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Thermooxidative Stabilization of Polymers Using Natural and Synthetic Melanins

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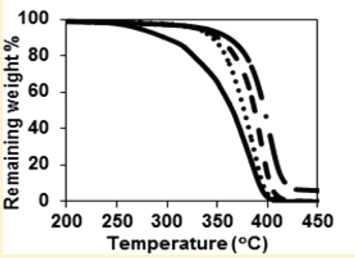
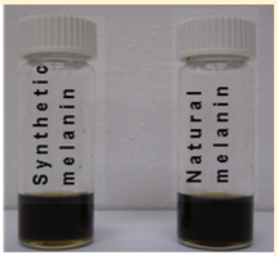
S *Supporting Information*

ABSTRACT: Melanin is a biopolymer well-known for its intriguing chemical structure and physiological functions including photoprotection, radical scavenging, and metal-ion chelation. Although it has a suite of properties not common to many known organic materials, efforts to exploit those properties in technologically relevant materials have been few compared to other biopolymers such as cellulose, chitin, or collagen. Besides its natural presence in many animals including humans, melanin is also commonly consumed by humans in soups, sauces, and pastas and is widely available in large quantities from a variety of natural sources, suggesting it could serve as a nontoxic additive for enhancing the properties of common polymers. To this end, we report for the first time the potential of natural and synthetic melanins as thermal stabilizers for common polymers by evaluating the addition of melanin to several model polymers with well-known degradation pathways. When added to poly(methyl methacrylate) (PMMA) in very low amounts (0.5−5 wt %), synthetic melanin-like polymers significantly altered the radical initiated chain scission behavior of PMMA and caused a dramatic increase (by about 50−90 °C) in its onset decomposition temperature in both inert and air atmospheres. Moreover, PMMA samples with up to 1 wt % melanin achieved nearly the maximum enhancement level yet retained more than 80% light transmission from 350 to 800 nm in 100 μm thick films. Natural melanin extracted from the ink sac of *Sepia officinalis* (commonly known as cuttlefish) also displayed significant thermal stabilization effects on PMMA and polypropylene at similar loadings. From molecular weight characterization studies, the associated delay in the molecular weight decrease of PMMA and other polymers at elevated temperature could be potentially beneficial for high-temperature processing or increasing their upper use temperature in demanding applications. It is likely that the thermal stabilization benefits of melanin could be realized in many polymers due to the diversity of its known radical scavenging capabilities in both living systems and the polymers presented in this article. Since natural and synthetic melanin additives are macromolecules, they are also less likely to leach from the base polymer in the same way that small molecule additives often do.





INTRODUCTION

In recent years, there has been tremendous interest in extracting and using biopolymers like cellulose,[1−3] chitin,[4,5] and collagen[6] as reinforcements in composites, tissue engineering scaffolds, transparent gas barrier films, etc. Melanins constitute another fascinating class of biopolymers found in the hair, skin, inner ear, eye, and brain of living animals.[7] They have been attributed to several different functions in the human body that include absorption of ultraviolet radiation (photoprotection) and dissipation into harmless heat, metal-ion chelation, thermoregulation, antibiotic activity, and free-radical quenching.[8,9] Among the different types of melanins, the most widely studied forms are eumelanins and pheomelanins. Both of these pigments are derived from the common precursor dopaquinone formed via the oxidation of L-tyrosine by tyrosinase.[10] Eumelanins are brown and black pigments derived from oxidative polymerization of 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA), while pheomelanins are red and yellow pigments derived from cysteinyl dopa units[11,12] (see Figure 1). Even given this knowledge of basic subunits, the comprehensive organization of the subunits in melanins is still not clear. It is under debate whether melanins are highly cross-linked heterogeneous polymers or oligomers condensed into nanoaggregates,[7,13] while accumulating evidence suggests supramolecular organization of protomolecules into stacked sheets with a regular spacing of about 3.7 Å.[14]

Natural melanins are amorphous pigments that are insoluble in almost all organic solvents, and this has limited physical and

