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Concentration-dependent anti-/pro-oxidant activity of natural phenolic compounds in bio-polyesters

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ABSTRACT

In this work, the potential of several naturally occurring phenolic compounds, such as Ferulic Acid (FA), Vanillic Acid (VA), Vitamin E (VE) and Quercetin (Q), as stabilizers against the photo-oxidative degradation of Polylactic acid (PLA) has been assessed. Specifically, PLA-based films containing different amounts of considered stabilizers have been formulated and their photo-stability under UVB exposure has been evaluated. The preliminary characterization of the formulated films shows that all used stabilizers exert plasticizing action, as probed by rheological analysis, due to their low molecular weight. Moreover, no significant modification of the PLA crystallinity has been noticed in presence of used natural compounds.

The study of the photo-oxidation behaviour of PLA-based systems suggests that, among all used natural phenolic compounds, FA and Q are suitable anti-oxidant for PLA, if they are added at low content. Surprisingly, all considered natural compounds, exert a pronounced pro-degradant action in PLA matrix, if their content overcomes a certain specific threshold. This finding has been related to the known concentration-dependent anti-/pro-oxidant activity of used phenolic compounds, that results exacerbated in presence of traces of transition metals, such as iron and copper.

1. Introduction

Polylactic acid (PLA) is a biodegradable biobased polyester of increasing industrial interest because of its unique properties, such as low toxicity, bio- and eco-compatibility. Indeed, PLA is a suitable material for several "green" applications in different fields, among other food packaging, textile fibres and biomedical devices [1–3]. However, like several conventional fossil-based polymers, PLA, when exposed simultaneously to oxygen and high temperatures or UV light, is susceptible to degradation processes. Indeed, PLA performances, in terms of durability, are limited by several chemical aging mechanisms, such as thermal decomposition, hydrolysis, photo-oxidation, natural weathering and thermo-oxidation at high temperature [4–6]. Therefore, to avoid the decay of its physical and mechanical properties, the addition of anti-oxidants and/or light stabilizers is imperative. The specific applications of PLA require the use of naturally occurring additives, which are able to enhance the resistance during processing, at typical processing conditions (around 200 °C), or during lifetime, in presence of high temperature or UV light. Several natural compounds with different chemical nature may be considered as stabilizers in polymers, and specifically in bio-polyesters [7,8]. The use of natural compounds as anti-oxidants in polymers and bio-polymers, provides similar stabilizing action to that of synthetic anti-oxidants [9–11]; additionally, they have low toxicity as many natural anti-oxidants are typical compounds used to protect human health. The potential of flavonoids, a class of natural polyphenols, as anti-oxidants and UV light stabilizers for polyolefins has been recently investigated by Samper et al. [12]. The effectiveness of used phenolic compounds as thermal stabilizers at high temperature has been probed. Moreover, among flavonoid compounds, the flavonols (quercetin and silibinin) provide the best results in stabilizing against both thermo- and photo-oxidation. Furthermore, flavonols have been demonstrated effective in protecting irradiated Ultra High Molecular Weight

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PolyEthylene (UHMWPE) against oxidation, becoming a potential alternative to vitamin E for the stabilization of UHMWPE for joint arthoplasty [13,14]. The anti-oxidant action of Vitamin E (α-tocopherol) was studied in detail by Al-Malaika et al. [11,15], demonstrating its excellent melt stabilizing effect, especially at very low concentrations.

In this work, the potential of Ferulic Acid (FA), Vanillic Acid (VA), Vitamin E (VE) and Quercetin (Q), as stabilizers against UV exposure in PLA was assessed. All considered natural compounds have been incorporated in PLA through melt-mixing. The preliminary characterization of PLA/natural compounds systems shows that all stabilizers act as plasticizers, without significant modification of the PLA crystallinity. Accurate analysis of photo-oxidation resistance of PLA-based systems has been performed, also considering the effect of natural compounds content.

2. Experimental part

2.1. Materials

The materials used in this work are:

- Polylactic Acid (PLA) 2002D has been purchased by NatureWorks LLC. Its main properties are: molecular weight (Mw) = 204456 g/mol; melting point = 150–160 °C; glass transition temperature = 58 °C; melt index (260 °C/2.16 Kg) = 5.0–7.0.
- 4-Hydroxy-3-methoxycinnamic acid, named Ferulic Acid (FA) has been purchased by Sigma-Aldrich. Molecular Weight 194.18.
- 4-Hydroxy-3-methoxybenzoic acid, named Vanillic Acid (VA) has been purchased by Sigma-Aldrich. Molecular Weight 168.15.
- 2,5,7,8-Tetramethyl-2-(4′,8′,12′-trimethyltridecyl)-6-chromanol,5,7,8-Trimethyltocol, named Vitamin E (VE) has been purchased by Sigma-Aldrich. Molecular Weight 430.71.
- 2-(3,4-Dihydroxyphenyl)-3,5,7-trihydroxy-4H-1-benzopyran-4-one hydrate, named Quercetin (Q) has been purchased by Sigma-Aldrich. Molecular Weight 302,24 (anhydrous basis).

