

# Investigations on Novel Ternary Green Polymer Composite

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## *Abstract:*

In this study, the novel ternary green polymer composites of poly(l-lactic acid) (PLLA)/poly(ethylene adipate)/hexagonal boron nitride (PLLA/PEA/h-BN) were synthesized and prepared. The crystallization rate of the biodegradable polymer PLLA in the composite was significantly increased with the addition of PEA and functional h-BN. In ternary PLLA/PEA/h-BN composites, PEA can be used as a plasticizer, while h-BN is a functional nucleation agent for PLLA. The analysis of the isothermal crystallization kinetics by the Avrami equation shows that the rate constant  $k$  of the ternary PLLA/PEA/h-BN composite represents the highest value, indicating the highest crystallization in the ternary composite. Adding h-BN in the composite can further increase the  $k$  value and increase the crystallization rate. Polarized optical microscopy (POM) images reveal that h-BN is an effective nucleation agent that increases the nucleation density of composites. Analysis of wide-angle X-ray diffraction (WAXD) further confirmed that the crystalline structures of PLLA were unchanged by the addition of PEA and h-BN. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that the h-BN particles are uniformly distributed in the composite. The distribution of h-BN having a particle size of a few hundred nm causes an effective nucleation effect and promotes the crystallization of the ternary composites.

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Communication

# Investigations on Novel Ternary Green Polymer Composite

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**Abstract:** In this study, the novel ternary green polymer composites of poly(L-lactic acid) (PLLA)/poly(ethylene adipate)/hexagonal boron nitride (PLLA/PEA/h-BN) were synthesized and prepared. The crystallization rate of the biodegradable polymer PLLA in the composite was significantly increased with the addition of PEA and functional h-BN. In ternary PLLA/PEA/h-BN composites, PEA can be used as a plasticizer, while h-BN is a functional nucleation agent for PLLA. The analysis of the isothermal crystallization kinetics by the Avrami equation shows that the rate constant  $k$  of the ternary PLLA/PEA/h-BN composite represents the highest value, indicating the highest crystallization in the ternary composite. Adding h-BN in the composite can further increase the  $k$  value and increase the crystallization rate. Polarized optical microscopy (POM) images reveal that h-BN is an effective nucleation agent that increases the nucleation density of composites. Analysis of wide-angle X-ray diffraction (WAXD) further confirmed that the crystalline structures of PLLA were unchanged by the addition of PEA and h-BN. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that the h-BN particles are uniformly distributed in the composite. The distribution of h-BN having a particle size of a few hundred nm causes an effective nucleation effect and promotes the crystallization of the ternary composites.

**Keywords:** biodegradable polymers; ternary composites; poly(L-lactic acid); hexagonal boron nitride; crystallization behavior

## 1. Introduction

Aliphatic polyesters represent an important family of green and biodegradable polymers. Poly(L-lactic acid) (PLLA) is one of the most promising materials of this family, due to its biocompatibility, biodegradability and renewability [1–3]. PLLA is a thermoplastic polymer with many excellent properties, such as having high strength, high modulus, low toxicity and transparency. The wide range of applications for PLLA includes biomedicine [4], packaging and textile industry [5] and agriculture [6]. However, the low crystallization rate and inherent brittleness of PLLA limits its application [7,8].

Generally, the crystallization process of a polymer is closely related to its physical properties. In order to increase the crystallization rate of the polymer, it is very useful to add a plasticizer or a nucleation agent. The plasticizer may increase the mobility of polymer chains to accelerate the crystallization rate of the polymer [9,10]. Conversely, the nucleating agent can add more nucleation sites, which can promote the nucleation and crystallization rate of the polymer [11–13].

Poly(ethylene glycol adipate) (PEA) is an aliphatic polyester and can be biodegraded in the natural environment due to its biodegradability. Okamoto et al. [14] have reported that PEA is a plasticizer for PLLA. The miscibility of PLLA/PEA blend was confirmed by the single glass transition temperature, and the ductility of PLLA was improved by the addition of PEA [14]. Adding the general nucleation agents such as silica [15], montmorillonite [16], magnesium oxide whisker [17] and

cellulose nanocrystal [18] can promote the crystallization behaviors of PLLA and its related composites. For example, cellulose nanocrystal can be used as a nucleation agent to promote the crystallization behavior of PLLA plasticized by a biodegradable polymer [18]. However, the application of functional nucleation agents to accelerate the crystallization rate of PLLA related composites is also an important issue. Unlike general nucleation agents, hexagonal boron nitride (h-BN) exhibits specific structural features similar to those of graphite and graphene. Moreover, h-BN is a functional material with high thermal and chemical stability and excellent thermal conductivity [19]. In terms of being used as a nucleation agent for biodegradable polymers, Puente et al. [20] have found that the addition of h-BN to poly(3-hydroxybutyrate) (PHB) can introduce an effective nucleation effect, thereby increasing the crystallization rate of PHB. Sijla Rosely et al. [21,22] have also discussed the influence of BN on the properties of PLLA.