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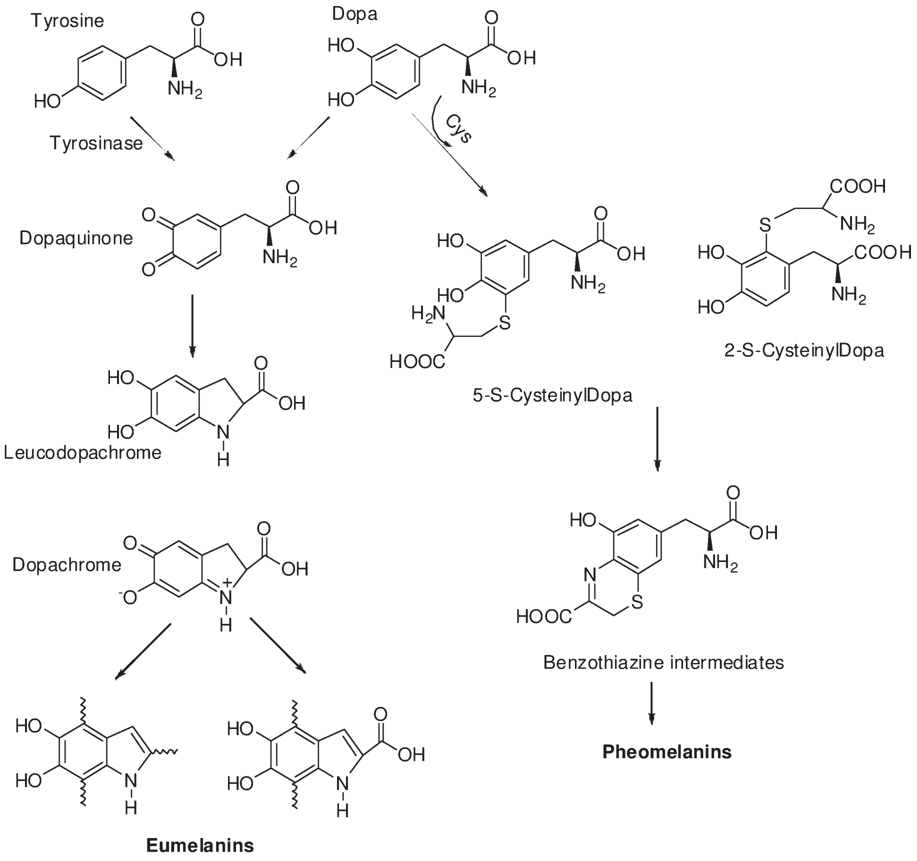

Figure 1. Biosynthetic pathways to eumelanins and pheomelanins.[10]

chemical analysis of these materials. In recent years, researchers have circumvented this issue to some extent by developing synthetic pathways for melanin-like polymers that are soluble in organic solvents like *N*,*N*-dimethylformamide and dimethyl sulfoxide.[8,15] Although exact structural differences between synthetic melanins and their natural counterparts are not completely clear, the fact that synthetic melanins exhibit similar physical and chemical properties to natural melanins has led to renewed interest in synthetic melanin-like polymers for their optical, electronic, and other properties.[16−18] Notwithstanding the voluminous research on the physiological functions of melanin and its related structural aspects, there have been few attempts[17,19,20] to create functional polymeric materials and composites which incorporate this biopolymer. In fact, exploiting the many desirable functional properties of melanins to augment the properties of other polymers still remains largely unexplored. Given that melanins can be extracted either from many natural sources such as cuttlefish (*Sepia officinalis*),[21,22] chicken feathers,[23,24] bacteria,[25] etc., or synthesized from various indole precursors makes it even more attractive for this purpose.

Toward this end, it is demonstrated here that natural melanins and melanin-like synthetic biopolymers have potential as antioxidant additives for certain commercial polymers explored here as model systems due to their well-known degradation pathways. There is increasing evidence suggesting that cellular melanin functions similarly as an antioxidant in the body by (1) scavenging free radicals, (2) deactivating electronically excited oxidizing species, (3) sequestering redox active metal ions such as iron and copper, and (4) scavenging intermediate radicals such as peroxyl and alkoxyl.[26] Dunford et al.[27] and Rozanowska et al.[11] studied the interaction of synthetic melanins with specifically generated oxidizing and reducing free radicals and found that synthetic melanins are good scavengers of carbon-centered radicals with corresponding rate constants in the range of 10^7−10^8 M^{-1} s^{-1}. The efficiency of scavenging depends on the redox potential, electric charge, and the lifetime of the radicals. Very recently, Ju et al. synthesized melanin-like nanoparticles from dopamine hydrochloride and studied their radical scavenging abilities by electron spin resonance spectroscopy.[28]

