

Biobased *myo*-inositol as nucleator and stabilizer for poly(lactic acid)

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ABSTRACT

myo-Inositol made from a biomass feedstock was used as an additive for poly(L-lactic acid) (PLLA) which was also made from biomass feedstock. The crystallization and stabilization of PLLA by the addition of *myo*-inositol were evaluated by the melt injection molding process. While the isothermal crystallization of PLLA at 100 °C had finished over 14 min after melting, that of PLLA with 5 wt% *myo*-inositol finished within 2 min. The crystal growth of PLLA started when the *myo*-inositol crystal was added, and the crystallization was promoted. Furthermore, the molecular weight of PLLA with *myo*-inositol did not decrease during the melt-mixed at 200 °C, different from that of PLLA without the *myo*-inositol. *myo*-Inositol prevented the degradation of PLLA during the thermal melting process. The biomass carbon ratio measured by the accelerator mass spectroscopy method showed that the PLLA with 5 wt% *myo*-inositol was a fully biobased material. It was demonstrated that *myo*-inositol was a multi-functional biobased additive for the modification of PLLA without decreasing its mechanical properties.

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1. Introduction

Recently, biorenewable materials have become more important for innovation regarding the sustainable development of a global society. Biorenewable materials are materials made from biomass feedstocks fixed with carbon dioxide from the atmosphere in modern times. The use of biorenewable materials allows a decreased oil consumption, and the emission of the CO₂ amounts to the atmosphere from the incineration of its waste is the same as the CO₂ amounts currently fixed during photosynthesis by plants from the atmosphere. This concept is called “Zero-emission”. Therefore, global warming will be alleviated. From these points of view, the use of biorenewable materials is promoted for the solution of environmental problems in addition to the use of biodegradable materials.

Poly(lactic acid) (PLA) as a biorenewable and biodegradable plastic [1] can degrade under some conditions; in soil [2], controlled compost [3,4], and anaerobic sludge [5,6]. Therefore, PLA as a disposable plastic has been used in agricultural applications [7,8] and packaging [9] for the solution of waste problems which cause serious environmental pollution by plastic products. In addition, PLA made from biorenewable resources such as corn, potato, sugar cane, and rice has been gaining significant attention as a biobased material for the previously mentioned reasons [10]. It

was also reported that the all CO₂ emissions of PLA were lower than petroleum-based polymers due to use of biomass feedstocks based on the life cycle assessment, *i.e.*, absorption from the atmosphere [11].

Since the large scale production of some companies started in the 1990s, the cost of PLA has decreased to equal to some commodity plastics. Accordingly, many researchers and companies have performed development targeting of commodity plastics for returnable platewares, electric appliance bodies, automobile components, and building materials. However, there are many difficulties for use as a commodity plastic due to some negative properties of PLA. When PLA is used as agricultural and packaging materials, the materials are molded into fibers, films, and sheets by extrusion molding and blow molding. In addition, injection molding, which is an effective and low-cost process to manufacture the end-use applications, is indispensable for the use as commodity plastics.

The native PLA material without any additives is difficult to mold the end-use applications by injection molding due to its crystallization characteristics. PLA is a crystalline plastic, and the crystallization rate of the native PLA is very low [12]. The crystallization of a plastic is the most useful and practical method to enhance its thermal and mechanical properties. In the case of molding fibers, films, and sheets, the crystallization of plastics is succeeded by a drawing process. On the other hand, in the case of injection molding, it is impossible to draw the molded plastics. Therefore, the crystallization process during the molding is often performed in the mold for crystalline plastics. If the crystallization

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rate is not enough fast, the molding process needs a long time and becomes a high-cost process. To promote the crystallization of PLA for thermal stable products, some crystallization additives called the nucleator have been developed for PLA such as a hydrazide compound [13], inorganic talc [14], clay nanocomposite [15], and stereocomplex of PLA [16–18]. For example, the crystallization temperature and enthalpy of PLA with the hydrazide compound were 131 °C and 46 J/g during cooling from 210 to 30 °C at the cooling rate of –20 °C/min measured by a differential scanning calorimeter (DSC), while that of only PLA were not observed.

Furthermore, the deterioration of the properties derived from the reduction of the molecular weight during the thermal molding process is a concern for general applications [19]. The terminal end-functional group of PLA, such as hydroxyl and carboxylic acid groups, moisture, residual catalyst and monomer, and impurities induce the hydrolysis and depolymerization to an oligo(lactic acid) and a lactide which is the starting material of PLA. To prevent their degradations, blocking the end-functional group, drying, and elimination of the residual catalyst and monomer [20] were performed. However, some degradation reactions like the back-biting reaction to give the lactide could not be perfectly prevented by these methods. Therefore, the stabilizers had been used for the thermal molding process. The carbodiimide compound, which could extend and cross-link the macromolecules possessing carboxylic and hydroxyl groups, is usually used for stabilizing some polyesters. In the case of PLA, carbodiimide compounds acted as an effective stabilizer and the degradation during thermal molding process was prevented [21]. On the other hand, it was reported that the addition of carbodiimide compounds causes the reduction of crystallinity in PLA. Organic phosphite could also prevent the reduction of the molecular weight of PLA resulting in the chain extension by transesterification during the thermal fiber process [22]. These reported nucleators and stabilizers were almost oil-based compounds, and a few biobased compounds, such as the stereocomplex nucleator, were reported. As mentioned above, the notable character of PLA is to be supplied from a biomass feedstock, therefore, it is desirable to use the additives made from biomass feedstocks even if the usage is a small amount.

