

Natural Anti-oxidants for Bio-polymeric Materials

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Abstract

In this work, three different bio-polymers, i.e. a commercial starch-based polymer (Mater-Bi®) a bio-polyester (PLA), and a bio-polyether (PEO) were additivated with quercetin, a natural flavonoid antioxidants, in order to formulate bio-based films for eco-sustainable packaging and outdoor applications. The photo-oxidation behavior of unstabilized and quercetin stabilized films has been evaluated and compared with that of films additivated with a commercial synthetic light stabilizer. Obtained results show that quercetin molecules are able to slow down the photo-degradation rate of all investigated bio-polymeric films, opening new avenues in the formulation of fully renewable polymer-based systems.

Keywords Anti-oxidants; Polymer; Starch

Introduction

Biodegradable polymers have been widely investigated to replace synthetic polymers, because of environmental concerns and decreasing availability of fossil resources [1]. The potential use of biodegradable polymers in the agricultural field as covering films or mulching films, and in biomedical applications is a very promising and challenging issue. However, the products formulated using biodegradable polymers must show properties, performances and durability comparable to those of the products formulated using conventional fossil fuel-based polymers [2]. In particular, the maintenance of the performance during their lifetime is a critical topic for successful applications. Indeed, the thermo- and photo-oxidative degradation of polymers and polymer-based systems is a key issue for these class of materials [3]. Usually, the protection against thermo- and photo-oxidative degradation is realized through the adding of suitable stabilizing systems, such as anti-oxidants, light stabilizers, thermal stabilizers, and fire retardants [4].

The specific applications of bio-polymers require the use of naturally occurring additives, which are able to enhance the resistance during processing, at typical processing conditions, or during lifetime, in presence of high temperature or UV light. So, in the recent years researchers have focused a growing attention

to formulations based on bio-polymer and natural stabilizing agent [5]. Several natural compounds with different chemical nature may be considered as stabilizers in polymers, and specifically in bio-polyesters [6,7]. The use of natural compounds as anti-oxidants in polymers and bio-polymers, provides similar stabilizing action to that of synthetic anti-oxidants; 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. [8]. The effectiveness of used phenolic compounds as thermal stabilizers at high temperature has been probed.

Quercetin is an abundant flavonoid suitable in stabilizing polymer against both thermo-oxidation during processing, and photo-oxidation during UV exposure. Its protective action is performed by reducing free radical formation, scavenging free radicals and, also, binding transition metal ions [9]. It is of fundamental importance to investigate and to verify the usefulness of flavonoids in the thermo- and photo-oxidation stabilization also for bio-polymers. The protection of biodegradable polymer provided by flavonoid compound is to be similar to that obtained using synthetic commercial light stabilizer.

Poly(lactic acid) PLA is a compostable thermoplastic made from renewable sources and able to degrade into innocuous lactic acid. PLA is used as medical implants and for the encapsulation of many therapeutic agents due to its high hydrophobicity, strong mechanical strength and slow drug release [7]. PLA, furthermore, can be used as a compostable packaging material. The maintenance of the performance during its lifetime, however, remains a critical point for successful application.

Mater-Bi® is completely biodegradable and compostable bio-polymer, made using natural and synthetic raw materials that does not involve the exploitation of virgin or deforested lands. Mater-Bi® is a recent bio-polymer that has, already, applications in the manufacture of film for agricultural mulching, biodegradable cotton buds, toys and bioplastic carrier bags [10].

Poly(ethylene oxide) PEO is an attractive biomaterial because of biocompatibility, hydrophilicity, and versatility. It is used in novel drug delivery systems and it finds potentially use in technological applications as solid electrolytes in

electrochemical devices such as batteries [11]. Premature degradation, that occurs due to aliphatic ethers, is a tricky issue for the use of PEO and the use of stabilizing systems is absolutely required.

