The Influence of Poly(Lactic Acid) Addition to Thermal Properties of the Blended Polypropylene for Food Packaging Materials

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Abstract

The commonly used food packaging materials are made from synthetic polymers derived from petroleum. However, the use of synthetic polymers has negative impacts on the environment, because it is difficult to degrade naturally either by the biotic or abiotic process. Although their complete replacement with eco-friendly packaging films is just impossible to achieve economically, at least for a specific application like food packaging the use of bioplastics should be the future. One of the alternatives is to blend synthetic polymer for instance polypropylene (PP) with a natural polymer like poly-lactic acid (PLA). Because their mixture is an immiscible blend because they have highly different polarity, it is necessary to add a compatibilizer such as polypropylene-grafted maleic anhydride (PP-g-MAH) in order to increase the properties of its blend miscibility. The objective of this research was to study the influence of PLA addition to the thermal properties of their blend product with PP. The combinations of PP with PLA in the ratios of (80:20); (90:10); (95:5) were prepared and then characterized for their thermal property behaviour by means of TG and DSC. The results showed that increasing the amount of PLA will decrease their enthalpy significantly.

1.   INTRODUCTION

The commonly used food packaging materials aremade from synthetic polymers from petroleum derivatives. Although the materials present several desired features like softness, lightness and transparency, however, the use of synthetic polymers has negative impacts on the environment, because the synthetic polymers are difficult to degrade naturally either by biotic components like microorganic decomposers or abiotic components for instance sun light [1]. This situation makes a problem for the environment and therefore assessment and mastery of technology to reduce the degree of degradation difficulty or development of new biodegradable materials are necessary. Bioplastics can be alternative food packaging materials and they need further deveopment.

Bioplastics may be produced by blending of synthetic polymers with natural polymers in certain ratios [2]. Polypropylene (PP) is one of the synthetic polymers which are often used as a food packaging materials while polylactic acid (PLA) is a natural polymer produced using renewable bio-based monomers. Some PLA properties are a heat resistant, strong, and elastic. The polymer can be decomposed in the soil either in aerobic or anaerobic conditions within a period of six months to five years [3]. PLA has the best properties of natural and artificial materials because this material is made from plant sugars, using renewable sources and can be fully decomposed [4]. In addition, this material also has similar properties with that of hydrocarbons plastics which are strong, flexible and cheap [3,4,5]. Blending PP with PLA, at certain ratios, to form a bio-plastic might still meet the standard

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properties for a good food packaging material and its waste is environmentally friendly [6]. Since the main functions of packaging are protection and preservation of food from external contamination involving retardation of deterioration, extension of shelf life, and maintenance of quality and safety of the packaged foods. These biodegradable polymers should fulfill all these functions without causing any threats to the environment.

Meanwhile, the development of polymer blending technology has grown rapidly, both in science and commercial use. The advantages of the blending technology are capability to of produce a product with properties that are better than that of the original materials at low cost; ability to improve the properties or performance of the materials, and that it can be used in recycling industry as well as matters relating to the reduction of plastic waste. However, most polyblends are immiscible, where the mix tends to very low entropy, resulting in the formation of polyblend with low mechanical properties during the process and use. PLA does not any reactive groups on the side chains [7,8]. A mixture of PP with PLA is an immiscible blend because they are very different in polarity, therefore it is necessary to add a compatibilizer such as polypropylene-grafted maleic anhydride (PP-g-MAH) in order to increase the properties of its blend miscibility. Parameswaranpillai [9] and Xin [10], have used PP-gMAH as a compatibilizer for PP blending with natural fibers [9,10].

The addition of PP-g-MA can improve homogeneity, tensile strength, and morphology as well as compatibility; and it is done using grafting techniques. This technique has been utilized in various fields of application to change the properties of the parent polymer with certainpurpose, for instance increasing the adhesive strength of the polymer [11] and the biodegradation of polymers [12].The objective of this research was to study the influence of PLA addition to thermal properties of their blend product with PP. The blends of PP with PLA in the ratios of (80:20); (90:10); (95:5) were prepared and then characterized for their thermal property behaviour by mean of TG and DSC.

2. EXPERIMENTAL SECTION

2.1. Materials and Instrument

All starting compounds, such as Maleic Anhydride (MAH) and Tetrachloroethylene, were purchased from E.Merck and used without any further purification; Polypropylene (PP) was made by Chandra Asri Petrochemical Ltd, while Poly Lactic Acid (Type 4043D PLA Pellet) was produced by Filabot Plastic; TG/DSC (LINSEIS STA Platinum Series) was performed to determine decomposition profile of bio-composite.