Crystallization of PLLA is critical in the processing of PLLA and can be closely related to the physical properties of PLLA. In this work, the study of the ternary PLLA/PEA/h-BN green polymer composite was presented. PEA may plasticize the polymer chain of PLLA. In addition, functional h-BN may create more nucleating sites to further promote the crystallization rate of PLLA. The crystallization kinetics, morphologies and crystalline structures of PLLA/PEA/h-BN composites were discovered in this study. The synthesized PLLA/PEA/h-BN composites could be the potential candidates for the applications of biodegradable plastics, packaging materials and the filaments of 3D-printing. The effective nucleation effect of h-BN in the ternary composite is highlighted.

## 2. Materials and Methods

### 2.1. Materials and Preparation

PLLA ( $M_w = 260,000$  g/mol), PEA ( $M_w = 10,000$  g/mol) and h-BN (average particle size 150 nm) were purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA). The PLLA/PEA blend and the PLLA/PEA/h-BN composites were prepared by solution casting using chloroform as a solvent at a concentration of about 3 wt%. To improve the dispersion of h-BN in solution, sonification treatment (30 min) was adopted prior to the final casting process. Film casting was carried out by evaporating the solvent at 45 °C and then vacuum drying for at least 4 days at 60 °C. The reminders for the sample preparation are provided in the Supplementary Materials.

### 2.2. Studies of Thermal and Crystallization Behaviors

The crystallization behaviors of the composites were investigated using Perkin-Elmer differential scanning calorimetry (DSC) (Perkin-Elmer DSC-8500, Perkin Elmer, Waltham, MA, USA). For isothermal crystallization, the samples were heated to 200 °C for 5 min to eliminate any thermal history and then quenched to 110 °C to record the isothermal crystallization process.

### 2.3. Morphological Observations and Characterizations

The spherulite morphologies were observed using an Olympus polarizing optical microscope (POM) (Olympus CX41, Olympus, Tokyo, Japan) equipped with a Linkam THMS-600 hot stage. The specimens were isothermally crystallized at 110 °C before observation. The dispersion and morphology of h-BN in composites were identified by scanning electron microscopy (SEM, Hitachi S3000, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-1400, JEOL, Peabody, MA, USA). All SEM samples were coated with gold to increase conductivity. TEM samples were fabricated by casting PLLA/PEA/h-BN solutions onto a copper grid.

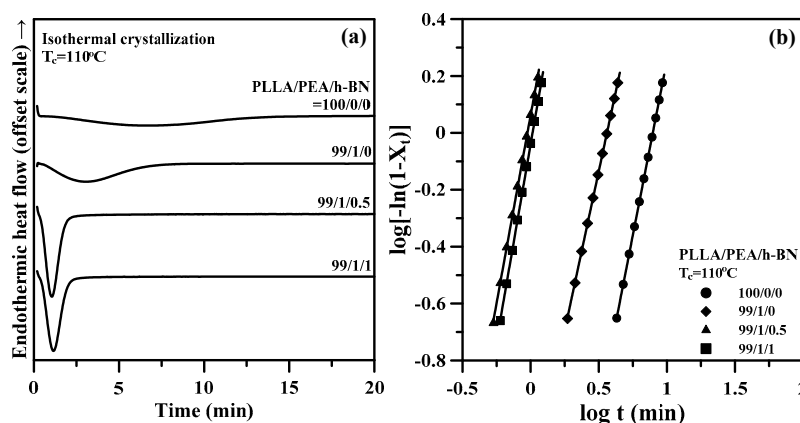
### 2.4. Discussions on Crystalline Structures

The crystalline structures of the composites were analyzed by wide-angle X-ray diffraction (WAXD) (Bruker D2 PHASER, Bruker, Billerica, MA, USA) with copper  $\alpha$  radiation (30 kV and 10 mA). All samples were isothermally crystallized at 110 °C and scanned at a step speed of 5°/min in the  $2\theta$  range of 5° to 50°.

