Eumelanin for Nature-Inspired UV-Absorption Enhancement of Plastics

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ABSTRACT. In the human body, the black-brown biopigment eumelanin blocks the harmful ultraviolet (UV) radiation. In the plastics industry, additives are often added to polymers to increase their UV-absorption properties. We herein report an assessment of the biopigment eumelanin as a nature-inspired additive for plastics to enhance their UV-absorption. Since eumelanin is produced by natural sources and is non-toxic, it is an interesting candidate in the field of sustainable plastic additives. In this work, eumelanin-including films of commercial ethylene-vinyl acetate copolymer (EVA), a plastic used for packaging applications, were obtained by melt-compounding and compression molding. The biopigment dispersion in the films was improved by means of the Melanin Free Acid treatment (MFA). It was observed that eumelanin amounts as low as 0.8% wt. cause an increase of the UV absorption, up to one order of magnitude in the UVA range. We also evaluated the effect of eumelanin on the thermal and photostability of the films: the biopigment proved to be double-edged, working both as UV-absorption enhancer and photo-prooxidant, as thermogravimetric analysis (TGA) and infrared (IR) spectroscopy revealed.

Introduction

The absorption in the ultraviolet (UV) region of plastics for packaging applications is paramount to protect the underlying wrapped material (e.g. food) [1]. Consequently, UV-absorbers are added in order to enhance the UV absorption of polymers and to stabilize them against UV-induced degradation.[2] In addition, the resistance to photodegradation is a requirement for plastics used in outdoor environments.[2]

Nature has been confronted with the need of providing a UV-absorber to the organ that "wraps" the human body (the skin), as harmful UV rays are part of the solar radiation that reaches the

Earth.[3] Such a natural UV-absorber, i.e. eumelanin, is a black-brown pigment that can be easily recognized, in our daily life, in the different skin complexations.[3] As a matter of fact, eumelanin exhibits featureless absorption in the UV and visible ranges (Figure 1-A).[4] It derives from the oxidative polymerization of 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA) (Figure 1, B-C).[5] DHI and DHICA form oligomers differing by number of units (up to tens), ratio DHI/DHICA and polymerization sites.[6] Such oligomers stack via π-π interactions, forming the so-called protomolecules, that, in turn, assemble in a complex supramolecular structure.[7] Eumelanin is widely investigated by both physicists and engineers.[8] The biopigment, indeed, features physico-chemical properties such as radical scavenging, redox activity, metal ion chelation, and hydration-dependent electrical conduction, all of interest for energy storage as well as bio and green electronics.[5,8–14]

The endeavor towards sustainability in the plastics field has involved not only the polymers but also their additives.[15] In this context, the advantages of eumelanin as a natural UV-absorber would be manifold. For instance, eumelanin is bio-sourced and non-toxic[16] (one of the requirements of additives for plastics[17]). These two features render the use of the biopigment greener with respect to several commercial additives.[18] Large scale production of melanin by microorganisms digesting food waste has been reported[19], and sustainable extraction from natural fibers (e.g. fleece from alpaca) has been demonstrated.[20] In addition, as eumelanin is formed of protomolecules,[7] it would be less likely to leach from the matrix polymer than small molecule additives.[17,21]

Natural eumelanin (Sepia Melanin, extracted from the ink sac of a cuttlefish), fungal melanin and polydopamine (a eumelanin-like material)[22] have been assessed as additives to improve the UV-absorption properties of polyimide (PI)[23], poly(lactic acid) (PLA)[24] and poly(vinyl alcohol) (PVA).[25] Other works regarding PVA[26] and bisphenol A polycarbonate (PC)[27] reported not only the improvement of the UV-absorption properties but also the long-term effects of UV-irradiation. In such works, the polymer matrix embedding the pigment was protected by eumelanin against photodegradation under prolonged UV irradiation.[26,27] Eumelanin was also assessed as a bio-

sourced thermal stabilizer for PI[23], PVA[28,29], polyhydroxybutyrate (PHB)[30], poly(methyl methacrylate) (PMMA)[21] and polypropylene (PP)[21], as it can scavenge the radicals that form during the thermal degradation of the polymers.[2,9.]