In this study the stabilization provided for biodegradable films by natural compounds was evaluated and compared to those provided by a commercial synthetic light stabilizer. The obtained results show that quercetin is suitable for the protection against photo-oxidation of bio-polymer matrices. Therefore bio-polymer films containing natural stabilizing molecules are excellent candidates for outdoor application and as smart and environmental-friendly packaging, where the release of bioactive compounds during lifetime of the packaging can improve food stability.

Experimental Part

Materials

The materials used in this work were:

- Polylactic acid PLA 2002D (PLA) supplied by Natureworks (USA);
- Mater-Bi® CF04P (MB), undisclosed composition, kindly supplied by Novamont spa (Italy);
- Polyethylene oxide (PEO) supplied by Sigma-Aldrich (USA);
- Quercetin hydrate, natural flavonoid compound (Q), supplied by Sigma-Aldrich srl. Molecular weight: 302.24 g/mol; Formula: C₁₅H₁₀O₇ xH₂O; Purity: >= 95%;
- Cyasorb® THT® 6460, synthetic heterocyclic Light Stabilizers (LS) – (1,6-Hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-, polymers with morpholine-2,4,6-trichloro-1,3,5-triazine reaction products, methylated and formaldehyde) kindly supplied by Cytec spa.

Formulation of polymer-based films

Both natural (quercetin) and synthetic (light stabilizer) stabilizing compounds have been added to the bio-polymers films at 0.5 wt% before the processing.

The PLA films were obtained using a single screw extruder equipped with a film head and equipped with a calender unit. The temperature profile was 210-210-200-200°C and the screw speed was 60 rpm. The film thickness was about 100 microns for all the samples.

The Mater-Bi® films were obtained using a single screw extruder equipped with a film blowing head and with a Brabender film blowing unit. The temperature profile was 90-120-130-145°C and the screw speed was 80 rpm. The film thickness was about 50 microns for all the samples.

The PEO films were obtained using a Brabender mixer at T=90°C at a mixing speed 50 rpm for 5 min. The films, with a thickness of about 100 microns, were obtained by compression molding.

Characterization

The accelerate weathering was performed on unstabilized film and stabilized films using a Q-UV (U.S.A.) chamber, containing eight UVB-313 (Q-Labs Corp., U.S.A) lamps. The exposure cycle conditions were: 8 h of light at T=55°C followed by 4 h condensation at T=35°C. The measured photon flux was 2 mW/cm².

Mechanical tests were carried out, at room temperature and humidity, using an Instron (U.S.A.) dynamometer mod. 3365, according to ASTM test method D882 (crosshead speed of 100 mm/min).

Statistical analysis of the data was performed through ANOVA by using the GraphPad Prism version 6 software (GraphPad Software Inc., La Jolla, CA, USA). Significant differences among mean values, where applicable, were determined by the means of ANOVA and by Tukey's HSD post hoc test for multiple comparisons. In all cases, a value of p<0.05 was considered statistically significant [7].

Results and Discussion

In **Table 1**, the main mechanical properties, i.e. the elastic modulus, E, tensile strength, TS and elongation at break, EB, of unstabilized films (PLA, MB and PEO) and all stabilized films before the photo-oxidative treatment are reported.

Table 1 Main mechanical properties, i.e. the elastic modulus, E, tensile strength, TS and elongation at break, EB, of unstabilized and stabilized films before the photo-oxidation (Values are given as means ± SD. Different letters in the same column, for each investigated system, indicate significant differences (p<0.05) when analyzed by Tukey's multiple comparisons tests)

