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Photooxidation of polylactide/calcium sulphate composites

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ABSTRACT

Stable $CaSO_4$ β-anhydrite II (**AII**), a specific type of dehydrated gypsum and a by-product of the lactic acid (**LA**) production process, was melt–blended with bio-sourced polylactide (**PLA**) to produce highly filled composites. Samples containing different amounts of filler (10–40 wt.%) with various granulometries were used for preparation of films by compression moulding. The influence of adding filler (calcium sulphate) on the photochemical behaviour of PLA–AII composites was studied by irradiation under photo-oxidative conditions ($\lambda > 300$ nm, temperature of 60 °C and in the presence of oxygen). Several analytical methods were used to characterise the polymer degradation. Oxidation of the polymer matrix was evaluated by infrared and UV–visible spectroscopies, differential scanning calorimetry (DSC) and size exclusion chromatography (SEC). The main photoproducts formed upon UV-light irradiation of the PLA were identified along with the influence of filler content and its particle size on the rate of oxidation. It was shown that oxidation of PLA and PLA–AII composites occurred without any induction time and that the presence of the $CaSO_4$ filler (AII) increased the oxidation rate of the polymer. Moreover, a faster degradation rate of PLA was observed in composites containing natural anhydrite of lower particle size (4 μm).

1. Introduction

In the market of biodegradable polymers, polylactide (PLA) is undoubtedly one of the most promising candidates for further developments as it is not only biodegradable but also produced from renewable resources, such as sugar beet and corn starch. Due to its attractiveness, PLA is currently receiving considerable attention for conventional applications such as packaging, textile fibres and more recently, as (nano)composites for technical applications.

In response to the demand for extending the range of PLA applications while reducing its production cost, it has recently been demonstrated that commercially available PLA can be effectively melt-blended with previously dehydrated gypsum (the so-called AII form), a direct by-product of the LA fabrication process [1]. Following melt mixing, these two products from the same source of origin can lead to polymer composites characterised by remarkable thermo-mechanical performances and other specific characteristic features, which are ascribed to the excellent filler dispersion and good interface between the polymer matrix and filler [1–4]. Moreover, just as with other mineral-filled polymers (e.g., PA, PET, PBT) the addition of a third component to the PLA–AII composites, (i.e., plasticisers, clays, flame retardants) have been considered in an effort to obtain new PLA grades with specific end-use properties [5–8].

Since the PLA–AII composites are potentially interesting as "clean and green bioplastics" [9], it is important to have information about their stability or modification during ageing under different conditions. The resistance to ageing, especially UV light, is a key factor for outdoor applications of polymeric materials [10] because degradation usually shortens the use-life of polymer-based products.

Following numerous applications of PLA-based materials (e.g., in the biomedical, packaging, fibres, and engineering industries) an important number of investigations have been devoted to the study of PLA and PLA-based products under different conditions of degradation (e.g., hydrolytic, enzymatic, microbial, UV irradiation, photo-oxidative, natural weathering) [11–18].

Despite these studies, to the best of our knowledge, our work represents the first investigation concerning the ageing of PLA–AII composites under photo-oxidative conditions. Moreover,

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Table 1
Composition of PLA–$CaSO_4$ composite samples with an AII average particle diameter of 9 μm (Codification of PLA samples containing different contents of AII ($d_{50} = 9$ μm)).

Code	Content of AII (wt.%)
PLA(G)	0
PLA/AII (90/10)	10
PLA/AII (80/20)	20
PLA/AII (70/30)	30
PLA/AII (60/40)	40

and interestingly enough, AII comes from the same source as PLA, i.e., the LA fabrication process. For the sake of comparison, natural gypsum was also considered in this study. Accordingly, this work mainly focuses on characterisation of the effect of $CaSO_4$ (AII), its content and particle size range, on the photo-oxidative degradation of PLA–AII composites, aspects that need to be evaluated when a potential end-use application is considered.

2. Experimental

2.1. Materials

Poly(L,L-lactide) (PLA) (number average molecular mass, M_n $_{(PLA)} = 74{,}500$ g mol^{-1} with an index of polydispersity, $M_w/M_n = 2.0$, D-isomer content = 4.3%, melting temperature ≈155 °C (DSC method)), commercial name “Galastic”, was kindly supplied by Galactic S.A.

Calcium sulphate hemihydrate ($CaSO_4$ $0.5H_2O$), a by-product obtained from the LA production process with mean particle diameters (d_{50}) ranging from 9 to 43 μm was provided by Galactic S.A. Starting from this filler, β-anhydrite II (AII) was obtained by drying in a Nabertherm 3 L furnace at 500 °C for 1 h as reported in a previous paper [1].

