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Determination of crystallization and melting behaviour of polylactic acid and polypropyleneblends as a food packaging materials by Differential Scanning Calorimeter

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Abstract

The food packaging materials commonly used is made from polymers synthetic base on petroleum derivatives. However, the use of synthetic polymers has negative impacts on the environment, because it is difficult to degrade naturally either by biotic or abiotic process. This is a problem for the environment and therefore it needs to do the assessment of the technology to reduce the degree of difficulty on its degradation or to find a new material that can be degradable naturally. One of the most important properties of food packaging materials is the polymer crystallinity. This refers to the overall level of crystalline component in relationship to its amorphous component. It is directly related to many of key properties exhibited by a semi-crystalline polymer including brittleness, toughness, stiffness or modulus, optical clarity, creep or cold flow, barrier resistance and long-term stability. Thus, in this study, PP blends with the PLA and melts at 250°C for 4 hours, and investigates their crystallization and melting behavior using DSC at cooling rate of 10 and 40°C/min. The results show that based on their thermograms, with increasing the cooling rate will decrease the crystallinity or increase the amorphous area under the peaks.

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1. Introduction

The food packaging materials commonly used is a film that is made from a polymer synthetic base on petroleum derivatives. Although the materials present several desired features like softness, lightness and transparency,

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however, the use of synthetic polymers has negative impacts on the environment due to their total non-biodegradability either by biotic process such as microorganism decomposition and by biotic process such as by sunlight¹. Although their complete replacement with eco-friendly packaging films is just impossible to achieve, at least for specific application like food packaging the use of bio-plastics should be the future. Since the main function of packaging is protection and preservation of food from external contamination, involves retardation of deterioration, extension of shelf life, and maintenance of quality and safety of packaged food. Biodegradable polymers are the one which fulfill all these functions without causing any threat to the environment. Bioplastics may be produced by blending of synthetic polymers with natural polymers in a certain ratios². Polypropylene (PP) is one of synthetic polymers which often be used as a food packaging material and Poly-lactic acid (PLA) is a natural polymer produced using renewable bio-based monomers. Blending PP with PLA to form a bio-plastic on the certain ratios might still meet the standard properties for a good food packaging materials and its waste are environmentally friendly³. Nowadays, there is a bio-technological advancement to produce PLA, which in this study is designed to produce a bio-composite products with industrial polymers such as polypropylene, polyethylene and polyethylene terephthalate that are used for food packaging. Some PLA properties are a heat resistant, strong, and an elastic polymer. The polymer can be decomposed in the soil either in aerobic or anaerobic conditions within a period of six months to five years⁴. PLA has the best properties within natural and artificial materials, because this material is made from plant sugars, using renewable sources and can be decomposed back fully⁵. In addition, this material also has properties similar to ordinary plastic made from hydrocarbons, strong, flexible and cheap price^{4,5,6}. One of the most important properties of food packaging materials is the polymer crystallinity. This refers to the overall level of crystalline component in relationship to its amorphous component. It is directly related to many of key properties exhibited by a semi-crystalline polymer including brittleness, toughness, stiffness or modulus, optical clarity, creep or cold flow, barrier resistance and long-term stability. Thus, in this study, we prepared PP blends with the PLA and investigate their crystallization and melting behavior^{2,7,8}.

2. Experimental

2.1. Materials and sample preparations

- Polypropylene (PP) homopolymer used in this study is commercial molding grade, Trilene HI10HO. Its melt index (MI) is 10 g/10min at 230°C (ASTM D-1238), Density: 0.903 g/cm³ (ASTM D-792).
- Poly-lactic acid (PLA) Ingeo Biopolymer 7001D. Its melt index (MI) is 6 g/10min at 210°C (ASTM D-1238), Specific Gravity: 1.24 (ASTM D-792)
- Blend of PP and PLA (50/50 wt.). Both granular were dissolved in their solvent (xylene for PP and dioxan for PLA). Its concentration is about 10% (w/v). Both solutions were stirred for 4 hours and then it was evaporated and the dry solid was then heated to temperature 250°C for 4 hours in temperature program of Termolyne furnace.

2.2. DSC measurements

DSC measurements were made on the LINSEIS STA Platinum 1600 Series (simultaneous thermal analysis) system. The sample was first rapidly heated up to 250°C and maintained at this temperature for 10 min in order to erase any previous morphological history, which the sample might be carrying. It was then non-isothermally crystallized when it was cooled down to room temperature at the cooling rate of 10 and 40°C/min. It was subsequently heated at heating rate of 10°C/min. The samples were approx. 10-20 mg. All curves were normalized to the unit weight of the sample. The percent crystallinity is determined using the following equation:

$$1. \% \text{ Crystallinity} = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100$$

ΔH_m is the heat of melting, ΔH_c is the cold crystallization. Both are determined by integrating the areas (J/g) under the peaks. Fig.1. is a typical area under the peaks calculated by Linseis TG/DSC. Depending upon the sample's given thermal history, a cold crystallization exothermic peak may or may not be observed during the DSC experiment. ΔH_m^0 is a reference value and represents the heat of melting if the polymer were 100% crystalline. The ΔH_m^0 value for polypropylene is 207.1 J/g and for PLA is 93 J/g⁸.