Sample	E, MPa	TS, MPa	EB, %
PLA	1556 ± 52 ^a	47.1 ± 2.5 ^a	9.3 ± 1.5 ^a
PLA/Q	1684 ± 56 ^b	44.8 ± 2.2 ^a	14.8 ± 2.0 ^b
PLA/LS	1843 ± 62 ^c	51.2 ± 2.5 ^b	19.5 ± 2.5 ^c
MB	105 ± 5 ^a	24.2 ± 1.2 ^a	435 ± 22 ^a
MB/Q	119 ± 6 ^b	27.0 ± 1.3 ^b	470 ± 24 ^b
MB/LS	120 ± 6 ^b	24.6 ± 1.2 ^a	440 ± 22 ^a
PEO	60.5 ± 2.3 ^a	3.5 ± 0.3 ^a	105 ± 5.0 ^a
PEO/Q	55.2 ± 2.5 ^b	3.1 ± 0.2 ^b	110 ± 6.0 ^a
PEO/LS	54.2 ± 2.3 ^b	3.2 ± 0.3 ^{a,b}	115 ± 7.5 ^b

As far as the PLA- and MB-based systems is concerned, the addition of both natural and synthetic stabilizers leads to an increase of the Elastic Modulus and of the properties at break. The slight increase of the EB for all PLA- and MB-based systems can be attributed to some plasticizing effect caused by the stabilizing molecules; indeed, it is known that the low molecular

weight molecules dispersed in polymer matrices are able to increase the free volume of the system, reducing the friction between the macromolecules. The rises of both E and TS values of the stabilized systems to the respect of those of neat matrices clearly suggest an increased rigidity of the stabilized films in the machine direction. This issue can be attributed to the higher orientation of the macromolecules achieved during the drawing in presence of a plasticizing agent. The increased orientation improves the rigidity of these samples and this effect overcomes the plasticizing action.

Concerning the PEO-based systems, the addition of stabilizing molecules causes a decrease of the E values and an increase of the properties at break. The obtained results can be explained considering the plasticizing action exerted by the stabilizing molecules, which leads to the obtainment of a more ductile material. In contrast to the PLA- and MB-based systems, the formulations based on PEO have not been subjected to drawing during processing, thus no preferential macromolecules orientation was achieved and the only observable effect is that due to the plasticizing action of added molecules.

Let us to discuss about the photo-oxidative behavior of investigated samples. According to the literature, the mechanism of PLA photo-oxidative degradation involves hydrogen abstraction on the polymer backbone, leading to the formation of macroradicals that, reacting with oxygen, form peroxy radicals and hydroperoxides [12]. The last decompose with the formation of alkoxy radicals that, in turn, degrade through three different β -scission reactions, leading mainly to the generation of anhydrides. Moreover, hydrolytic degradation of PLA needs to be taken into account; the hydrolytic chains cleavage occurs mainly in the bulk of the material and not only on its surface and proceeds preferentially in the amorphous regions, leading to the formation of carboxylic acid end groups.

The photo-oxidative behavior of MB is a very complex issue, given that this polymer matrix is a multi-component system and hence a large amount of radicals coming from different components needs to be taken into account, along with the possible reactions/interactions between them [13].

Concerning PEO, the first step of its oxidative pathway is the hydrogen abstraction on the polymer backbone by a free radical, with the formation of a macroradical that, reacting with oxygen, gives a peroxy radical that evolves in a hydroperoxide. The photochemical decomposition of this hydroperoxide leads to the formation of an alkoxy radical that can evolve following three routes: (1) β -scission, leading to the formation of formate end groups; (2) cage reaction with HO which gives ester functions formation; (3) hydrogen abstraction reaction with formation of a hemiacetal that, in turn, decomposes to form alcohols and carboxylic acids [11]. Therefore, the main oxidation products of PEO formed upon UVB irradiation are essentially formats, esters, carboxylic acids, and alcohols.

The chemical modifications of polymeric materials which occur during the photo-oxidation process due to the degradation reactions, are detrimental for the mechanical properties of the materials. In particular, all the chemical modifications result in a severe embrittlement of the material.