In this work, we evaluated the biopigment eumelanin as an additive for the UV-absorption enhancement of a commercial grade of the copolymer ethylene-vinyl acetate, EVA (ELVAX®3128-1), used as plastic material for packaging applications (Figure 1-D).[31] Both natural Sepia Melanin and two synthetic counterparts based on only one of the two building blocks (DHI-melanin and DHICA-melanin) were tested. Our work is the first where eumelanin was not merely added as-polymerized or as-extracted nor functionalized.[23] Indeed, the dispersion of the biopigment in the polymer matrix was improved by the Melanin Free Acid (MFA) treatment. Such treatment opens the biopigment supramolecular structure and causes the reduction of the size of the oligomers.[32,33] Both the π-π stacking featured by the supramolecular structure and the size of the oligomers affect the electronic delocalization.[32] An extended π-π stacking and a large oligomer size generate extended delocalization, in turn leading to the red shift of the optical absorption spectrum.[32,33] The MFA treatment causes therefore the shift of the eumelanin absorption towards the UV.[33,34] The assessment included the evaluation of possible synergistic or antagonistic effects between eumelanin and the thermal stabilizer (butylated hydroxytoluene), already present in the commercial grade EVA.[35–37] Finally, eumelanin's UV-absorption properties in nature can have a dichotomous role, either photoprotective or photodamaging.[38] The latter effect was suggested to prevail after prolonged UV-exposure of the biopigment.[39,40] Consequently, we also assessed whether, in the polymeric matrix, the photoprotective or the photodamaging role of the biopigment prevails upon prolonged UV irradiation.
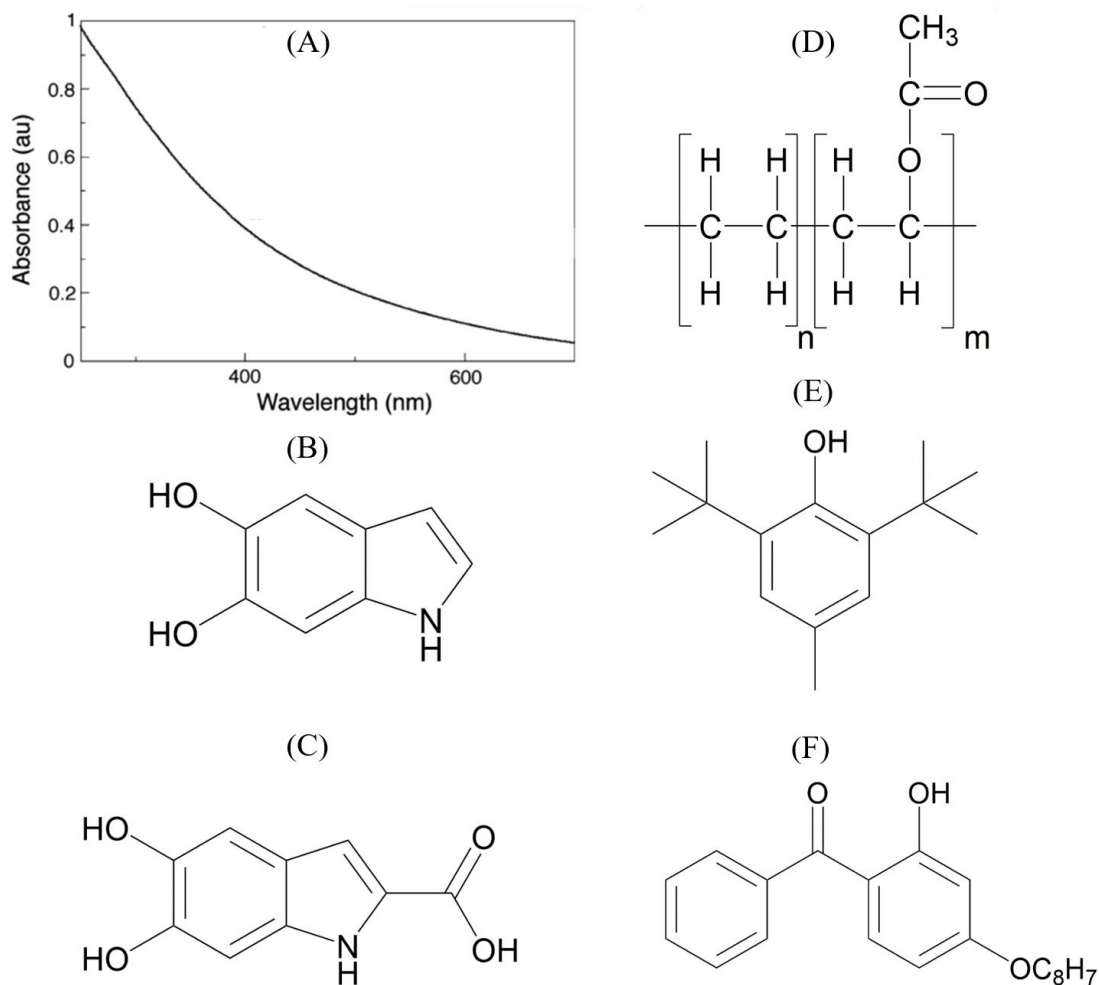
Figure 1 (A) Featureless UV-visible absorbance of eumelanin (adapted from[4]); Molecular structure of the building blocks of eumelanin, (B) DHI (5,6-dihydroxyindole) and (C) DHICA (5,6-dihydroxyindole-2-carboxylic acid); (D) Monomer of polyethylene-vinyl acetate copolymer, EVA; (E) Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl- or butylated hydroxytoluene (BHT), a commercial anti-oxidant; (F) 2-hydroxy-4-(octyloxy) benzophenone or BLS®531, a commercial UV-absorber.

