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Studies of Poly(L-lactic acid) Composites: Influence of 1H-Benzotriazole on Thermal and Mechanical Performance in Matrix

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Abstract: This study reported the effect of the functional additive 1H-benzotriazole (BTA) on the thermal behaviour and mechanical properties of Poly(L-lactic acid) (PLLA) through differential scanning calorimeter (DSC), infrared spectra (IR), thermogravimetric analysis (TGA) and tensile testing. The DSC measurement showed that both BTA and cooling rate greatly affected the crystallization process of PLLA, the introduction of BTA led to a positive effect on promoting PLLA's crystallization, but an increase of a cooling rate was negative. Compared with other concentration of BTA, 0.5 wt% BTA had the best crystallization accelerating effect. Second, thermal decomposition indicated that the onset decomposition temperatures of all PLLA/BTA composites were higher than that of BTA at same heating rate; as well as the onset decomposition temperature of BTA increased with increasing of the heating rate. Third, the mechanical performance showed that PLLA/BTA samples presented the irregular trend in the elongation at break with increasing of BTA content, and the PLLA/3%BTA had the maximum value 2.87%.

1. Introduction

1H-benzotriazole, as a type chemical intermediates, was widely used in corrosion inhibitors [1-3], chemical synthesis [4, 5], high-energy materials [6, 7], etc. Srinivas and his colleagues [6] synthesized a number of derivatives of 1H-benzotriazole with amino, azido and nitro groups. The energetic properties and thermal analyses of these 1H-benzotriazole derivatives indicated that 1H-benzotriazole derivatives existed a comparable performance to that for TNT, which showed that these 1H-benzotriazole derivatives might be used in the area of energetic materials. In aspect of corrosion inhibitors, three benzotriazole derivatives were investigated for the corrosion of copper in acidic medium by both experimental and theoretical approach [2]. The nature of the inhibitors and concentration determined the inhibition efficiency of the benzotriazole derivatives. Theoretical calculation results further indicated that the heteroatoms and benzotriazole ring were the key active sites of inhibitors, and the benzotriazole derivatives could adsorb on the copper surface *via* the benzotriazole ring and heteroatoms.

Enhancing the performance of Poly(L-lactic acid) (PLLA) has been the interest of many researchers around the globe over the last two decades [8, 9]. In general, the performances of the neat PLLA cannot satisfy the requirements for application in industry and agriculture field. Thus, it is necessary to improve the defects of PLLA to cause PLLA to compete with the traditional plastic products including Polyethylene, Polypropylene, etc. Joo et al reported that the cellulose nanowhiskers



could promote crystallization of PLA, moreover, the modulus and tensile strength of the PLA composite also increased with an increasing of cellulose nanowhiskers loading. However, the glass transition of PLA with the cellulose nanowhiskers still depended on PLLA itself [10]. In addition, the reinforcing the performance of PLA through polymer materials also was reported. Effects of dendritic hyperbranched polymer and starch on mechanical properties of PLA were evaluated [11]. The dendritic hyperbranched polymer could improve significantly mechanical properties of PLA. However, a small amount of starch had no effect on tensile strength. And the crystallization behavior showed that both the dendritic hyperbranched polymer and starch could promote the PLA's crystallization.

In generally, the excellent crystallization and mechanical properties of PLLA are very key role in increasing the heat resistance and widening the application. Thus, 1H-benzotriazole (BTA) was incorporated into PLLA matrix to evaluate its role in the crystallization and mechanical performance, and relevant research work were performed using DSC, TGA, tensile testing, etc. Those results may be useful to rich the PLLA composites and explore the application of PLLA composites in more fields.

2. Experimental section

2.1. PLLA and BTA

The 2002D PLLA and chemical pure BTA were purchased from Nature Works LLC of USA and Chongqing Chuandong Chemical Reagents Company of China, respectively.

2.2. Preparation of modified PLLA samples

The PLLA and BTA was dried firstly overnight, and the similar and detailed melt-blended processing procedure had been described in our previous work [12].

2.3. Characterization

TGA: Thermogravimetric analysis of BTA and PLLA/BTA composites was performed on Q500 TGA with a different heating ramp with 50 ml/min air flow.

DSC: The non-isothermal crystallization process of PLLA and PLLA/BTA under different conditions was measured by DSC Q2000 with 50 ml/min nitrogen.

FT-IR: Infrared spectra of PLLA, BTA and PLLA/BTA composites were performed on a Nicolet iS50 spectrophotometer.

Tensile testing: The Dumbbell-shaped tensile test specimens with dimensions of 25 mm×6 mm×1.0 mm were prepared by pneumatic-controlled impact shaping machine. Normal tensile tests were conducted on a D&G DX-10000 electronic tensile tester at the speed of 50 mm/min at room temperature.

