Journal of Food Engineering 93 (2009) 308–312

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Effect of high pressure treatment on thermal properties of polylactides

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ARTICLE INFO

Article history:
Received 9 July 2008
Received in revised form 24 January 2009
Accepted 26 January 2009
Available online 3 February 2009

Keywords:
Amorphous
Glass transition temperature
Crystallinity
Melting
Enthalpy

ABSTRACT

Effect of high pressure treatment on thermal properties of amorphous and semi-crystalline polylactides (PLA) was studied. Three different PLA isomers (D, L and DL) with molar mass in the range of 3800–6200 were pressurized (350, 450 and 650 MPa) for a holding time of 15 min and the process temperature was maintained in the range of 22–26 °C. Thermal properties (glass transition temperature, melting behavior and crystallinity) of post-process samples were analyzed by a differential scanning calorimetery (DSC) and compared with untreated sample. The glass transition temperature (T_g) was found to decrease as pressure was applied to lactides. During pressure treatment, it was observed that both melting and crystallization peak of L-isomer were significantly reduced at 650 MPa and the observation was quantified by decrease in fusion (ΔH_m) and crystallization enthalpy (ΔH_c). Fourier transform infrared (FTIR) spectroscopy could not detect the change in the crystalline band (1300–1150 cm^{-1}) of pressure treated L-isomer. This study suggests that PLA could be further experimented for development of food packaging material under high pressure treatment either individually or in combination with other materials.

1. Introduction

Biodegradable polymers are current research focus in bio-medical and environment friendly packaging materials. Among biopolymers, lactic acid based polymers known as polylactides (PLA) are extensively used in various medical applications including carriers in drug delivery, scaffolds in tissue engineering (Fetters et al., 1994; Tullo, 2000) and coronary stents for treating vascular disease (Varshney et al., 2007). PLA has good biodegradability, biocompatibility, a high mechanical strength, and excellent shaping and molding properties. Therefore, it becomes a good candidate for packaging materials due to its close similarity with poly(ethylene terephthalate) (PET). PLA production is derived from renewable sources (e.g. corn, sugarcane) and therefore, it gained attention as an alternative to synthetic polymers. PLA can be hydrolysed quite easily to produce lactic acid, lactide and oligomers, which are afterward decomposed into water and carbon dioxide by microorganisms (Tuominen et al., 2002).

PLA has already been approved as GRAS (generally regarded as safe) status for food packaging (Jin and Jhang, 2008). Presently, it is used for manufacturing lunch boxes and for fresh food packaging in Japan (Mutsuga et al., 2008) whereas, PLA containers have been used for packaging bottled water, bottled juices, and yogurts in European and North American market. Blends of PLA and starch/protein to develop biodegradable packaging materials have been studied extensively (Ke and Sun, 2003; Huneault and Li, 2007) due to enormous environment concerns across the globe. Attention is also paid to PLA due to solid waste accumulation (Sinclair, 1996) and thus, there are significant efforts to produce newer biodegradable packaging materials based on PLA. In the same time, there is an urgent need to develop suitable packaging materials for novel food processing technologies like microwave, high pressure processing, Ohmic heating etc. PLA based packaging materials with added advantages could be tested for those processes.

There has been renewed interest in crystallization of lactides. Nature derived lactides (agricultural source) are mostly in L-form and exhibit crystalline behavior. The crystallization behavior of polylactides depends on the thermal history (i.e. annealing) (Tsuji and Ikada, 1995), amount and type of additives (Brochu et al., 1995), and stereosequence distribution (Thakur et al., 1996). The heat of crystallization measured by differential scanning calorimetry may depend on the sterosequence distribution in the polymer. It is important to know the percent of crystallinity since it strongly influences the physical properties of the polymer (Perego et al., 1996). Understanding of thermodynamic properties of lactides requires quantitative thermal analysis and reliable interpretation of the underlying molecular mobility (Pyda, 2004). Interestingly, polylactides exhibit both amorphous and semi-crystallinity and a wide variation in thermal properties among various polylactides are expected. In our earlier communication (Ahmed et al., 2009), effect of isomer, microstructure and molar mass on thermal properties of PLA have been reported.