Materials and Methods

Materials and Processing: The plastic material studied was a commercial grade ethylene-vinyl acetate copolymer (EVA), namely ELVAX®3128-1 from DuPont™, containing butylated

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hydroxytoluene, BHT (Figure 1,D-E). The vinyl acetate content was 9.3% wt. and the melting point 99 °C.

ELVAX®3128-1 pellets were dried at 60 °C overnight prior to processing. Films of pure ELVAX®3128-1 were prepared from the pellets received from the company. The dried pellets were melted in a batch mixer (Brabender Plasticorder DDRV501), compression-molded in a hot press and stabilized in a cold press (Tables S1-S2). The size of the so-obtained films was 20.1 cm × 15.0 cm. Such films will be from now on referred to as "control films".

Three types of eumelanins were used in this study, two synthetic and one bio-sourced. The two synthetic eumelanins were obtained from only one of the two monomers (DHI or DHICA), i.e. DHI-melanin and DHICA-melanin. Such synthetic eumelanins were synthesized by a solid-state polymerization method already reported in the literature.[41] Natural eumelanin was extracted from the ink sac of a cuttlefish (Sepia Melanin), following procedures established in the literature[42,43] ("Sepia Melanin Extraction" in SI). Eumelanin was added to the polymers by melt compounding in the batch mixer. The processing parameters to obtain the eumelanin-including films were the same as the control films (Tables S1-S2).

Prior to the addition of eumelanin to the plastics, the Melanin Free Acid (MFA) treatment of eumelanin was deemed necessary, in order to properly homogenize the product obtained by melt compounding commercial EVA and eumelanin in the batch mixer.[44,45] The MFA treatment was carried out following existing protocols ("Melanin Free Acid Treatment" in SI and Figure S1).[45]

The lowest amount of eumelanin added to the plastic was 0.2% wt. Higher amounts (0.3% wt., 0.6% wt. and 0.8% wt.) were tested for synthetic DHICA-melanin that, compared to the other two types (synthetic DHI-melanin and natural Sepia Melanin), has been reported to have lower visible absorption and more intense absorption in the UV region.[46,47]

For the sake of comparison, a commercial UV-absorber, 2-hydroxy-4-(octyloxy)benzophenone, also called BP12[48] (commercial name BLS®531 from Mayzo), was also considered (Figure 1-F).

Characterizations: The absorption was measured using a PerkinElmer LAMBDA 1050 spectrophotometer equipped with a Labsphere integrating sphere on samples (approximately 2 cm × 3 cm) cut from the center of the compression-molded films and placed inside the sphere at a 20-degree angle with respect to the incident beam (5 samples for the control films, 3 samples for the films containing the different additives). This center-mount setup allowed for the total reflected R and transmitted T radiation to be measured simultaneously in the 250-800 nm range and the resulting absorption of the films obtained by posing $A = 1 - (R + T)$. As the films have different thicknesses, an equivalent absorption coefficient α was inferred by assuming a Beer-Lambert-like attenuation ("Equivalent absorption coefficient" and Figure S2 in SI). The ratio $\alpha_{ADD}/\alpha_{CON}$ indicates the relative increase of absorption provided by the additive in the films with respect to the control film.

Thermogravimetric analyses (TGAs) reveal whether the addition of the biopigment shifts the degradation temperature towards lower or higher temperatures, due to antagonistic or synergistic effects with the anti-oxidant butylated hydroxytoluene present in ELVAX®3128-1. Thermogravimetric analyses were carried out in argon and air atmosphere (90 cm^3 min^{-1}), at a heating rate of 10 °C min^{-1}, in the range of 25 – 600 °C, using a TA Instruments TGA 2950 thermogravimetric analyser. The onset degradation temperature, T$_{on}$, was calculated following ASTM E 2550-07, setting 0.1 %/°C as the value for which the initial plateau of the derivative of the TGA (DTG) was considered over. The temperature of the maximum rate of degradation is also reported. For the average values, 4 samples for the control films and 2 samples for all the other cases were considered.