Since radical-initiated chain scission is a common thermooxidative degradation pathway for most synthetic commercial polymers, it was of interest in the present study to determine whether melanins could be used as an effective thermal stabilizer in polymers such as poly(methyl methacrylate) (PMMA), polypropylene (PP), and polystyrene (PS), which have well-known thermooxidative degradation pathways. Most dramatically, synthetic melanins derived from oxidation of L-3-(3,4-dihydroxyphenyl)alanine (L-Dopa) (Figure 1) significantly enhance PMMA's onset of thermal and thermooxidative stability by 50−90 °C when incorporated in small amounts (0.5−5 wt %). Further, similar thermooxidative stabilization of PMMA and PP can be attained by incorporating natural melanin extracted from the ink sac of *Sepia Officinalis* at similar loadings.

EXPERIMENTAL SECTION

Materials. L-3-(3,4-Dihydroxyphenyl)alanine (L-Dopa), benzoyl peroxide, dimethyl sulfoxide (DMSO), and acetonitrile were all purchased from Sigma-Aldrich. All reagents were used as received without

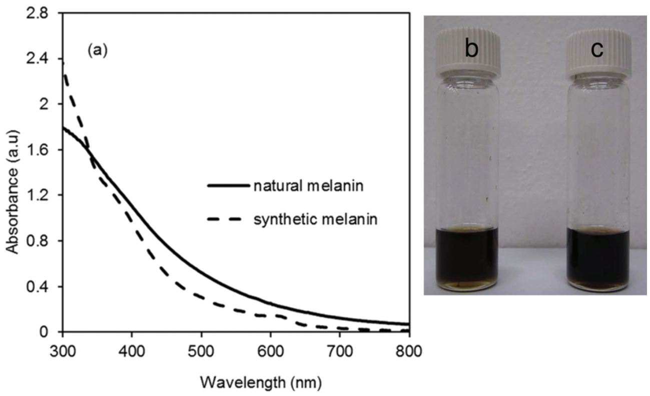

Figure 2. (a) UV−vis absorbance spectra of natural and synthetic melanin in Soluene (both at 0.05 mg/mL). Solutions of (b) synthetic melanin and (c) natural melanin dispersed in Soluene at a concentration of 1 mg/mL.

further purification. PMMA (M_w = 350 000 g/mol) and PS (M_w = 350 000 g/mol) were purchased from Sigma-Aldrich and used as received. PP (grade 3746G) was kindly provided by Exxon Mobil and used as received.

Synthesis of Melanin-like Polymers from L-Dopa. Melanin-like polymers were synthesized by oxidation of L-Dopa following the procedure outlined by Deziderio et al.[8] In a typical procedure, 3.0 g of L-Dopa and 3.7 g of benzoyl peroxide were added to about 400 mL of anhydrous DMSO in a round-bottom flask. The flask was quickly sealed with an airtight stopper, and the solution was stirred with a magnetic stir bar for 28 days at room temperature. The solution turned pink and then black within 2 h, and after 28 days a black solution was obtained. To collect the synthetic melanin product, excess DMSO was evaporated using a rotary evaporator with the water bath set to 100 °C, leaving behind a viscous, concentrated black melanin solution. Dropwise addition of this solution into about 600 mL of acetonitrile resulted in precipitation of melanin-like black aggregates. The precipitate was extracted by centrifugation at 3000 rpm for 10 min, redispersed in acetonitrile, and centrifuged several times until the supernatant was clear. Then the material was dried in vacuum for 2 days to yield black powder of synthetic melanin. This melanin powder was readily redissolvable in DMF and DMSO.

Extraction of Sepia Eumelanin. Ink of *Sepia Officinalis* was provided by Epitek, Inc. (Medford, NJ). Natural melanin was extracted from this ink using the procedure outlined by Liu and Simon.[21] Briefly, 24 mL of the ink was dispersed in 225 mL of deionized water in a polycarbonate centrifuge tube and stirred for 20 min. The solution was centrifuged in an ultracentrifuge (Sorvall RC5B, Sorvall Instruments, Newton, CT) at RCF 20000*g* and 4 °C for 15 min. The top solution was decanted, and the viscous mass at the bottom was redispersed in about 225 mL of deionized water by stirring for 15 min. This was centrifuged, and the solid in the bottom was redispersed again. After six such cycles, the solid mass deposited at the bottom was dried in vacuum for 2 days to yield dry powder of natural eumelanin.

