (T_g). This effect is enhanced not only by the low molecular weight but also by its higher content. The tensile properties demonstrated that the addition of PEG-200 to PLA led to an increase of elongation at break (>7000%), but a decrease of both tensile strength and tensile modulus. The plasticization of the PLA with PEG-200 effectively lowers T_g as well as cold-crystallization temperature, increasing with plasticizer content. SEM micrographs reveal plastic deformation and few long threads of a deformed material are discernible on the fracture surface. The use of low molecular weight PEG-200 reduces the intermolecular force and increases the mobility of the polymeric chains, thereby improving the flexibility and plastic deformation of PLA. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4576–4580, 2013

INTRODUCTION

In recent years, bio-based products have been of great interest as sustainable development policies have tended to expand with decreasing reserves of fossil fuels and growing concern for the environment. Consequently, biodegradable and renewable polymers have been the topic of significant research. These polymers can mainly be classified as agro-polymers (starch, chitosan) and biopolyesters (polyhydroxyalkanoates, poly(lactic acid)). Unfortunately, for certain applications, these bio-based polymers cannot be fully competitive with conventional thermoplastics as some of their properties are too weak. Therefore, to extend the range of their applications, current bio-based polymers have to be reformulated. Some of the most promising are nano-biocomposites, where nano-sized fillers are dispersed into a bio-polymer matrix, which could yield a range of improved properties (stiffness, permeability).
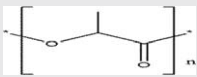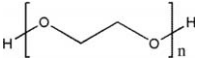
Poly(lactic acid) (PLA) is one of the most frequently used bio-degradable polymer, especially in packaging applications because of its high strength, high modulus, good transparency, process-ability, and biocompatibility. However, PLA also has the draw-backs of inherent brittleness and poor toughness, which impede its wide application. Many efforts have been carried out to improve the properties of PLA so as to compete with low cost and flexible commodity polymers. These attempts include blending PLA with other polymers, modifying PLA with plasti-cizers, or blending with inorganic nano-fillers.

Attempts have been made to improve flexibility by blending PLA with other polymers such as poly(ε-caprolactone), poly(bu-tylene succinate),[1] poly(ether urethane), and poly(butylene adi-pate-co-terephthalate).[2] Plasticizers such as epoxidized palm oils,[3] poly(propylene glycol),[4] citrate esters,[5] oligomeric malo-nate esteramides,[6] polyglycerol esters,[7] poly(1,3-butylene adi-pate)[8] glucosemonoesters,[9] and oligomeric lactic acid[10] were used to improve the flexibility and impact resistance of PLA. The resulting plasticized PLA materials gained in deformation and resilience.

Polyethylene glycols (PEG), also known as macrogols, are liquid or solid polymers of the general formula $H(OCH_2CH_2)_n OH$. Low molecular weight of PEG is in the liquid form, whereas the higher molecular weight of PEGs are in the solid form at room temperature. PEGs are suitable plasticizer for PLA because of their miscibility, biodegradability, and food contactable applica-tion. There is no literature examining the plasticizing effect of low molecular weight PEG on PLA. Most of the researchers use high molecular weight PEG as plasticizer.[11–16] High molecular weight of PEG will slow down the diffusion of PEG plasticizer

Table I. Properties of PLA and Plasticizer Used in This Study

Materials	Mn (g/mol)	T_m (°C)[a]	T_g (°C)[a]	Chemical formula
Poly(lactic acid), PLA, 4042D	66,000	149.79	62.85	
Poly(ethylene glycol), PEG	200	−65	−41	

[a] Determined by Differential Scanning Calorimetry (DSC).

from interlamellar amorphous phase to polymer melt.[4] In this study, low molecular weight of PEG-200 is used as plasticizer on PLA. The effect of PEG-200 plasticizer on the tensile properties, thermal and morphology of PLA at various PEG-200 contents is investigated.

EXPERIMENTAL

Materials
Poly(lactic acid) resin, commercial grade 4042D, was supplied by NatureWorks® LCC, MN, USA. Low molecular weight Poly (ethylene glycol) (Mn = 200 g/mol) purchased from Sigma-Aldrich. The materials used and their properties are listed in Table I.

