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# Effect of Compatibilizer on PLA/PP Blend for Injection Molding

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# Abstract

Polymer blends of poly(lactic acid) and polypropylene were prepared for the application to injection molding products. Due to the phase separation of PLA and PP, the addition of polypropylene-graft-maleic anhydride (PP-g-MAH) as a compatibilizer was studied. The polymer blends were comprised of PLA:PP ratios 80:20 and 20:80 with addition of 1, 3 and 5 wt% of PP-g-MAH. The product samples were processed dry blend with injection molding process and the products were subjected to thermal, mechanical properties and morphology analysis. The thermal analysis confirmed that addition of PP-g-MAH has no effect on crystalline melting temperature of the polymer components as well as no effect on the mechanical properties. The morphology study of the polymer blends confirmed the adhesion of PLA and PP by assistance of PP-g-MAH. The addition of more amount of PP-g-MAH resulted in high polarity of a compatibilizer and decreased the compatibility with PLA. The tensile strength of polymer blends increased with increasing amounts of PLA. The research results confirmed the application of polymer blend system to injection molding process.

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#### 1. Introduction

Poly(lactic acid) (PLA) is one of the well-known bio-based materials. Lactic acid is produced from various sources such as starches, sugars, and other biomass materials through biological fermentation, and then is chemically converted to poly(lactic acid) [1,2]. PLA has high transparency and elastic modulus, can be thermoplastically processed like conventional plastics, and has been widely used in the development of disposable products, such as disposable cutlery, cups, and films [3–5]. However, since PLA is quite brittle (low strain at break and high modulus) at room temperature and easily hydrolysable, its applicability has been limited [6]. Thus, blending PLA with soft and tough polymers can enhance mechanical properties and biodegradability [7,8]. Polypropylene (PP) is a useful commodity polymer with outstanding properties such as low density, sterilizability, good surface hardness, very good abrasion resistance, excellent electrical properties, as well as good mechanical and barrier properties to water. It also has low cost, worldwide production, simplicity of processing, capability to burn without producing toxic emissions, working security, and recyclability. Its blends and composites find wide applications in home appliances, automotive parts, extruded profiles, packaging industry, construction, etc. [9,10]. Though the blended polymers exhibited certain improved mechanical properties compared to virgin non-blended parts, immiscible polymer blends may lead to less desirable properties that were anticipated from blending. Thus, compatibilizers are often used to improve the miscibility between the immiscible polymer blends [11]. Chengjun Zhou et al. reported that the thermoplastic matrix was modified by grafting, and the compatibility of the bamboo fiber (BF) matrix was improved with the use of the graft copolymer as a compatibilizer [12]. Similarly, Marsilla et al. [13] studied the compatibility of a Novatein thermoplastic from bloodmeal (NTP)/linear low-density polyethylene (LLDPE) composite modified by polyethylene-g-MAH as a compatibilizer. Wang et al. [14] introduced the polar groups on maleic anhydride (MAH) to the nonpolar molecules of LLDPE to first obtain an LLDPE-MAH copolymer, which was later blended with BF. Ya-nan Wang et al. studied the PLA/BF biocomposites by blending PLA (85 wt%) and BF (15 wt%) with different concentrations of PLA-g-GMA. The phase morphology, thermal stability and mechanical properties of the composites prepared with PLA-g-GMA were improved over those of PLA/BF composites without compatibilizer [15].

In this work poly(lactic acid)/polypropylene blends with different content were prepared with the objective of application for producing the injection molding products. The effect of addition of polypropylene-*graft*-maleic anhydride (PP-*g*-MAH) compatibilizer to the blend was studied. Thermal, mechanical properties and morphology of the blends were investigated.

# 2. Experimental

## 2.1. Materials

Poly(lactic acid) (grade: 3052D,  $M_n$  1.39 x 10<sup>5</sup> g/mol,  $M_w$  2.07 x 10<sup>5</sup> g/mol, polydispersity 1.48) was purchased from Natureworks LLC. Polypropylene (grade: HP500N) was produced by HMC Polymers Company Ltd. PP-g-MAH was produced from DuPont functionalized with maleic anhydride.