We selected *myo*-inositol as a candidate for the biobased nucleator and stabilizer. Inositol exists as a phosphate ester within the organism both of animals and plants, and has six hydroxyl groups at each carbon of the cyclohexyl ring, and consists of nine stereo isomers with the difference in the steric conformation of the hydroxyl groups [23]. The stereo isomers of inositol are denoted by with prefix such as *cis*-, *epi*-, *allo*-, *muco*-, *neo*-, *D-chiro*-, *L-chiro*-, *scyllo*-, and *myo*- [24]. Six isomers of inositol; *muco*-, *neo*-, *D-chiro*-, *L-chiro*-, *scyllo*-, and *myo*-, have been found in nature. The structure of *myo*-inositol is shown in Fig. 1. *myo*-Inositol is the most general

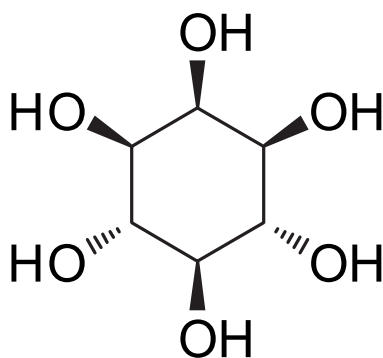


Fig. 1. Chemical structure of *myo*-inositol.

isomer of inositol in nature with a single axial hydroxyl group and five equatorial hydroxyl groups, and isolated as a commercially available reagent from rice bran after hydrolysis of *myo*-inositol-1,2,3,4,5,6-hexaphosphate (phytic acid). *myo*-Inositol has biological roles and is safe for humans [25], therefore, it was usually used as a food additive, such as a nutritious drink in Japan.

Furthermore, it is important to evaluate the biomass carbon ratio of the material, which is produced from biomass feedstocks, for certification and reliance of biobased applications. The method to distinguish the biomass carbon ratio is to measure the radioisotope ^{14}C ratio. The accelerator mass spectroscopy (AMS) measurement method for determining the biomass carbon ratio based on the American Society for Testing and Materials (ASTM) D6866 method entitled “Standard test methods for determining the biomass carbon ratio of solid, liquid, and gaseous samples using radiocarbon analysis” has become a very important and efficient method in the field of biomass materials [26–29]. The AMS method has been used for the carbon dating of archaeological and geological samples. In addition, the method can be applied to a mass balance study using a lower amount of ^{14}C -labelled metabolic compounds for biological systems. AMS can measure very low ^{14}C concentrations, and determine the ratio of the radiocarbon-14 to carbons-12 and 13. The ratio $^{14}\text{C}/^{12}\text{C}$ in biomass carbon is around 1×10^{-12} . Fossil resources and materials derived from them contain no ^{14}C because all the ^{14}C atoms that have a 5730-year half-life, have been changed to ^{14}N during a very long burial time. Thus, the ratio of $^{14}\text{C}/^{12}\text{C}$ for oil-based carbon is found to be zero. The origin of compounds made from carbon, and the ratio of the biobased resource to oil-based resource (the biomass carbon ratio) can be determined by measuring the $^{14}\text{C}/^{12}\text{C}$ ratio.

In this study, we developed a PLA melt-mixed with *myo*-inositol, which had fast crystallization and better stability, during processing. We evaluated the nucleation effect of *myo*-inositol at the isothermal condition of 100 °C after melting at 200 °C, and the stabilization effect of *myo*-inositol during the thermal melting process on PLA. It was expected that the hydroxyl groups on the crystal surface of *myo*-inositol act as the starting point of crystallization of PLA and promote the crystallization. To confirm whether the mixed materials were fully biobased materials, the biomass carbon ratio was measured by the AMS method.

2. Experimental

2.1. Reagent and material

myo-Inositol derived from rice bran was kindly supplied from Tsuno Co., Ltd. (Japan). Poly(L-lactic acid) (PLLA) (L-lactic acid rich PLA, $M_n = 1.0 \times 10^5$) as H-100 made from biomass feedstock was purchased from Mitsui Chemical, Inc. (Japan). *myo*-Inositol was separated using sieves of 120 mesh (125 μm) then dried at 120 °C for 12 h in *vacuo*.

2.2. Melt mixing of PLLA with *myo*-inositol

To prepare the samples for the measurement of the thermal properties and molecular weight, *myo*-inositol (4.0 g) and PLLA (76.0 g), containing 5 wt% *myo*-inositol, were melt-mixed using a melt-mixer (Toyo Seiki Seisaku-sho, Ltd.; Labo Plastomil) equipped with a twin screw and 100 ml interior volume at various temperatures for various times. To prepare the samples for the measurement of the mechanical properties, after the dry blending of the *myo*-inositol (0.10 kg) and PLLA (1.90 kg), containing 5 wt% *myo*-inositol, the melt-extrusion was carried out using the twin screw extruder ($L/D = 31.5$) (Ikegai Co., Ltd.; PCM 30). The melt-extrusion was

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