Preparation of PLA/PEG-200 Blend
The PLA/PEG-200 blends were prepared by melt blending technique using Brabender internal mixer with 25 rpm of the rotor speed, at 160°C for 10 min. The weight of PEG-200 studied was varying from 0 to 10 wt%. The blends obtained were then molded into sheets of 1 mm in thickness by hot pressing at 160°C for 10 min with pressure of 110 kg/cm², followed by cooling to room temperature. The sheets were used for further characterization.

Characterizations
Tensile Properties Measurement. Tensile properties test was carried out by using Instron 4302 series IX. The samples were cut into dumbbell shape follow ASTM D638 (type V) standard. Load of 1.0 kN was applied at constant crosshead speed of 10 mm/min at room temperature. Tensile strength, tensile modulus, and elongation at break were evaluated from the stress-strain data. Each sample included seven tested replicates to obtain a reliable mean and standard deviation.

Thermal Properties. Differential scanning calorimetry (DSC) analysis was performed to study the nonisothermal crystallization kinetics. The DCS procedure was consisting of three steps.

At the first step, the films were heated from 30°C to 180°C with a heating rate of 10°C/min, then they were held at this temperature for 5 min to eliminate the thermal history, and they were cooled to 30°C at cooling rate of 10°C/min and held at 30°C for 5 min. In the last step, they were reheated to 180°C at a heating rate of 10°C.

The degree of crystallinity of all samples were calculated by

$$\text{Crystallinity } (\%) = \frac{\Delta H_m - \Delta H_{cc} \; / \; \Phi_{\text{PLA}}}{\Delta H_m^o} \times 100$$

where ΔH_m is the measured heat of fusion, ΔH_{cc} is the heat of cold crystallization, Φ_{PLA} is the PLA content in the blend and ΔH_m^o is melting enthalpy of the 100% PLA (93.6 J/g).

Thermaogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris 7 TGA analyzer with scan range from 35° to 800° at a constant heating rate of 10°C/min and continuous nitrogen flow. The thermal degradation temperature taking into account were the temperature at onset (T_{onset}) and the temperature of maximum weight loss (T_{max}).

Morphology. The samples were submerged in liquid nitrogen and broken down. The fracture surfaces were studied under a JEOL scanning electron microscopy (SEM) instrument JSM-6400 (Japan) at an accelerating voltage of 30 kV. The fractured surfaces were coated with a thin layer of gold prior to observation.

RESULTS AND DISCUSSION

Mechanical Properties
Results of tensile experiments are shown in Table II. The neat PLA was typically rigid and brittle. It had high tensile modulus as well as tensile strength, but with very limited elongation at break. After the addition of PEG-200, the tensile strength and modulus of the blend decreased, whereas the elongation at break significantly increased. The neat PLA shows tensile

Table II. Summary of Tensile Properties of PLA and Plasticized PLAs

	Tensile strength (MPa)	Elongation (%)	Tensile modulus (MPa)
PLA	57.98 ± 2.86	5.37 ± 0.06	1209 ± 61
PLA/1 wt% PEG	54.53 ± 1.34	5.53 ± 2.44	1135 ± 32
PLA/3 wt% PEG	49.13 ± 1.37	6.93 ± 1.63	1077 ± 26
PLA/5 wt% PEG	42.90 ± 2.69	8.17 ± 0.72	1016 ± 58
PLA/7 wt% PEG	31.13 ± 2.90	70.30 ± 15.60	827 ± 122
PLA/10 wt% PEG	20.76 ± 1.62	413.1 ± 14.30	424 ± 17

