INFLUENCE OF FAST PYROLYSIS BIO-OIL-DERIVED PHENOLIC-RICH FRACTION ON PLLA UV STABILITY

D. Duraccio[1], M. Di Maro [1], G. Gomez d'Ayala [2], G. Dal Poggetto[2], Taina Ohra-aho[3], Elmeri Pienihäkkinen[3], Petri Widsten[3], Giulio Malucelli[4]

[1] Istituto di Scienze e Tecnologie per L'Energia e La Mobilità Sostenibili CNR Sede Secondaria Strada Delle Cacce, 73 10135 Torino, Italy
[2] Istituto per i Polimeri, Compositi e Biomateriali (IPCB) Via Campi Flegrei 34, Comprensorio "A. Olivetti" 80078 Pozzuoli (Na), Italy
[3] VTT Technical Research Centre of Finland Ltd., Tekniikantie 21, 02150 Espoo, Finland
[4] Politecnico di Torino - Dipartimento di Scienza Applicata e Tecnologia, Viale Teresa Michel 5, 15121 Alessandria, Italy
e-mail: donatella.duraccio@stems.cnr.it

Introduction

Poly-L-lactic acid (PLLA) is a thermoplastic polymer derived from renewable resources, which is emerging as an alternative polymer matrix with a wide spectrum of applications in medicine, packaging, agriculture, electronics, and the automotive industry [1,2]. It possesses good mechanical properties, can be easily melt-processed and also mechanically recycled. However, given its biodegradable nature, it is inherently more prone to photodegradation than conventional polymers (i.e. polypropylene, polyethylene) derived from fossil fuels [3].
In this work, we investigated the ability of phenolic-rich fraction obtained by fast pyrolysis bio-oil (PRF-BO) from logging residues to mitigate the effects of ageing on PLLA when exposed to UV irradiation. The ageing was evaluated by assessing changes in the structure, morphology, thermal, and mechanical properties of a PLLA blend containing 2 wt.% PRF-BO.

Methods

Fast pyrolysis bio-oil (FPBO) was produced from logging residues using a circulating fluidized bed pilot unit operated with the feed capacity of 20 kg/h biomass feedstock. A detailed description of the unit and fractionation procedure can be found elsewhere [4]. The water insoluble phenolic-rich fraction was separated from FPBO via water addition, using a water/organics ratio of 1:1. PRF-BO was collected from the bottom of the separation vessel for further use. Based on the NMR results, shown in Figure 1, PRF-BO shows different phenolic hydroxyls in which the p-hydroxyphenyl-, cathecol- and guaiacyl-type phenolic OH beared the important active sites. 2wt.% of PRF-BO was then added to PLLA by melt mixing using a Brabender W50E internal mixer (175°C and 100rpm). Unfilled PLLA was processed at the same conditions as reference. The materials were labeled as PLA0 for the unfilled polymer and PLA2 for the blend containing 2wt.% of PRF-BO. PLA0 and PLA2 were compression-molded using a Collin P200T laboratory press at 170 °C (100 bar for 5 min) to obtain several plates suitable for the ageing process.

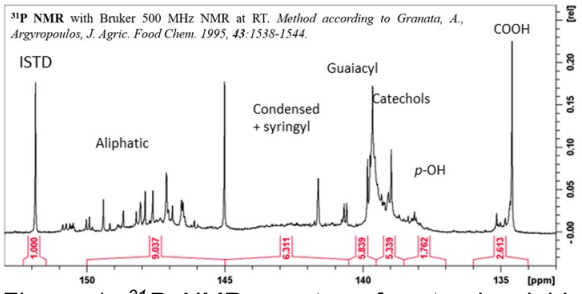

Figure 1. ^{31}P NMR spectra of water insoluble phenolic rich fraction.

The ageing process was conducted in a climate chamber equipped with a mercury UV lamp (λ > 250 nm) under dry conditions (RH = 0%, T = 40 °C) for two different times (t_1 = 180 h; t_2 = 560 h). PLA0 and PLA2 were analyzed by Gel Permeation Chromatography (GPC) to evaluate the change in molecular weights (M_w, M_n and IV) of PLLA as a result of ageing process. The analysis was carried out using a GPC Omnisec system equipped with a triple detector and a Phenogel (Phenomenex) column set after dissolution in $CHCl_3$.
Structural analysis was performed by X-ray diffraction (XRD) in Bragg-Brentano geometry using a PANalytical X'Pert PRO diffractometer with CuK_α radiation (λ = 0.15418 nm), operating at 45 kV and 40 mA, to analyze the change in crystallinity of PLLA during the ageing.
Mechanical tests were conducted with an Instron 5966 dynamometer in tensile configuration. The test was performed at RT at a constant crosshead speed of 2 mm/min until break.