# 2.2. Preparation of injection molding

Prior to mixing, PLA and PP were dried at 80 °C under vacuum for 12 h. The blends of PLA and PP with ratios PLA:PP of 80:20 and 20:80. Varying amounts of PP-g-MAH compatibilizer (1, 3 and 5 wt%) were dried at 80°C in oven for 8 hours before mixing with polymers in the injection molding (Toyo Machinery & Metal Co., Ltd (TI-30F6)). The temperature setting was 200/180/180/180/170°C. The injection samples were subjected to mechanical property analysis.

# 2.3. Morphology

Samples for morphology analysis are from tensile test specimens. The morphology of polymer blends was examined by scanning electron microscopy (SEM) (JEOL, JSM-S410LV), operated at 15 kV. The samples were fixed on supports and coated with gold.

#### 2.4 Differential scanning calorimeter (DSC)

DSC scans were recorded on a differential scanning calorimeter Perkin Elmer, DSC 800 in inert atmosphere (nitrogen), with a heating rate of 10 °C/min. The samples (~10 mg) were placed into alumina crucibles. After the first heating from 20 °C to 250 °C at a rate of 10 °C/min, held at that temperature for 5 min, then cooled to 20 °C with cooling rate of 10 °C/min before second step where the samples were heated again and thermograms for second heating were recorded. Glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_c$ ), melting temperature ( $T_m$ ) were recorded.

# 2.4. Tensile Properties

Young's modulus, tensile strength, and elongation at break were determined according to ASTM method D638 under ambient conditions, using tensile testing machine LR10K Plus series (LLOYD Instrument). The testing conditions used were: cross head speed of 5 mm/min and load cell of 10 N. Dumbbell samples  $(25 \times 197 \times 3 \text{ mm})$  (thickness x width x length) were tested with a gauge length was adjusted for each sample and each sample's width and thickness were measured before testing. The reported values were the average of at least 10 measurements.

# 2.5 Izod Impact Test

Samples for izod impact test were prepared using injection molding process. The dimensions of a standard specimen for ASTM D256 are  $63.5 \times 12.7 \times 3.2$  mm. Izod test sample usually have a V-notch cut into them. Impact strength is calculated by dividing impact energy in J by the thickness of the specimen. The test result is typically the average of 10 specimens.

#### 3. Results and Discussion

## 3.1 Thermal properties

The thermal property of polymer blends of PLA/PP ratios 100:0, 80:20, 20:80 and 0:100 by weight using polypropylene-*graft*-maleic anhydride (PP-*g*-MAH) 0, 1, 3 and 5 wt% as a compatibilizer. The results are shown in Fig. 1(a-d).

Fig. 1(a) shows the thermogram of DSC analysis of neat PLA without and with addition of 1, 3 and 5 wt% of PP-*g*-MAH. The results confirm that PP-*g*-MAH has no effect to the melting temperature of PLA. However, the crystallization temperature of PLA was clearly seen and shift to lower temperature. From Fig. 1(b) the polymer blends of PLA/PP (80/20 by weight) show two peaks of melting temperature of PLA at 153 °C and PP at 164 °C. Addition of PP-*g*-MAH resulted in slightly shift of both peaks together implied that partial compatibility of both polymers. With 5 wt% of PP-*g*-MAH, the glass transition temperature of PLA was not observed. The thermogram of PP/PLA (80/20) in Fig. 1(c) shows opposite shape of peaks due to high contents of PP. With 5 wt% of PP-*g*-MAH, the shoulder peak of PLA is slightly shift to higher temperature shows better mixing of both polymers. Fig. 1(d) shows thermogram of neat PP with addition of PP-*g*-MAH. The unchanged  $T_m$  of PP without and with addition of PP-*g*-MAH confirmed no effect of a compatibilizer on PP similar to PLA.