Table III. Characteristic Temperature and Percentage of Crystallinity of PLA and Plasticized PLAs
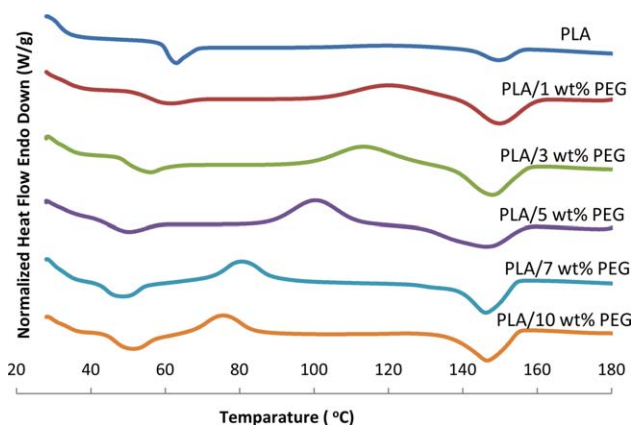
	T_g (°C)	T_{cc} (°C)	T_m (°C)	X_c (%)
PLA	62.85	124.11	149.79	13.87
PLA/1 wt% PEG	61.35	119.60	149.72	59.32
PLA/3 wt% PEG	55.88	112.94	147.78	58.15
PLA/5 wt% PEG	50.29	98.97	146.46	57.18
PLA/7 wt% PEG	48.54	79.14	146.18	50.76
PLA/10 wt% PEG	51.63	74.30	146.48	49.43

Table IV. Thermal Degradation Temperatures of PLA and Plasticized PLAs

	T_{onset} (°C)	T_{max} (°C)	T_{50} (°C)
PLA	274.26	345.12	339.16
PLA/1 wt% PEG	253.41	341.86	340.16
PLA/3 wt% PEG	245.47	337.92	327.93
PLA/5 wt% PEG	221.76	326.79	309.80
PLA/7 wt% PEG	202.34	296.39	290.47
PLA/10 wt% PEG	194.50	291.00	285.66

strength of 53 MPa and exhibited very low ability to the plastic deformation. With 7 wt% of PEG plasticizer caused the decrease of the tensile strength to 31.13 MPa, whereas the elongation at break was increased to 70.3%. The increase of PEG plasticizer content to 10 wt% further decreased the tensile strength to 20.76 MPa, and dramatically increased the elongation at break to 413.1%. Increase of elasticity means that brittleness of samples decreased since the elongation at break and brittleness are inversely proportional. Brittleness of the samples can be observed from the tensile modulus results. Tensile modulus of PLA/PEG-200 gradually decreased from 1209 to 424 MPa when 10 wt % of PEG-200 was used. In a meantime, a gradually decrease in tensile strength of PLA/PEG-200 from 57.98 to 20.76 MPa was also observed as the content of PEG increased from 0 to 10 wt%.

Thermal Properties

Thermal properties of pristine PLA and PLA/PEG blend were investigated by means of DSC and TGA. DSC measures the amount of heat energy absorbed or released when the material is heated or cooled. For polymeric materials, which undergo important property changes near thermal transition, DSC is a very useful technique to study the glass transition temperature, crystallization temperature, and melting behavior.

Table III summarizes the glass transition temperature (T_g) of pristine PLA and plasticized PLAs as well as crystallization and

melting temperatures (T_c and T_m). The first heating scan of pristine PLA showed an endothermic peak (melting, $T_m = 149.79°C$). A minor decrease in the melting temperature of 3–4°C was observed, indicating that the melting temperature of PLA was not greatly affected by the addition of PEG plasticizer.