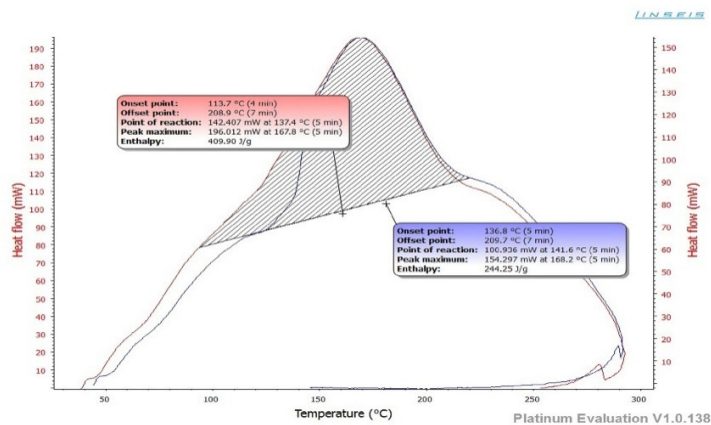


Fig.1. The typical area under the peak calculated by LINSEIS STA Platinum 1600 Series

3. Results and Discussion

This study, non-isothermal crystallization conducted according to the method described in the section 2.1. The DSC measurement use two cooling rates, such as 10°C/min represent of the low cooling rate and 40°C/min represent of the high cooling rate. The curves then were grouped base on polymer samples such as PP, PLA and PP/PLA (1:1). Their thermograms were compiled in Fig.2.

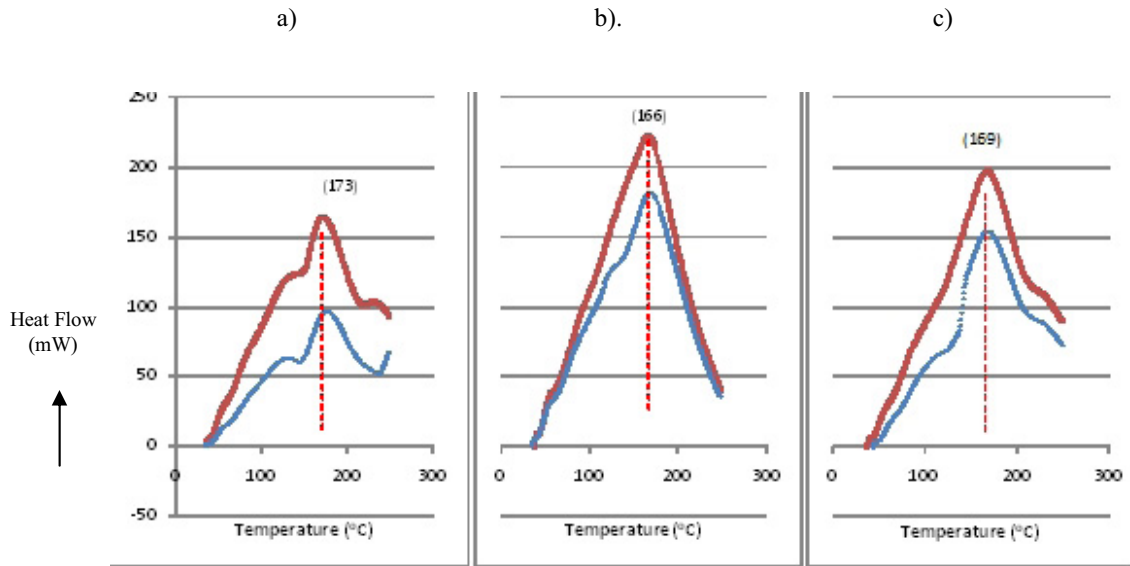


Fig. 2. DSC fusion endotherms for specimens of (a) PP, (b) PLA, and (c) the PP/PLA (50/50) blend prepared by non-isothermal crystallization at 10 and 40°C/min of cooling rate. The heating rate is 10°C/min.

Table 1. The effect of cooling rate to the % crystallinity of polymer samples

Cooling rate (°C/min)	Heat of Melting (J/g)			% Crystallinity		
	PP	PLA	PP/PLA (50/50)	PP	PLA	PP/PLA(50/50)
10	123.0	206.75	244.25	59.39	amorph	Crystalline/amorph
40	117.8	248.59	409.90	56.88	amorph	amorph

From the figure 2, the DSC curve for the high cooling rate lie above the lower ones. Fig 2.a and Fig.2.b are the individual polymer (PP, PLA) and Fig 2.c is a blending polymer PP/PLA (50/50).