Results and discussion

Slab images of PLA0 and PLA2 after 180 and 560h of UV-treatment are reported in Figure 2. From a visual standpoint, PLA0 sheets exhibit an increase in surface roughness and a transition from a transparent to a white color, indicating an increase in the material's crystallinity. PLA0 also appears extremely brittle when cut. These effects are considerably less pronounced in PLA2 after UV-ageing: the sample is significantly less brittle and does not change its color.

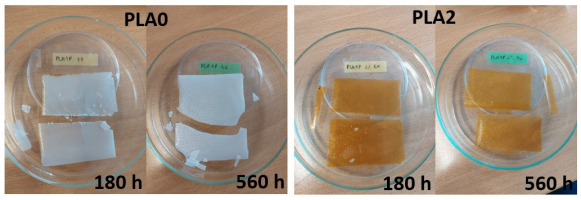

Figure 2. PLA0 and PLA2 after 180 h (t_1) and 540 h (t_2) of UV exposure.

The increase in crystallinity of PLA0 is confirmed by the XRD results. In Figure 3, the amorphous PLA0 crystallizes already after 180h (7 days) in the α-form of PLLA. Conversely, PLA2 remains amorphous even after 560h irradiation.

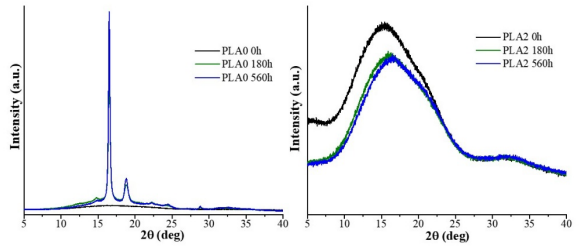

Figure 3. XRD diffractograms of PLA0 and PLA2 before and after the UV-ageing.

PLA0 and PLA2 before UV exposure exhibit a significant difference in molecular weights (Table 1), suggesting that the presence of PRF-BO aleardy acts as a stabilizing agent during melt mixing.

Table 1. Molecular weights of a of PLA0 and PLA2 before and after ageing process.

Sample	M_n (Da)	M_w (Da)
PLA0	87277	112511
PLA0 t_1	9717	18511
PLA0 t_2	3962	10761
PLA2	109007	131904
PLA2 t_1	78263	108841
PLA2 t_2	58448	106985

After UV irradiation, both M_n and M_w of PLA0 drastically decrease as time of exposure increases. After 580h irradiation, M_n and M_w decrease by about 90-95% with respect to those measured at t_0. Conversely, in the presence of PRF-BO, the decrease in molecular weight is significantly attenuated, evidencing the protective effect exerted by PRF-BO.

The mechanical properties of PLA0 and PLA2 before and after ageing are collected in table 2. The ability of PRF-BO to slow down the degradation of PLLA is supported by the mechanical properties of the filled material. More specifically, PLA0 after ageing becomes very brittle already after 180h, so that it is not possible to prepare specimens suitable for mechanical tests. In contrast, PLA2 shows a slightly reduction in mechanical parameters (i.e., Young's modulus and elongation at break) but exhibits significantly better mechanical properties than PLA0.

Table 2. Mechanical properties of PLA0 and PLA2 before and after ageing process.

Sample	E (MPa)	ε_b (%)	σ_b (MPa)
PLA0	2972 ± 115	5.9 ± 3.0	38.0 ± 4.8
PLA0 t_1	n.d.	n.d.	n.d.
PLA0 t_2	n.d.	n.d.	n.d
PLA2	2651 ± 106	3.8 ± 0.7	38.7 ± 3.1
PLA2 t_1	2785 ± 122	2.0 ± 0.2	39.4 ± 2.5
PLA2 t_2	2150 ± 121	2.0 ± 0.2	32.2 ± 2.3

Conclusions

Preliminary results of this work indicate that UV ageing of PLLA causes a decrease in molecular weight, an increase in crystallinity and a dramatic drop of the mechanical properties already after 7 days of exposure. The presence of 2 wt.% of PRF-BO drastically slows down the ageing of PLLA, allowing it to maintain its mechanical properties for up to 23 days.

References

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