Natural calcium sulphate anhydrate (commercial name, USG CAS-20-4) with an average diameter of 4 μm was kindly supplied by the United States Gypsum Company. Manufactured by the controlled calcination of natural gypsum rock and fine grinding, this product was used only for a comparative evaluation as microfiller of smaller dimensions.

2.2. Melt-blending procedure and preparation of films

Composites were obtained by melt-compounding PLA pellets with up to 40 wt.% of AII at 190 °C, with a Brabender bench scale kneader, using the procedure described in a previous paper [1]. PLA–AII composites were prepared with different amounts and granulometries of $CaSO_4$. The composition of the samples is reported in Tables 1 and 2.

Films with an average thickness of 150 μm were prepared from these samples by compression moulding at 200 °C using an Agila PE20 hydraulic press (processing conditions: low pressure for 200 s with two degassing cycles, followed by a high-pressure cycle at 150 bars for 150 s and finally, cooling with tap water for 300 s at 50 bars of pressure).

Table 2
Composition of PLA–$CaSO_4$ composite samples with 30% of AII (Codification of PLA–30% AII composites containing filler of different granulometry).

Code	AII particle size (d_{50}, μm)
PLA/AII (70/30) 4 μm	4
PLA/AII (70/30) 9 μm	9
PLA/AII (70/30) 18 μm	18
PLA/AII (70/30) 43 μm	43

2.3. UV-light irradiations

UV-light irradiation was carried out for up to 500 h under polychromatic light at wavelengths higher than 300 nm in a SEPAP 12.24 unit, in the presence of oxygen (under air), at 60 °C. The accelerated weathering device was equipped with four medium pressure mercury lamps (400 W) (a borosilicate envelope filters wavelengths below 300 nm) and the samples were placed on a rotating carousel positioned in the centre [19].

2.4. Characterisation

2.4.1. IR analysis

Infrared spectra in transmission mode were recorded with a Thermo Scientific Nicolet 6700 FTIR spectrometer, with OMNIC software. Spectra were obtained using 32 scan summations and a 4 cm^{-1} resolution. Depth profiling of the photo-oxidised samples was performed with a FTIR Continuum Thermo Scientific microscope. Spectra were obtained using 128 scan summations and a 4 cm^{-1} resolution.

2.4.2. UV–visible analysis

UV/Visible spectra were recorded on a Shimadzu UV-2550 scanning spectrophotometer equipped with an integrating sphere. Considering the chemical structure of PLA, it was expected that PLA would be transparent in the UV ($\lambda > 300$ nm) and visible regions. The UV–visible spectra of the PLA films did not show any absorption bands.

2.4.3. Size exclusion chromatography (SEC)

The changes in molecular characteristics were obtained by size exclusion chromatography (SEC) using the Viscotek SEC-TDA equipment. It consisted of a TDA 302 module (triple detector array) that included a column oven and triple detector consisting of an RI detector, a four-bridge viscometer and LS detector. The latter consisted of a right-angle light scattering (RALS) detector and an innovative low-angle light scattering (LALS) detector. Two TSK-GEL columns (GMHXL and G3000HXL) in series that were preceded by a TSK-GEL guard column HXL-L were used. The analyses were performed with THF as the eluent at a flow rate of 1 ml min^{-1}. The PLA solutions were prepared in THF (10 mg polymer/5 ml solvent) and were filtered before injection. The OmniSEC software program was used for acquisition and analysis of the Viscotek data.

2.4.4. Differential scanning calorimetry (DSC)

The differential scanning calorimeter used to measure the thermal characteristics of the PLA and PLA composites was a Mettler Toledo DSC 822. The thermal characteristics of the films were determined from the first scan using a heating rate of 10 °C/min from 0 to 200 °C. The events of interest, i.e., the glass transition temperature (T_g), cold crystallisation temperature (T_c), enthalpy of cold crystallisation (ΔH_c), melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from the first scan. The degree of crystallinity was determined by subtracting ΔH_c from ΔH_m and by considering a melting enthalpy of 93 J/g for 100% crystalline PLA as in a previous report [1]. Additional DSC measurements were performed on the initial films using a DSC Q200 from TA Instruments under nitrogen flow following a similar procedure.

2.4.5. Chemical treatments

The photo-oxidised samples were submitted to chemical treatment in order to identify the photoproducts. The irradiated films