



# A comparison of annealing process and nucleating agent (zinc phenylphosphonate) on the crystallization, viscoelasticity, and creep behavior of compression-molded poly(lactic acid) blends



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## ABSTRACT

In this study, the thermal crystallization, viscoelastic property, and creep behavior of poly(lactide acid)/zinc phenylphosphonate (PLA/PPZn) blends were compared with those of annealed PLA. The results revealed that PPZn exhibited an excellent nucleating effect for the crystallization of PLA. The isothermal crystallization half-time ( $t_{1/2}$ ) of amorphous PLA (PLA<sub>am</sub>) at 130 °C was 28.1 min, whereas all the  $t_{1/2}$  values of PLA/PPZn blends were less than 1 min. In addition, the blends showed better thermal resistance than the annealed PLA. The storage modulus ( $E'$ ) of all the PLA/PPZn blends was higher than that of the annealed PLA at temperatures higher than the  $T_g$  of PLA. However, the modulus of rupture (MOR) of PLA/PPZn blends decreased with increasing PPZn concentration in the PLA matrix, whereas there was no noticeable difference for all the annealed PLA. Regarding the creep behavior, the predicted modulus reduction of PLA<sub>am</sub> was 42.9% at 60 years by time–temperature superposition principle (TTSP) method. In contrast, the reductions in modulus levels of all the PLA/PPZn blends and the annealed PLA were still less than 33% over the 60-year period.

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## 1. Introduction

Poly(lactic acid) (PLA) is renewable, biomass-derived, biocompatible, and nontoxic to the environment and human body; thus, it has attracted considerable attention for its broad application in the biomedical, agricultural, and packaging industries. Additionally, PLA has raised considerable interest as a potential substitution for petroleum-based polymers because of its favorable biodegradability, versatile fabrication, and good mechanical properties [1]. However, one of the general drawbacks of PLA-based materials is its low glass transition temperature (ca. 56 °C), which severely limits the application of PLA. It is well known that most properties of PLA are mainly dependent on the crystalline morphology, spherulite size, and crystallinity [2–4]. The crystalline form is required to increase the thermal resistance of PLA. Therefore, annealing treatment is commonly used to develop the crystal region of amorphous PLA (PLA<sub>am</sub>), which results in the formation of the crystallized polymer. According to previous studies [5–8], the minimum

crystallization half-time or the maximum crystallization rate was reached in the range of 105–110 °C.

The other drawback of PLA-based materials is the slow crystallization rate that causes almost no crystallization under a high cooling rate during the practical molding process [9]. The heterogeneous nucleation, in which additional impurities are present in the polymer matrix as heterogeneous nuclei, reduces the free energy needed for the formation of a critical nucleus to increase the crystallization rate. The overall nucleation and crystallization rates of PLA in heterogeneous conditions are relatively higher than in homogenous conditions. In general, nucleating agents that can be added to the PLA matrix have been developed, and they have been shown to be an effective approach to reduce the nucleation induction time and increase the number of primary nucleation sites. Changes in the properties of nucleating agents that are added to polymers could be attributed to the quantity of spherulite, the filler loading, and the interfacial adhesion between the filler and the polymer matrix.

Recently, several researchers have attempted to reduce the induction time of nucleation and increase the nucleation density of PLA composites with inorganic fillers [10–16]. Pan et al. [17] reported that a few metal phosphonate filler-loaded PLA composites

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can accelerate the crystallization rate and improve the mechanical properties. Zinc phenylphosphonate (PPZn), one of the most famous nucleation agents, has a layered structure similar montmorillonite clay [18], and it can increase significantly the crystallization rate of PLA [17,19]. Although several studies have focused on the effects of homogeneous or heterogeneous nucleations on the crystallization rate and thermal and mechanical properties, a limited number of studies have investigated the difference between these two crystallization processes on various properties in a PLA matrix. In addition, polymer composites exhibit a time-dependent degradation in modulus and strength as a consequence of the viscoelasticity of the polymer matrix [20]. In most practical applications, creep behavior, which is a time-dependent response, is of considerable significance because isothermal compliance of the polymeric material depends not only on stress but also on time. Therefore, the creep behavior is a critical issue for many engineering fields, such as aerospace and biomedical engineering. Several studies have been conducted on the creep behavior of polymer matrix composites. For example, the flexure creep properties of E-glass reinforced polymers were studied by Abdel-Magid et al. [21]. Wang et al. [22] reported the creep behavior of basalt fiber-reinforced polymer tendons. For polymeric matrix with natural fibers, Doh et al. [23] studied the creep behavior of liquefied wood–polymer composites based on polypropylene (PP), low-density polyethylene (LDPE), and high-density polyethylene (HDPE). For PLA composites, Suryanegara et al. [24] studied the creep deformation of microfibrillated cellulose-reinforced partially crystallized PLA composites. The creep behavior of PLA with lignin-based flax composites subjected to tensile loading was reported by Rozite et al. [25]. Kontou et al. [26] implemented nonlinear viscoelastic/viscoplastic response under monotonic loading and creep recovery tests of PLA composite with flax fibers. However, creep research that considers the difference between homogeneous and heterogeneous nucleations for PLA-based materials has not been conducted. To the best of our knowledge, there has not been any prior research on the comparison of nucleating agents and annealing on the thermal properties, mechanical properties, and creep behavior of compression-molded PLA blends. In this study, the thermal crystallization, viscoelastic property, and creep behavior of PLA/PPZn blends compared with the annealed PLA were investigated.