To assess whether the absorption enhancement provided by eumelanin (MFA) prevents or favors photodegradation, a UV-aging test entailing prolonged UV-exposure was carried out. Such test was conducted for 144 days in air, at 25 °C, using a lamp of ~10 W·m^{-2} in the 290 nm – 440 nm spectral range, with the films held at a 10 cm-distance from the lamp.

At day 48 and day 144 of UV irradiation, the possible presence of photodegradation products was assessed, by means of infrared spectroscopy (IR), UV-visible spectroscopy and thermogravimetric analyses. Optical images of the samples were taken at days 0, 48, 96 and 144 of UV irradiation.

IR spectra of the films were recorded in the attenuated total reflection (ATR) mode using a Bruker Optics Tensor 27 FT-IR spectrometer equipped with a HgCdTe detector. Samples were pressed against the silicon ATR element of a MIRacle accessory (Pike Technologies). All spectra were obtained with a resolution of 4 cm^{-1} by averaging at least 250 scans. Absorbance was normalized with respect to the maximum value of each spectrum.

Results and Discussion

We initially compared the UV-visible equivalent absorption coefficient (i.e. the absorption coefficient normalized by the thickness) of the control film (α_{CON}) with that of films including eumelanin (α_{ADD}). We used both natural Sepia Melanin and two synthetic counterparts based solely on one of the two building blocks (DHI-melanin and DHICA-melanin). The addition of 0.2% wt. eumelanin brings about a UV-absorption enhancement, with $\alpha_{ADD}/\alpha_{CON}$ = 6-8 in the UVA and UVB regions for the three types of eumelanin (Figure 2).

The peak located at about 285 nm is due to the presence of the anti-oxidant butylated hydroxytoluene in the control film (see "Materials and Methods"). Furthermore, two peaks located at ca. 320 nm and 370 nm are observable in the films containing eumelanin. Both peaks may result from the overlap of the absorption of collections of oligomers.[34,49] A further contribution to the peak at 320 nm could be ascribed to polypyrroles resulting from the peroxidation of eumelanin during the MFA treatment.[50,51]
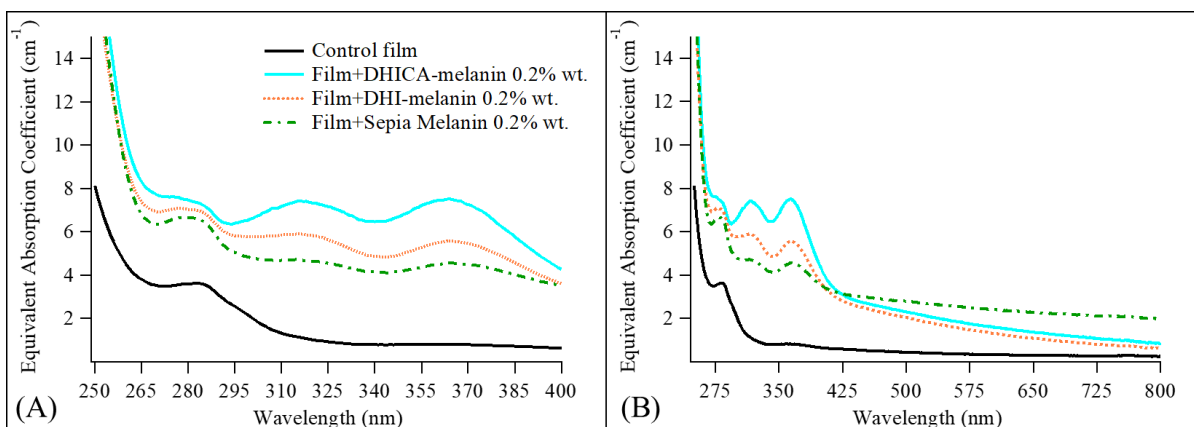
Figure 2 Equivalent absorption coefficient of the control film and films including different types of eumelanin 0.2% wt. (A) in the UV range and (B) in the UV and visible ranges.

For applications where color matters, a negligible absorption increase is ought in the visible range ($\alpha_{ADD}/\alpha_{CON}$ close to 1). In this context, DHICA-melanin and DHI-melanin perform better than Sepia eumelanin. For Sepia Melanin, $\alpha_{ADD}/\alpha_{CON}$ keeps increasing in the visible range, up to $\alpha_{ADD}/\alpha_{CON}$ = 8 at 800 nm. On the other hand, for applications where a black color is desired, Sepia Melanin could represent a bio-sourced alternative to petroleum-based UV-absorbers (e.g. carbon black[52]).

