IMPROVEMENT IN MECHANICAL PROPERTIES OF FLEXIBLE POLY(L-LACTIDE)-*b*-POLYETHYLENE GLYCOL-*b*-POLY(L-LACTIDE) BIOPLASTIC BY MELT BLENDING WITH BORON NITRIDE

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ABSTRACT: Poly(L-lactide)-*b*-polyethylene glycol-*b*-poly(L-lactide) triblock copolymer (PLLA-PEG-PLLA)/boron nitride (BN) composites with BN contents of 1, 2 and 4 wt.% were prepared by melt blending. Scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and tensile testing were carried out to characterize the phase morphologies, thermal properties and mechanical properties of composite films. The BN particles showed good distribution and dispersion throughout the film matrices as observed from SEM. DSC analysis showed that increasing crystallinity content and decreasing half crystallization-time of PLLA-PEG-PLLA/BN composites were obtained when the BN content was increased. The ultimate tensile stress significantly increased and strain at break steadily decreased with an increase in the BN content. These results showed that the BN particles enhanced crystallizability and mechanical properties of PLLA-PEG-PLLA.

Keywords: Bioplastics, Polymer composites, Poly(L-lactide), Block copolymer, Boron nitride

1. INTRODUCTION

Poly(L-lactic acid) or poly(L-lactide) (PLLA) is a potential bioplastic to replace petroleum-based plastics in many fields, such as biomedical, tissue engineering, drug delivery and packaging applications because of its excellent biocompatibility, biodegradability, bio-renewability and compo-stability as well as good mechanical strength and processability [1−3]. Unfortunately, slow crystallization and poor flexibility of PLLA limit some of its applications [4,5]. PLLA-*b*-polyethylene glycol-*b*-PLLA triblock copolymers (PLLA-PEG-PLLA) were found to be more flexible than PLLA because of flexible PEG middle-blocks enhanced plasticizing effect for PLLA end-blocks by reducing glass-transition temperature and increasing film extensibility [6, 7]. PLLA-PEG-PLLA have been widely investigated for use in medical and pharmaceutical applications due to their being biocompatible and biodegradable polymers [8−10]. However, high-molecular-weight PLLA-PEG-PLLA has lower mechanical strength than PLLA [7].

Previous studies reported that various fillers including natural fibers [11], cellulose nanocrystals [12], nano-clay [13] and boron nitride [14] can be used to improve the mechanical strength of PLLA. Among these fillers, boron nitride is one of the most interesting reinforcing fillers because of its good thermal and chemical stability, low reactivity and high mechanical strength [15, 16]. Boron nitride has been used as a reinforcing filler for PLLA [14]. The tensile stress of PLLA increased by of about 132% as compared to pure PLLA by the addition of 2%BN. Moreover, boron nitride powder can accelerate the crystallization of PLLA [16] and poly(3-hydroxybutyrate) (PHB) [17] by acting as a heterogeneous nucleating agent to increase their crystallinity content.

To the best of our knowledge, there have not been any reports on the effect of boron nitride on crystallization behavior and mechanical properties of PLLA-PEG-PLLA. In this study, we aimed to improve the crystallization and mechanical strength of PLLA-PEG-PLLA by blending it with boron nitride.

2. RESEARCH SIGNIFICANCE

High-molecular-weight PLLA-PEG-PLLA triblock copolymer showed potential for use as a flexible biodegradable bioplastic to resolve the plastic-waste problem. However, PLLA-PEG-PLLA had lower tensile strength than PLLA home that restricting its use for a wider range of applications. Therefore, this works aim to improve the the mechanical properties of PLLA-PEG-

PLLA using boron nitride as a reinforcing filler. It was found that the mechanical strength of PLLA-PEG-PLLA was improved by melt blending with boron nitride. Moreover, boron nitride also acted as a heterogeneous nucleating agent to improve crystallizability of PLLA-PEG-PLLA. Hence, it could be a reference for further research and development on flexible PLLA-based bioplastics with good mechanical strength and crystallization properties.

