Polymer Testing 41 (2015) 124–132

Contents lists available at ScienceDirect

Polymer Testing

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

Material behaviour

The influence of a hydrolysis-inhibiting additive on the degradation and biodegradation of PLA and its nanocomposites

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ARTICLE INFO

Article history:
Received 23 September 2014
Accepted 29 October 2014
Available online 11 November 2014

Keywords:
Biodegradability
PLA
Layered silicates
Abiotic hydrolysis
Thermal degradation
Carbodiimide

ABSTRACT

A carbodiimide-based additive, intended to stabilize PLA based materials to avoid hydrolytic degradation during processing, was incorporated into a series of PLA and nanofiller containing PLA films. The influence of the additive on the subsequent degradability of the materials was studied under the conditions of melt processing, biodegradation in compost and abiotic hydrolysis. Identical films without the additive were used as reference materials. Adding an anti-hydrolysis agent significantly retarded the decomposition of PLA in all the degradation processes tested. Both biodegradation and the abiotic hydrolysis of the PLA-based materials investigated were substantially retarded. This effect was much less pronounced in a material with organically modified montmorillonite.

1. Introduction

Biodegradable polymers that can be decomposed by microorganisms with no negative environmental impact appear to be a promising alternative to conventional polymers for some specific applications [1,2]. Of these, aliphatic polyester polylactid acid (PLA) seems to be one of the most attractive materials due to its thermoplastic behaviour, good processability, biocompatibility and some interesting physical properties e.g. transparency after processing. Moreover, PLA can be fully obtained from renewable resources [3]. Recently, new techniques which allow for economical production of high molecular weight (MW) PLA (greater than 100,000 Da), with relatively good mechanical and processing properties, have brought further expansion of utilization from the biomedical area to a wider spectrum of products, particularly short service life applications in agriculture and the food industry [4]. These disposable products that benefit from the advantage of PLA biodegradability may be processed along with other organic waste in industrial composting facilities. Nevertheless, propensity to degradation along with poor thermal and mechanical resistance, as well as restricted gas barrier properties, significantly limit specific industrial applications, particularly for durable products with long-term performance such as in the automotive and electronic industries [5]. For items such as these, resistance to degradation is required unlike for disposable applications [6].

In the natural environment, the degradation of PLA proceeds either through hydrolytic or enzymatic chain scission of the ester bonds to low molecular weight oligomers and

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http://dx.doi.org/10.1016/j.polymertesting.2014.10.015
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monomers, enabling assimilation by microorganisms [7]. It is well known [8,9] that biodegradation of PLA proceeds readily in a compost environment, especially during the thermophilic phase of the composting process, characterized by relatively high temperatures. In particular, abiotic hydrolysis was suggested as a major depolymerisation mechanism and the rate-controlling step of PLA biodegradation in compost [10]. Therefore, any factor affecting the rate of hydrolysis could either accelerate or retard the whole biodegradation process [11]. The presence of weak hydrolyzable linkages also makes material more sensitive to heat and moisture during its thermal processing, which may lead to degradation and molecular weight reduction [12]. Moreover, ester hydrolysis can be autocatalyzed by any carboxyl end groups initially present or formed during the chain cleavage [13]. The thermal stability of polyesters could be enhanced by adding appropriate reagents, which work as chain extenders and react with carboxylic groups [14]. Recently, the use of compounds acting on the above-mentioned principle, e.g. polycarbodiimides [16] and tris(nony1-phenyl) phosphite [17], have been studied to improve the thermal stability of PLA during processing. However, their impact on stability during biotic and abiotic degradation has yet to be substantially investigated.