The three types of eumelanin considered in this work were added to the commercial grade EVA after the MFA treatment. The MFA treatment causes the opening of eumelanin's supramolecular structure, by the dissociation of eumelanin aggregates into smaller protomolecules.[44] The treatment also reduces the oligomers' length.[44] Both effects reduce the absorption in the visible range.[33,34] The more intense optical absorption in the visible region provided by Sepia Melanin with respect to the synthetic eumelanins may be due to the less complex initial supramolecular assembly of the synthetic eumelanins, which are easier to "open" by the MFA treatment with respect to Sepia.[53] This hypothesis is confirmed by the darker color of the pellets and films including Sepia Melanin with respect to its synthetic counterparts (Table S2). It is worthy of note

that adding an as-polymerized synthetic powder (DHICA-melanin and DHI-melanin) or as-extracted natural powder (Sepia Melanin) to the batch mixer entailed films with black dots after compression molding.

As DHICA-melanin has been reported to have lower visible absorption and more intense absorption in the UV region[46,47] with respect to the other two types of eumelanin (DHI-melanin and Sepia Melanin), higher concentrations of DHICA-melanin were also tested (0.6 and 0.8% wt.) (Figure 3).
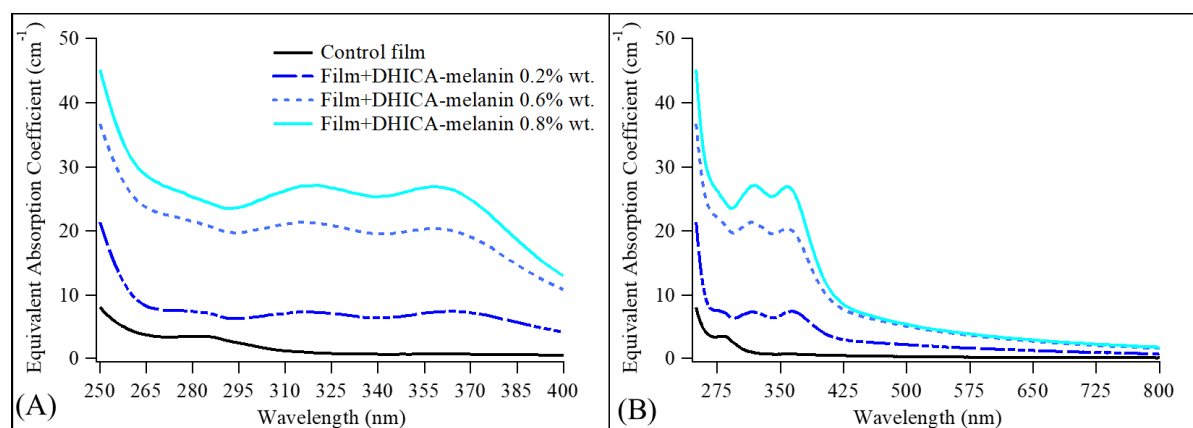

Figure 3 Equivalent absorption coefficient of the control film and films including different DHICA-melanin amounts (A) in the UV range and (B) in the UV and visible ranges.

The absorption coefficient increases more remarkably in the UV range than in the visible range with increasing DHICA-melanin amount from 0.2% to 0.8% wt. Such an increase is stronger in the UVA, where $\alpha_{ADD}/\alpha_{CON}$ = 27 for the 0.8% wt. concentration.

Overall, the results of Figure 2 and Figure 3 prove that eumelanin works as a UV-absorption enhancer for our commercial EVA. However, the absorption enhancement takes place also in the visible range, pointing to the residual presence of some oligomers with a high level of conjugation and still assembling via π-π stacking.

The thermogravimetry in inert atmosphere (Figure S3) of the commercial grade EVA shows an initial stage involving the deacetylation of the vinyl acetate fraction[54], with maximum rate at ≈ 355 °C. Such a step leaves a poly[ethylene-co-(acetylene)] backbone[54] and is followed by the degradation of the main chain, i.e. random splitting of the carbon skeleton, with maximum rate at ≈ 470 °C. In air, the thermo-oxidative degradation rate is faster. Indeed, the onset degradation temperature and the main degradation peak are located at lower temperatures with respect to the inert atmosphere (Figure S3).[55] The thermo-oxidative degradation starts with an initial gain in mass, ascribed to an oxygen uptake by the polyethylene fraction, bringing about the formation of alkyl-hydroperoxides.[56–58] The subsequent drop is due to the deacetylation[59] and thermo-oxidative cleavage of the backbone chains.[56–58]

