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Research article

Dual effect of wood fiber as bio-nucleating agent and reinforcement material in wood fiber/poly(lactic acid) composites

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Abstract. Biodegradable plastics such as poly(lactic acid) (PLA) are gaining considerable interest as promising substitutes for conventional petroleum-based plastics due to ecological, health, and environmental concerns. PLA possesses good biodegradability and biocompatibility but is limited by its slow crystallization rate, low impact resistance, and high costs. In this study, a small amount of natural wood fiber (WF) was incorporated into PLA to improve mechanical and crystallization properties as well as cost reduction. The effects of WF size (20–40, 80–100, and 140–160 mesh) and loading content (0.5–8 wt%) on the mechanical and crystallization properties were investigated and compared. Results indicated that WF of 80–100 mesh (WF₈₀₋₁₀₀) exhibited a better reinforcement effect on PLA than the other two sizes of WF. The optimal loading content for WF₈₀₋₁₀₀ was 1 wt%, at which the flexural and tensile strength increased by about 18% compared to neat PLA, and the elongation at break increased by 27%. Moreover, the degree of crystallinity and crystallization rate significantly increased in 1WF₈₀₋₁₀₀/PLA composite and the spherulite size decreased compared to neat PLA. These findings confirmed that WF, even at a low addition level, could act as both a reinforcement material and an efficient nucleating agent for PLA, which is closely related to its size.

Keywords: biocomposites, mechanical properties, reinforcements, poly(lactic acid), bio-nucleating agent

1. Introduction

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In recent years, the disposal of plastic waste has become a serious environmental issue. Biodegradable plastics from renewable resources have been receiving increasing attention as potential alternatives to petroleum-based plastics [1]. Poly(lactic acid) (PLA) is a fully bio-based and bio-degradable plastic produced completely from renewable resources and can be degraded into carbon dioxide and water without any pollution. It shows great superiority in the aspect of biodegradability, biocompatibility, and processability, which makes it a promising alternative to traditional petroleum-based polymers in fields of medical, packaging, cutleries, etc. [2, 3].

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However, PLA is limited by its low crystallization rate, brittleness, and high production price for specific fields of applications [4, 5]. Also, PLA has a lower crystallization rate as compared to conventional synthetic plastics such as polypropylene and polyethylene, which requires longer molding cycle time and leads to low productivity [6, 7]. Another major drawback of PLA is its poor toughness, with low elongation at break and relatively poor impact strength, thereby limiting its applications as films, fiber or biomedical materials that require plastic deformation [8, 9].

Various strategies, including blending with other polymers, adding nucleating agents, incorporating fillers, compounding with plasticizers, and copolymerizing chemicals, have been investigated to overcome the aforementioned drawbacks of PLA [10–12]. Among all these technologies, adding a nucleating agent is a simple but effective method to facilitate the crystallization process and improve crystallization temperature during cooling [6]. Nucleating agents could increase the number of primary nucleation sites and accelerate nucleation by reducing the surface free energy nuclei barrier [13]. The common nucleating agents used in PLA mainly include mineral, organic, bio-based, and stereocomplex categories. Previous studies have identified some effective nucleating agents for PLA, such as talc [14], calcium carbonate [15, 16], and silica [17]. The nucleation effect largely depends on the properties of the nucleating agent including types, particle size, geometry, and dispersion in the matrix [18, 19]. Recently, introducing bio-based nucleating agents have attracted more interest owing to preserving the green properties of PLA, which is attractive for broadening the utilization of PLA for biodegradable product development. For instance, starch [20], cellulose [4], and lignin [21] have been evaluated as heterogeneous nucleating agents to improve the crystallization rate of PLA. Wood filler (wood flour and fiber) is also a promising natural bio-nucleating agent for PLA. It was found that the addition of 4 wt% wood flour increased the nucleation density of PLA and reduced half-crystallization time [22].

As the most widely known and used natural filler, wood filler has raised a lot of interest in recent years, and its composite with other polymers is extensively investigated. Many researchers have investigated the use of wood filler as reinforcement of PLA due to its low cost, easy availability, and bio-based nature [23]. In these studies, a high amount of wood filler was often incorporated into PLA for the purpose of cost reduction and achieving a balance between sustainability and performance. Previous studies on wood filler/PLA composites show differences in their mechanical properties. Huda et al. [24] found that the incorporation of 20 wt% wood fiber (WF) into PLA resulted in a considerable increase in the tensile strength and modulus but a decrease in notched Izod impact strength.Dobrzyńska-Mizera et al. [25] prepared PLA-based composites with WF content of 30 wt% and found that the tensile strength was decreased while Young's modulus was improved. Petinakis *et al.* [26] found that the addition of up to 40 wt% wood flour into PLA caused a significant decrease in break elongation. Generally, under the same manufacturing parameters, the effect of wood filler on the physical and mechanical properties of PLA depends largely on the nature of wood filler, such as the size and distribution of wood particles, wood filler species, and contents [27]. For instance, wood fiber provides higher plastic reinforcement than wood flour [19]. Moreover, a high amount of fillers cause difficulties in fabrication and may not generate a significant reinforcement effect.

