Polymer Degradation and Stability 142 (2017) 244–254

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Nucleating efficiency and thermal stability of industrial non-purified lignins and ultrafine talc in poly(lactic acid) (PLA)

Adriana Kovalcik [a, b, *], Ricardo A. Pérez-Camargo [c], Christian Fürst [a], Pavel Kucharczyk [d], Alejandro J. Müller [c, e, **]

[a] Kompetenzzentrum Holz GmbH (Competence Centre for Wood Composites and Wood Chemistry, Wood K Plus), Department of Wood Polymer Composites, Altenberger Strasse 69, 4040 Linz, Austria
[b] Institute of Food Science and Biotechnology, Chemical Faculty, Brno University of Technology, Purkynova 118, 612 00 Brno, Czech Republic
[c] POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel Lardizabal 3, 20018. Donostia, San Sebastián, Spain
[d] Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Tr. T. Bati 5678, 760 01 Zlin, Czech Republic
[e] IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

ARTICLE INFO

Article history:
Received 22 February 2017
Received in revised form
30 June 2017
Accepted 9 July 2017
Available online 10 July 2017

Keywords:
Biodegradable polymers
Crystallization kinetics
Differential scanning calorimetry
Lignin
Nucleation efficiency
Poly(lactic acid)
Thermal stability

ABSTRACT

Poly(lactic acid) (PLA) with *D* − lactide content of 1.2 wt% has been modified by melt mixing with 3 wt% of lignin (Kraft or Organosolv). Gel permeation chromatography and thermogravimetric analysis were employed to determine the thermal stability of PLA and nucleated PLA compounds during melt blending. The nucleating efficiency of industrial lignins was compared with the nucleation efficiency of ultrafine talc (UT). The feasibility of using industrial lignins and UT as nucleating agents for PLA was investigated by polarized light optical microscopy and differential scanning calorimetry, through non-isothermal and isothermal crystallization, whereas their structure was studied through *in-situ* synchrotron X-ray diffraction at wide and small angles. Both lignins, as well as UT induced heterogeneous nucleation and their nucleating action in PLA increased the crystallization rate and shortened the overall crystallization half time for isothermal crystallization. All tested nucleating agents increased the degree of crystallinity of PLA. The nucleation efficiency of Kraft and Organosolv lignin and ultrafine talc was 31%, 27%, and 80%, respectively. It was found that the thermal processing window of PLA was not influenced by the addition of lignins or ultrafine talc.

1. Introduction

The global production of bio-based polymers including bio-based polyethylene, poly(ethylene terephthalate), starch blends, poly(lactic acid), polyhydroxyalkanoates, polyamide, cellulose acetate and others, reached 5.1 million tons approximately in 2013. The production growth of poly(lactic acid) (PLA) is expected to almost quadruple between 2013 and 2020 [1]. Despite some promising properties, the applicability of PLA is restricted by its slow crystallization, high brittleness, low softening temperature and a high tendency to shrinkage (during polymer processing and storage). Given these limitations, the best way to improve its properties and enhance its application range is to prepare blends, copolymers or to reinforce it with various inorganic and organic fillers.

The production of new compounds and mixtures based on PLA, as well as the modification of polymer processing methods, are under constant development to meet industrial customers' needs [2].

A number of nucleating agents based on (1) inorganic materials, e.g., talc and kaolin [3,4], (2) organic materials, e.g., sorbitol derivatives [5], oxalamide derivatives [6], aromatic phosphonates [7], aromatic sulphonates [8,9], benzoyl hydrazide compounds [10–13], (3) inorganic-organic hybrid materials, e.g., epoxy functionalized poly(hedral oligomeric silsesquioxane) [14], and (4) oligomers or polymers, e.g., lignin [15,16] or (5) hybrids based on inorganic