The addition of eumelanin to our commercial EVA, containing the anti-oxidant butylated hydroxytoluene, leaves both the onset degradation temperature and the main degradation peak unaltered (Figure S3). Eumelanin, in the MFA form, did not show any antagonistic nor synergistic effects with the butylated hydroxytoluene stabilizer, as it does not interfere with the thermal nor thermo-oxidative stabilization imparted by such a stabilizer. On the other hand, it has been reported that other polymers loaded with eumelanin presented higher degradation temperatures, suggesting thermal stabilization imparted by the biopigment.[21,23,28–30] As this effect was associated in the literature to the radical scavenging properties of the biopigment[21,23,28–30], we make the hypothesis that the Melanin Free Acid treatment reduced the radical scavenging power of eumelanin. This reduction following the MFA treatment has already been reported in the literature.[40,60–62]

The long-term effects on our commercial EVA of the UV-absorption enhancement were then evaluated by means of a UV-aging test. Findings from both medical doctors and physicists point to a dichotomous role, either photoprotective or photodamaging, conferred to eumelanin by its broad UV-absorption.[38] When eumelanin converts the energy of the photons into heat (photothermal effect), it can act as a photoprotector.[63,64] This is the effect by which UV-absorbers

protect polymers against photo-oxidation.[35] Another photoprotective path entails the quenching of reactive oxygen species (ROS) generated upon UVA irradiation.[65–67] However, a prolonged exposure to UV could lead to eumelanin photodegradation[65,68], with fission of the indolequinone moiety. Such photo-induced chemical modification of eumelanin's building block can result in the loss of its radical scavenging abilities.[39] In that case, eumelanin can become a pro-oxidant.[40]

To chemically identify possible photo-oxidation products in the control films during the UV-aging test, IR spectroscopy was used. The IR spectra revealed that the prolonged UV irradiation caused photodegradation of the control film, with the appearance of photo-oxidation products: in the first time range of UV-aging (48 days), only at 1715 cm^{-1} (carbonyl groups of ketones[69–75]), and, in the time frame 48 – 144 days, also at 1780 cm^{-1} (γ-lactone)[74,76], 1170 cm^{-1} (C-O stretching of a backbone ester)[77] and 909 cm^{-1} (vinyl groups)[77,78] (Figure S4). Such photo-oxidation products are common to the photodegradation of the polyethylene fraction and to the UV-induced elimination of the vinyl acetate.[79] Because of such an elimination process, the intensity of the bands of the photo-oxidation products increases with time with respect to the intensity of the vinyl acetate band at 1740 cm^{-1}, which decreases with irradiation time (Table S3).[79]

In line with the IR results, the UV-visible absorption spectra of the control films, after UV-aging, feature a strong UV absorption increase, particularly in the UVC, peculiar of the photodegradation products (Figure 4).[80]
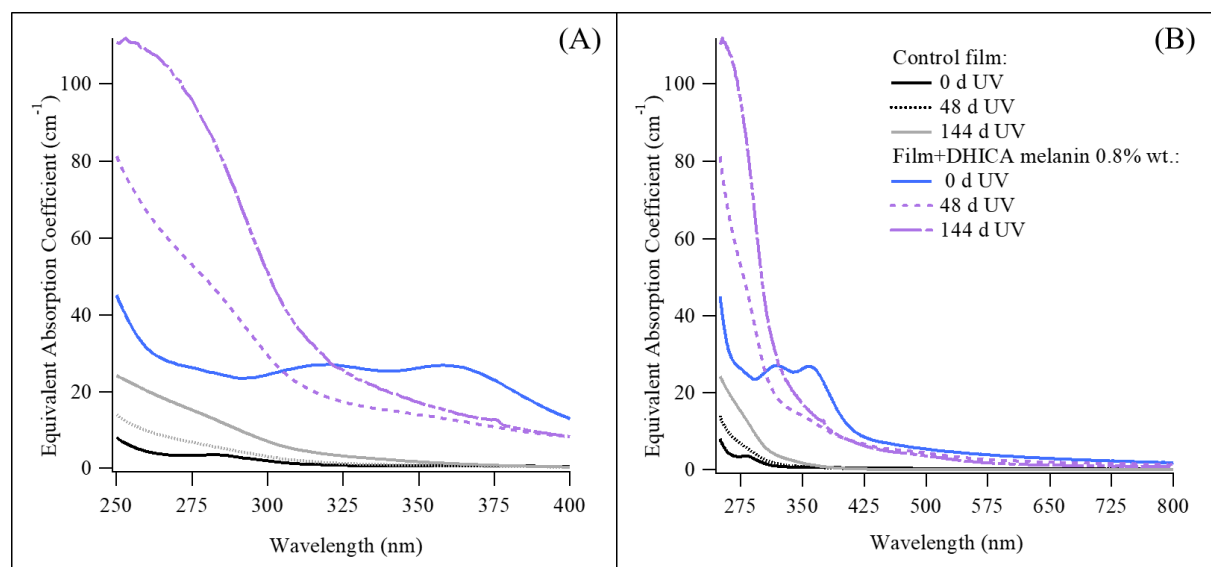
Figure 4 Equivalent absorption coefficient (A) in the UV range and (B) in the UV and visible ranges (B) of the control film and films including DHICA-melanin 0.8% wt. at different times of UV-aging (0, 48 and 144 days).