A review of the literature shows that the comparative studies of the PLA-based composites containing different sizes of WF are very limited. Moreover, few studies pay attention to the effect of a small amount of WF as a reinforcement and bio-nucleating agent for PLA. Therefore, the aim of this study was to systematically evaluate the role of a small amount of WF with different sizes and contents in WF/PLA composites. Herein, poplar WF was sieved into three distinct size grades and respectively compounded with PLA. The mechanical properties of PLA composites with three sizes of WF were comparatively studied, and the optimal WF size was determined. After that, a small amount of WF with the selected size was incorporated with PLA to prepare WF/PLA composites. The crystallization behavior, crystalline morphology, and structure of WF/PLA composites with different WF contents were further investigated. This work indicates that WF at appropriate size and content plays the role of both reinforcement material and nucleating agent for PLA, which promotes producing completely biodegradable PLA-based composite and broadening application fields of PLA.

2. Experimental 2.1. Materials

Extrusion grade PLA 2002D, Natureworks, Minnesota, USA) was used as the polymer matrix. It's comprised of 4% D-lactic, and its melt flow index is 4–8 g/10 min (210 °C, 2.16 kg). Poplar (*Populus tomentosa* Carr.) WF was provided by Yongdeshun mineral processing factory (Hebei Province, China). The WF was sieved to three sizes: 20–40 mesh (WF₂₀₋₄₀), 80–100 mesh (WF₈₀₋₁₀₀), and 140–160 mesh (WF₁₄₀₋₁₆₀) by using an automatic vibratory sieve shaker (JEL 200, Engelsmann, Ludwigshafen, Germany).

2.2. Preparation of WF/PLA composites with varying WF sizes

After drying in an oven at 103 °C for 6–8 h, 1 wt% WF of each size was mixed with PLA in a high-speed mixer. Then the mixture was extruded using a single-screw extruder (SJ35, Orodes machinery Co. Ltd, Zhangjiagang, China) and crushed into about 4 mm long granules. The extrusion temperature was 180 °C, and the screw speed was 20 rpm. Then the pellets were molded using a hydraulic press (type 3889, Carver Inc., USA) at 190 °C with a pressure of 4 MPa for 5 min. After that, the samples were cold pressed at 6 MPa for another 5 min at room temperature to obtain WF/PLA composites (1WF₂₀₋₄₀/PLA, 1WF₈₀₋₁₀₀/PLA, and 1WF₁₄₀₋₁₆₀/PLA).

2.3. Preparation of WF/PLA composites with varying WF contents

According to our preliminary experiment results, WF_{80-100} was selected to explore the optimum WF content for reinforcing and nucleating PLA. Subsequently, 0.5, 1, 2, 4, and 8 wt% of WF_{80-100} were compounded with PLA for preparing 0.5 WF_{80-100} /PLA, $1WF_{80-100}$ /PLA, $2WF_{80-100}$ /PLA, $4WF_{80-100}$ /PLA, and $8WF_{80-100}$ /PLA, $2WF_{80-100}$ /PLA, $4WF_{80-100}$ /PLA, and $8WF_{80-100}$ /PLA composites, respectively. WF/PLA composites containing 0.5–8.0 wt% WF₈₀₋₁₀₀ were mixed, extruded, crushed, and molded using the same procedures as mentioned above. Figure 1 shows the process of preparing WF_{80-100} /PLA composites containing varying contents of WF_{80-100} .

2.4. WF morphology and size distribution

The microscopic morphology of WF_{20-40} , WF_{80-100} , and $WF_{140-160}$ was observed by optical microscope (BX53, Olympus, Japan). The length and diameter distributions of WF_{20-40} and WF_{80-100} were measured by an optical lab fiber screen analyzer (FIBERCAM 100, IMAL-PAL Group, Italy). The wood fibers were separated using compressed air and imaged by a digital camera, and the length and diameter of individual fibers were measured. Approximately 100 000 fibers were evaluated for each size of WF. This method was inapplicable for fibers below 1 mm. Therefore, the size distribution of $WF_{140-160}$ was determined by a laser diffraction particle size analyzer (Mastersizer 2000, Malvern Panalytical, UK). The surface of WF/PLA composites containing different sizes of WF was observed by an optical microscope to investigate the distribution of WF in the PLA matrix.

2.5. Scanning electron microscopy (SEM)

The fracture surface of the WF/PLA composites after impact tests was gold sputter-coated and observed using a field emission scanning electron microscopy (Gemini 300, ZEISS, UK) with an accelerating voltage 3 kV. The overall morphology of the composites and the interaction of WF with PLA was investigated.

2.6. Mechanical properties

Izod notched impact strength was measured using a HIT50P pendulum impact tester (Zwick/Roell, German) referred to ISO 180:2000. The 80×10×4 mm standard specimens were notched for impact tests. The flexural properties of samples were tested on a 5582 Universal mechanical testing machine (Instron, USA) for three-point bending at a 2 mm/min loading rate referred to ISO 178:2001. The standard specimens of 80×10×4 mm dimensions were placed between two supports at a distance of 64 mm for the flexural test. Tensile properties were tested on a 5582 Universal mechanical testing machine (Instron, USA) at a crosshead speed of 5 mm/min, referred to ISO 527:2012. Samples for tensile tests were molded into dog-bone-shaped specimens with a thickness of 4 mm. Tensile properties including elongation at break, tensile strength, and modulus, were measured. All presented results are the average values of ten measurements.