3. MATERIALS AND METHODS

3.1 Materials

Chain-extended PLLA-PEG-PLLA were synthesized through ring-opening polymerization in the bulk of L-lactide monomer under nitrogen atmosphere in the presence of 2 parts per hundred of resin (phr) Joncryl® ADR4368 as described in our previous work [18]. The Melt flow index of this PLLA-PEG-PLLA at 190˚C under 2.16 kg load was 31 g/10 min. Boron nitride (BN) powder with the particle size of 1 μm was obtained from Qinghe Chuangya Welding Material Co., Ltd. (China) was used without further modification. The morphology of BN particles is shown in Fig. 1.
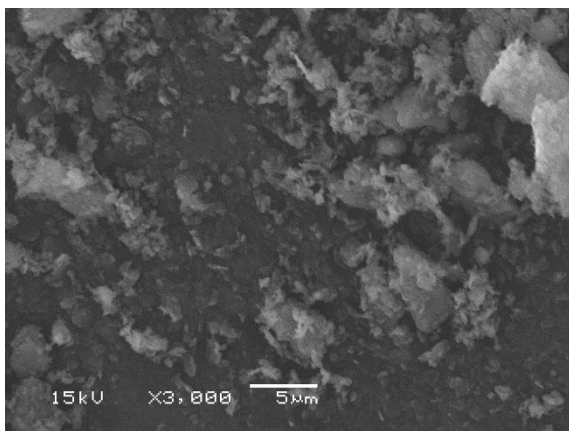

Fig. 1   SEM images of BN particles. Bar scale = 5 μm.

3.2 Preparation of PLLA-PEG-PLLA/BN Composites

PLLA-PEG-PLLA and BN were dried *in vacuo* at 50˚C overnight to remove moisture before melt blending using a Rheomix batch mixer (HAAKE Polylab OS). Melt blending was performed at 190˚C with a rotor speed of 100 rpm for 4 min. PLLA-PEG-PLLA composites with different BN contents (1, 2 and 4 wt.%) were prepared. PLLA-PEG-PLLA without BN was also prepared by the same method for comparison.

The composites were dried *in vacuo* at 50˚C overnight before film formation with a compression molding machine (Auto CH Carver). The composites were heated at 200˚C for 3 min without any force before compressing unde5-tonon load for 1 min. The obtained films were 150 × 150 mm in size and were quickly cooled to 25˚C with water flow for 1 min under the same compression force. The films were stored in a desiccator at room temperature for 24 h before characterization.

3.3 Characterization of PLLA-PEG-PLLA/BN Composites

Thermal transition properties of the composites were determined using a differential scanning calorimeter (DSC, Perkin-Elmer Pyris Diamond) under nitrogen gas flow. The composites were first heated at 200˚C for 3 min to remove thermal history, then fast quenched before heating from 0 to 200˚C at a rate of 10˚C/min to detect glass transition (T_g), cold crystallization (T_{cc}) and melting (T_m) temperatures as well as enthalpies of melting (ΔH_m) and cold crystallization (ΔH_{cc}). The degree of crystallinity (X_c) of the PLLA phases was calculated from Eq. (1).

$$X_C(\%) = [(\Delta H_m - \Delta H_{cc})/(93.7 \times W_{PLLA})] \times 100 \quad (1)$$

where the 93.7 J/g is the ΔH_m for 100%X_c PLLA [19]. W_{PLLA} is the PLLA weight-fraction of the composites calculated from PLLA fraction (PLLA-PEG-PLLA = 0.83 obtained from ^{1}H-NMR [7]) and the BN content.

For half crystallization-time ($t_{1/2}$) determination, the composites were first heated at 200˚C for 3 min to completely erase thermal history, then quenched to 120˚C at a rate of 50˚C/min and then isothermal scanned at 120˚C until the completion of crystallization [20]. The $t_{1/2}$ is the time required to achieve half of the final crystallinity.

Thermal decomposition behaviors of the composites were determined using a thermogravimetric analyzer (TGA, TA-Instrument SDT Q600). TGA was carried out in the range of 50 to 800˚C at a heating rate of 20˚C/min under a nitrogen gas flow.