### 3. Results

We preliminarily confirmed the miscibility of the PLLA/PEA = 99/1 blend. The relevant results are demonstrated in Figure S1 in the Supplementary Materials. For the PLLA/PEA = 99/1 blend, only one  $T_g$  (55.8 °C) is shown, indicating the miscibility of the blend. Moreover, the  $T_g$  of the PLLA/PEA = 99/1 blend is lower than that of the neat PLLA (60.3 °C). This result suggests the plasticizer effect of PEA is present in the blend and the chains of PLLA are plasticized by PEA.

The isothermal crystallization results from the neat PLLA to ternary PLLA/PEA/h-BN composites are presented in Figure 1a at the crystallization temperature ( $T_c$ ) of 110 °C. Typical results for the neat PLLA, PLLA/PEA = 99/1 binary blend, and PLLA/PEA/h-BN = 99/1/0.5 and 99/1/1 ternary composites are displayed. It shows that the peak value of crystallization time from neat PLLA to ternary PLLA/PEA/h-BN composite is gradually shortened. The PLLA/PEA/h-BN = 99/1/0.5 composite shows the shortest peak value of crystallization time. The relevant results indicate that the addition of PEA can first cause a plasticizer effect to promote crystallization, and the addition of h-BN can further lead to a nucleation effect to accelerate crystallization. The isothermal crystallization behavior of the composites was further analyzed by the conventional Avrami equation. The detailed description and related analysis of the Avrami equation are shown in the Supplementary Materials. Figure 1b displays the Avrami plots from neat PLLA to ternary PLLA/PEA/h-BN composites. It demonstrates the linear fit of all samples studied in this work, representing that the Avrami equation can describe isothermal crystallization kinetics. The relevant kinetic parameters estimated by the fitting results of the Avrami equation are summarized in Table 1. It shows that the  $n$  values of neat PLLA, PLLA/PEA blend and PLLA/PEA/h-BN composites are between 2 and 3, suggesting that the addition of PEA and h-BN does not significantly change the isothermal crystallization mechanism of PLLA. Regarding the values of the rate constant ( $k$ ) and the reciprocal of the crystallization half-life ( $1/t_{0.5}$ ), they first increase with the addition of PEA and increase again with the incorporation of h-BN. The addition of h-BN in the composite can further increase the crystallization rate. The largest  $k$  (1.153) and  $1/t_{0.5}$  (1.213) appear on the ternary composite of PLLA/PEA/h-BN = 99/1/0.5. It should also be noted that the additional loading of the nucleation agent of h-BN will slow down the acceleration of crystallization. This may indicate that excess h-BN can retard crystal growth at the crystallization front.

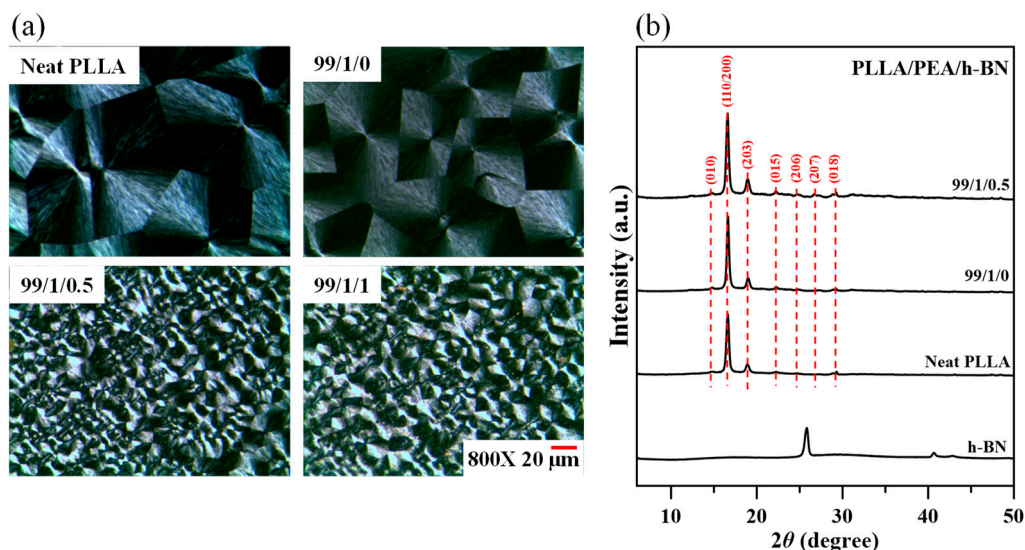


**Figure 1.** (a) Differential scanning calorimetry (DSC) traces at an isothermal crystallization temperature of 110 °C; (b) The Avrami plots of neat poly(L-lactic acid) (PLLA), PLLA/poly(ethylene adipate) (PEA) blend, and PLLA/PEA/hexagonal boron nitride (h-BN) composites.

