Polymer Degradation and Stability 143 (2017) 9–19

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Relevant factors for the eco-design of polylactide/sisal biocomposites to control biodegradation in soil in an end-of-life scenario

J.D. Badia [a, b], E. Strömberg [c], T. Kittikorn [c, d], M. Ek [c], S. Karlsson [c], A. Ribes-Greus [a, *]

[a] Instituto de Tecnología de Materiales (ITM), Universitat Politècnica de València (UPV), Camino de Vera S/N, 46022, Valencia, Spain
[b] Departament d' Enginyeria Química, Escola Tècnica Superior d'Enginyeria, Universitat de València, Av. de la Universitat, s/n, 46100, Burjassot, Spain
[c] School of Chemical Science and Engineering, Fibre and Polymer Technology, KTH – Royal Institute of Technology, Teknikringen 56-58, SE-10044, Stockholm, Sweden
[d] Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Songkhla, 90112, Thailand

ARTICLE INFO

Article history:
Received 13 March 2017
Received in revised form
22 May 2017
Accepted 4 June 2017
Available online 6 June 2017

Keywords:
Polylactide (PLA)
Natural fibre
Sisal
Biocomposite
Degradation
Biodegradation in soil
Design of experiments
Statistical factorial analysis
Size exclusion chromatography
Differential scanning calorimetry

ABSTRACT

The eco-design considers the factors to prepare biocomposites under an end-of-life scenario. PLA/sisal biocomposites were obtained from amorphous polylactide and sisal loadings of 10, 20 and 30 wt% with and without coupling agent, and subjected to biodegradation in soil according to standard ISO846. Mass-loss, differential scanning calorimetry and size-exclusion chromatography were used for monitoring biodegradation. A statistical factorial analysis based on the molar mass M_n and crystallinity degree X_C pointed out the relevance and interaction of amount of fibre and use of coupling agent with the time of burial in soil. During the preparation of biocomposites, chain scission provoked a similar reduction of M_n for coupled and non-coupled biocomposites. The amount of fibre was relevant for the increase of X_C due to the increase of nucleation sites. The coupling agent accelerated the evolution of both factors: reduction of M_n and the consequent increase of X_C, mainly during biodegradation in soil. Both factors should be balanced to facilitate microbial assimilation of polymer segments, since bacterial digestion is enhanced by chain scission but blocked by the promotion of crystalline fractions.

1. Introduction

The use of bio-based composites based on renewable polymer matrixes and natural fibres as alternative materials are continuously increasing in several applications such as packaging or household and agricultural equipment [1–3]. The eco-design of plastic materials from renewable resources for high-consume applications such as packaging or agricultural mulches moves towards the design of sustainable polymers with controlled degradability and enhanced bio-reintegration. Cradle-to-cradle design enables the establishment of completely beneficial industrial systems driven by the synergistic search of positive economic, environmental and social goals [4].

The use of sisal [5] has been reported for biopolymers such as polylactide [6–8], poly(hydroxyl butyrate-co-valerate) [9,10], starch-based matrixes [11–13] or chitosan [14]. Natural fibres such as sisal present low densities, low cost, non-abrasive nature, high filling level, low energy consumption, high specific properties, biodegradability, etc., over synthetic fibres. However, the absorption of moisture by untreated biofibres, poor wettability, and insufficient adhesion between the polymer matrix and fibre deteriorate the performance of the biocomposites [15]. In order to overcome the drawbacks, surface modifications of fibres [16] by means of processes such as esterification [17], silanization [17–19] or the use of maleic anhydride as coupling agent [20–22] are reported. Due to stability of biocomposites, there is a risk of wide scale environmental contamination and environmental issues similar to that seen with conventional plastics [23]. The balance of long-term properties of bio-based polymers and biocomposites is not usually connected to a proper end-of-life scenario [24]. Actually, most of them retain their properties after their service life and are uncontrolledly discarded [25], which could be approachable by means of burial in soil, that might induce biodegradation.

* Corresponding author.
E-mail address: aribes@ter.upv.es (A. Ribes-Greus).

http://dx.doi.org/10.1016/j.polymdegradstab.2017.06.004
0141-3910/

In order to understand and control the biodegradation state of these materials after disposal, several standards can be followed [26]. The use of the ISO846 [27], consisting in burial in active soil at 28 °C and controlled humidity is feasible to simulate the uncontrolled disposal of polymers, has been shown for polylactide [28–30], polyurethane [31], silicon rubber [32] or plasticised starch [33]. The biodegradation rate in this norm is usually followed by mass-loss after the disintegration state, which seldom represents a proper indicator to monitor biodegradation [30]. Indeed, before disintegration, the materials undergo structural and morphological modifications that are not assessable by the methods foreseen in the standard. Therefore, specific techniques such as size-exclusion chromatography and differential scanning calorimetry offer a fast and cost-reliable alternative to monitor the degradation state of biopolymers and biocomposites [24]. It is well-stated that degradation induces chain scission, which may ease the assimilation of oligomeric species by microorganisms in soil. However, it is also well-known that degradation mainly takes place in the amorphous fraction of polymers and therefore the formation of crystalline phase may difficult the chain scission and ulterior incorporation into the C-cycle by microorganisms. Therefore, the monitoring of both the molar mass and the degree of crystallinity may help interpret the biodegradation profile of biocomposites according to the balance between both competitive processes. Indeed, the abiotic and biotic environmental degradation of the bioplastics such as polylactide is reported [34], but it becomes more complex when other factors such as the amount of fibre and coupling agent in biocomposites are taken into account [35].