Phase morphology of the composite films was observed using a scanning electron microscope (SEM, JEOL JSM-6460LV). The composite films were cryogenically fractured after immersing in liquid nitrogen for 10 min and were sputter-coated with gold to avoid charging before scanning at an acceleration voltage of 15 kV.

Tensile properties of the composite films were measured using a universal mechanical testing machine (Liyi Environmental Technology LY-

1066B) with a load cell of 100 kg, a crosshead speed of 50 mm/min and a gauge length of 50 mm. The film sizes were 100 mm × 10 mm. The averaged tensile properties were obtained from at least five measurements.

4. RESULTS AND DISCUSSION

4.1 Thermal Transition Properties

DSC has been widely used to determine the thermal transition properties of PLLA-based composites [1, 16]. The DSC heating curves of pure PLLA-PEG-PLLA and their composites are shown in Fig. 2 and DSC results are reported in Table 1. It was found that the T_g of pure PLLA-PEG-PLLA and PLLA-PEG-PLLA/BN composites were in range 27–29°C, indicating that the T_g was not significantly changed by the addition of BN.

However, blending of BN caused shifting of T_{cc} peaks of PLLA-PEG-PLLA to lower temperature. This indicates that the BN enhanced stronger PLLA crystallizability by acting as a heterogeneous nucleating agent by increasing the nucleation density and reducing the nucleating barrier [16, 21–24]. Therefore, the X_c of composites increased as the BN content increased. The T_m peaks of the composite did not change with the BN content. The T_m of PLLA-PEG-PLLA/BN composiwaswere in rthe ange 160–161°C.
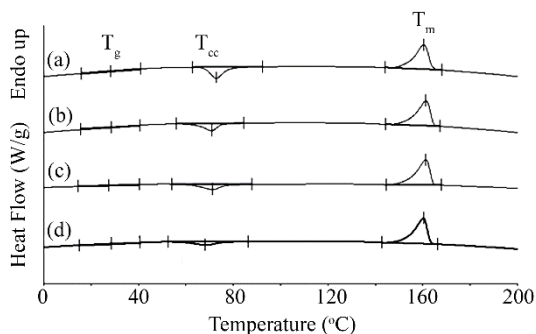

Fig. 2 DSC heating curves of PLLA-PEG-PLLA/BN composites (a) without BN and with BN contents of (b) 1, (c) 2 and (d) 4 wt.%.

The crystallizability of PLLA-PEG-PLLA composites and the effectiveness of nucleating agents was also determined in terms of half crystallization-time ($t_{1/2}$) [25]. Isothermal crystallization of pure PLLA-PEG-PLLA and its composites was observed from DSC exothermic curves as shown in Fig. 3. Sharper isothermal crystallization-peaks were assigned to a shorter time for crystallization [26]. It is clearly found that isothermal crystallization peaks of PLLA-PEG-

PLLA matrices became sharper by addition of the BN.

The $t_{1/2}$ values are also reported in Table 1. The pure PLLA-PEG-PLLA had slow crystallization and its $t_{1/2}$ was 1.8 min. The $t_{1/2}$ of PLLA-PEG-PLLA matrices decreased to 1.0, 0.9 and 0.8 min when 1%, 2% and 4%BN were added, respectively. This confirms that the addition of BN can accelerate crystallization of PLLA end-blocks and BN was an effective nucleating agent for the PLLA-PEG-PLLA corresponding to non-isothermal crystallization results as described above.
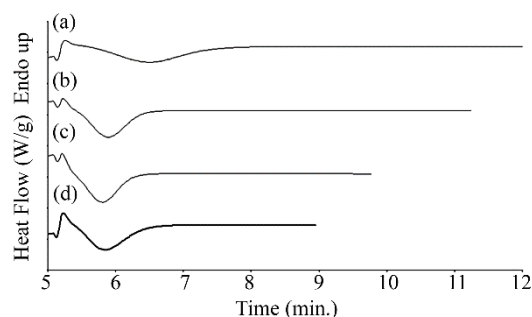

Fig. 3 DSC exothermic curves for the isothermal crystallization temperature at 120°C of PLLA-PEG-PLLA/BN composites (a) without BN and with BN contents of (b) 1, (c) 2 and (d) 4 wt.%.