**Table 1.** The isothermal crystallization kinetics parameters from Avrami equation.

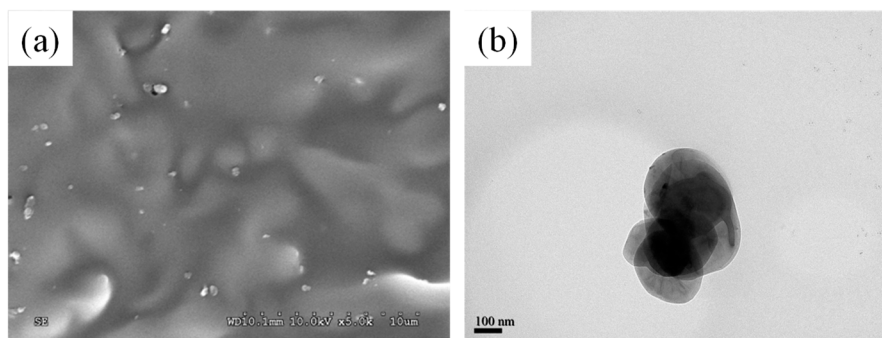
PLLA/PEA/h-BN (Relative Weight Ratio)	T <sub>c</sub> (°C)	n	K (min <sup>-n</sup> )	t <sub>0.5</sub> (min)	1/t <sub>0.5</sub> (min <sup>-1</sup> )
100/0/0	110	2.46	6.268 × 10 <sup>-3</sup>	6.79	0.147
99/1/0	110	2.24	5.56 × 10 <sup>-2</sup>	3.08	0.324
99/1/0.5	110	2.64	1.153	0.82	1.213
99/1/1	110	2.78	9.137 × 10 <sup>-1</sup>	0.91	1.105

Figure 2a presents the POM images of neat PLLA and PLLA/PEA/h-BN composites crystallized at 110 °C. It is apparent that the amount and size of spherulites increase and decrease, respectively, with the addition of h-BN. By adding h-BN, the ternary composites have a higher nuclei density than neat PLLA. The h-BN in the composite provides sufficient sites for the crystallization of PLLA to drive and promote the crystallization. Figure 2b displays the WAXD results. Under the current experimental condition of WAXD, it presents diffraction peaks at  $2\theta = 14.7^\circ, 16.6^\circ, 18.9^\circ, 22.4^\circ, 24.5^\circ, 27.1^\circ$  and  $28.8^\circ$  caused by the reflection planes of (010), (110/200), (203), (015), (206), (207) and (018), respectively [23,24]. The two diffraction peaks at  $16.6^\circ$  and  $18.9^\circ$  show relatively strong intensity. All diffraction patterns of the composites are identical to that of neat PLLA, indicating that the crystalline structures of PLLA are not altered by the addition of PEA and h-BN.



**Figure 2.** (a) Polarized optical microscopy (POM) images of neat PLLA and PLLA/PEA/h-BN composites crystallized at 110 °C; (b) Wide-angle X-ray diffraction (WAXD) results of neat PLLA and PLLA/PEA/h-BN composites crystallized at 110 °C.

Figure 3a reveals the SEM image for the ternary PLLA/PEA/h-BN = 99/1/0.5 composite. The image shows that h-BN particles are uniformly distributed in the composite without significant aggregation. TEM was also used to confirm the morphology of the composites for higher resolution. Figure 3b displays the TEM image of the ternary PLLA/PEA/h-BN = 99/1/0.5 composite. Obviously, the h-BN particles in the composite exhibit a lateral dimension <600 nm at submicron scale. The fine distribution of h-BN causes an effective nucleation effect to further accelerate the crystallization of the composites.



**Figure 3.** (a) Scanning electron microscopy (SEM); (b) Transmission electron microscopy (TEM) image of PLLA/PEA/h-BN = 99/1/0.5 composite.