2.2. Methods

2.2.1. Preparation of PP-g-MAH:

100 mL of tetrachloroethylene was heated in three-neck round bottom flask until the temperature reached 130°C. Then, 5.79 grams of polypropylene was added to the flask and stirred for 90 minutes. Later, 0.579 grams of maleic anhydride was added and the solution was heated for 15 minutes until the maleic Anhydride was dissolved completely. The solution was poured into a petri dish and cooled for 24 hours in a fume hood.

2.2.2. Preparation of PP/ PP-g-MAH / PLA:

100 mL of Tetrachloroethylene was heated in three-neck round bottom flask and heated until the temperature reached 50°C. 0.30 mg PP-g-MAH and 10 grams of w/w ratio of PP:PLA (100:0); (95:5); (90:10); (80:20) were added to the flask. Each composition was stirred for 90 minutes. Then, the hot solution was poured and cooled for 24 hours in a fume hood.

2.2.3. Characterization of Samples:

The dry samples were then crushed using a grinder until they form powder. About 8 mg of samples were characterized by TGA/DSC. TGA analysis was used for detection of temperature degradation (Te) from pure and blended sample. The TGA analysis was run at

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the maximum temperature of 500°C and DSC of 240°C, with the heat flow rate at about 10°C per minute under nitrogen atmosphere rate of 20 mL/minute.

3. RESULTS AND DISCUSSION

3.1. Thermogravimetry Analysis

TG thermal degradation of all the samples is shown in Fig.1 and Fig.2. Fig.1 shows the TGA curves of the pure PLA and PP; Fig.2 shows the TGA curves of PP-gMA-PLA in the ratio of PP/PLA (80:20); (90:10) and (95:5).
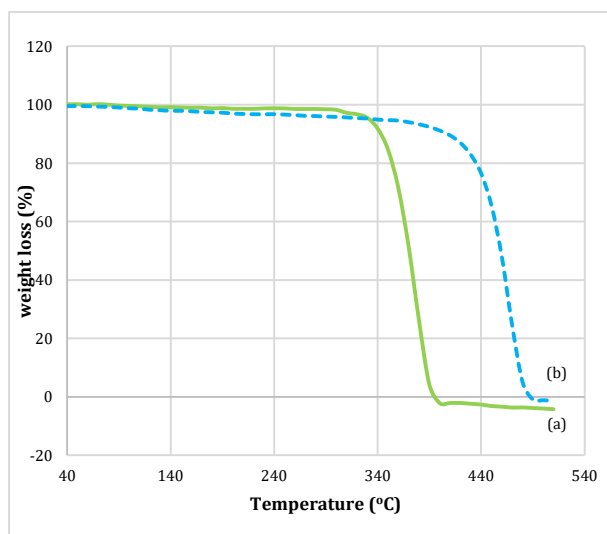

Fig. 1.TGA curves of PP/PLA (a) 0/100; (b) 100/0

There were two characteristic temperatures investigated in the TGA curves which were onset temperature where the degradation process started and end temperature where the combustion completed. It could be seen from Fig.1 that thermal degradation of pure PLA and PP was clearly different and there was only a single step degradation process. Therefore this curve had a set of the characteristic temperature. The onset temperature of PLA was about 300°C and while that of PP was 440°C. Meanwhile, the end temperature of PLA was 391°C and for PP it was 483°C. Therefore the blend (PP/PLA) products could be degraded at a temperature about 300°C to 483°C. According to ASTM E 1131-03, polymer degradation product in the temperature range 200 to 750 ^{o}C was classified as amedium volatile matter [13].
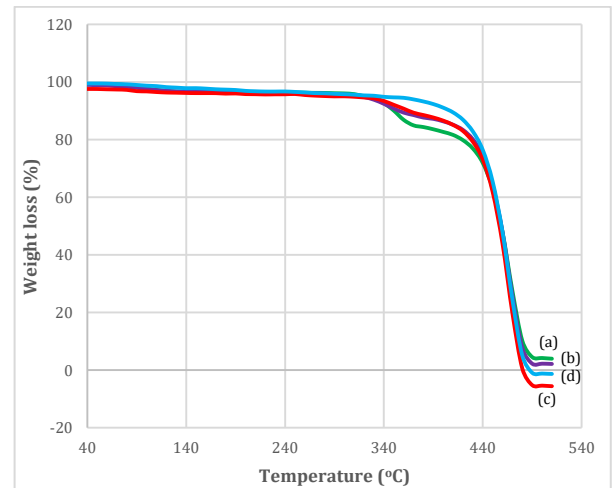

Fig. 2. TGA curves of PP/PLA (a) 100/0; (b) 95/5; (c) 90/10; (d) 80/20

From Fig.2 it could be seen that there was a single step of degradation process of PP with T-onset of 440°C. When PLA was incorporated into the blend, a two-step degradation process appeared with a change in T-onset(1) to 337-318°C, and T-onset(2) to 441-445 This confirms Zhou's research above that there is two-stage degradation process in immiscible polymer PP/PLA blends[14].