The pristine PLA showed a sharp T_g and its value decreased gradually with increasing PEG content as shown in Figure 1. At 1 wt% PEG the T_g decreased from 62.85°C for pristine PLA to 61.35°C and down to 51.63°C when 10 wt% of PEG plasticizer was added. The plasticization of the PLA with low molecular weight poly(ethylelne glycol) effectively lowers T_g. The DSC thermograms show clearly a decrease of T_g because of enhanced segmental mobility of PLA chains caused by the presence of PEG plasticizer. No trace of separate melting or crystallization of PEG was found confirming that the phase separation of PEG did not occur.
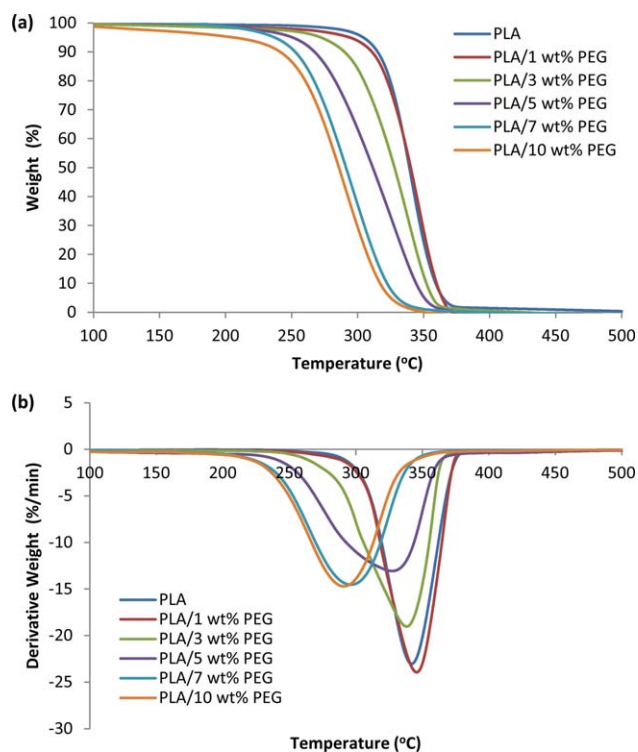
Figure 2. Effect of PEG on thermal stability of PLA/PEG (a) TGA and (b) DTG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
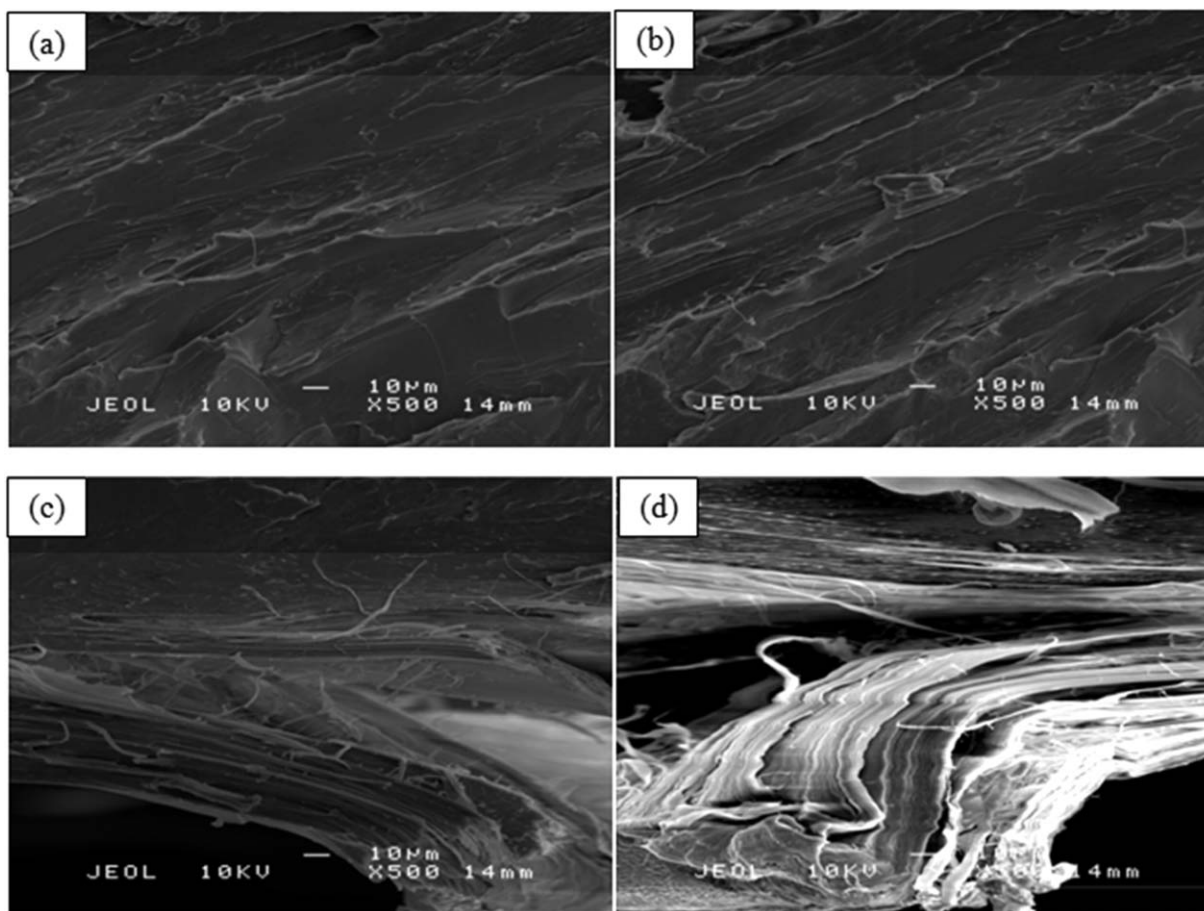

