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Crystallization, Melting Process and Optical Property of PLLA/PABBH System

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Abstract: The goal of this research was developing a new organic nucleating agent and investigating its influence on the non-isothermal crystallization including melt-crystallization and cold-crystallization, melting behavior and optical property of Poly(L-lactic acid) (PLLA). The results from the melt-crystallization indicated that the *N, N'*-bis(benzoyl) phenylmalonic acid dihydrazide (PABBH) could be used as an effective role in nucleation, and 2 wt% PABBH had the best crystallization promoting effect for PLLA. However, the increase of PABBH content made the cold-crystallization peak shift toward the higher temperature. The melting behavior of PLLA/PABBH sample depended on the crystallization time, and the double-melting peaks were ascribed to the melting-recrystallization. The introduction of PABBH seriously decreased the transmittance of PLLA resulting from an increase of crystallinity and the yellowish-brown of PABBH itself.

1. Introduction

PLLA is commonly considered to be environment-friendly materials because of its complete degradability, excellent compatibility and nontoxicity [1]. Thus PLLA as the substitute for petroleum-based plastic has a very wide range of applications in food packaging [2], biomedical materials [3], disposable tableware [4]. However, the slow crystallization rate of PLLA itself results in many defects of the product such as poor heat resistance, poor dimensional stability, low crystallinity [5-6], which seriously restricts the development of PLLA industry. To overcome this defect, some methods like adding the plasticizer or nucleating agent, decreasing the amount of D-lactide isomers were used to accelerate PLLA's crystallization. Among these strategies, using the nucleating agent in PLLA is thought to be the easiest industrialized way to accelerate the crystallization of PLLA [5]. Many compounds were used to investigate their effects on the crystallization process of PLLA. These typical compounds includes talc [7], montmorillonite [8], calcium carbonate [9], 1H-benzotriazole derivatives [10], benzoyl hydrazine derivatives [11], oxamide derivatives [12], etc. For example, Cai et al reported that the half-time of crystallization of PLLA reduced to 22.9 s at 115 °C after using 3 wt% *N, N'*-dodecanedioic bis(benzoic acid) dihydrazide, which was of the great significance for the shortening of PLLA crystallization time. This result indicated a potential usage in producing the PLLA products with the high crystallinity [13].

In this study, *N, N'*-bis(benzoyl) phenylmalonic acid dihydrazide (designated here as PABBH), was prepared to be used as a crystallization promoter for PLLA, and the melt-crystallization, cold-crystallization, melting process and optical property of the PABBH-nucleated PLLA were investigated using differential scanning calorimeter (DSC) and a light transmittance meter.



2. Experimental section

2.1 Materials

The PLLA matrix was obtained from USA Nature Works LLC. The PABBH was synthesized in our lab through acylation and amination of the phenylmalonic acid, the molecular structure of PABBH is shown in Fig.1.

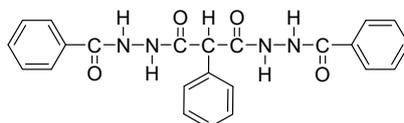


Figure 1. The molecular structure of PABBH

2.2 Melting blend of PLLA/PABBH samples

The preparation of the dried PLLA/PABBH mixture was carried out by a counter-rotating mixer. The processed parameters were set as follows: the blending temperature 190 °C, a rotation speed of 32 rpm for 7 min, and then a rotation speed of 64 rpm for 7 min. Finally, the blend was further pressed *via* hot treatment and cool treatment.

3. Results and discussion

3.1 Non-isothermal crystallization

Figure.2 shows, upon the cooling of 1 °C/min, DSC curves of melt-crystallization of the neat PLLA and PLLA/PABBH samples. For PLLA, the melt-isothermal crystallization peak can not almost be observed in DSC curve, showing the very slow crystallization process of PLLA itself, the similar result was reported by other researchers [14, 15]. In contrast, the presence of PABBH causes PLLA to exhibit the discernible melt-crystallization peak, indicating that the PABBH can be acted as a heterogeneous crystallization promoter for PLLA in cooling. However, it is also noted that the crystallization peaks are slightly wide, showing that the role of PABBH in promoting PLLA's crystallization is medium. Additionally, Figure.2 displays the effect of PABBH concentration on the melt-crystallization behavior of PLLA. With increasing of PABBH content from 0.5 to 3 wt%, the melt-crystallization peak firstly shifts toward the higher temperature, and then the peak shifts to low temperature, when the PABBH loading is higher 2 wt%. And the melt-crystallization peak of the PLLA/2%PABBH sample located at the highest temperature, as well as that the PLLA/2%PABBH has the sharpest melt-crystallization peak, implying that the 2 wt% PABBH exhibits the best crystallization accelerating effect for PLLA.