Tabel 1. T-onset and T-end temperatures of PP/PLA blends

PP/PLA	Ti-1	Te-1/Ti-2	Te-2
100:0	440	-	483
95:5	337	441	483
90:10	329	444	482
80:20	318	445	482
0:100	300	-	391

Note: Ti = the onset temperature-1; Te= the end temperature

The percentage of weight loss in the first and second decomposition stage and their T-onset value were related to the amount of PLA and PP in the blend. Therefore PLA was more thermal stable than PP. The incorporation of PLA into a PP/PLA blend led to a decrease of T-onset of the blend to 318 ^{o}C at (80:20) ratio.

Similarly, an increase in the temperature range of decomposition wa shown in Table 1. Improved thermal stability and thermal

sensitivity was observed for PP and PLA blending.

According to Fig. 2, the generated peaks were directly proportional to the amount of PLA in the blend. As the amount of PLA increased, the peak became steeper; the end point decreased and the onset point also somewhat decreased. The initial temperature of thermal degradation (T-onset) and the decomposition temperature range for the polymer were essential for evaluating thermal stability and their respective thermal sensitivity [15].

3.2. Differential Scanning Calorimeter Analysis

Typical DSC endotherm curve was shown in Fig. 3 and DSC curves of PP-gMA-PLA in the ratio of PP/PLA (100: 0); (95: 5); (90:10) and (80:20) were shown in Fig. 4. Table 2 showed data generated from the DSC endotherm curves at several PP/PLA blending ratios.
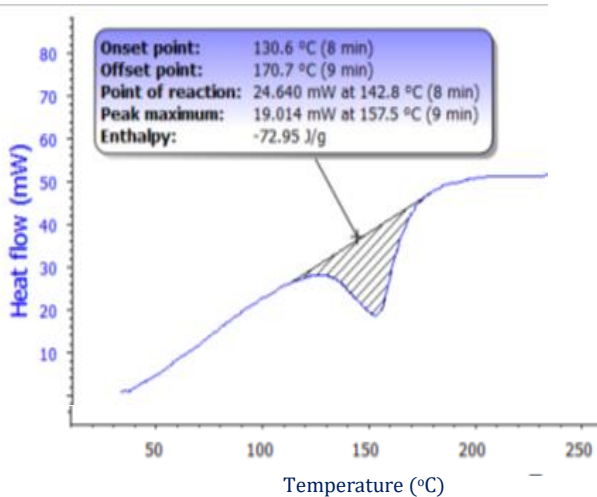

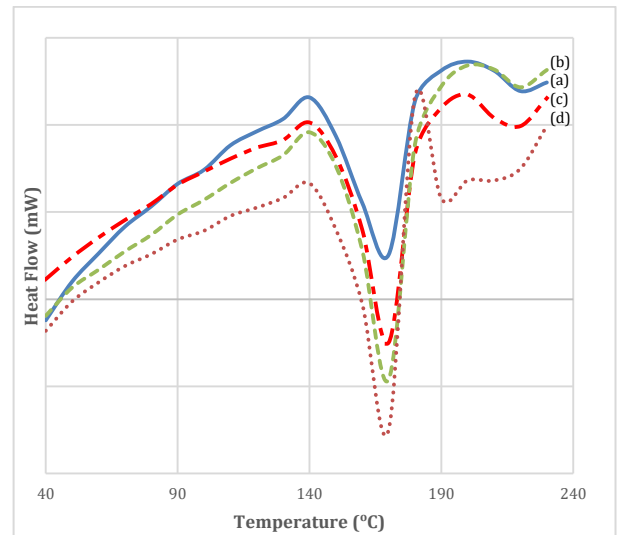**Fig. 3.** Typical DSC endo-thermogram of PP/PLA

Fig. 4. DSC endotherm of PP/PLA blending (a) 80/20; (b) 90/10; (c) 95/5; and (d) 100/0

As shown in Table 2, the DSC measurements indicated that the T_m values (temperature at maximum heat flow) of the blends decreased with increasing of PLA content. This was confirmed by Kim.et.al. [16], that in the crystalline/amorphous immiscible blend system, the presence of separate domains of PLA (amorphous component) in the molten PP (crystalline component) during the crystallization process might cause a depression of the observed T_m.

Table 2 also showed that the blended enthalpy values decreased with increasing PLA content. The low enthalpy also reflected a lower degradation temperature to break up the bond between molecules. The PP/PLA blend films were compatibilized with PP-g-MA prepared with liquid mixing and cast film extrusion technique. Increasing the PLA content led to a decrease in T_m and crystallinity of blend films. From the thermal results, the PP/PLA blend exhibited the typical behaviour of the immiscible polymer blend.

