



Pressure dependence of equilibrium melting temperature of poly(lactic acid)



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ABSTRACT

The behavior of the equilibrium melting temperature (T_m^0) of poly(L-lactic acid) with pressure estimated using the Gibbs-Thomson method is presented. Differential scanning calorimetry and a High pressure differential thermal analyzer have been used to determine the melting temperatures of samples isothermally crystallized at atmospheric pressure and at pressures ranging from atmospheric to 300 MPa respectively. Lamellar thickness of the crystals was determined from small angle X-ray scattering. The $\left(\frac{dT_m^0}{dP}\right)_0$ was found to follow the second order polynomial $T_m^0 = 206 + 0.309P - 3.86 \times 10^{-4}P^2$. The enthalpy and entropy of fusion of the perfect crystal up to 300 MPa determined through the Clapeyron equation remained more or less similar up to 200 MPa but increased significantly at 300 MPa. The ΔH_f^0 and ΔS^0 at atmospheric pressure were calculated to be 94.5 Jg^{-1} and $0.197 \text{ JK}^{-1}\text{g}^{-1}$, respectively while the fold surface energy was calculated to be $64 \times 10^{-3} \text{ Jm}^{-2}$.

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1. Introduction

Biopolymers are now attracting much attention because they are renewable, and are derived or produced from natural sources and living organisms which create a sustainable industry. These polymers are classed as carbon neutral because the crops from which these biopolymers are derived reabsorb the CO_2 released during their degradation. Biopolymers are mainly polyesters and are finding applications in several areas ranging from packaging to medicine. Among the biopolyesters, poly(lactic acid) (PLA) has been given much attention because it is considered as both biodegradable, adapted for short term packaging application, and biocompatible with living tissues suitable for biomedical applications. PLA synthesis is a multistep process where the monomer lactic acid, largely produced by the fermentation of carbohydrates, is polymerized. There are two main ways to synthesize PLA; one is from the condensation of lactic acid which yields low-molecular weight and the other is from the ring opening polymerization of lactide

which yields high molecular weight PLA. PLA biodegrades into harmless natural products through hydrolysis and enzymatic catalysis. Because the raw material is from renewable resources, this polyester is classified as an environmentally friendly material. Mechanically, this polyester is a high strength and high modulus thermoplastic and can be easily processed on standard equipment such as injection, extrusion or blow molding to yield molded parts [1]. PLA has two isomers, the D form, poly(D-lactic acid) (PDLA), and the L form poly(L-lactic acid) (PLLA) and both isomers are crystalline. However, poly(DL-lactic acid) which is the combination of the L and the D form is amorphous. PDLA is expensive compared to PLLA, thus the latter is used for the manufacture of commercial goods. Although PLLA is semicrystalline, the crystallization rate is very slow. This has delayed PLLA's widespread commercial use. Extensive investigations are undertaken to improve the crystallization rate for this polyester [2–6]. Recently, development of stereo-complex of PLLA and PDLA has also progressed with improved properties [7]. Despite the extensive literature available on the crystallization behavior of this polyester, very limited literature [8,9] are available at elevated pressures. Reported works under high pressure on this polyester are through the use of pressurized gas and are mainly on the crystallization and melting behavior [10–12].

According to the European Bioplastics Association [13], only one third of the total lactic acid produced is being used for PLA

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production annually. This indicates that this polyester has a high potential for development. As the application of this polyester as plastic products increases, it will often be exposed to elevated pressures during processing. Pressure has been shown to affect the crystallization behavior of polymers, therefore, information about crystallization at elevated pressures is important to envisage the processing conditions of this polyester in order to control the physical properties. Of interest, is the behavior of the equilibrium melting temperature (T_m^0) with pressure. The T_m^0 is defined as the melting temperature of an infinite stack of extended chain crystals. This entity is one of the most important thermodynamic properties of crystallizable polymers, as it is the reference temperature from which the driving force for crystallization is defined. The lateral growth rate, the fold surface energy and the nucleation rate are all controlled by the degree of supercooling (ΔT) according to the secondary nucleation crystallization growth theory of Lauritzen and Hoffman [14]. ΔT is defined as $T_m^0 - T_c$, where T_c is the crystallization temperature. Due to the difficulty in growing extended chain crystals, T_m^0 is normally determined using extrapolative method such as the Hoffman-Weeks (HW) or Gibbs-Thomson plot. The theory related to these methods has been well described in the literature [15–20]. Of these two methods, the Gibbs-Thomson method is considered to give an accurate and reliable estimate of the T_m^0 because it is directly derived from thermodynamic arguments with few assumptions used [17–20]. In this method, the polymer is isothermally crystallized at different T_c 's and the melting temperatures (T_m 's) of the corresponding crystal lamellar thickness (l) are measured. The measured T_m 's are plotted against the inverse of (l). The T_m is well known to depend on the crystal form and the lamellar thickness of the crystals. To estimate the accurate value of T_m^0 , the T_m should be stable at the corresponding T_c at which it was crystallized, i.e., the crystals should not undergo reorganization, premelting or lamellar thickening during the heating measurement. It has been reported [20] that thin lamellar crystals formed at large supercoolings, when heated at slow heating rates, readily undergo thickening. To overcome this shortcoming, thick lamellar crystals crystallized at small supercoolings should be used and scanned at faster heating rates to determine the T_m . However, the latter condition contributes to thermal lag, which needs to be corrected, and methods for eliminating this is well described in the literature [16,18].

