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Effect of chain extenders on thermal and mechanical properties of poly(lactic acid) at high processing temperatures: Potential application in PLA/Polyamide 6 blend

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ABSTRACT

Poly(lactic acid) (PLA) is vulnerable to severe thermal degradation when it was processed at high temperature, especially above 200 °C. An undesired molecular weight reduction and weight loss caused by both hydrolysis and depolymerization reactions result in poor mechanical performance of final products. Thus, the aim of this work was to study the effect of chain extenders on the thermal and mechanical properties of PLA processed at high temperatures in a twin screw extruder having four different sets of temperature profiles. Two types of chain extenders, multifunctional epoxide (ECE) and polycarbodiimide (PCD) were used with the constant amount of 0.5 phr. All samples were characterized using GPC, MFI, DSC, TGA, FT-IR tensile and impact tester. The GPC results showed that the molecular weight (Mw) of processed PLA tended to decrease when increasing the processing temperatures and its molecular weight distribution (MWD) shifted towards lower molecular weights whereas Mw of all PLA added chain extenders samples increased and MWD exhibited bimodal distribution and slightly shifted towards higher molecular weight population. The addition of both chain extenders also improved elongation at break and impact strength. For processed PLA samples, these mechanical properties decreased. TGA thermograms of PLA added chain extenders samples showed the increase in onset and deflection temperatures when compared to processed PLA ones. The investigation of PLA based matrix (70%wt of total polymer) was also performed by blending with Polyamide 6 (30%wt of total polymer) with 0.5 phr of ECE or PCD in a twin screw extruder within the temperature profile of 170–250 °C. The blend with chain extenders proved to ease the effect of molecular weight reduction without sacrificing the mechanical properties. Both of PCD and ECE provided the improvement in modulus and tensile strength, especially elongation and impact strength for PLA/PA6/ECE blend. They increased by 92.2% and 65.1% respectively when compared to blend without ECE.

1. Introduction

Biodegradable polymers are currently materials of considerable interest due to their advantages such as an environmental benign, an origin of renewable resources and comparable mechanical properties with conventional plastics. Despite numerous advantages, thermal properties are considered to be the major drawback, which limits their use for specific products. Among the bio-based and biodegradable polymers, poly(lactic acid) (PLA) is the one of popular choices as it possesses high mechanical strength and modulus and is now available largely in a commercial scale, thus PLA is most likely to replace commodity and even engineering plastics. However, some properties such as brittleness, limited gas barrier properties, low melt strength and low thermal stability [1] are major drawbacks of PLA. Especially, thermal properties, PLA is vulnerable to severe thermal degradation when processed at high

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temperature. The decrease of molecular weights and weight loss occurred via hydrolysis reactions and back-biting depolymerization respectively [2,3]. During processing, the moisture content in the polymer (for PLA usually >200 ppm) and heat absorbed by the polymer can accelerate the hydrolysis reaction. The weight loss of PLA can occur via the depolymerization, releasing the oligomers or the lactide monomer as a consequence.

Sodergard et al. [4] studied the melt degradation of poly(l-lactide) at temperature above 180 °C and the result showed that the thermal degradation was found to proceed by random main-chain scission. Wachsen et al. also reported that the temperature of above 200 °C led to the formation of cyclic oligomers [5]. Moreover, PLA could be degraded at 160 °C under injection molding as described by Gogolewski et al. [6]. To enlarge its processing window and thereby also its applications field, the thermal degradation protection of PLA at high process temperature is very important. In order to minimize or avoid the thermal degradation of aliphatic polyesters, many methods such as non-reactive and reactive blending, copolymer synthesis and the addition of additives are available. Above all, using a chain extender as an additive is considered to be an easy-to-apply alternative for many industries. Many authors have shown the interest of using a chain extender, which is able to reconnect cleaved chains by increasing molecular weight of polymer [7–9], strength of melt [10] and can also be used as a reactive compatibilizer in blends [10–12]. In general, the chain extender can have bi or more functional groups such as diisocyanate [9,13], dianhydride [14,15], diamine [16], epoxy, etc. to couple the two end groups of low molecular weight polymer chains. The variety of these compounds allows the bonding of specific chain structures.