The chemical structure of used natural compounds is reported in Fig. 1.

2.2. Processing

The preparation of PLA-based samples were carried out using a Brabender mixer at T = 170 °C and mixing speed 50 rpm for 5 min. The stabilizers have been added at 0.1 and 0.5 wt%; further formulations have been produced considering 0.05 wt% and 2 wt% of some natural molecules. PLA matrix has been subjected to the same processing conditions. Prior to melt mixing process, PLA pellets have been dried in a vacuum oven at 70 °C overnight, in order to keep the moisture content of less than 0.025%. Thin films (thickness about 100 μm) of neat PLA and all stabilized systems have been obtained through compression molding in a Carver Laboratory Press at a pressure P = 1500 psi for 5 min and at T = 170 °C.

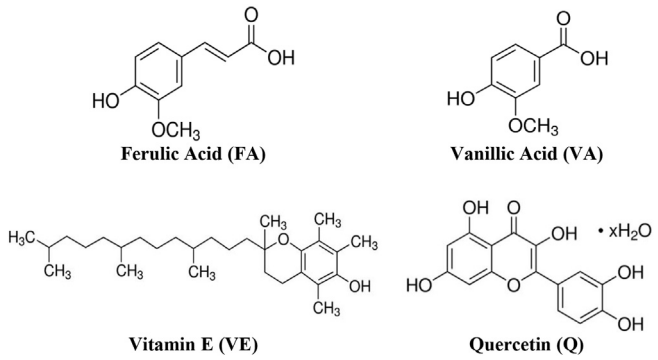

Fig. 1. Chemical structure of used natural compounds.

2.3. Characterizations

Rheological tests were performed using a strain-controlled rheometer (mod. ARES G2 by TA Instrument) in parallel plate geometry (plate diameter 25 mm). The complex viscosity (η^*) was measured performing frequency scans from $\omega = 10^{-1}$ to 10^2 rad/s at $T = 170$ °C. The strain amplitude was $\gamma = 2\%$, which preliminary strain sweep experiments proved to be low enough to be in the linear viscoelastic regime.

The SEM analysis was performed on cryogenically fractured and gold sputtered surfaces of thin films using a Philips (Netherlands) ESEM XL30 scanning electron microscope.

The calorimetric data were evaluated by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7 calorimeter. All experiment were performed under dry N_2 on samples of around 10 mg in 40 μl sealed aluminium pans. Four calorimetric (two heating: 30–220 °C and two cooling: 220-30 °C) scans were performed for each sample at scanning heating/cooling rate of 5 °C/min.

The crystallinity degree (X_c) is calculated using the formula:

$$X_c(\%) = \frac{\Delta H_m + \Delta H_{cc}}{\Delta H^\circ} \times 100 \quad (1)$$

where ΔH_m is the heat of melt of sample, ΔH_{cc} corresponds to the heat of cold crystallization, ΔH° is the heat of fusion for 100% crystalline PLA (93.6 J/g) [16].

FT-IR analyses were performed on photo-oxidized films for different exposure time. The spectra were collected by performing 16 scans between 4000 and 400 cm^{-1}. The spectra have been normalized using as internal standard the peak at 2995 cm^{-1}, which correspond to the asymmetric stretching of CH_3 groups [17].

Photo-oxidation of PLA and PLA-based films (about 100 μm thick) was carried out using a Q-UV-Solar Eye weatherometer (from Q-LAB, USA) equipped with UVB lamps (313 nm). The weathering conditions were 8 h of light at T = 55 °C followed by 4 h of dark/condensation at T = 35 °C.

Inductively coupled plasma–mass spectrometry (ICP-MS) analysis was performed by using a NEXION 300X (PERKIN ELMER). About 200 mg of PLA were mineralized with 2.5 mL of nitric acid and 1.5 mL of hydrogen peroxide (700W, 40 min). 10 ppb of internal standards (Y, Re, Ge) were added and 100 ppb of Au (for a more efficient determination of Hg) and diluted up to 50 mL.

3. Results and discussion

3.1. Preliminary characterization of PLA/Natural compounds systems

First of all, the rheological behaviour of neat PLA and PLA-based systems containing different natural occurring stabilizers has been fully investigated, considering oscillatory tests. In Fig. 2 the complex viscosity (η^*) as a function of frequency is plotted. Neat PLA shows a well distinguished Newtonian behaviour, i.e. η^* remains almost frequency-independent, in the frequency range between 0.1 and 10 rad/sec, followed by a weak shear-thinning behaviour in the high frequency region. The adding of all natural occurring