For this reason, the progress of the degradative process can be followed by analysing the variation of the polymer mechanical properties as a function of the photo-oxidation time. In Figures 1-3, the dimensionless Elongation at break of all investigated systems based on PLA, MB and PEO as a function of the exposure time are reported. All dimensionless values have been calculated by dividing the values of EB at a given exposure time by the value measured before the photo-oxidation. The EB is the mechanical property more sensitive to all morphological and structural changes occurring during photo-oxidation process. The dashed lines in the Figures 1-3 indicates the time at 50%, i.e. the time at which the EB value is one half of the initial one (0.5EB). The time at 50% can be considered as the maximum time at which a film can be used; after this time severe mechanical damages occur. For all investigated bio-polymers-based systems, a beneficial effect can be noted by adding the quercetin, especially at short exposure times. Otherwise, for long exposure times, the values of the dimensionless EB for unstabilized and stabilized systems are very similar. It is noteworthy that the three investigated bio-polymers show different photo-oxidation behavior due to the different chemical nature and different absorption ability in the UV-B range. The photo-oxidation of PLA is a slow process: after about 1200 h of exposure, the value of its dimensionless EB is slightly lower than the 0.5EB value. MB and PEO, instead, show faster photo-oxidation and the values of dimensionless EB reach the 0.5EB values after 12 h and 24 h, respectively. To sum up, all obtained results indicate that quercetin molecules are able to protect all the investigated bio-polymers in a similar way to what observed for commercial synthetic light stabilizer.

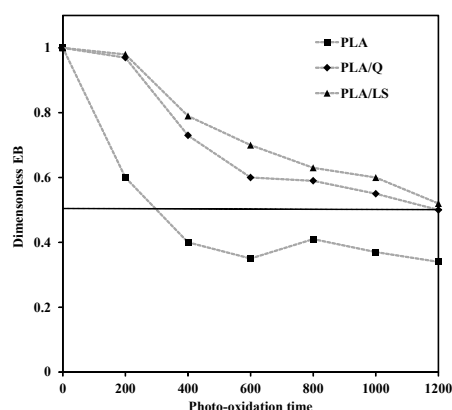


Figure 1 Variation of dimensionless EB for neat PLA and PLA-based systems as a function of photo-oxidation time.

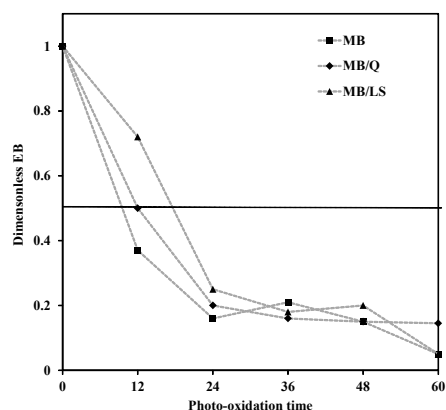


Figure 2 Variation of dimensionless EB for neat MB and MB-based systems as a function of photo-oxidation time.

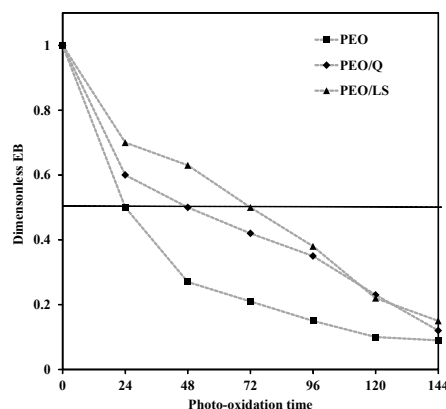


Figure 3 Variation of dimensionless EB for neat PEO and PEO-based systems as a function of photo-oxidation time.

Conclusions

Biopolymers-based films containing a natural phenolic compounds have been formulated and their photo-oxidation behaviour has been investigated and compared to that of systems containing a synthetic commercial light stabilizer. All obtained results indicate that Quercetin is able to offer a remarkable stabilizing action against the photo-oxidative degradation of polymeric materials. In all, obtained results open new perspectives in the use of natural compounds as eco-friendly stabilizers, to get fully bio-based polymer systems with enhanced photo-oxidative stability.

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