Figure 1. DSC thermograms of PLA/PEG at various PEG contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. SEM images of PLA/10 wt% PEG at different locations.

Cold-crystallization was chosen as a crystallization method because it leads to more intense spherulite nucleation resulting in shorter crystallization time and smaller spherulite sizes.[17] Pristine PLA showed cold-crystallization temperature at about 124.11°C. The cold-crystallization temperature of PLA decreased as the PEG content increased in parallel with the shift in T_g as shown in Figure 2. The cold-crystallization decreased to 74.30°C for the blend containing 10 wt% PEG plasticizer. The significant depression of T_{cc} and the decrease in T_g indicated that the PEG was compatible with PLA. It clearly appeared that the decreasing of T_{cc} and T_g of PLA because of enhanced chain mobility as the plasticizer content increased.[18] Enhanced chain mobility increased the rate of crystallization, which allowed PLA to crystallize at lower temperature. Furthermore, the crystallization peak was narrowed as the content plasticizer increases because of increased ability of PLA to crystallize.[19]

When a polymer molecule crystallizes, this high degree of organization becomes a major factor in overall structure. Low crystallinity of PLA (13.87%) in this study was destroyed by the addition of PEG-200 plasticizer. However, high crystallinity polymer prevents compatibility with plasticizers, because they are unable to separate the polymer molecules sufficiently to move in between them. Generally, the elongation at break of PLA/PEG blend increase as crystallinity decrease because of the increasing mobility of the system. Crystallinity, if well devel-oped, increases the elongation at break and further decreases the drawability of PLA.[20]

The impact of the plasticizer on the thermal stability often takes into account when studying a plasticized polymer. One of most accepted methods to study the thermal properties of polymeric materials is thermogravimetry. The integral (TGA) and derivative (DTG) thermogravimetric curves provide information about the nature and extent of degradation of the polymeric materials. The TGA and DTG thermograms of PLA/PEG blends are given in Figure 2. A detailed evaluation of the thermograms is presented in Table IV.

The decomposition onset temperature (T_{onset}) and maximum decomposition temperature (T_{max}) as well as the decomposition temperature at 50% weight loss (T_{50}) of PLA shift systematically to lower temperatures when PEG plasticizer is added. This shift is globally more important when the amount of PEG is higher. For example, a shift from 274°C to 194°C and from 345°C to 291°C is observed for the decomposition onset temperature and the maximum decomposition temperature of the sample PLA/10 wt% PEG, respectively. The decrease of the PLA thermal stability is mainly because of the presence of PEG as plasticizer. PEG promotes a decrease in thermal stability by its action to intersperse itself around polymers and by breaking polymer–polymer interactions, which are predicted in the lubricity theory and gel theory of plasticization.[21]

Morphology

Micrographs of PLA/10 wt% PEG at different location are shown in Figure 3. Figure 3(a,b) reveal little plastic deformation and few long threads of a deformed material are discernible on the fracture surface of the sample. A large amount of plastically deformed part is clearly visible in Figure 3(c,d). This shows that the plasticized PLA with low molecular weight PEG gained the ability to plastic deformation leading to about 7600% increment in elongation at break in the case of 10 wt% plasticizer content.