At present, the information on the pressure dependence of the T_m^0 of PLLA and the thermodynamic data at high pressures are lacking because of the difficulty in growing extended chain crystals and measuring the T_m of such crystals at elevated pressures directly, except for polyethylene, which can grow extended chain crystals at pressures above 300 MPa [21–26].

In this study, our objective is how best can we determine the T_m^0 of PLLA using the Gibbs-Thomson method at elevated pressures and calculate the enthalpy and entropy of fusion at different pressures using the Clapeyron equation. To the best of our knowledge, this is the first experimental approach to measure the pressure dependence of melting temperature and the thermodynamic variables of PLLA using this technique. A lot of attention has been focused on minimizing the effects of lamellar thickening and thermal lag. The melting temperature of the isothermally crystallized PLLA samples of different lamellar thickness was determined at atmospheric pressure and at elevated pressures using a DSC and a high pressure differential thermal analyzer (HP-DTA), respectively. The T_m at zero heating rate, ($0\text{ }^\circ\text{C min}^{-1}$) was evaluated using the principle of "heating kinetics" to minimize thermal lag. Small angle X-ray scattering (SAXS) and the one dimensional correlation approach was used to determine the long period and the lamellar thickness of the crystals. The behavior of the T_m^0 at elevated pressures will help to understand the crystallization behavior better.

2. Experimental

2.1. Materials

PLLA was supplied by Mitsui Chemicals, Inc., Japan. The sample was purified by dissolving it in chloroform and precipitating it from methanol and vacuum dried at $80\text{ }^\circ\text{C}$ for several days before use. The M_w was 115,833, M_n 69,303 and M_w/M_n 1.67 determined from gel permeation chromatography (GPC) calibrated by polystyrene standards.

2.2. Sample preparation

Melt isothermal crystallization of PLLA was performed as follows: about 10 g of the polymer was melted at $220\text{ }^\circ\text{C}$ for 5 min and pressed to a thickness of 1 mm using a hot press. The molten sample was quickly transferred to an annealing box equilibrated at a preset temperature. After 7 days (completion of crystallization), the sample was removed from the annealing box and quenched to room temperature. For high pressure measurements, about 8 mg of the polymer sample was melted directly in the aluminum DTA sample cup and crystallized following the procedure mentioned above for atmospheric pressure. Before high pressure analysis, the sample was coated with epoxy resin to prevent direct contact with the pressure transmitting silicon oil. Care was taken not to coat the Al cup in order to maintain high accuracy of the thermal signals and reduce noise. Fresh sample was used for each high pressure analysis because of the possibility of PLLA decomposing at high temperature required for melting at high pressures.

2.3. Measurements

2.3.1. Differential scanning calorimetry

Thermal analysis at atmospheric pressure was performed on a DSC (EXTER6200, SEIKO Instruments Inc., Japan) using about 7 mg of the isothermally crystallized samples. Heating was done from 20 to $220\text{ }^\circ\text{C}$ at different heating rates, $5\text{--}20\text{ }^\circ\text{C min}^{-1}$ with a nitrogen gas flow at 20 mL min^{-1} .

2.3.2. High pressure DTA

The high pressure DTA (Hikari High-Pressure Machinery Co., Ltd., Japan) apparatus was modified to suit our investigation. The heating rate was controlled by PID heater controller within $\pm 0.1\text{ }^\circ\text{C}$. Type K (chromel-alumel) thermocouples were used to measure the temperatures of a sample and a reference material (aluminum). The sample cup, which was made from aluminum, was fitted directly onto the ceramic tube containing the thermocouple and the junction of the thermocouple was in direct contact with the aluminum cup just below the sample separated by 0.5 mm thickness of the aluminum cup as shown in Fig. 1.

At ambient temperature, desired pressure was applied and the temperature was raised at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ while the pressure was maintained and monitored using a Heise gauge within $\pm 1\text{ MPa}$. The temperature of the sample and reference pans were recorded with a two channel recorder and the temperature difference between them was plotted against the reference temperature and the absolute minimum of the curve was taken as the melting temperature.

2.3.3. Small angle X-ray scattering (SAXS)

SAXS measurement was carried out using a Nano-Viewer (RIGAKU Corp., Japan). A Cu $K\alpha$ radiation (40 kV, 20 mA) was used as an X-ray source. The two dimensional scattered intensity data were detected using an imaging plate (IP). The pinhole slits, samples, and IP were set in a vacuum chamber and the two

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