Figure 1. Process of preparing WF₈₀₋₁₀₀/PLA composites containing varying contents of WF₈₀₋₁₀₀.

2.7. Differential scanning calorimetry (DSC)

The melting and crystallization behavior of the samples were performed on a DSC apparatus (DSC8000, PerkinElmer, USA) under a nitrogen atmosphere. Fragment-shaped samples of 5–6 mg were cut from neat PLA and WF/PLA composite films and placed into sealed aluminum pans with lids. For non-isothermal crystallization, samples were firstly heated to 200 °C at a heating rate of 20 °C/min and held for 5 min to eliminate thermal history. Then samples were cooled to 30 °C at a cooling rate of 10 °C/min and reheated to 200 °C at a heating rate of 10 °C/min. In the analysis of isothermal crystallization, the sample was heated from room temperature to 200 °C at a heating rate of 20 °C/min and held for 5 min to eliminate thermal history. Then it was rapidly cooled to 120, 110, and 100 °C at a cooling rate of 50 °C/min and held at this temperature until crystallization was completed, respectively. After that, the samples were reheated to 200 °C at a heating rate of 10 °C/min. The degree of crystallinity (X_c) was calculated according to Equation (1) [14]:

$$X_{\rm c} = \frac{\Delta H_{\rm m} - \Delta H_{\rm cc}}{f \cdot \Delta H_{\rm m}^0} \cdot 100\% \tag{1}$$

where $\Delta H_{\rm m}$ and $\Delta H_{\rm cc}$ are the melting enthalpy and cold crystallization enthalpy of the samples, respectively. $\Delta H_{\rm m}^0$ is the standard melting enthalpy of 100% crystalline PLA, which value is 93.6 J/g [14]. *f* is the weight fraction of PLA in the WF/PLA composite.

2.8. Polarized optical microscope (POM)

Crystalline morphology of PLA and WF/PLA composite were observed by a polarized optical microscope (BX53, Olympus, Japan) equipped with a hot stage. The samples were firstly pressed into films of about 20 μ m thickness. Then each film was put into between two cover glasses and placed in the hot stage. The sample was first heated to 200 °C at a heating rate of 20 °C/min and maintained for 5 min, then cooled to 110 °C at a rate of 50 °C/min and maintained at this temperature until the crystallization was completed. Images were taken automatically by a digital camera during the isothermal crystallization process.

2.9. Wide angle X-ray diffraction (WAXD)

WAXD was used to probe the crystalline structure of neat PLA and WF/PLA composite. The experiment was performed using a D8 Advance X-ray diffraction (Bruker, Germany) under a voltage of 40 kV and current of 40 mA with Cu-K_{α} tube ($\lambda = 1.5418$ Å) between $2\theta = 5-40^{\circ}$ at a scan rate of 6 °/min.

3. Results and discussion

3.1. Morphology and size distribution of WFs

Figure 2 shows the morphology of WF₂₀₋₄₀, WF₈₀₋₁₀₀, and WF₁₄₀₋₁₆₀ and their size distributions. The WF₂₀₋₄₀ and WF₈₀₋₁₀₀ exhibited a slim shape, whereas the $WF_{140-160}$ appeared as a fine powder. The average length/diameter ratio was determined to be 13, 10, and 5 for WF₂₀₋₄₀, WF₈₀₋₁₀₀, and WF₁₄₀₋₁₆₀, respectively. WF₂₀₋₄₀ exhibited the highest length/diameter ratio. For fiber length distribution (Figures 2b and 2e), in comparison to WF₂₀₋₄₀, WF₈₀₋₁₀₀ showed lower amounts of longer fibers (>3 mm) and higher amounts of shorter fibers (<3 mm). In the case of diameter distribution (Figures 2c and 2f), in comparison to WF_{20-40} , WF_{80-100} showed higher amounts of fibers with smaller diameters (<0.16 mm). For $WF_{140-160}$ (Figure 2h), the average particle size was 51 μ m, which was much lower than that of WF₂₀₋₄₀ and WF₈₀₋₁₀₀.

3.2. Microstructure of WF/PLA composites containing varying sizes of WF

Figure 3 shows the distribution of three sizes of WF in the PLA matrix observed under an optical microscope. It was clearly seen that the small-sized WF (WF₁₄₀₋₁₆₀) did not distribute evenly in the PLA matrix and formed agglomerates, as indicated by the dark area in Figure 3c. Figure 4 shows the fracture surface of 1WF/PLA composites containing three different sizes of WF. The fiber size has a direct influence on the microstructure of composites. The microstructure of the failure surface in Figure 4a suggested weak interfacial adhesion between large-sized WF and PLA matrix. It is evident that fiber/matrix debonding and fiber pull-out occurred at the interface of large fibers (WF₂₀₋₄₀) with the matrix, which indicated weak points in the composite. The composites prepared with the medium-sized fibers (WF_{80-100}) show a better cohesive structure between the fibers and the PLA compared to WF_{20-40} ; however, fiber fracture and pull-out remained to be visible (Figure 4b). The composites prepared with the small-sized fibers (WF₁₄₀₋₁₆₀) show a more homogeneous and compacted structure compared to the larger fibers, with the small fibers embedded into the PLA (Figure 4c).