Table 1 DSC results of PLLA-PEG-PLLA/BN composites

BN (wt.%)	T_g [a] (°C)	T_{cc} [b] (°C)	T_m [c] (°C)	X_c [d] (%)	$t_{1/2}$ [e] (min)
-	28	73	160	23.7	1.8
1	29	71	161	30.3	1.0
2	27	71	161	30.0	0.9
4	28	68	160	35.0	0.8

[a] Glass transition temperature obtained from DSC heating curves in Fig. 2; [b] Cold-crystallization temperature obtained from DSC heating curves in Fig. 2; [c] Melting temperature obtained from DSC heating curves in Fig. 2; [d] Degree of crystallinity calculated from Eq. (1); [e] Half crystallization-time obtained from DSC exothermic curves in Fig. 3

4.2 Thermal Decomposition Behaviors

The thermal-decomposition behavior of composites provides important information on the processing window for melt processing that was investigated from thermogravimetric (TG) curves as reported in Fig. 4.

The TG curves of pure PLLA-PEG-PLLA are shown in Fig. 4 (black line) indicating that it had two thermal-decomposition steps in ranges 250–350°C and 350–450°C assigned to the

"unzipping" mechanism at the chain ends of PLLA and thermal decompositions for PEG blocks, respectively [18, 27]. The addition of BN did not change thermal-decomposition behaviors of PLLA-PEG-PLLA. This indicates BN has poor shielding effect for improving the thermal stability on PLLA-PEG-PLLA. The movement of polymer chains of composites was restricted and gas barrier property was developed for obstructing the diffusion of decomposition products to improve thermal stability of polymer composites [28].

The remaining weights at 1,000˚C for composites without and with BN contents of 1, 2 and 4 wt.% were 0.2%, 1.4%, 2.5% and 4.1%, respectively. Undoubtedly, the remaining weights of composites increases with increasing BN content. This suggested homogeneity of the BN within the composites [14].
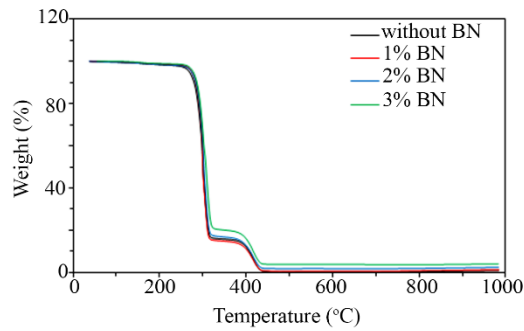

Fig. 4 TG curves of PLLA-PEG-PLLA/BN composites with and without BN.

4.3 Phase morphology

Phase morphology including distribution and dispersion of BN particles in the composite films was observed from SEM images of film cross-sections as shown in Fig. 5. It can be seen that the number of BN particles increased with the BN content. It could be obviously observed that good distribution and dispersion of the BN particles were found for all the composite films corresponding to the TGA results as described above. This suggests that the BN particles were well compatible with PLLA-PEG-PLLA. In addition, there have no voids between dispersed BN particles and PLLA-PEG-PLLA matrix, which suggests that the interfacial between BN and PLLA-PEG-PLLA was stronger than the PLLA/BN composites [28]. The results indicated the PEG middle-blocks enhanced phase compatibility between BN and PLLA end-blocks.

4.4 Tensile Properties

Selected tensile curves of composite films are presented in Fig. 6. The averaged tensile properties are summarized in Table 2. All the PLLA-PEG-