3. Results and discussion

3.1. Non-isothermal crystallization

Studying on the melt crystallization of polymer composites is key and more practical value for application. Figure.1 showed the melt crystallization procedure of PLLA/BTA composites upon cooling of 1 °C/min. As shown in Figure.1, there exists a very weak crystallization peak for the PLLA during cooling process. However, the crystallization peaks of PLLA containing BTA are very obvious upon cooling of 1 °C/min, indicating that addition of BTA induces the PLLA's crystallization. At the same time, it is also clear from Figure.1 that the melt-crystallization peaks for all PLLA/BTA composites are much sharper during the cooling process compared with the neat PLLA, but the crystallization peak of PLLA with 0.5 wt% BTA is the sharpest, showing the best nucleation effect for crystallization at 0.5 wt% BTA content. In addition, the cooling rate is another important fact for the PLLA's crystallization process (See Fig.2), with the continuous increase of cooling rate, the crystallization peak of PLLA containing 0.5 wt% BTA (labeled as PLLA/0.5%BTA) shifts to lower temperature, and the crystallization peak also become much wider, the possible reason of this

phenomenon is that a decrease of the cooling rate makes the PLLA's crystal become more perfect in cooling crystallization, and increasing of crystal perfection leads to the sharper the melt-crystallization peak become. The similar result can be observed in other study [12].

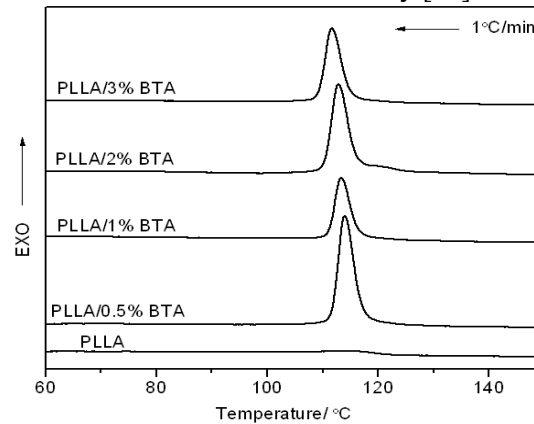


Figure 1. The melt-crystallization process of PLLA/BTA

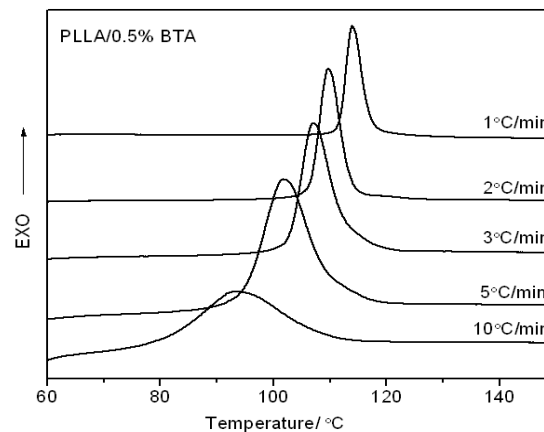


Figure 2. The melt-crystallization process of PLLA/0.5%BTA at different cooling rate

The crystallization of PLLA/BTA composites was also investigated by IR (See Figure. 3). There is a strong absorption of all PLLA/BTA samples at about 1753 cm^{-1} which attributes to the C=O stretching vibration of PLLA. What is more, the intensity trend of carbonyl group absorption peak of PLLA/BTA composites has the same change with the melt-crystallization of PLLA/BTA composites in cooling of $1\text{ }^{\circ}\text{C/min}$, which further confirms that 0.5 wt% BTA creates the most advanced crystallization ability for PLLA.