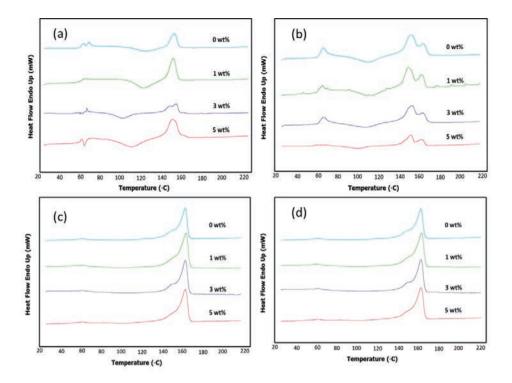


Fig. 1. DSC curve of (a) neat PLA with PP-*g*-MAH (b) PLA/PP (80/20) with PP-g-MAH (c) PLA/PP (20/80) with PP-*g*-MAH (d) neat PP with PP-g-MAH.

#### 3.2 FT-IR Analysis

The analysis of functions of PP, PLA and PP/PLA blends and a compatibilizer was carried out by FT-IR analysis. The results are shown in Fig. 2(a-d).

The transmittance bands of PP (Fig. 2(a)) at 2950-2838, 1455-1453, and 1376 cm<sup>-1</sup> were assigned to C-H stretching, -CH<sub>3</sub> bending, and C-H bending, respectively [16,17]. However, the characteristic spectrum of C=O stretching of PP-*g*-MAH was not clearly observed. The transmittance bands of PLA (Fig. 2(b)) at 1750, 1180, and 1080 cm<sup>-1</sup> referred to C=O stretching, symmetric C-O-C stretching, and asymmetric CH<sub>3</sub>, respectively [18]. However, the characteristic spectrum of ester linkage of PP-*g*-MAH and PLA was not clearly observed. For PLA/PP blends of ratios 80/20 and 20/80 the transmittance bands that represents PP and PLA were observed in the polymer blends. However, the characteristic spectrum of ester linkage of PP-*g*-MAH and PLA between 1800 cm<sup>-1</sup> and 1700 cm<sup>-1</sup> was not observed.

#### 3.3 Mechanical property

The tensile test of PLA/PP blends ratio 100:0, 80:20, 20:80 and 0:100 wt% with PP-g-MAH 0, 1, 3 and 5 wt% was carried out according to ASTM D 638. The results are shown in Fig. 3(a-c).

The tensile strength of PLA is much higher than PP. The polymer blends show conventional trends of decreasing of strength with PP content. PP-*g*-MAH has no effect on the tensile strength of the blends.

Young's Modulus of PLA/PP blends follows the mixing rule. PP-g-MAH has no effect on the Young's Modulus of the blends.

The PP-g-MAH shows small effect to the PLA, PP and PLA/PP blends due to weak bonding of a compatibilizer to PLA.

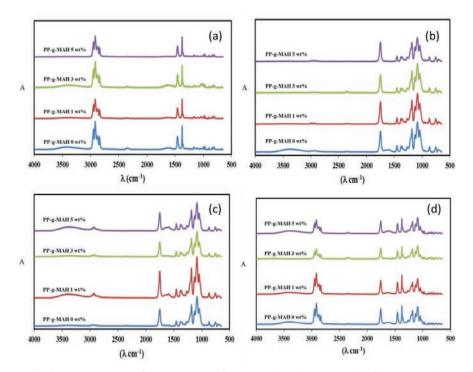


Fig. 2 FT-IR spectra of (a) neat PP with PP-g-MAH (b) neat PLA with PP-g-MAH (c) PLA/PP (80/20) with PP-g-MAH (d) PLA/PP (20/80) with PP-g-MAH