#### 4. Conclusions

The novel green polymer composites of PLLA/PEA/h-BN were synthesized and investigated in this study. Adding PEA can increase the crystallization rate of PLLA. Moreover, the incorporation of h-BN to form the ternary composite can further promote the crystallization rate. The results of kinetic analyses indicate that the ternary PLLA/PEA/h-BN composite reveals the highest crystallization rate. The POM images show that by adding h-BN, the ternary composites have a higher nucleation density than neat PLLA. The WAXD results confirmed that the crystal structures of PLLA did not change with the incorporation of PEA and h-BN. SEM and high resolution TEM demonstrate that h-BN particles are uniformly distributed in the composite at a particle size of a few hundred nm, which leads to an effective nucleation effect on the crystallization of PLLA.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2227-9717/8/1/31/s1>, Figure S1: DSC thermograms of neat PLLA and PLLA/PEA = 99/1 blend.

**Author Contributions:** T.-C.H. and X.-Y.W. were responsible for performing the experiments and data analysis. L.-T.L. was responsible for developing the research outline, designing the experiments, and writing most of the paper. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Singh, N.K.; Singh, S.K.; Dash, D.; Gonugunta, P.; Misra, M.; Maiti, P. CNT Induced  $\beta$ -phase in polylactide: Unique crystallization, biodegradation, and biocompatibility. *J. Phys. Chem. C* **2013**, *117*, 10163–10174. [CrossRef]
2. Ni'mah, H.; Woo, E.M. A novel hexagonal crystal with a hexagonal star-shaped central core in poly(L-lactide) (PLLA) induced by an ionic liquid. *Crystengcomm* **2014**, *16*, 4945–4949. [CrossRef]
3. Hughes, A.; Tai, H.; Tochwin, A.; Wang, W. Biodegradable and biocompatible P<sub>DL</sub>LA-PEG<sub>1k</sub>-P<sub>DL</sub>LA diacrylate macromers: Synthesis, characterisation and preparation of soluble hyperbranched polymers and crosslinked hydrogels. *Processes* **2017**, *5*, 18. [CrossRef]
4. Pawar, R.P.; Tekale, S.U.; Shisodia, S.U.; Totre, J.T.; Domb, A.J. Biomedical applications of poly(lactic acid). *Recent Pat. Regen. Med.* **2014**, *4*, 40–51. [CrossRef]
5. Vink, E.T.H.; Rábago, K.R.; Glassner, D.A.; Springs, B.; O'Connor, R.P.; Kolstad, J.; Gruber, P.R. The sustainability of NatureWorks™ polylactide polymers and Ingeo™ polylactide fibers: An update of the future. *Macromol. Biosci.* **2004**, *4*, 551–564. [CrossRef] [PubMed]
6. Czekalski, J.; Krucińska, I.; Kowalska, S.; Puchalski, M. Effect of twist stabilisation and dyeing on the structural and physical properties of agricultural strings. *Fibres Text. East. Eur.* **2013**, *21*, 39–44.