It was reported that poor thermal stability, along with the other drawbacks mentioned above, can also be improved by mixing the polymer with various nanoclays even at low final contents [18,19]. Montmorillonites (MMT) represent the most frequently studied group of nanofillers as an additive in PLA polymer systems, which are of particular interest due to their modifications with organic compounds that provide greater compatibility with the polymer [20,21]. In order to improve the performance of the material significantly, nanoparticles have to be properly dispersed throughout the polymer on the nanoscale level to achieve a high specific surface area, hence better interfacial interactions between the polymer matrix and the layered silicates [22]. Of the various preparation methods, twin-screw melt extrusion has emerged as the approach of choice for precise PLA/silicate nanocomposite processing, as a result of the high level of organo-modified MMT intercalation that might be achieved [23]. Consequently, the degradation of PLA in the melt could intensify due to the high shear stress mixing needed for good intercalation of clays [24].

The incorporation of nanoclay fillers into PLA could also, in some cases, increase the susceptibility of PLA towards hydrolysis in comparison with the unfilled material [25–27]. The differences have mainly been attributed to the relatively high hydrophilicity of nanoclays, which could increase the diffusion of water into the polymer matrix, resulting in faster activation of the hydrolytic degradation processes [28]. According to other authors [29,30] the hydrolytic process during thermal and abiotic degradation may be enhanced due to the presence of terminal hydroxyl groups of silicates as well as the excess of hydroxyl groups in some organic modifiers.

In the present work, the authors investigated the stabilization effect of a commercially available aromatic carbodiimide-based anti-hydrolysis agent (AHA), intended to improve the hydrolysis resistance of bio-based polyesters and prevent their degradation during processing [31] by scavenging of the free carboxylic groups and water molecules (Fig. 1). It was stated that AHA should improve the hydrolytic stability of PLA during its melt processing by up seven times in comparison to unstabilized material. However, further information is missing about the additive influence in other phases of the material life cycle and its interference with common fillers like nanoclays. In order to evaluate the extent of stabilization during thermal processing and during the subsequent lifetime of the products, PLA films stabilized with AHA were tested and monitored by different experimental techniques in the processes of thermal degradation, abiotic hydrolysis and microbial decomposition under compost conditions. The effect of AHA was also tested for PLA nanocomposite films filled with commercially available native and organo-modified MMTs equally loaded at 5% w/w.

2. Materials and methods

2.1. Materials

Polylactic acid PLA2003D was purchased from NatureWorks® Ingeo™, USA. The aromatic carbodiimide-based anti-hydrolysis additive Bioadimide100, containing about 10% of the active ingredient, was purchased from Rhein Chemie Corporation, Chardon, USA. The nanofillers used in the study, native MMT Cloisite Na^+ and organo-modified MMT Cloisite 10A (Dimethyl benzyl hydrogenated tallow quaternary ammonium modifier), were supplied by Southern Clay Products, Inc., Gonzales, USA.

2.2. Material processing

2.2.1. Preparation of PLA/clay nanocomposites

Prior to compounding, the PLA and clays were dried at 60°C under reduced pressure for at least 24 hours. A co-rotating twin screw extruder ZSK 25 compounder (Coperion GmbH, Stuttgart, Germany), operating at 200°C, was used. The feed rate of materials was set to 6 $kg.h^{-1}$ and the screw speed to 100 RPM. Table 1 lists the clay types along with the process conditions, including torque, head pressure and real temperature profiles.

2.2.2. Preparation of films

Prior to the film extrusion process, PLA and PLA/clay nanocomposite pellets were pre-dried at 40°C for 24 h. Then they were extruded with a single-screw extruder type PlastiCorder (Brabender, Germany) equipped with a flat extrusion die (width: 250 mm) at a processing temperature of 200°C, providing thin films of about 20 μm thickness. The films were quenched by a chill roll at 40°C.

2.3. Characterization

2.3.1. Gel permeation chromatography

The weight average molecular weight (M_W) and MW distribution of samples and its changes during degradation

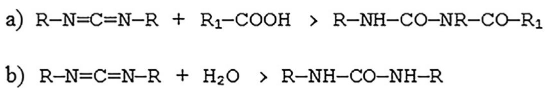

Fig. 1. Reaction of carbodiimide with carboxylic group (a) and water (b).