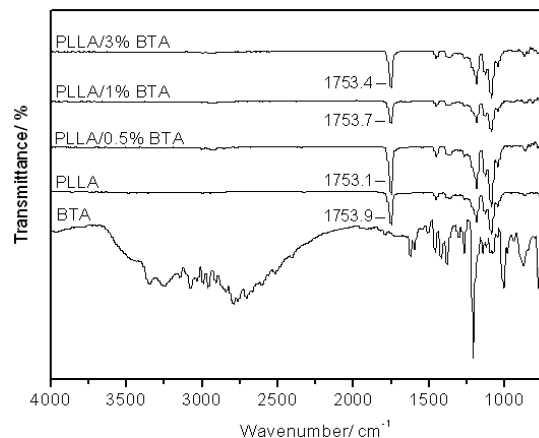


Figure 3. IR of BTA, PLLA and PLLA/BTA composites

3.2. Thermal decomposition and mechanical property

The thermal decomposition and mechanical properties of polymer materials are also very important testing contents to know the relationship between structure and performance. Firstly, the thermal decomposition process of the BTA, PLLA and PLLA/BTA samples were investigated by TGA. Figure.4 shows that the thermal decomposition curves of the PLLA, BTA and PLLA/BTA samples in heating of 10 °C/min. It is found from Fig.4 that the onset decomposition temperatures (T_o) of all PLLA/BTA composites are higher than that of BTA, though the T_o of the PLLA/BTA composites decreases with increasing of BTA content because of the blending of BTA with low decomposition temperature, and this result is very promising application in higher temperature zone. In addition, the TGA results about the influence of the heating rate on the decomposition temperature shows that the thermal decomposition process of BTA is affected significantly by the heating rate (See Fig.5), with the increasing of heating rate, the T_o of BTA shifts to higher temperature, and the pot of the maximum decomposition rate also is different due to different heating rate, this phenomenon could be also observed in decomposition process of other compounds [13].

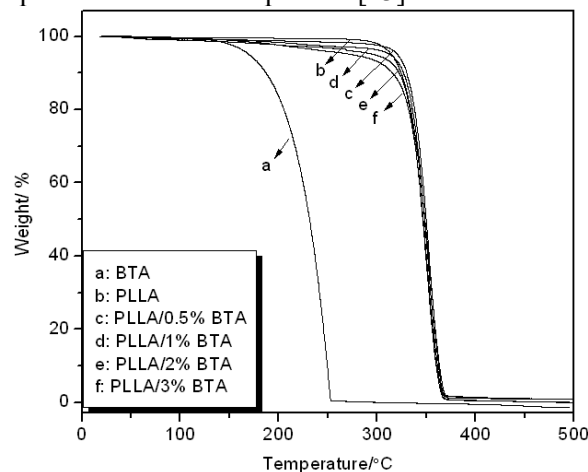


Figure 4. The thermal decomposition curves of BTA, PLLA and PLLA/BTA composites

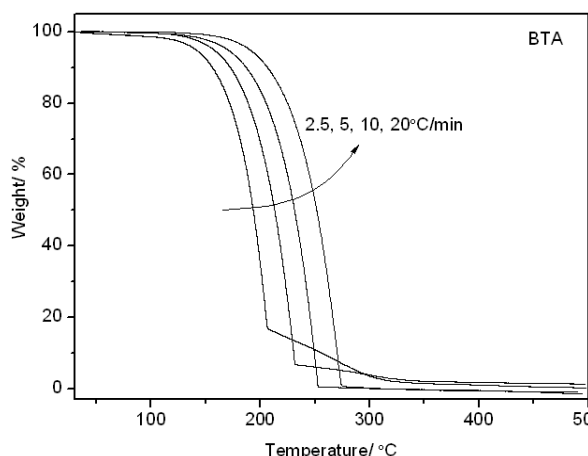


Figure 5. Thermal decomposition process of BTA at different heating rates

The effect of BTA on the mechanical property of PLLA was also further investigated, and the stress-strain curves of the pure PLLA and PLLA/BTA composites are displayed in Figure. 6. The elongation at break of the neat PLLA is 2.83%, then the addition of BTA causes the elongation at break of PLLA to present irregular trend, upon addition of 3 wt% BTA, the elongation at break of PLLA has the maximum value of 2.87%, and PLLA with other content has smaller value compared with the neat PLLA. The complex trend of elongation at break of PLLA with BTA not only may result

from the influence of BTA, but also result from operation, testing environment, sample preparation, etc.

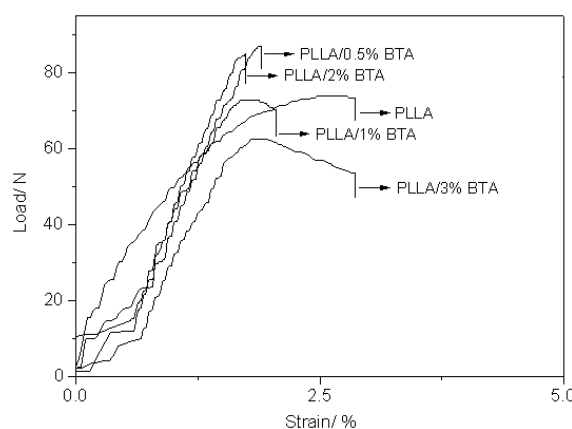


Figure 6. The stress-strain curves of the pure PLLA and PLLA/BTA

4. Conclusions

This study is a useful attempt in improving the performance of PLLA through the addition of BTA. And the testing results showed that the BTA could promote the PLLA's crystallization, the 0.5 wt% BTA exhibited the best nucleation effect for PLLA through the melt-crystallization and IR analysis. Besides, the BTA could also promote the thermal decomposition temperature of PLLA. However, both the melt-crystallization and thermal decomposition process of PLLA/BTA composites were affected significantly by the relevant rate. The elongation at break of PLLA/BTA presented irregular trend, and PLLA/3% BTA had the largest elongation at break.

Acknowledgements

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