Analysis of crystallization and melting behavior of composites before and after annealing

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Abstract
The crystallization and melting behavior of sisal fibers reinforced PLA composites were studied in this work. It can be found that the addition of sisal fiber as reinforcement shortened the nucleation period of PLA and promoted the formation of transverse crystals in PLA composites. Annealing treatment can improve the transition temperature and crystallinity of PLA composites.

1. Introduction
PLA has good physical properties, biocompatibility and biodegradability which has been widely used in various fields. [1] Whereas, the production cost and poor mechanical properties limit the extensive application of PLA. Researchers have done a lot of work to modify PLA and optimize the processing process to promote the industrialization of PLA. [2] Among them, blending modification of PLA with natural fibers is a better method. Natural fibers have many excellent properties over synthetic fibers and can be used to reinforce the polylactide (PLA). They can not only improve the properties of PLA, but also expand the application to achieve the sustainable development. [3]
PLA is a semi-crystalline polymer and natural fiber has a high specific surface area. [4] Therefore, the addition of natural fiber has a great influence on the crystallization behavior of PLA composites. Many tests can be used to study the crystallization behavior of polymers. Differential scanning calorimetry (DSC) has been widely used because of its simplicity and reliability, which was also used to analyze the crystallization and melting behavior of PLA/natural fiber composites in this study.

2. Experiment

2.1. Materials
PLA 3051D, Nature Works™, was purchased by Shenzhen Bright China Industrial Company
SF bundles (GB/T 15031-94) were provided by Guangxi Sisal Company of Guangxi Province, China. Other chemical reagents were commercial products.

2.2. Samples Preparation
SFs were submerged into 10% NaOH solution (mass concentration) for 3 h. Then, ASFs were washed with distilled water and dried in the open air for 48 h. USFs were mixed with ASFs to fabricate HSFs in a mass ratio of 1:1 and then PLA, ASFs, USFs and HSFs were dried at 100 degrees for 4 h. Then PLA was compounded with SFs with a mass ratio 4:1 using a two-roll plastic mill (SK-160B, Shanghai Rubber Machinery Factory, china) at 180 degrees. Four kinds of samples were made: pure PLA, PLA/USFs, PLA/ASFs, and PLA/HSFs. Then, they were compressed into sheets by a hot press (QBL-350, Wuxi No.1 Rubber Plastics Mechanical Co. Ltd, China). The compression molding temperature and pressure were 190 degrees and 10 MPa, respectively.

2.3. DSC test
About 5 mg of the PLA composites and the pure PLA were placed in the crucible respectively, the scanning temperature range was set as 25-200 °C, the protective gas was nitrogen atmosphere, and the purge flow rate was set as 20 ml/min.

2.4. Polarizing Microscope
Polarizing microscope (POM) investigation was performed with a POM (Axioskop 40 POL, ZEISS, Germany)

3. Results and discussion

3.1 DSC analysis of pure PLA and PLA composites
DSC curves of PLA and PLA composites during the secondary heating process are shown in figure 1. The thermal properties and the calculated crystallinity of PLA and three composites are also given in table 1. It can be seen that both PLA and composites have a cold crystallization peak on the DSC curve, and the cold crystallization peak temperature of PLA is 128.7 °C. It was also found that the crystallization peak of pure PLA was small and wide which fully proved that PLA was a polymer with difficulty in crystallization. However, the crystallization peak of PLA/USFs PLA/ASFs and PLA/HSFs is sharp and narrow and the temperature of the cold crystallization peak of the three composites also decreased to 109.6 °C 110.0 °C and 113.7 °C, respectively. This indicates that the addition of sisal fiber can obviously improve the crystallization performance of PLA, which is mainly due to the heterogeneous nucleation of sisal fiber. [5-6] Effect of sisal fiber on the crystallization of PLA can also be seen from the crystallinity data of table 1. The crystallinity of PLA composites was 24.3%, 22.1% and 29.6%, respectively, which were higher than that of pure PLA of 18.0%.

| materials    | cold crystallization temperature (°C) | melting point (°C) | crystallinity (%) |
|--------------|----------------------------------------|--------------------|-------------------|
| PLA          | 128.7                                  | 156.5              | 18.0              |
| PLA/USFs     | 109.6                                  | 151.5/159.8        | 24.3              |
| PLA/ASFs     | 110.0                                  | 150.0/156.6        | 22.1              |
| PLA/HSFs     | 113.7                                  | 154.1/161.8        | 29.6              |
In addition, it can be found that PLA has only one melting peak, while the three composites have a small and obvious melting peak near 150°C and a large melting peak. Due to the complexity of polymer crystallization, multiple melting behavior exists widely in the heating process of crystalline polymer. It has been pointed out in literatures [134-136] that transverse crystals may appear on the surface of fibers when fibers and semi-crystalline polymers are blended. Therefore, it may be speculated that the reason why there is a small melting peak near 150°C on the DSC curves of the composites may be the occurrence of transverse crystals.