PLLA/BN composite films showed a yield point indicating that they were flexible. This can be explained by the flexible PEG middle-blocks enhanced flexibility of PLLA-PEG-PLLA/BN composite films [6, 7].
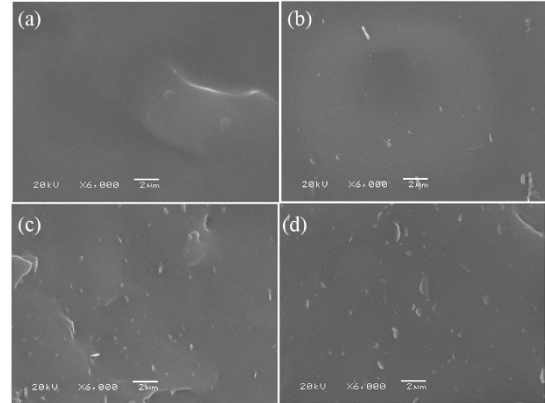

Fig. 5 SEM images of cryo-fractured cross-sections of PLLA-PEG-PLLA/BN composite films (a) without BN and with BN contents of (b) 1, (c) 2 and (d) 4 wt.%. All bar scales = 2 μm.
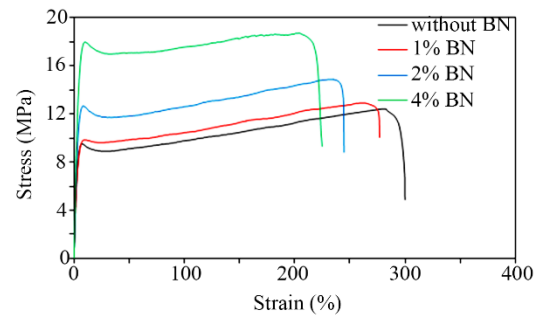

Fig. 6 Tensile curves of PLLA-PEG-PLLA/BN composite films with and without BN.

Table 2 Tensile properties of PLLA-PEG-PLLA/BN composited films

BN (wt.%)	σ [a] (MPa)	ε [b] (%)	E [c] (MPa)
-	10.1 ± 1.9	288 ± 11	132 ± 18
1	12.9 ± 1.4	277 ± 15	163 ± 25
2	14.9 ± 2.6	245 ± 12	182 ± 15
4	18.7 ± 3.4	225 ± 27	252 ± 23

[a] Ultimate tensile stress; [b] Strain at break; [c] Young's modulus.

The ultimate tensile stress, strain at break and Young's modulus of pure PLLA-PEG-PLLA film were 10.1 MPa, 288% and 132 MPa, respectively. It was found that the ultimate tensile stress and Young's modulus of the composite films increased while strain at break decreased steadily when the BN content was increased. The increase in the

tensile stress of PLLA-PEG-PLLA/BN composite films shows an effective interaction between PLLA-PEG-PLLA and BN. The results indicated the BN particles induced a reinforcing effect on PLLA-PEG-PLLA films similar to that in PLLA films [14].

It should be noted that the ultimate tensile stress of composite films did not drop when the BN content was higher than 2 wt.%. This can be explained by good distribution and dispersion of BN particles in the PLLA-PEG-PLLA matrices as previous described from SEM analysis. The results suggested that the interfacial adhesion on PLLA-PEG-PLLA/BN composites was strong enough to enhance stress transfer from the PLLA-PEG-PLLA matrix to the BN particle surfaces to improve the stress at break and Young's modulus of these composite films [14]. This indicates the BN acted as an effective reinforcing filler for PLLA-PEG-PLLA.

However, from results of tensile properties, all the PLLA-PEG-PLLA/BN composite films were still more extensible than the pure PLLA films (5−10% strain at break) [7].

5. CONCLUSIONS

PLLA-PEG-PLLA/BN composite films have been successfully prepared by melt blending following compression molding. The effect of BN content on the thermal, morphological and mechanical properties of composites was investigated. DSC study indicated that the addition of BN enhanced PLLA crystallization. The %X_c of PLLA-PEG-PLLA increased significantly with increasing BN content. Good phase compatibility between the PLLA-PEG-PLLA matrix and BN filler was found as observed from SEM images. Tensile properties of the composite films indicated that the ultimate tensile stress significantly increased with increasing BN content. It was concluded that the crystallizability and mechanical properties of PLLA-PEG-PLLA can be improved by BN blending. Thus, the PLLA-PEG-PLLA/BN composites could be appropriate for use as highly flexible bioplastics in packaging applications.

6. ACKNOWLEDGEMENTS

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