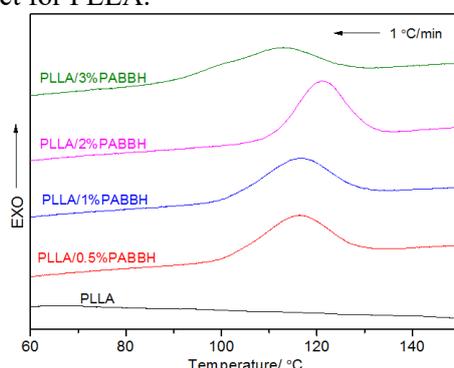


Figure 2. Melt-crystallization of the neat PLLA and PLLA/PABBH samples

Differing from the aforementioned melt-crystallization process, the cold-crystallization process has higher nuclear rate because of the additive PABBH and homogeneous nucleation of PLLA itself. Figure.3 is the DSC of PLLA/PABBH samples from 40 °C at a heating rate of 1 °C/min. It is clear that all PLLA/PABBH have the sharp cold-crystallization peaks, and the crystallization peak shifts toward

the higher temperature with a higher PABBH concentration. The reason may be that a larger amount of PABBH in PLLA matrix has a greater inhibition for the mobility of PLLA molecular chain, and the PLLA molecular chain possesses a good mobility only at a higher temperature, and then forms the crystals. In addition, the perfection of the crystals formed at a higher temperature is better, which results in the higher melting temperature of PLLA containing a larger amount of PABBH.

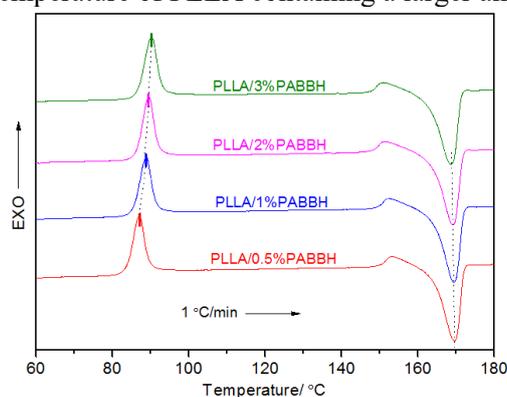


Figure 3. Cold-crystallization of PLLA/PABBH samples

3.2 Melting process

The melting behavior of PLLA/PABBH after crystallization is displayed in Fig.4. With increasing of crystallization time, the double-melting peaks gradually develop into the single melting peak, because crystallization process can be completed after crystallization at 120 °C for the enough time, leading to the appearance of the single melting peak. On the other hand, the melting process of PLLA/PABBH samples depends on the crystallization time. As to the double-melting peaks, there exist two melting mechanisms including the melting-recrystallization and crystal polymorphism. Here, according to the aforementioned transformation, the double-melting peaks are assigned to the melting-recrystallization.

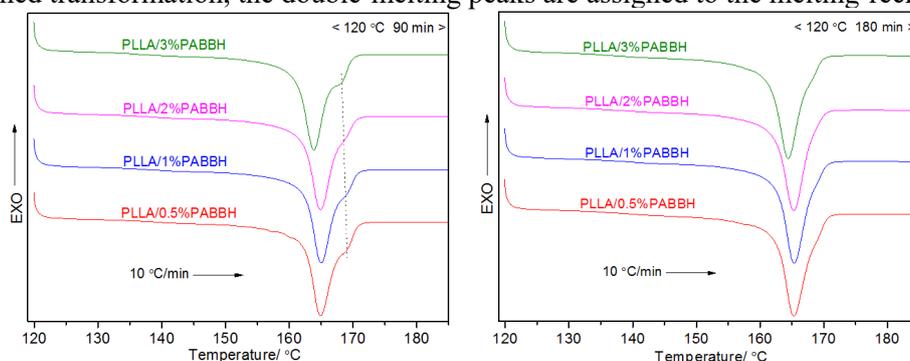


Figure 4. Melting process of PLLA/PABBH samples after crystallization

3.3 Optical property

As aforementioned, the influences of PABBH on the melt-crystallization, cold-crystallization and melting process are obvious. Undoubtedly, the PABBH must affect the optical property of PLLA. Figure.5 is the effect of PABBH on the optical property of PLLA, the addition of PABBH seriously decreases the transmittance of PLLA, even when the PABBH is 2 wt%, the transmittance of PLLA/PABBH sample is zero, and two probable reasons are employed to explain this result. First, the addition of PABBH increases the crystallinity of PLLA; secondly, the yellowish-brown of PABBH itself can also result in the decrease of transmittance.

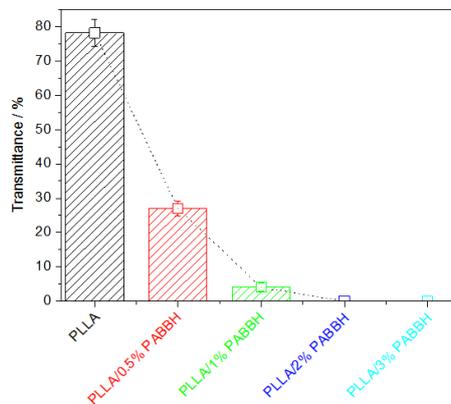


Figure 5. The transmittance of PLLA and PLLA/PABBH

4. Conclusions

PABBH was prepared to study its effect on the melt-crystallization, cold-crystallization, melting process, and transmittance of PLLA. The results confirmed that PABBH could improve the crystallization of PLLA, but the promoting effect was medium. Compared to the other concentration of PABBH, 2 wt% PABBH exhibited the best crystallization ability. For cold-crystallization process, a larger amount of PABBH made the PLLA crystallize at a higher temperature. The melting process of PLLA/PABBH samples depended on the crystallization time, with increasing of crystallization time, the double-melting peaks degenerated into the single melting peak, resulting from the melting-recrystallization. Finally, the influence of PABBH on the transmittance of PLLA was negative.

Acknowledgements

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