Figure 2. Optical micrograph and size distribution of WF with three sizes: a)-c) WF₂₀₋₄₀, d)-f) WF₈₀₋₁₀₀, g) and h) WF₁₄₀₋₁₆₀.



Figure 3. Distribution of three sizes of WF in PLA matrix observed under optical microscopy: a) WF₂₀₋₄₀/PLA,
b) WF₈₀₋₁₀₀/PLA, c) WF₁₄₀₋₁₆₀/PLA.

3.3. Mechanical properties of the composite containing varying sizes of WF

Notched impact strength represents the energy absorbed by a material when it is ruptured [28]. The variation in notched impact strength with varying WF sizes is shown in Figure 5a. It is clearly seen that neat PLA shows lower notched impact strength of 1.49 kJ/m². Adding 1 wt% WF₂₀₋₄₀ or WF₁₄₀₋₁₆₀ had no remarkable effect on the notched impact strength of PLA. The notched impact strength of $1WF_{80-100}$ / PLA composite significantly increased by 14% compared with neat PLA, indicating WF₈₀₋₁₀₀ exhibits a better toughening effect than the other two sizes of WF. The value of elongation at break also reflects



Figure 4. Scanning electron micrographs of the fracture surface of WF/PLA composite with varying WF sizes: a) WF₂₀₋₄₀/PLA, b) WF₈₀₋₁₀₀/PLA, c) WF₁₄₀₋₁₆₀/PLA.

the toughness of the composite. Figure 5b shows the elongation at break of neat PLA and 1WF/PLA composites containing three sizes of WF. The elongation at break for neat PLA, $1WF_{20-40}/PLA$, $1WF_{80-100}/PLA$, and $1WF_{140-160}/PLA$ was 1.63, 1.57, 2.07, and 1.60%, respectively. Among the three sizes of WF, the incorporation of 1 wt% WF₈₀₋₁₀₀ resulted in the highest elongation at break, which increased by 27% compared with neat PLA. Adding 1 wt% WF₂₀₋₄₀ or WF₁₄₀₋₁₆₀ had no significant effect on elongation at

break. According to the above results, the addition of WF_{80-100} contributed to enhancing the toughness of PLA.

The flexural test measures the force required to bend a beam under the action of the applied load [29]. The variation of flexural strength and modulus for varying WF sizes is shown in Figure 5c. The flexural strength and modulus of neat PLA were 71.6 and 2788 MPa, respectively. In comparison to neat PLA, the highest elevation in flexural strength (13.1 MPa)



Figure 5. Mechanical properties of neat PLA and WF/PLA composite containing 1 wt% of WF with three sizes: a) Notched impact strength, b) elongation at break, c) flexural properties, d) tensile properties. Samples with the same alphabetical designation are not significantly different using Tukey paired t-tests (*P* > 0.05).

was observed with the addition of 1 wt% WF_{80-100} . The flexural strength of WF_{20-40} /PLA and $WF_{140-160}$ /PLA composites was inferior to that of WF_{80-100} /PLA composite. In the case of flexural modulus, the incorporation of WF increased the modulus compared to neat PLA, but the difference between the three sizes of WF was not statistically significant.

The tensile properties exhibited the ability of a material to withstand the applied pulling force [30]. Figure 5d displays the tensile properties of PLA and WF/PLA composite containing 1 wt% WF of various sizes. Neat PLA exhibited tensile strength and modulus of 43.9 and 2985 MPa, respectively. The presence of WF resulted in an increasing tensile modulus. The size of WF did not have a remarkable influence on the tensile modulus. In the case of tensile strength, the incorporation of WF₂₀₋₄₀ and WF₁₄₀₋₁₆₀ had no significant influence compared to neat PLA. However, the tensile strength of WF_{80-100}/PLA (51.4 MPa) was significantly higher than the other groups. This indicated that medium-sized WF (WF₈₀₋₁₀₀) showed better reinforcing potential in PLA than the other two sizes of WF.

Through a comprehensive comparison of WF/PLA made with three sizes of WF, WF of medium size (WF₈₀₋₁₀₀) had the greatest reinforcing effect on PLA. Similarly, a previous study by Golmakani *et al.* [31] prepared wood flour-reinforced polyethylene composites using three different sizes of wood flour (30–40,

70–80, and 100–120 mesh). They also found that the maximum tensile strength and flexural strength were related to the composites comprised of 70–80 mesh wood flour. The better reinforcing effect of medium-sized WF (WF₈₀₋₁₀₀) than the other two sizes of WF is due to several factors. On the one hand, when using the larger fibers (WF₂₀₋₄₀), the fractured composite showed discontinuous microstructure with fiber/matrix debonding and fiber pull-out, which indicated weak interfacial bonding. On the other hand, the aspect ratio of WF₁₄₀₋₁₆₀ was the lowest among the three sizes of WF, indicating an inferior strengthening effect. Besides, WF₁₄₀₋₁₆₀ did not disperse evenly in the PLA matrix (as shown in Figure 3c), resulting in inefficient stress transfer and reduced strength.