IR spectra show that the films including the three types of eumelanin, 0.2% wt., after 48 days of UV irradiation, featured the same extent of photodegradation as the control film (Figure 5 and S5). Conversely, after 144 days, only the film containing natural Sepia Melanin showed the same extent of photo-oxidation as the control film. Films containing synthetic eumelanin underwent photo-oxidation to a higher extent with respect to the control counterparts (increased relative intensity of the bands at 1715, 1780, 1170 and 909 cm^{-1}) (Figure 5 and S5).

Increasing the DHICA-melanin amount entailed a more pronounced photo-oxidation (Figure 5). Mechanical embrittlement and surface crazing of the films with higher DHICA-melanin loadings, 0.6% and 0.8% wt. (Table S2), which are consequences of photo-oxidation, were also observed.[81]
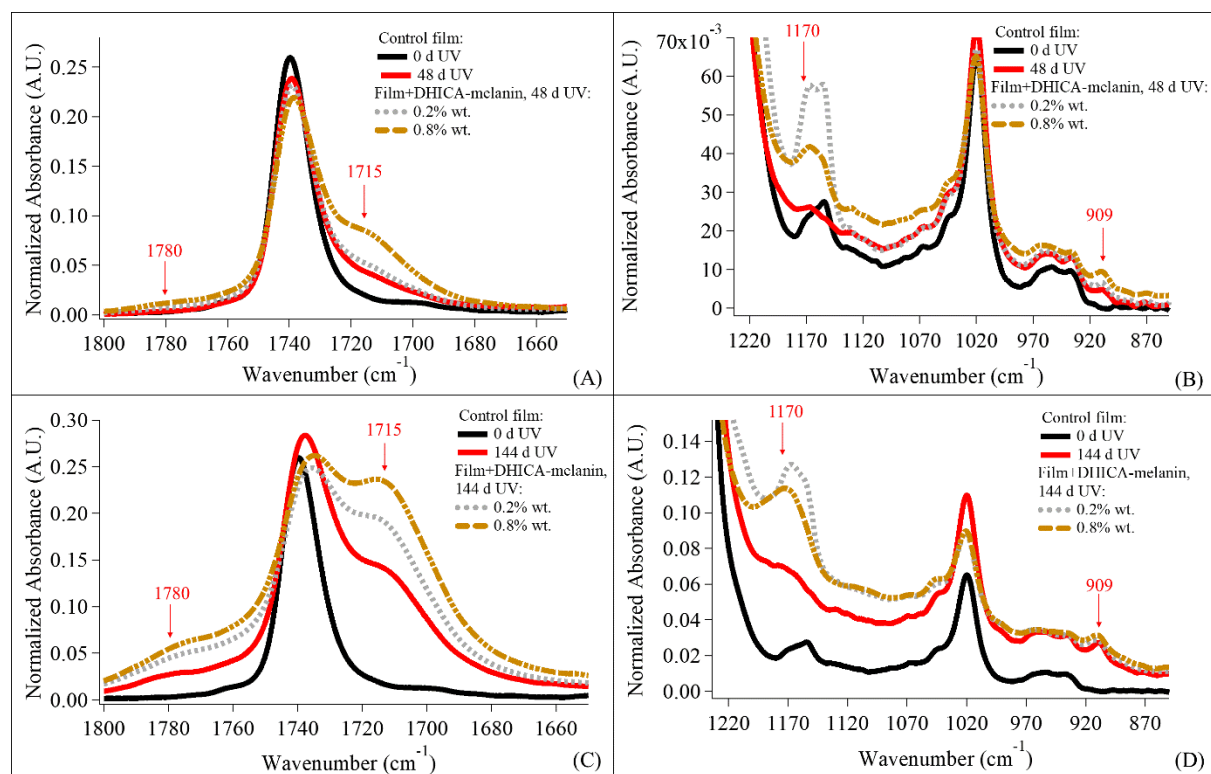
Figure 5 IR spectra of the control film and the films including different concentrations of DHICA-melanin at: 48 days of UV-aging in the range (A) 1800 cm^{-1} – 1650 cm^{-1} and (B) 1230 cm^{-1} – 850 cm^{-1}; 144 days of UV-aging, in the range (C) 1800 cm^{-1} – 1650 cm^{-1} and (D) 1230 cm^{-1} – 850 cm^{-1}. The control film at day 0 of UV-aging is reported for the sake of comparison.