3.2 DSC analysis of pure PLA and PLA composites after annealing

It was well known that crystallization temperature has a very important effect on the structure and morphology of polymer crystallization, such as crystal integrity, wafer thickness, crystal shape and so on. In the process of production and molding of polymer products, the uneven crystal orientation and shrinkage are caused by the inconsistent cooling speed during the molding of the products, which leads to the internal stress of the products. It is necessary to annealing the molded products in order to eliminate or reduce the internal stress in the molded products to avoid the deformation or cracking. Annealing is an effective method for the properties of polymer products, through which the crystallinity, crystal structure and crystal size of the polymer can be adjusted to obtain different physical properties.

Figure 2 shows the DSC curves of PLA and composites before and after annealing treatment, in which AT110 represents the annealing temperature of 110°C. It can be seen from figure 2 that all the melting peaks becomes sharp after annealing treatment, which indicates that the crystal perfection of pure PLA and composites increases after annealing treatment. In addition, the disappearance of cold crystallization peak on DSC curve after annealing in figure 4-5 also indicates that annealing can improve the crystal perfection of PLA and PLA composites. It can also be seen from table 2 that the crystallinity of pure PLA and PLA composites after annealing treatment are higher than that before annealing treatment, which is because the frozen molecular chain of PLA is rearranged in chain segments, and the molecular structure becomes more perfect and regular during annealing treatment and thus the crystallinity is improved.
The glass transition temperatures of pure PLA and PLA composites before annealing treatment were higher than that before annealing treatment. It is because the crystal perfection of the materials is improved, the movement ability of the molecular chain segment is reduced and thus the glass transition temperature is increased. In addition, it can be found that the small melting peaks of the annealed composites near 150°C do not disappear, which also indicates that a new crystal structure generated because of the addition of sisal fiber.

(a) PLA; (b) PLA/USF(AT110); (c) PLA/ASF(AT110); (d) PLA/HSF(AT110)

Fig. 2 DSC curves before and after annealing of PLA and composites

| materials         | glass temperature (°C) | crystallization temperature (°C) | melting point (°C) | crystallinity (%) |
|-------------------|------------------------|----------------------------------|-------------------|------------------|
| PLA(AT110)        | 68.7                   | —                                | 157.9             | 29.3             |
| PLA/USF(AT110)    | 66.4                   | —                                | 151.6/157.6       | 31.6             |
| PLA/ASF(AT110)    | 69.6                   | —                                | 150.7/158.5       | 30.1             |
| PLA/HSFAT110)     | 68.2                   | —                                | 150.7/158.1       | 39.8             |

3.3. POM analysis

POM of PLA and PLA composites are presented in figure 3. It can be seen that the crystals of PLA are like branches. However, a layer of crystals perpendicular to the axial direction of sisal fibers appears around SFs which indicated that a new crystal morphology namely transcry stallization appeared because of the addition of SFs in PLA matrix. The reason is mainly because some factors make the fiber become the nucleating material that induces the crystallization of the polymer matrix and thus a large number of crystal nuclei and crystals produced on the fiber surface which squeeze against each other and grow in a directed way. The appearance of transcry stallization also explained why the DSC curves of PLA composites showed a small melting peak near 150°C.
Fig. 3 POM investigation of PLA and composites

4. Conclusion
The crystallinity of the PLA composites was higher than that of pure PLA because of the addition of sisal fiber as reinforcement which also shortened the nucleation period of PLA and promote the formation of transverse crystals in PLA composites. Annealing treatment can improve the transition temperature and crystallinity of PLA composites.

Reference
[1] Auras R, Harte B, Selke S. An overview of polylactides as packaging materials. Macromol. Biosci. 2004, 4, 835-864.
[2] Agopyan V, Savastano H, John V M, et al. Developments on vegetable fibre-cement based materials in Sao Paulo, Brazil: an overview[J]. Cement & Concrete Composites, 2005, 27(5):527-536
[3] John M J, Thomas S. Biofibres and biocomposites. Carbohyd. Polym. 2008, 71, 343-364.
[4] Gottschalk C, Frey H. Hyperbranched polylactide copolymers[J]. Macromolecules, 2006, 39(5):1719-1723
[5] Wang C, Liu C R. Transcrystallization of polypropylene composites: nucleating ability of fibres[J]. Polymer, 1999, 40(2):289-298
[6] Campbell D, Quayum M M. Melt crystallization of polypropylene: effect of contact with fiber substrates[J]. Journal of Polymer Science, Polymer Physics Edition, 1980, 18(1):83-93

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