3.4. Microstructure of WF/PLA composites containing varying contents of WF

Figure 6 shows the SEM images taken from the fracture surface of composites containing varying contents of WF₈₀₋₁₀₀. More fibers were visible with the increasing WF content in the composite. The composites prepared with lower contents of WF (0.5 and 1 wt%) exhibited a more homogeneous and continuous microstructure, with few small holes and cracks visible. As the WF content increased to 2 wt%, the cavities caused by fibers being pulled out of the matrix during the impact test were seen clearly. With the WF further increased to 8 wt%, more traces of



Figure 6. Scanning electron micrographs of the fracture surface of WF_{80-100} /PLA composite with varying WF contents: a) 0.5 wt% WF₈₀₋₁₀₀; b) 1 wt% WF₈₀₋₁₀₀; c) 2 wt% WF₈₀₋₁₀₀; d) 4 wt% WF₈₀₋₁₀₀; e) 8 wt% WF₈₀₋₁₀₀.

WF pull-out from the matrix could be observed, and the fracture surface was less continuous than the lower WF contents. These results suggested that when more WF was incorporated, there were more weak points caused by the weak interfacial adhesion between WF and the PLA matrix.

3.5. Mechanical properties of the composite containing varying contents of WF₈₀₋₁₀₀

Based on previous experiments, WF_{80-100} was selected to further investigate the effects of varying WF contents on the mechanical properties of WF/PLA composite. The notched impact strength of WF/PLA composite as a function of WF_{80-100} contents is shown in Figure 7a. The notched impact strength of WF/PLA composite containing 0.5–4.0 wt% WF₈₀₋₁₀₀ had a significant improvement compared to neat PLA. However, the addition of 8 wt% WF₈₀₋₁₀₀ caused a reduction in impact strength, and the difference between neat PLA and PLA composites with 8 wt% WF₈₀₋₁₀₀ was not significant. For elongation at break, the maximum value of 2.46% was obtained by adding

0.5 wt% WF₈₀₋₁₀₀ (Figure 7b). Beyond 0.5 wt% WF₈₀₋₁₀₀ loading, the elongation at break of WF/PLA composite gradually decreased with increasing WF₈₀₋₁₀₀ contents. When WF₈₀₋₁₀₀ content increased to 4 wt%, the elongation at break of the composite decreased to the same level of neat PLA. With the further increase in WF₈₀₋₁₀₀ content to 8 wt%, the elongation at break was significantly lower than that of neat PLA. This result indicated that lower content of WF₈₀₋₁₀₀ improved the toughness of the WF/PLA composite.

The variation in the flexural strength and modulus of the WF/PLA composite as a function of WF₈₀₋₁₀₀ content is shown in Figure 7c. The addition of 0.5– 2 wt% WF₈₀₋₁₀₀ significantly increased the flexural strength compared to neat PLA, but the difference between composites of these WF₈₀₋₁₀₀ loadings was not statistically significant. Flexural strength reached a maximum of 84.7 MPa in composites containing 1 wt% WF₈₀₋₁₀₀. Beyond 2 wt% WF₈₀₋₁₀₀ loading, a steady decrease in flexural strength was observed with the increasing WF₈₀₋₁₀₀ loading up to 8 wt%.



Figure 7. Mechanical properties of WF/PLA composite with varying WF₈₀₋₁₀₀ contents: a) Notched impact strength, b) elongation at break, c) flexural properties, d) tensile properties. Samples with the same alphabetical designation are not significantly different using Tukey paired t-tests (P > 0.05).

For flexural modulus, adding 0.5 wt% WF had no significant effect on PLA. Adding 1–8 wt% WF₈₀₋₁₀₀ into PLA significantly increased the flexural modulus, and the highest flexural modulus was observed for composites containing 8 wt% WF₈₀₋₁₀₀. The results of flexural properties indicated that WF₈₀₋₁₀₀ at appropriate loadings (1–2 wt%) played a reinforcing effect on PLA, which increased flexural strength as well as stiffness.