---

* Corresponding author. Institute of Food Science and Biotechnology, Chemical Faculty, Brno University of Technology, Purkynova 118, 612 00 Brno, Czech Republic.
** Corresponding author. POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel Lardizabal 3, 20018. Donostia, San Sebastián, Spain.
E-mail addresses: adriana.kovalcik@gmail.com (A. Kovalcik), alejandrojesus.muller@ehu.es (A.J. Müller).

http://dx.doi.org/10.1016/j.polymdegradstab.2017.07.009
0141-3910/© 2017 Elsevier Ltd. All rights reserved.

material and polymer [17] have been studied. The essential requirements for nucleating agents are their proper distribution in PLA, high nucleation efficiency already in low concentrations, high ability to increase the crystallization rate and to induce the crystallization into the preferred crystalline form. The following nucleating agents are commercially available for PLA: talc, kaolin, calcium carbonate, ethylenebis(12-hydroxystearylamide) (EBHSA), ethylene bis-stearamide (EBS), N,N′,N″-tricyclohexyl-1,3,5-benzenetricarboxylamide (TMC-328), 1,3:2,4-Dibenzylidene-*D*-sorbitol (DBS), Ecopromote, phthalhydrazide, tetramethylenedicarboxylic dibenzoylhydrazide (TMC-306), potassium salt of 5-dimethyl sulfoisothalate (Lak-301). Other non-commercial crystal nucleating agents for PLA have been synthesised and investigated, such as various inorganic and organic materials like hydrazide compounds [12,13,18,19], *myo*-Inositol [20], benzenetricarboxylamide (BTA) derivatives [21], dilithium hexahydrophthalate [22], oxalamide derivatives [6], amino acids and poly(amino acids) [23], phenylphosphonic acid zinc salt [24], bibenzoylhydrazinepropane (BBP) [25]. The effective concentration of inorganic materials was found to be in the range of 1–5 wt% depending on their efficiency. Nano- and micro-talc are amongst the most effective nucleating agents for PLA. The superior nucleating efficiency of talc as compared to kaolin and calcium carbonate was explained by the formation of orthotropic crystalline textures due to the presence of specific interfacial interactions between talc and PLA [4].

Lignins can be used as renewable organic nucleating agents for polymeric matrices. Lignins are natural amorphous polymers with a complex mutative structure consisting of phenylpropane units predominantly with hydroxyl, methoxyl, carbonyl, and carboxyl substitutions. It has been accepted that lignin's structure and properties are not stable and can vary during individual isolation step, while every operation involves some cleavages of linkages between lignin and carbohydrates that are accompanied by condensation reactions that modify the resulting chemical and physical properties of derived materials. The substantial heterogeneity of lignin structures makes difficult the determination of their overall chemical structure. The main issue limiting the use of lignins in other applications besides fuel is mainly their different structure as well as acquired properties after delignification during industrial processes (pulp and paper industry). The main detected differences are in the purity (e.g., content of Klason lignin, ash, cellulose and hemicelluloses), macromolecular weight properties, elemental composition, and functional groups.

A number of PLA blends with physically and chemically modified lignins have been studied [15,17,26–41]. Only a few works have employed commercial lignins without additional chemical modifications used as additives for PLA in concentrations up to 5 wt% [15,29,32]. Some authors have shown that the addition of lignin can improve the thermal stability of PLA [29,33,34]. Other studies confirmed the existence of PLA-lignin interactions (carbonyl groups of PLA with hydroxyl groups of lignin) and a formation of hydrogen bonds [26,27,34,35,42,43]. The flame retardant effect of lignin in PLA due to the formation of char has been reported by Costes et al. [37]. The ability of lignins (derived from cornstalk [15] and lignin nanoparticles (LNP) prepared by steam explosion and enzymatic modified pristine lignin [38,41]) to serve as nucleating agents for the heterogeneous crystallization of PLA has been demonstrated by non-isothermal DSC and polarized light optical microscopy analyses. Additionally, an antioxidative and antibacterial activity of lignin particles has been reported [44].