## 2. Experimental

### 2.1. Materials and preparation of blends

Semicrystalline grade comprised of approximately 2% D-LA oligomer PLA was purchased from Natureworks (PLA 4032D, Blair, NB). PPZn was purchased from Nissan Chemical Industries, Ltd. (Tokyo, Japan). PLA with various PPZn concentrations was compounded at 150 °C by a twin-screw extruder at a speed of 60 rpm. The mixtures were extruded and pelleted, then the plate samples with a thickness of 4.0 mm were hot-pressed at 180 °C after melting for 3 min, followed by quenching to room temperature. The PLA/PPZn blends are denoted as  $N_x$ , where  $x$  is the weight percent of PPZn in the blends. The annealed PLA are denoted as  $A_y$ , where  $y$  is the duration (min) of annealing at 110 °C.

### 2.2. Differential scanning calorimetry (DSC)

The crystallization behavior was measured by DSC 8500 (Perkin–Elmer, UK) with an intracooler II cooling accessory. The samples were weighed and sealed in an alumina pan. To measure the melt crystallization temperature, the samples were cooled from the melt state to room temperature at 10 °C/min after melting at 200 °C

for 5 min (non-isothermal crystallization). The degree of crystallinity ( $X_{mc}$ ) was obtained as a function of the PPZn concentration using the following equation (1):

$$X_{mc}(\%) = \frac{\Delta H_m}{\Delta H_m^0 \times W_p} \times 100 \quad (1)$$

where  $\Delta H_m$  is the experimental heat of fusion determined from the DSC measurement,  $\Delta H_m^0$  is the assumed heat of fusion of the fully crystalline PLA (93 J/g) [27], and  $W_p$  is the weight percentage of PLA in the blends. In addition, to investigate the crystallization half-time from isothermal conditions, the samples were rapidly cooled at 100 °C/min from the melt state to the desired temperature.

### 2.3. X-ray diffraction (XRD)

X-ray diffractograms were recorded with a MAC science MXP18 instrument (Japan) using Ni-filtered  $\text{CuK}\alpha_1$  radiation ( $\lambda = 0.1542$  nm) at 40 kV and 30 mA. XRD patterns of samples were recorded in the  $2\theta$  ranges of 4–40° with a scan rate of 2°/min. The crystallinity index ( $CrI$ ) of the samples was calculated by the following equation (2) according to the previous study [28]:

$$CrI(\%) = \frac{A_{cry}}{A_{cry} + A_{am}} \times 100 \quad (2)$$

where  $A_{cry}$  is the area of the PLA crystallographic form at  $2\theta = 16.5^\circ$  (planes 110 and 200) and  $18.9^\circ$  (plane 203), and  $A_{am}$  is the area of diffraction of the amorphous region.

### 2.4. Gel permeation chromatography (GPC)

A gel permeation chromatography (GPC) equipped with a PU-2080 pump (Jasco, Japan), a RI-2031 refractive index detector (Jasco, Japan), and 10E3A/10E4A columns (Phenogel, USA) was used to measure the number average molecular weight ( $M_n$ ) and the weight average molecular weight ( $M_w$ ) of the PLA/PPZn specimens. Tetrahydrofuran (THF) was used as the isocratic mobile phase at a flow rate of 1 mL/min. A series of polystyrene calibration standards was used to calculate  $M_n$  and  $M_w$ . Before sample injection, the specimens were dissolved in THF and then filtered through a 0.2- $\mu\text{m}$  hydrophilic polypropylene (GHP) membrane to remove insoluble particles.

### 2.5. Dynamic mechanical analysis (DMA)

The dynamic mechanical properties were measured in a single-cantilever bending mode (DMA 2000, PerkinElmer, Buckinghamshire, UK) with a span of 20 mm at a frequency of 1 Hz and a heating rate of 2 °C/min from room temperature to 170 °C. The samples were thin rectangular strips with dimensions of  $30 \times 10 \times 4$  mm<sup>3</sup>.

The creep compliance master curves and activation energy of the glass transition relaxation were also determined by DMA. Creep and creep recovery cycles were conducted at isotherms between 20 and 50 °C in intervals of 5 °C. A three-point bending mode with a span of 40 mm was used. For each isotherm, 10% of the average flexural strength was applied for 1 h, followed by a 1 h recovery period. According to the principle of time–temperature superposition, each curve was shifted by an appropriate shift factor,  $\log a_T$ . This shift factor can be related to temperature and activation energy using the following Arrhenius equation (3):

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