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0260-8774/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jfoodeng.2009.01.026

High pressure processing (HPP) is one of the non-thermal processing technologies currently being exploited to produce value-added food products by keeping adequate sensory attributes. The low molar mass compounds are not affected by high pressure whereas large molecules like proteins and starches have been significantly affected by pressure treatment. Under high pressure, proteins denature and starches gelatinize and consequently lose their structures and functionality (Hayashi, 1992). HP treatment has been shown to influence the functional properties of proteins through the disruption and reformation of hydrogen bonds and hydrophobic interactions leading to denaturation, aggregation and gelation (Cheftel, 1992).

Numerous research works have been carried out in the area of pressure assisted starch gelatinization and protein denaturation and subsequent structural modification followed by change in functionality. Limited research works are carried out on packaging materials and heat sensitive nanoparticle under high pressure to assess its suitability for the food packaging and sterilization (Schmerder et al., 2005; Brigger et al., 2003). In that direction, studies on PLA under high pressure are very relevant and, in the same time food processors are looking for suitable packaging material that could be used for HPP.

The main objectives of the present study are to explore high pressure effect on thermal properties and crystallinity of the PLA isomers to elucidate the influences of high pressure on the properties and characteristics of PLA using calorimetric and infrared techniques.

2. Materials and methods

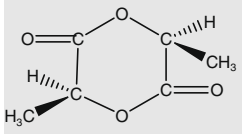
2.1. Materials

Polylactides (PLA) samples (D, L and DL) were synthesized at Polymer Source Inc. (Montreal, Canada). Both poly L(−), D(+) and racemic (DL±)-lactides were synthesized by tin-catalyzed ring-opening bulk polymerization of monomer (Purac, USA). The number average (M_n) and the weight average (M_w) molar masses of D, L and DL samples were 3500, 4500, 5200 and 3800, 5800, 6200, respectively based on size exclusion chromatography (SEC) measurement on a Varian instrument (Varian Inc., CA, USA) equipped with refractive index, UV and dual detectors (light scattering, and viscosity detectors). Details are available in another publication (Ahmed et al., 2009). It is worth to mention that L-form was monohydroxy terminated and other two isomers were dihydroxy terminated. Isomeric and molecular structures of studied polylactides are presented in Table 1.

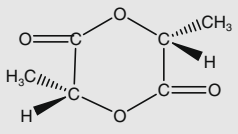
2.2. High pressure treatment

Polylactide samples (powdered form, about 2 g each) were packed in low-density polyethylene bags (Whirl-Pak®, USA) and the bags were heat sealed. The air in the bag was squeezed out as much as possible before sealing. All lactide samples were wrapped with another similar bag to prevent water absorption during pressurization. Samples were then transferred to the 5 L

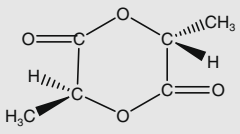
Table 1
Isomeric and molecular structures of polylactides used in the experiment.



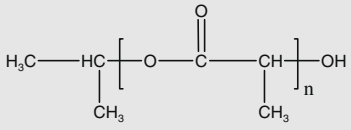
L-Lactide



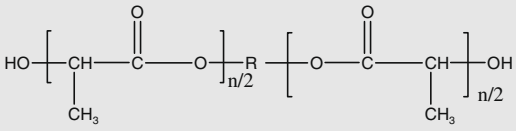
D-Lactide



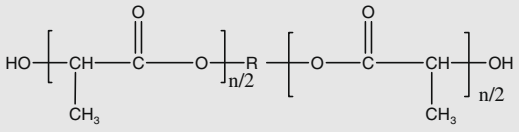
DL-Lactide



Poly(L-lactide)



Poly(D-lactide) where R=ethylene glycol



Poly(DL-lactide) where R=diethylene glycol