Some works have reported anti-nucleation effects of several types of lignins (i.e., almond shell lignin [29], Kraft lignin derived from lignoBoost process [32,34], organosolv lignin from birch wood [34] and methanol fractionated softwood Kraft lignin (Indulin AT) [42]) on PLA. On the other hand, it has been reported that the crystallization kinetics of PLA can be accelerated by a silica/lignin hybrid filler, while half-time values and crystallinity rates increase with the amount of silica in the compound [17]. As far as we are aware, isothermal crystallization kinetics of PLA/industrial (unmodified) lignin blends have not been reported yet. Only the isothermal crystallization kinetics of PLA with lignin coated cellulose nanocrystals has been reported [45]. It has been accepted that the influence of lignin on the thermal properties of polymers depends on the chemical nature of the polymer matrix, as well as its origin, concentration, particle dimensions, distribution in the polymer matrix and polymer-lignin interactions.

In this study, industrial lignins without any purification or other treatment step were evaluated as nucleating agents for PLA by using differential scanning calorimetry (DSC). The nucleating efficiency of lignins and talc in PLA was determined by self-nucleation experiments employing the Fillon et al. [46] nucleating efficiency scale. The overall crystallization kinetics of PLA nucleated compounds were evaluated by isothermal crystallization experiments. The morphology of the samples was observed by polarized light optical microscopy. The influence of industrial lignins and ultrafine talc on the thermal stability of PLA compounds after melt blending was studied by thermogravimetric analysis and gel permeation chromatography.

2. Experimental part

2.1. Materials

Poly(lactic acid) (PLA) used in this study was Ingeo™ Biopolymer 3251D type (NatureWorks, MN, USA), with a $D-$lactide content of 1.2%, a density of 1.24 g cm^{-3}, a melt flow index (MFI) of 35 g 10 min^{-1} (at 190 °C and 2.16 kg). The glass transition temperature and melting temperature of the PLA resins (moisture in the range of 0.02–0.03%) were 59.5 °C and 170.9 °C, respectively.

Kraft lignin (KL) with M_w 3.8 kDa, $Đ$ of 3.8 and with particle size distribution d90 of 63 μm (Indulin AT, Mead Wesvaco corp., USA), and Organosolv lignin (OL) with M_w of 3.2 kDa, $Đ$ of 2.9 and with particle size distribution d90 of 75 μm (Chemicalpoint) were used as received. Ultrafine talc (UT) (Jetfine 3CA) with particle size distribution d95 of 3.3 μm and specific gravity of 2.78 g cm^{-3} was obtained from Luzenac. It is composed of 62% SiO_2, 31.5% MgO, 0.4% Al_2O_3, 0.3% CaO and 0.2% Fe_2O_3. Physical properties and chemical composition of lignins and ultrafine talc, namely data concerning Brunauer-Emmett-Teller BET surface area analysis, elemental analysis, carbohydrate and ash content are shown in Table 1.

2.2. Preparation of blends

PLA and nucleating agents were dried in an oven at 80 °C for 24 h. Melt blending of neat PLA and PLA with nucleating agents was carried out in a Brabender Plasti-Corder (Brabender 250 EHT, Germany) at a temperature of 190 °C, a screw speed of 60 rpm for 6 min. The samples were coded as follows: PLA/UT, PLA/KL, and PLA/OL with a constant amount of 3 wt% nucleating agent.

2.3. Characterisation methods

2.3.1. Polarized light optical microscopy (PLOM)

A polarized light optical microscope, Olympus BX51, was employed incorporating a λ plate in between the polarizers at 45° to facilitate observation and determine the sign of the birefringence. The microscope was equipped with an Olympus SC50 digital camera. A Mettler Toledo FP82 hot stage was coupled to the microscope. Film samples with 10 μm thickness were sandwiched between two glass slides. The samples were first heated to 190 °C to