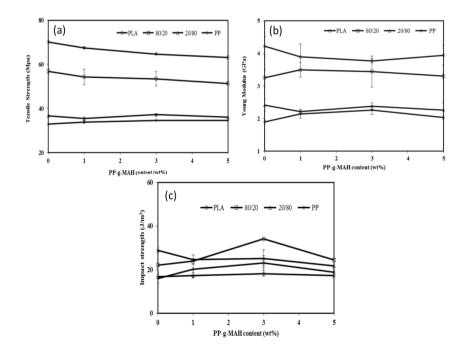


Fig. 3 (a) Tensile strength (b) Young's Modulus (c) Impact strength of PLA/PP blend with PP-g-MAH

# 3.4 Morphology

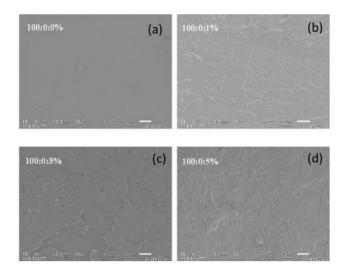


Fig. 4. SEM image of neat PLA with PP-g-MAH (1,000X).

Fig. 4. shows morphology of fracture surface of tensile specimen of neat PLA with PP-*g*-MAH 1, 3 and 5 wt%. In Fig. 4 (a) PLA shows brittle fracture while PLA/PP-MAH show ductile fracture ((b),(c),(d)). The fracture shows interaction of PP-*g*-MAH and PLA. However, the fracture surface of PP without and with addition of PP-*g*-MAH show ductile fracture due to high toughness of PP (Fig.5).

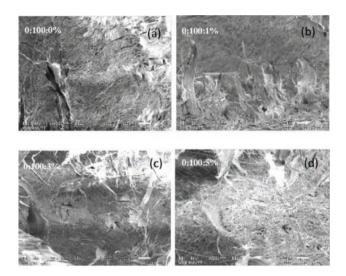


Fig. 5. SEM image of neat PP with PP-g-MAH (1,000X).

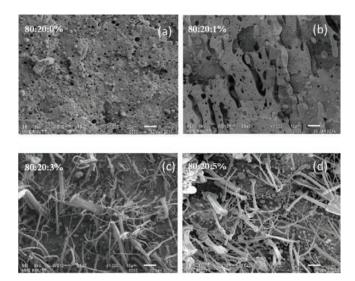


Fig. 6. SEM image of PLA/PP (80/20) with PP-g-MAH (1,000X).

Fig. 6 (a) show morphology of PLA/PP blend (80/20). It was found that phase separation occurred. PP dispersed as small particles in the PLA matrix. The tensile force applied to the sample resulted in pulling PP particles out of the PLA matrix and small holes could be observed. The fracture surface of sample with addition of 1 wt% of PP-*g*-MAH to the polymer blend shows agglomeration of PP in PLA matrix. The morphology of Fig. 6 (b) shows different phenomena that extension of fracture surface can be observed. The morphology of ductile fracture is clearly shown in the polymer with content of PP-*g*-MAH 3 and 5 wt%. The results show effect of PP-*g*-MAH as a compatibilizer of PLA and PP.

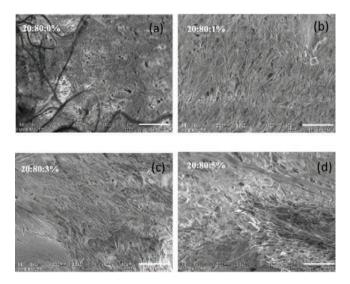


Fig. 7. SEM image of PLA/PP (20/80) with PP-g-MAH (1,000X).

The morphology of fracture surface of polymer blends with opposite ratio of PLA and PP shows different phenomena. The PLA/PP blend (20/80) show ductile fracture due to much content of PP (Fig. 7 (a)). The PLA/PP blends with addition of PP-g-MAH to shows clearly ductile fracture confirmed the compatibility of PLA and PP.