Therefore, the aim of this work was to study the effect of chain extenders on the thermal and mechanical properties of PLA and chain extenders processed at high temperatures in a twin screw extruder having four different sets of temperature profiles with the die temperature ranged from 220 to 250 °C. Two types of chain extenders, polycarbodiimide (PCD) and multifunctional epoxide chain extender (ECE) were selected for comparison. In addition, the application of PLA blended with high melting temperature plastics was also investigated. Polyamide 6 (PA6) was selected as a model polymer due to high tensile strength, stiffness and hardness, excellent abrasion resistance, good gas barrier properties, good chemical resistance in oils, fats, and petrol [17,18]. Thermal and mechanical properties of PLA/PA6 (70/30 w/w) blend with 0.5 phr of ECE or PCD were investigated and discussed.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA) 2003D was purchased from NatureWork® LLC, USA. Two types of chain extenders, multifunctional epoxide chain extender (ECE) and polycarbodiimide (PCD) were chosen for comparison. The multifunctional epoxide chain extender (ECE) (Joncry® 4368) was kindly supported from BASF, Thailand. Its molecular weight (Mw) was 6800 Da with the epoxy equivalent weight of 285 g/mol. Polycarbodiimide (PCD) or Bioadimide™, RheinChemie, Germany, was kindly supplied by Optimal Tech Co., Ltd, Thailand. PCD with carbodiimide content higher than 13.0% has the melting temperature in range of 70–80 °C. Polyamide 6, nylon resin Zytel® 7331J NC010 (DuPont™) was purchased from Global Connection (Public) Co., Ltd, Thailand.

2.2. Processing

PLA pellets were first dried in a vacuum oven at 60 °C for 24 h before further use. PLA and 0.5 phr of chain extenders were mixed and then introduced to the twin screw extruder (SHJ-25, China) with length to diameter ratio (L/D) of 40. The barrel temperature was divided to eight zones from feed zone to die. The mixture was mixed under the four temperature profiles from feed zone to die set at: (1) 140/160/190/210/220/220/220/220, (2) 150/170/200/220/230/230/230/230, (3) 160/180/210/230/240/240/240/240 and (4) 170/190/220/240/250/250/250/250 °C. The die temperature 220, 230, 240 and 250 °C was referred to the processing temperature and is used for further discussion. The rotation speed was kept at 50 rpm. The processing of processed PLA was also carried out at the same four conditions. The extrudates were cut, dried at 60 °C for 12 h. Then the moisture content was measured with moisture analyzer (METTLER TOLEDO, HX204) and kept the samples in zip-lock plastic bags to avoid the moisture adsorption.

2.3. Preparation of PLA/PA6 blends

PLA pellets and PA6 resin were first dried in the vacuum oven at 60 °C for 24 h. Then PLA pellets were premixed with PA6 and chain extenders before blending in the twin screw extruder (SHJ-25, China). The processed polymers and blend of PLA/PA6/chain extenders were prepared where the ratio of PLA and PA6 was 70/30 and the amount of chain extender was fixed at 0.5 phr. The blends were prepared in the twin screw extruder under the temperature profile from feed zone to die set at 170/190/220/240/250/250/250/250 °C, the rotation speed was kept at 50 rpm. The extrudate was cooled in the water bath, then granulated and dried at 60 °C for 12 h. The moisture content of samples were measured and kept it in zip-lock plastic bags.

2.4. Molecular weight measurement

Molecular weight and polydispersity index of PLA and modified PLA with chain extenders samples at various process temperatures were measured by gel permeation chromatography (GPC). The sample of 10 mg was dissolved in the tetrahydrofuran (THF) 3 ml for measurement. Gel permeation chromatograph (GPC) analyses were carried out on Waters 2414 refractive index (RI) detector, equipped with Styragel HR5E 7.8 × 300 mm column (molecular weight resolving range of 2000–4,000,000 Da). The GPC columns were eluted using tetrahydrofuran with a flow rate of 1.0 mL/min at 40 °C and calibrated with polystyrene standards.

2.5. Melt flow index

Melt flow index of all samples were performed on a melt flow indexer (Intro D7053, KAYENESS) operating at 190 °C with 2.16 kg load according to ASTM D1238.

2.6. Thermal properties

2.6.1. Thermogravimetric analysis (TGA)

The thermal stability of processed PLA and PLA added chain extenders samples were analyzed by TGA (PERKIN ELMER, TGA7). The 3–5 mg of sample was heated from 50 °C to 550 °C with heating rate at 10 °C/min under nitrogen atmosphere.

2.6.2. Differential scanning calorimetry (DSC)

The measurements were carried out with METTLER TOLEDO, DSC1 operated with STARe system software. 7–10 mg samples were weighted. The temperature scan was performed with a heating and cooling rate of 10 °C/min under nitrogen atmosphere. The samples were heated from 30 to 200 °C, held for 1 min to erase thermal history effects and cooled to 30 °C, held for 1 min and then heated to 200 °C again for the second scan. The glass transition