Summing up, the design of biocomposites is performance-focused, and therefore the addition of certain fibres and the improvement of the interfaces to achieve certain mechanical specifications are usually pursued. However, the eco-design of the same biocomposites should also consider the impact of these factors once the service life has been fulfilled, under an end-of-life scenario. In this work, PLA/sisal biocomposites were therefore prepared from amorphous polylactide and sisal loadings of 10, 20 and 30 wt% with and without coupling agent, and subjected to biodegradation in soil according to standard ISO846. The eco-design factors under study were the amount of fibre and the use of coupling agent. The variable of monitoring biodegradation was the time if burial. The effects under consideration were the molar mass, as obtained from size exclusion chromatography, and the crystallinity degree and thermal properties, as obtained by differential scanning calorimetry. The aim was to qualitatively assess the correlation between molar mass and crystallinity degree during biodegradation in soil before disintegration. The use of a statistical factorial analysis [36] to understand the relevance and possible interaction of the factors under study was used to shed more light on the understanding of the effects of biodegradation in soil on the biocomposites.

2. Experimental procedure

2.1. Materials and reagents

Polylactide (PLA) 3251D was purchased from Natureworks (Minnetonka, USA) as pellets with a glass transition in 65–70 °C range. Sisal fibres, a farming crop, were supplied by the Thai Royal Project [37]. Their length was about 0.5–1 mm, tensile strength of 550 MPa, tensile modulus of 30 GPa and density about 1.5 g/cm^3. Dicumyl peroxide (DCP) 98% (Sigma-Aldrich, Sweden AB) and maleic anhydride (MAH) M188-99% (Sigma-Aldrich, Sweden AB) were used as free radical initiator and coupling agent, respectively.

2.2. Preparation of PLA/sisal biocomposites

Prior to processing, neat PLA and sisal fibre were dried in an oven at 80 °C during at least 12 h and kept in zip bags. The fibre contents in the biocomposite were formulated as 10%, 20% and 30% by weight with and without coupling agent. In case of not using MAH, the biocomposites were prepared in an internal mixer (Brabender, Germany) during 5 min at 180 °C and at the speed of 50 rpm. The resulting biocomposites were labelled as PLA10, PLA20 and PLA30. The biocomposites containing the coupling agent were prepared by incorporating MAH 2.5% and DCP 0.3% by weight in molten polymer and mixing during 5 min at 180 °C and at the speed of 50 rpm. These samples were labelled as PLA10C, PLA20C and PLA30C. The compounded PLA/sisal biocomposites were then ground and the granules dried at 80 °C in the oven during at least 12 h. The final 500 μm thick specimens were obtained by means of a compression moulding equipment (Fontijne Presses, Netherlands), by preheating the press to 200 °C for 2 min, and applying a compression force of 150 kN during 2 min under vacuum conditions. Finally, all compounded biocomposites were dried at 50 °C in a vacuum oven (Heraeus Vacutherm 6025, Germany), then kept in zip bags and placed in a desiccator for further analyses at normalized lab conditions according to ISO 291 [38].

2.3. Biodegradation in soil test

The PLA/sisal biocomposites were subjected to a controlled degradation in soil test under controlled conditions, following the ISO 846–1997 International Norm, method D [27] during 135 days. The specimens were buried in biologically active soil and kept in a Heraeus B12 (Hanau, Germany) culture oven at 28 °C. The soil used in these tests was a red soil extract taken from a real agriculture field in Alginet (Valencia). The microbial activity of soil was monitored with cotton along the extension of the experiment. The soil was maintained at approximately pH 7 and a relative humidity of 0.87 g water/g wet soil. To ensure the oxygenation of the soil, a protocol of periodical air oxygen supply was followed. Three specimens of each sample were extracted after certain times of burial in soil, cleaned and kept in a desiccator during 4 days in order to ensure water desorption before being analyzed.

2.4. Analytical characterisation

2.4.1. Mass-loss variance

The specimens of PLA/sisal biocomposites were weighed using a scale (Mettler Toledo AB135-S) with a precision of 0.1 mg. Three samples of each material were used to assess reproducibility.

2.4.2. Size exclusion chromatography (SEC)

The molar mass of PLA/sisal biocomposites was analysed by size exclusion chromatography (SEC). The samples were dissolved in chloroform (Fluka, purity of 99%) at 80 °C for 2 h. The sample solution was filtered for removal of contaminants and fibres before injecting the sample into the SEC column. The polymers were analysed with a Verotech PL-GPC 50 Plus system equipped with a PL-RI Detector and two PLgel 5 mm Mixed-D columns. The samples were injected by a PL-AS RT auto-sampler for PL-GPC 50 Plus, in which chloroform was used as mobile phase (1 mL min^{-1}, 30 °C). The calibration was created using polystyrene standards with a narrow molar mass distribution. Corrections for the flow rate fluctuations were performed using toluene as internal standard. Triplicates were performed to ensure reproducibility of results.

2.4.3. Differential scanning calorimetry (DSC)

DSC characterization of PLA/sisal biocomposites was carried out