CONCLUSIONS

The use of low molecular weight PEG-200 reduces the intermolecular force and increases the mobility of the polymeric chains, thereby improving the flexibility and plastic deformation of PLA. Mechanical characteristic of PLA/PEG showed a decrease in tensile strength and tensile modulus, but an increase in percentage elongation at break. This means the transition of PLA from brittle to ductile behavior occurs. The temperature of cold-crystallization was decreased and the crystallization peak was narrowed. PEG promotes a decrease in thermal stability by its action to intersperse itself around polymers and by breaking polymer–polymer interactions.

ACKNOWLEDGMENTS

REFERENCES

1. Bhatia, A.; Gupta, R. K.; Bhattacharya, S. N.; Choi, H. J. *J. Appl. Polym. Sci.* **2009**, *114*, 2837.

2. Signori, F.; Coltelli, M. -B.; Bronco, S. *Polym. Degrad. Stab.* **2009**, *94*, 74.

3. Silverajah, V. S. G.; Ibrahim, N. A.; Yunus, W. M. Z. W.; Hassan, H. A.; Chieng, B. W. *Int. J. Mol. Sci.* **2012**, *13*, 5878.

4. Piorkowska, E.; Kulinski, Z.; Galeski, A.; Masirek, R. *Polymer* **2006**, *47*, 7178.

5. Labrecque, L. V.; Kumar, R. A.; Davé, V.; Gross, R. A.; McCarthy, S. P. *J. Appl. Polym. Sci.* **1997**, *66*, 1507.

6. Ljungberg, N.; Colombini, D.; Wesslén, B. *J. Appl. Polym. Sci.* **2005**, *96*, 992.

7. Uyama, H.; Ueda, H.; Doi, M.; Takase, Y.; Okubo, T. *Polym. Prepr. Jpn.* **2006**, *55*, 5595.

8. Wang, N.; Zhang, X.; Yu, J.; Fang, J. *Polym. Polym. Compos.* **2008**, *16*, 597.

9. Jacobsen, S.; Fritz, H. G. *Polym. Eng. Sci.* **1999**, *39*, 1303.

10. Martin, O.; Avérous, L. *Polymer* **2001**, *42*, 6209.

11. Gumus, S.; Ozkoc, G.; Aytac, A. *J. Appl. Polym. Sci.* **2011**, *123*, 2837.

12. Pluta, M.; Paul, M.-A.; Alexandre, M.; Dubois, P. *J. Polym. Sci. Part B: Polym. Phys.* **2006**, *44*, 299.

13. Sungsanit, K.; Kao, N.; Bhattacharya, S. N. *Polym. Eng. Sci.* **2012**, *52*, 108.

14. Hu, Y.; Hu, Y. S.; Topolkaraev, V.; Hiltner, A.; Baer, E. *Polymer* **2003**, *44*, 5681.

15. Gui, Z.; Xu, Y.; Gao, Y.; Lu, C.; Cheng, S. *Mater. Lett.* **2012**, *71*, 63.

16. Baiardo, M.; Frisoni, G.; Scandola, M.; Rimelen, M.; Lips, D.; Ruffieux, K.; Wintermantel, E. *J. Appl. Polym. Sci.* **2003**, *90*, 1731.

17. Pluta, M.; Galeski, A. *J. Appl. Polym. Sci.* **2002**, *86*, 1386.

18. Pillin, I.; Montrelay, N.; Grohens, Y. *Polymer* **2006**, *47*, 4676.

19. Kulinski, Z.; Piorkowska, E. *Polymer* **2005**, *46*, 10290.

20. Dhanvijay, P. U.; Shertukde, V. V. *Polym. Plast. Technol. Eng.* **2011**, *50*, 1289.

21. Daniels, P. H. *J. Vinyl Addit. Technol.* **2009**, *15*, 219.