The tensile strength and tensile modulus of the WF/ PLA composite are displayed in Figure 7d. Neat PLA possessed a tensile strength and modulus of 43.9 and 2985 MPa, respectively. The incorporation of 0.5-1 wt% WF₈₀₋₁₀₀ into the PLA matrix significantly increased the tensile strength, which ranged from 43.9 to 52.2 MPa. Tensile strength of 0.5WF₈₀₋₁₀₀/PLA reached the highest value of 52.2 MPa with an insignificant difference with 1WF₈₀₋₁₀₀/PLA composite. Beyond 1 wt% WF₈₀₋₁₀₀ loading content, tensile strength decreased significantly with increasing WF₈₀₋₁₀₀ content up to 8 wt%. Higher content of WF₈₀₋₁₀₀ resulted in lower tensile strength may be due to mingling or agglomeration of WF in PLA. Adding 0.5-8 wt% WF₈₀₋₁₀₀ significantly improved the tensile modulus of PLA. The difference between composites of 0.5-4 wt% WF₈₀₋₁₀₀ loadings was not statistically significant. But the addition of 8 wt% WF₈₀₋₁₀₀ effectively improved the tensile modulus of PLA, which is similar to the results of flexural modulus. The tensile results showed $0.5-1WF_{80-100}$ / PLA composite has a better tensile strength through tensile properties analysis.

Through a comprehensive comparison of the above mechanical properties, the optimal loading of WF_{80-100} was found to be 1 wt% among the loadings used in this study. At this WF_{80-100} addition level, the overall mechanical properties of WF/PLA composite were significantly enhanced compared to neat PLA. The mechanical test results suggested that WF_{80-100} , even at low dosages, can play the role of reinforcement in WF/PLA composites.

3.6. Non-isothermal crystallization behaviors

Non-isothermal crystallization behaviors of neat PLA and WF/PLA composite were analyzed by DSC. The second heating curves of WF/PLA composites containing different contents of WF₈₀₋₁₀₀ are presented in Figure 8. The characteristic parameters, including glass transition temperature ($T_{\rm g}$), cold crystallization temperature ($T_{\rm cc}$), melting temperature



Figure 8. Melting curves after non-isothermal crystallization of WF/PLA composite with varying WF_{80-100} contents.

 $(T_{\rm m}), \Delta H_{\rm m}, \Delta H_{\rm cc}, \text{ and } X_{\rm c} \text{ derived from DSC, are list-}$ ed in Table 1. The melting curves displayed three main transitions, which were related to $T_{\rm g}$ around 62–63 °C, T_{cc} around 121–126 °C, and T_{m} around 152-155 °C. There was an exothermic peak in the melting curves belonging to the cold crystallization of PLA. The cold crystallization peak reflects the ability of a material to crystallize below the melting temperature [32]. The incorporation of WF_{80-100} slightly decreased the T_{cc} , indicating the crystallization window was moving to a lower temperature. For processing, the decrease of T_{cc} is desirable as by expanding this window, the crystallinity for the material can be increased, or the processing temperature can be lowered, leading to more efficient processes [33]. The DSC curves of neat PLA and WF_{80-100} / PLA composite containing 0.5-4.0 wt% WF₈₀₋₁₀₀ exhibited a single melting peak belonging to the α -crystal [34], indicating the addition of WF₈₀₋₁₀₀ did not change the crystal form of PLA. However, there was a double melting peak in 8WF₈₀₋₁₀₀/PLA composite. The melting peak at lower temperatures corresponded to the melting of less ordered α '-crystal,

 Table 1. Non-isothermal crystallization parameters of WF/PLA composite with varying WF₈₀₋₁₀₀ contents.

Samples	<i>T</i> g [°C]	<i>T</i> _m [°C]	$\Delta H_{\rm m}$ [J/g]	<i>T</i> _{cc} [°C]	ΔH _{cc} [J/g]	X _c [%]
PLA	63.3	155.1	21.2	126.2	-18.8	2.6
0.5WF ₈₀₋₁₀₀ /PLA	63.3	154.9	29.1	126.3	-24.4	5.0
1WF80-100/PLA	62.1	153.4	23.4	124.0	-18.0	5.8
2WF80-100/PLA	62.3	154.1	23.5	125.3	-18.6	5.3
4WF80-100/PLA	62.7	154.1	25.2	125.9	-19.3	5.0
8WF80-100/PLA	62.1	152.8	29.4	121.6	-24.9	5.3

and the peak at higher temperatures corresponded to the melting of the thermodynamically more stable α -crystal [35]. Furthermore, it was found that adding WF₈₀₋₁₀₀ into PLA increased the crystallinity. The crystallinity of 1WF₈₀₋₁₀₀/PLA composite reached 5.8%, exceeding by 3.2% that of neat PLA (2.6%). Nonisothermal crystallization behaviors of the WF/PLA composite indicated WF improved the crystallinity and heterogeneous nucleation ability of PLA.