3.1. Individual Polymer

Fig 2.a shows the corresponding DSC thermograms for PP obtained at the both cooling rate. Unlike isothermally crystallized specimens reported by Yadav et.al.⁹ the general feature of cooling rate these curves is the dominance of the single fusion endotherm at 173°C followed by a shoulder peak at about 128°C. The temperature point where the curves reach zero heat-flow was 36.5 °C. As the cooling rate increases, the main peak position remains constant but the shoulder appears in the low cooling rate trend to more shoulder and merger with the main peak. This means that increasing its cooling rate affect to the decreasing their crystalline and it can be said increasing their amorphous. Table 1 confirmed that the % crystalline at the low cooling rate is 59% and at high rate is about 57%. For the specimen prepared at a lower cooling rate, the molecules have enough time to form perfect

crystals. However, as the cooling rate increases, the crystallized fraction may consist of defective crystals would undergo perfection during heating. Thus, this shoulder is due to the recrystallization or reorganization of crystals initially formed during non-isothermal crystallization. However, it follows that at a rapid cooling rates only a small amount of originally formed crystals will undergo recrystallization in the heating process, which can be qualitatively evaluated in terms of the relative areas under the resolvable melting peaks. The main melting peaks are, therefore, not influenced by the recrystallization.

Fig 2.b shows the fusion endotherms for PLA specimens crystallized under the same condition as in Fig 2.a. Similarity with PP, the DSC curve for PLA also shows a dominance single main endotherms peak at 166°C. The point where the curve reach zero heat flow, the temperature was 38.2 °C. It is only a small shoulder peaks at the low cooling rate and might disappear at the higher cooling rate. There is the effect of cooling rate to the relative area under main peak, the higher cooling rate, the wider its area. From the curves, it is observed that with increasing in cooling rate, the area under main peak also increase and the shoulder was disappear, merge to the main peak. Thus, the shoulder peak represents the melting of the crystal formed during the non-isothermal crystallization process, while the main peak is attributed to the melting of PLA of higher stability formed amorphous due to the reorganization of molecule initially formed during the non-isothermal crystallization. Non-isothermal crystallization is comparable in the sense of super cooling. When the cooling rate is low, it is similar to isothermal crystallization at higher temperature. Crystallization proceeds at a slower rate, resulting in more perfect and stable crystals. As the cooling rate increases, super cooling become greater and more defective crystals are obtained, which would undergo perfection during heating. Thus, the area under this peak also increases with the increasing of the cooling rate. This trend is very similar to the case isothermal crystallization of PP by Yadav and cho.^{9,10} It follows that in non-isothermal crystallization, recrystallization would be obvious in PP but not in PLA.

3.2. Blending Polymer PP/PLA (50:50)

Fig 2.c gives the heating DSC thermographs for the PP/PLA (50/50 wt) blends prepared at the low and high cooling rates. The results show that the melting characteristic for the blends are closely related with the cooling rate. For the blend specimen prepared at cooling rate. The top single melting peak at 169°C is the main peaks. The point where the curve reach zero heat flow, the temperature was 39.0 °C. This figure indicates that with addition of PLA content the melting temperature (T_m) values of the blends less than the melting of PP. 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 may cause a depression of the observed T_m ¹¹. There are the shoulder peaks at the both sides of the main peak. As the cooling rate increases, the area under the peak is also increase; however, it seems the crystallinity decrease. At the high cooling rate, a single broad melting point for the blends is obtained. As shown in Table 1, glass transition temperature (T_g) of PLA in the blends slightly decrease compared with pure PLA, whereas no significantly changed for crystallization temperature (T_c). Since in non-compatible blends the phase were physically separated, the same heterogeneities that nucleate the homopolymer at T_c of pure polymer may nucleate the stability of crystalline matrix during cooling from melt phase¹². Therefore, T_c

values of the blends were similar to those of the pure component. The Crystallinity value of the blends decrease with increasing of PLA content. Such a result was probably due to the decreasing in primary crystalline density of PP phase and the increasing in the interlamellar amorphous regions, which inhibited the crystallization process¹³.

4. Conclusion

Combining the discussion of pure PP and PLA in Fig.2.a and Fig.2.b, the results can be summarized as follow: At the lower cooling rate (10°C/min), the peak of blend is observed to be almost the same as peak of PP. As the cooling rate increases, the shoulder peak were disappears, and only one single melting peak is observed, the peaks look closely to the peak of PLA. On the other hand, only at very slow cooling rate the blends becomes close to the melting temperature of pure PP. It seems that, for the blend sample prepared at a lower cooling rate PP and PLA crystallized melt separately, indicating the existence of phase separation between PP and PLA in the blend. For those specimens prepared at relatively high cooling rates, co-crystallization as characteristics of the single melting peak by DCS.

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