7. Xiang, S.; Feng, L.; Bian, X.; Zhang, B.; Sun, B.; Liu, Y.; Li, G.; Chen, X. Toughening modification of PLLA with PCL in the presence of PCL-*b*-PLLA diblock copolymers as compatibilizer. *Polym. Adv. Technol.* **2019**, *30*, 963–972. [[CrossRef](#)]
8. Zaldua, N.; Mugica, A.; Zubitur, M.; Iturrospe, A.; Arbe, A.; Re, G.L.; Raquez, J.M.; Dubois, P.; Müller, A.J. The role of PLLA-g-montmorillonite nanohybrids in the acceleration of the crystallization rate of a commercial PLA. *Crystengcomm* **2016**, *18*, 9334–9344. [[CrossRef](#)]
9. Singh, S.; Maspoche, M.L.; Oksman, K. Crystallization of triethyl-citrate-plasticized poly(lactic acid) induced by chitin nanocrystals. *J. Appl. Polym. Sci.* **2019**, *136*, 47936. [[CrossRef](#)]
10. Kodal, M.; Sirin, H.; Ozkoc, G. Non-isothermal crystallization kinetics of PEG plasticized PLA/G-POSS nanocomposites. *Polym. Compos.* **2017**, *38*, 1378–1389. [[CrossRef](#)]
11. Chen, P.Y.; Lian, H.Y.; Shih, Y.F.; Chen Wei, S.M.; Jeng, R.J. Preparation, characterization and crystallization kinetics of Kenaf fiber/multi-walled carbon nanotube/poly(lactic acid) (PLA) green composites. *Mater. Chem. Phys.* **2017**, *196*, 249–255. [[CrossRef](#)]
12. Chen, J.; Xu, C.; Wu, D.; Pan, K.; Qian, A.; Sha, Y.; Wang, L.; Tong, W. Insights into the nucleation role of cellulose crystals during crystallization of poly( $\beta$ -hydroxybutyrate). *Carbohydr. Polym.* **2015**, *134*, 508–515. [[CrossRef](#)] [[PubMed](#)]
13. Lee, L.-T.; Hsu, C.-Y.; Hung, S.-P. Promoted crystallization kinetics of biodegradable poly(butylene succinate) by a nucleation agent of green chemical. *J. Polym. Res.* **2019**, *26*, 255. [[CrossRef](#)]
14. Okamoto, K.; Ichikawa, T.; Yokohara, T.; Yamaguchi, M. Miscibility, mechanical and thermal properties of poly(lactic acid)/polyester-diol blends. *Eur. Polym. J.* **2009**, *45*, 2304–2312. [[CrossRef](#)]
15. Wu, J.H.; Yen, M.S.; Kuo, M.C.; Chen, B.H. Physical properties and crystallization behavior of silica particulates reinforced poly(lactic acid) composites. *Mater. Chem. Phys.* **2013**, *142*, 726–733. [[CrossRef](#)]
16. Wu, T.; Tong, Y.; Qiu, F.; Yuan, D.; Zhang, G.; Qu, J. Morphology, rheology property, and crystallization behavior of PLLA/OMMT nanocomposites prepared by an innovative eccentric rotor extruder. *Polym. Adv. Technol.* **2018**, *29*, 41–51. [[CrossRef](#)]
17. Zhao, Y.; Liu, B.; You, C.; Chen, M. Effects of MgO whiskers on mechanical properties and crystallization behavior of PLLA/MgO composites. *Mater. Des.* **2016**, *89*, 573–581. [[CrossRef](#)]
18. Li, J.; Qiu, Z. Significantly enhanced crystallization of poly(L-lactide) by the synergistic effect of poly(diethylene glycol adipate) and cellulose nanocrystals in their fully biodegradable ternary composite. *Ind. Eng. Chem. Res.* **2019**, *58*, 15526–15532. [[CrossRef](#)]
19. Liu, Q.; Hu, C.; Wang, X. One-pot solvothermal synthesis of water-soluble boron nitride nanosheets and fluorescent boron nitride quantum dots. *Mater. Lett.* **2019**, *234*, 306–310. [[CrossRef](#)]
20. Puente, J.A.S.; Esposito, A.; Chivrac, F.; Dargent, E. Effect of boron nitride as a nucleating agent on the crystallization of bacterial poly(3-hydroxybutyrate). *J. Appl. Polym. Sci.* **2013**, *128*, 2586–2594. [[CrossRef](#)]
21. Sijla Rosely, C.V.; Shaiju, P.; Bhoje Gowd, E. Poly(L-lactic acid)/boron nitride nanocomposites: Influence of boron nitride functionalization on the properties of poly(L-lactic acid). *J. Phys. Chem. B* **2019**, *123*, 8599–8606. [[CrossRef](#)] [[PubMed](#)]
22. Sijla Rosely, C.V.; Nagendra, B.; Sivaprasad, V.P.; Bhoje Gowd, E. Influence of boron nitride nanosheets on the crystallization and polymorphism of poly(L-lactide). *J. Phys. Chem. B* **2018**, *122*, 6442–6451. [[CrossRef](#)] [[PubMed](#)]
23. Pan, P.; Zhu, B.; Kai, W.; Dong, T.; Inoue, Y. Polymorphic transition in disordered poly(L-lactide) crystals induced by annealing at elevated temperatures. *Macromolecules* **2008**, *41*, 4296–4304. [[CrossRef](#)]
24. Li, F.J.; Zhang, S.D.; Liang, J.Z.; Wang, J.Z. Effect of polyethylene glycol on the crystallization and impact properties of polylactide-based blends. *Polym. Adv. Technol.* **2015**, *26*, 465–475. [[CrossRef](#)]