3.7. Isothermal crystallization behaviors

Isothermal crystallization analysis was performed to further study the effect of WF_{80-100} on the crystallization of PLA. Figures 9a and 9b displays the isothermal crystallization behaviors under certain crystallization temperatures (100, 110, and 120 °C) for neat PLA and $1WF_{80-100}$ /PLA composite. The width of the exothermic peak reflects the crystallization rate. The wider the exothermic peak, the slower the crystallization rate [22]. The exothermic peak of the isothermal crystallization of PLA was flatter than that of the WF/PLA composite under the same crystallization temperature, indicating that WF accelerated the crystallization of PLA. For the same sample, the exothermic peak of isothermal crystallization at 110 °C was sharper than that at 100 and 120 °C. It can be concluded that the optimal isothermal crystallization temperature of PLA and WF/PLA composite was 110 °C in this study. The isothermal crystallization kinetics can be analyzed by the Avrami model, which describes the change of relative crystallinity (X_t) with crystallization time t [36] (Equation (2)):

$$1 - X_{t} = \exp(-kt^{n}) \tag{2}$$

where X_t is time-dependent relative crystallinity, n is Avrami exponent, and k is the overall crystallization rate constant related to nucleation and crystal growth. Avrami model can be expressed in linear form and is given by the Equation (3):

$$\lg\left[-\ln(1-X_t)\right] = \lg k + n \lg t \tag{3}$$



Figure 9. a) and b) isothermal crystallization exotherms and c) and d) relative crystallinity (X_t) versus crystallization time at different isothermal crystallization temperatures for neat PLA and 1WF₈₀₋₁₀₀/PLA.

 X_t can be calculated from the isothermal DSC heat flow curve as Equation (4) [37]:

$$X_{t} = \frac{\int_{0}^{t} \frac{\mathrm{d}H}{\mathrm{d}t} \mathrm{d}t}{\int_{0}^{\infty} \frac{\mathrm{d}H}{\mathrm{d}t} \mathrm{d}t}$$
(4)

where dH/dt is the respective heat flow; the sum of dH/dt from 0 to *t* is the enthalpy at time *t*; and the sum of dH/dt from 0 to t^{∞} is the enthalpy at time t^{∞} , which can be obtained as the total area under the crystallization DSC curve. The half-crystallization time $(t_{1/2})$ is another important crystallization kinetics parameter, which is defined as the time of achieving 50% crystallinity of samples. It can be calculated by the Equation (5) [38]:

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \tag{5}$$

Avrami parameters calculated from the isothermal curves were summarized in Table 2. For the ideal isothermal crystallization process, *n* should be an integer, which depends on the nucleation mechanism and the growth mode. The *n* value ranged from 1.8 to 2.7 due to the heterogeneous nucleation mechanism [22]. Figures 9c and 9d shows the relative crystallinity X_t versus crystallization time *t* for neat PLA and 1WF₈₀₋₁₀₀/PLA composite, which exhibited typical S-type curves. The X_t versus *t* curve of 1WF₈₀₋₁₀₀/PLA composite extraordinarily shifted to the left

compared with neat PLA at 100 and 110 °C. At the same isothermal crystallization temperature, neat PLA showed longer $t_{1/2}$ than that of 1WF₈₀₋₁₀₀/PLA composite. As listed in Table 2, $t_{1/2}$ of neat PLA was 23.6 min at 110 °C. A shorter $t_{1/2}$ of 7.2 min was observed for 1WF₈₀₋₁₀₀/PLA composite isothermally crystallized at 110 °C, which indicated that 1 wt% WF₈₀₋₁₀₀ was efficient in promoting crystallization rate. Figure 10 shows the $t_{1/2}$ plots as a function of WF₈₀₋₁₀₀/PLA composite at three crystallization temperatures. The crystallinity of 1WF₈₀₋₁₀₀/PLA composite after isothermal crystallization at 100, 110, and 120 °C were 30.1, 31.7, and



Figure 10. Half-crystallization time $(t_{1/2})$ at different isothermal crystallization temperatures for WF/PLA composite with varying WF₈₀₋₁₀₀ contents.

Table 2. Isothermal crystallization kinetic parameters of WF/PLA composite with varying contents of WF₈₀₋₁₀₀.

Samples	<i>T</i> c [°C]	п	k [min ⁻ⁿ]	<i>t</i> _{1/2} [min]	$\Delta H_{\rm m}$ [J/g]	X _c [%]
PLA	100	2.0	1.5.10-3	22.8	28.6	30.6
	110	2.1	8.9.10-4	23.6	29.7	31.7
	120	1.8	$1.7 \cdot 10^{-3}$	27.1	13.7	14.6
0.5WF ₈₀₋₁₀₀ /PLA	100	2.7	2.1.10-3	8.3	27.8	29.9
	110	2.3	5.9.10-3	7.6	29.6	31.8
	120	2.4	4.3.10-4	21.6	27.4	29.4
1WF ₈₀₋₁₀₀ /PLA	100	2.5	4.0.10-3	8.1	27.9	30.1
	110	2.4	5.9.10-3	7.2	29.4	31.7
	120	2.0	1.1.10-3	24.4	29.7	32.1
2WF ₈₀₋₁₀₀ /PLA	100	2.6	$2.8 \cdot 10^{-3}$	8.4	27.2	29.7
	110	2.6	4.9.10-3	6.9	29.6	32.3
	120	2.3	4.5.10-4	25.7	29.5	32.2
4WF ₈₀₋₁₀₀ /PLA	100	2.6	$2.2 \cdot 10^{-3}$	9.2	28.0	31.2
	110	2.5	5.6.10-3	7.0	30.7	34.2
	120	2.5	2.0.10-4	25.1	30.3	33.7
8WF ₈₀₋₁₀₀ /PLA	100	2.6	3.8.10-3	7.7	28.4	33.0
	110	2.6	6.1.10 ⁻³	6.3	28.9	33.6
	120	2.3	$1.2 \cdot 10^{-3}$	15.2	28.3	32.9