# 4. Conclusion

Polymer blends of PLA/PP with ratio of PLA:PP 80:20 and 20:80 was prepare by injection molding method. The effect of addition of PP-g-MAH as a compatibilizer to the blends was studied. The thermal analysis confirmed that addition of PP-g-MAH has no effect on crystalline melting temperature of the polymer components but the impact strength was increased. The FTIR analysis confirmed the transmittance bands that represent PP and PLA but the characteristic spectrum of ester linkage of PP-g-MAH and PLA was not clearly observed. The compatibilizer does not show significant improvement of mechanical property. However, the morphology study confirmed effect of PP-g-MAH as a compatibilizer for PLA and PP.

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# References

- Kamm B, Gruber PR, Kamm M, Biorefineries Industrial Processes and Products: Status Quo and Future Directions, John Wiley & Sons, 2010.
- [2] Nampoothiri KM, Nair NR, John RP, An overview of the recent developments in polylactide (PLA) research. J Bioresour Technol 2010; 101:8493–8501.
- [3] Tsuji H, "Polylactic Acid -Shokubutsu Yurai Plastic no Kiso to Ouyou", Yoneda Shuppan Co., (2008), in Japanese.
- [4] Auras R, Harte B, Selke S. An overview of polylactides as packaging materials. J Macromolecular Biosci 2004;4:835–864.
- [5] Auras RA, Singh SP, Singh JJ. Evaluation of oriented poly(lactide) polymers with existing PET and oriented PS for fresh food service containers. J Packag Technol Sci 2005;18:207–216.
- [6] Vainionpaa S, Rokkanen P, Tormal P. Surgical Application of Biodegradable Polymers in Humman Tissues. J Prog Polym Sci 1989;14: 679-716.
- [7] Engelberg I, Kohn J. Physico-mechanical properties of degradable polymers used in medical applications: a comparative study. J Biomater 1991;12:292–304.
- [8] Dollinger HM, Sawan SP. Polym Prepr 1990;31:429-430.
- [9] Rohlmann CO, Failla MD, Quinzani LM. Linear viscoelasticity and structure of polypropylene–montmorillonite nanocomposites. Polymer 2006;47:7795–804.
- [10] Zhang QX, Yu ZZ, Xie XL, Mai YW. Crystallization and impact energy of polypropylene/CaCO3 nanocomposites with nonionic modifier. Polymer 2004;45:5985–94.
- [11] Pilla S, Kim SG, Auer GK, Gong S, Park CB. Microcellular extrusion foaming of poly(lactide)/poly(butylene adipate-co-terephthalate) blends. Mater Sci Eng 2010;30:255–262.
- [12] Zhou C, Shi Q, Guo W, Terrell L, Qureshi TA, Hayes DJ, Wu Q. Electrospun bionanocomposite scaffolds for bone tissue engineering by cellulose nanocrystals reinforcing maleic anhydride grafted PLA. J ACS Appl Mater Interfaces 2013;5:3847–3854.
- [13] Marsilla KIK, Verbeek CJR. Properties of bloodmeal/linear low density polyethylene blends compatibilized with maleic anhydride grafted polyethylene. J Appl Polym Sci 2013;130:1890–1897.
- [14] Wang Q, Wang W. Wood-plastic Composites and Products. China Chemical Industry Press:Beijing; 2007.
- [15] Wang YN, Weng YX, Wang L. Characterization of interfacial compatibility of polylactic acid and bamboo flour (PLA/BF) in biocomposites. J Polym Test 2014;36:119–125.
- [16] Ploypetchara N, Suppakul P, Atong D, Pechyen C. Blend of polypropylene/poly(lactic acid) for medical packaging application: physicochemical, thermal, mechanical, and barrier properties. Energy Procedia 2014;56:201–210.
- [17] Riga A, Collins R, Mlachak G. Oxidative behavior of polymers by Thermogravimetric analysis, differential thermal analysis and pressure differential scanning calorimetry. Thermochim Acta 1998;324:135-49.
- [18] Hoidy WH, Ahmad MB, Jaffar Al-Mulla EA, Ibrahim NAB. Preparation and characterization of polylactic acid/polycaprolactone clay nanocomposites. Appl Sci 2010;10:97-106.