Table 2. Data generated from the DSC endotherm curves at several PP/PLA blending ratios

PP/PLA BLENDING RATIOS	ONSET POINT ^{O}C	OFFSET POINT ^{O}C	POINT OFREACTION mW	PEAK MAXIMUM mW/^{O}C	ENTHALPY J/g
80:20	140.3	176.8	10.818	0.7889/167.3	-48.14
90:10	140.5	179.0	9.426	-2.770/169.0	-59.44
95:5	140.3	178.9	18.873	-5.127/168.8	-72.83
100:0	140.3	183.0	5.953	-7.584/170.7	-73.12

4. CONCLUSION

The presence of PLA in the blends may affect the point of onset and end temperature and enthalpy of blend, as confirmed by TGA and DSC analysis. As the amount of PLA increased, the offset point decreased while the onset point was generally stable. As the result, the enthalpy also decreased.

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REFERENCES

[1]. Pawar,P.A., Purwar, A.H., Biodegradable polymers in food packaging, American Journal of Engineering Research, vol 02, Issue-05, pp:151-164.

[2]. Siracusa,V., Rocculi,P., Romani S.,and Rosa,M.D., Biodegradable polymers for food packaging: Review. Trends in Food Science & Technology 19 (12), 634-643

[3]. Jamshidian, M., Tehran, E.A, Imran,M., Jacquot,M., and Desobry, S. Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies, Comprehensive Reviews in Food Science and Food Safety, Vol. 9,2010, pp 552-571

[4]. Avérous, L., 2008. Polylactic Acid: Synthesis, Properties and Applications. *Monomers, Polymers and Composites from Renewable Resources* (Ed Mohamed Naceur Belgacemdan Alessandro Gandini), 1st Edition, Chapter 21. Amsterdam: Elsevier Ltd.

[5]. Auras, R., Harte, B., Selke, S. An Overview of Polylactides as Packaging Materials, Macromolecular Bioscience, 2004, 4/9:835-864.

[6]. Hamad K, Kassem M, Deri F. Rheological and mechanical characterization of poly (lactic acid)/polypropylene polymer blends. J Polym. Res 2011;18:1799-806.

[7]. Rasal, R. M., & Hirt, D. E. (2009). Improving the properties of the polylactic acid. Plastics Research online, Ed by soap engineers, Clemson, SC

[8]. Wang, J. H., & Schertz, D. M. (2010). Synthesis of grafted polylactic acid and polyhydroxyalkanoate by a green reactive extrusion process. In ACS Symposiumseries (Vol. 1043, pp. 439-453).Oxford University Press.

[9]. Parameswaranpillai, J., Joseph, G., Jose, S., & Hameed, N. (2015). Phase morphology, thermomechanical, and Crystallizationbehaviour of compatibilized and PP-g-MAH compatibilized polypropylene / polystyrene blends. Journal of Applied Polymer Science, 132 (24).

[10]. Xin, L., June, Z., Lin, Z., Hongxia, J., & Ruofei, J. (2014). Study on Mechanical Properties and Thermal Stability Behaviours of PP/PP-g-MAH/ABS-g-MAH Blends. Plastics Science and Technology, 9, 012.

[11]. Song Y. W., Do H. S. Joo H. S., Lim D. H., Kim S., and Kim H. J., (2006), Effect of Grafting of Acrylic Acid onto a PET Film Surfaces by UV Irradiation on the Adhesion of PSAs, J. Adhesion Sci. Technol., 20 (12): 1357-1365

[12]. Hendry, J., I. Ginting, and Laila A. (2008), Gamma radiation studies on the binding of acrylic acid grafted chitosan polyethylene. Proceeding of 2nd National Science and Technology Seminar, Lampung University. 17-18 November 2008.

[13]. ASTM E 1131-03: Standard Test Method for Compositional Analysis by Thermogravimetry, ASTM International, West Conshohocken, PA 2003, www.astm.org

[14]. Zhou S, Chen Y, Zou H, Liang M. Thermally conductive composites obtained by flake graphite filling immiscible polyamide 6/polycarbonate blends. Thermochimica Acta 2013; 566:84-91.

[15]. Ploypetcharaa, N, Panuwat S., Duangduen A., Chiravoot P. Blend of polypropylene/poly (lactic acid) for medical packaging application: physicochemical, thermal, mechanical, and barrier properties. Energy Procedia 56 (2014) 201–210

[16]. Kim YF, Choi CN, Kim YD, Lee KY, Lee MS. Compatibilization of immiscible poly(l-lactide) and low-density polyethylene blends. Fibers and Polymers 2004, 5, 270-4.