32.1%, respectively. In comparison to neat PLA, the incorporation of 1% $WF_{\rm 80-100}$ resulted in a higher

0 min 2 min 50 µm 50 µm a) b) 50 µm d) c) 0 min 2 min 50 µm 50 µm e) f) 6 min 4 mir 50 µm 50 µm h) g)

Figure 11. Crystalline morphology evolution observed by polarized optical microscope (POM) during isothermal crystallization at 110 °C of a)–d) neat PLA and e)–h) 1WF₈₀₋₁₀₀/PLA.

level of crystallinity. The reduced crystallization halftime and cold crystallization temperature, as well as increased crystallinity, suggested that 1% WF₈₀₋₁₀₀ promoted the nucleation and crystallization process of the PLA matrix.

3.8. Crystalline morphology

Crystalline morphological evolution for neat PLA and 1WF80-100/PLA composite under POM observation during isothermal crystallization at 110 °C was shown in Figure 11. The spherulites in neat PLA slowly grew with time. Relatively large spherulites with a diameter of about 20 µm were observed for neat PLA until isothermal crystallization was completed. Neat PLA exhibited a typical maltase cross phenomenon. In the presence of WF_{80-100} , the spherulite size was smaller, and the crystal growth rate was much faster. This result is consistent with the $t_{1/2}$ results of the DSC analysis. It was also noticed that the crystals of $1WF_{80-100}$ /PLA composite were denser than neat PLA, which was attributed to the increasing nucleation density of PLA [22]. The spherulite sizes of 1WF₈₀₋₁₀₀/PLA composite were so fine that it was hard to be figured out, indicating WF₈₀₋₁₀₀ provided more nucleation sites for PLA. PLA crystals grew along the WF until WF was coated with crystals completely. Such a phenomenon further demonstrated that WF₈₀₋₁₀₀ was an effective nucleating agent for PLA.

3.9. Crystalline structure

Diffraction peaks of WAXD spectra reflect the crystalline structure of WF and WF/PLA composite with varying WF₈₀₋₁₀₀ contents shown in Figure 12. WF



Figure 12. Wide angle X-ray diffraction (WAXD) spectra of WF and WF/PLA composite with varying WF_{80-100} contents.

showed obvious diffraction peaks at $2\theta = 15.7$ and 22.2° corresponding to $(10\overline{1})$ and (002) lattice planes, respectively, which indicated a typical cellulose I structure with high crystallinity of 66.7%. Neat PLA is amorphous, as evidenced by a broad WAXD curve. The WAXD pattern of WF/PLA composites with varying WF₈₀₋₁₀₀ contents shows obvious diffraction peaks around $2\theta = 16.6$ and 19.0° , which was associated with (110)/(200) and (203) lattice planes of α-crystal in PLA. In 1WF₈₀₋₁₀₀/PLA composite, a shift of the above-mentioned lattice planes towards higher 2θ values (16.8°) attributed to the crystalline structure of PLA transformed from a disorder α '-crystal to an ordered α -crystal [25]. This phenomenon indicated WF₈₀₋₁₀₀ contributed to enhancing PLA crystallization, which is consistent with DSC results.

4. Conclusions

The effect of a small amount of WF on the mechanical and crystallization properties of PLA was investigated in this study. WF/PLA composite containing 1 wt% WF₈₀₋₁₀₀ exhibited better mechanical properties in notched impact strength and flexural and tensile properties compared to neat PLA, 1WF₂₀₋₄₀/PLA, and 1WF₁₄₀₋₁₆₀/PLA composite. Thus, WF₈₀₋₁₀₀ was determined as the optimal size of WF for reinforcing PLA. Then the mechanical properties of WF_{80-100} PLA composites containing varying WF₈₀₋₁₀₀ contents (0.5, 1, 2, 4, and 8 wt%) were further studied. The optimal loading content for WF₈₀₋₁₀₀ was 1 wt%, at which the notched impact strength, flexural and tensile strength increased by 14, 18, and 18%, respectively. Elongation at break of 1WF₈₀₋₁₀₀/PLA composite significantly increased by 27% compared to neat PLA. Furthermore, adding WF₈₀₋₁₀₀ could significantly reduce half-crystallization time, meanwhile improving crystallinity. The phenomenon indicated WF accelerated crystallization and contributed to the heterogeneous nucleation of PLA. Crystalline morphology evolution of WF/PLA composite observed by polarized optical microscope showed that WF increased the nucleation sites companies with decreasing the size of spherulites. Meanwhile, WF₈₀₋₁₀₀ significantly enhanced the formation of α-crystal of PLA based on wide-angle X-ray diffraction results. These results indicated that the presence of a small amount of WF with appropriate size acted as both a bio-nucleating agent and reinforcement material for the PLA matrix. This study provides a

simple and feasible strategy for enhancing the processing and properties of PLA and ensures its complete biodegradability.

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