In line with the IR results, after 144 days of UV-aging, films containing eumelanin showed higher absorption in the UVC and UVB than the non-UV-aged counterparts due to the presence of photo-oxidation products (Figure 4). In particular, the absorption at ca. 320 nm decreases during the first 48 days of UV-aging, but, then, in the time frame 48 – 144 days, it increases reaching values equal or higher than the non-UV-aged films (Table S4). This can be explained with an initial photo-degradation of the small oligomers and polypyrroles responsible for the peak at ca. 320 nm[82], followed by a rise in absorption related to the formation of photodegradation products of our commercial EVA. Such photodegradation products feature a broad absorption in the UVB and UVC.[80] The decrease of the absorption peak at ca. 370 nm (resulting from collections of

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oligomers[34,49]) after 144 days is in agreement with the UVA-induced oxidative degradation of eumelanin, with formation of pyrrole-2,3,5-tricarboxylic acid and fission of indolequinone.[68] Literature reports that, during prolonged UV irradiation of eumelanin in solution, concomitantly to the formation of such photodegradation products, reactive oxygen species (ROS) are also generated.[39,65,83]

We make the hypothesis that the ROS formation takes place also when eumelanin is embedded in the polymer matrix. Considering that eumelanin was in the MFA form, with reduced radical scavenging ability, ROS cannot be efficiently quenched by eumelanin, contributing to the propagation of the photo-oxidation process of our commercial EVA.[17] This may explain the pro-oxidant behavior of eumelanin.

Thermogravimetry revealed that the onset degradation temperature (T_{on}) of films containing eumelanin decreases after UV-aging (Figures S6 and S7). The thermal decomposition of the photodegradation products can explain the lower thermal stability of the films. As a matter of fact, the decrease of T_{on} reaches a maximum for films with the highest eumelanin content (~ 17 °C in argon and ~ 83 °C in air). Such films feature the highest extent of photo-oxidation products, as revealed by IR spectroscopy. We cannot rule out chain scission as a further photodegradation path causing the T_{ON} decrease after UV-aging (Figures S6 and S7).[79,84]

Finally, we compared the effects of the addition of eumelanin to a commercial synthetic UV-absorber, the benzophenone BLS®531. Such an additive belongs to a category of compounds that gave evidence of carcinogenic effects.[85–87]

BLS®531 provides to our commercial EVA a one order of magnitude increase of the absorption coefficient in the UV range with a sharp absorption cut-off between the UV and the visible (Figure S8). BLS®531 limited, but did not completely avoid, the formation of photodegradation products after UV-aging, as shown by IR spectroscopy (Figure S9). As the UV-aging time elapses, the absorption coefficient in the UV-range of the film containing the commercial benzophenone decreases (by 10% - 20% after 48 days and by 20% - 50% after 144 days) (Table S4 and Figure

S8), similarly to what happens to the eumelanin related absorption enhancement in the UVA. The depletion of BLS®531 can be due both to its photodecomposition and to physical loss, because of its relatively low molecular weight.[84]

Conclusions

We investigated the use of eumelanin, a dark-brown biopigment, as UV-absorber for packaging polymers. Three types of eumelanin were investigated: one bio-sourced (extracted from cuttlefish ink) and two synthetic (DHICA-melanin and DHI-melanin). In our work, eumelanin underwent the Melanin Free Acid treatment, prior to the addition to the commercial grade ethylene-vinyl acetate copolymer, EVA. The treatment aimed at dispersing the biopigment in the polymer matrix and limiting its absorption in the visible. The addition of amounts of eumelanin as low as 0.2% wt. caused a UV absorption increase, mainly in the UVA. Bringing the amount to 0.8% wt. for DHICA-melanin provided a substantial absorption increase (1 order of magnitude in the UVA). Such increase was partially lost during prolonged UV-irradiation, due to the additive depletion (mainly by indole fission), with photo-oxidation of the embedding polymeric matrix. Work is in progress to optimize the Melanin Free Acid treatment to favor the photo-stabilizing role of eumelanin through radical scavenging and to provide a sharp absorption cut-off between UV and visible ranges. Furthermore, the use of oligomers, not yet assembled in a supramolecular fashion, obtained by controlling eumelanin polymerization in its very early stages, is expected to selectively enhance the optical absorption in the sole UV range.

Supporting Information

Optical images, additional graphs and tables of TGA, UV-visible spectroscopy as well as IR spectroscopy are provided in the Supporting Information.

Funding Sources

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