Preparation of Polymer−Melanin Blends. Specific weight fractions of synthetic or natural eumelanin were incorporated into various polymers by melt compounding in a twin-screw DSM microcompounder at 100 rpm for 10 min at compounding temperatures typical for each commercial polymer with a dry nitrogen purge: PMMA (220 °C), PS (220 °C), and PP (180 °C). Neat polymers were also run through the microcompounder at similar conditions to have identical thermomechanical history and serve as appropriate controls.

Thermogravimetric and Chromatographic Analysis. Thermal decomposition behavior of the various polymer−melanin blends was determined using a thermogravimetric analyzer (DSC/TGA 1, Mettler Toledo). Samples were heated in the TGA furnace from 30 °C at indicated heating rates in nitrogen or air atmosphere. To determine activation energies, PMMA and PMMA−5 wt % synthetic melanin blends were heated in a nitrogen atmosphere in TGA at different heating rates: 2, 5, 10, and 20 °C/min. For molecular weight analysis by gel permeation chromatography (GPC), samples were heated in the TGA up to 320 °C; the residue was then completely dissolved in HPLC grade *N,N*-dimethylformamide (DMF) and filtered with 0.2 μm pore size filters. These samples were analyzed using an Agilent 1100 series GPC (Agilent Technologies) equipped with Viscotek I-series mixed bed high and medium molecular weight columns and refractive index and diode-array absorbance detectors.

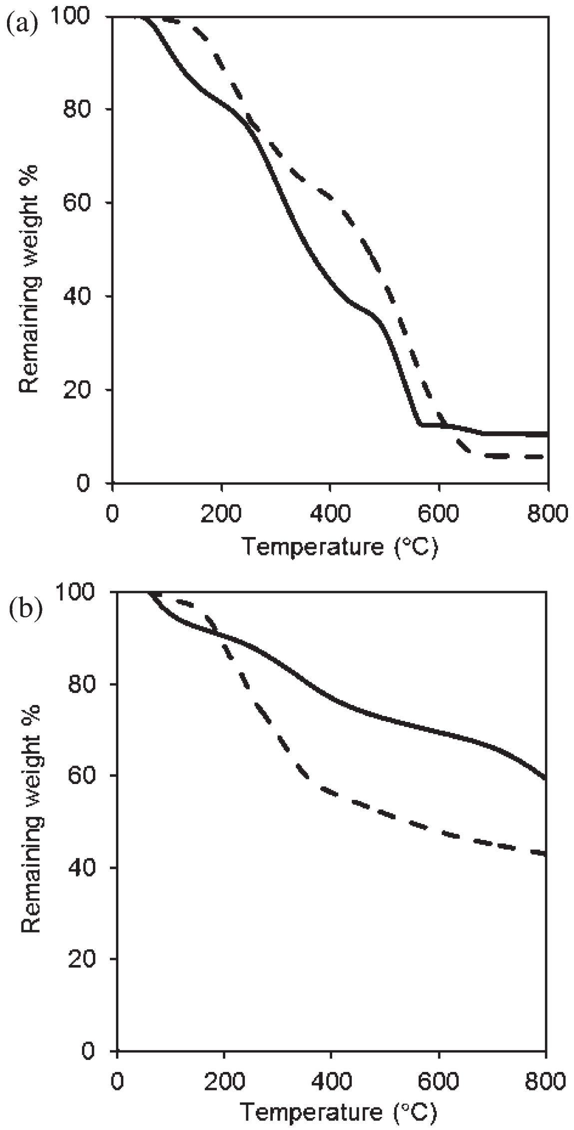

Figure 3. Thermogravimetric analysis plots of synthetic (dashed line) and natural melanin (solid line) (a) in air (b) in nitrogen at 20 °C/min.

UV−vis Spectroscopy. Photoabsorbance behavior of synthetic and natural eumelanins was obtained from a 0.05 mg/mL solution in Soluene (Perkin-Elmer), a solvent that disperses both eumelanins, using a UV−vis spectrophotometer (Hewlett-Packard 8452A diode array).

■ RESULTS AND DISCUSSION

Melanins have been difficult to characterize owing to their heterogeneous structure, intractable chemical properties, and

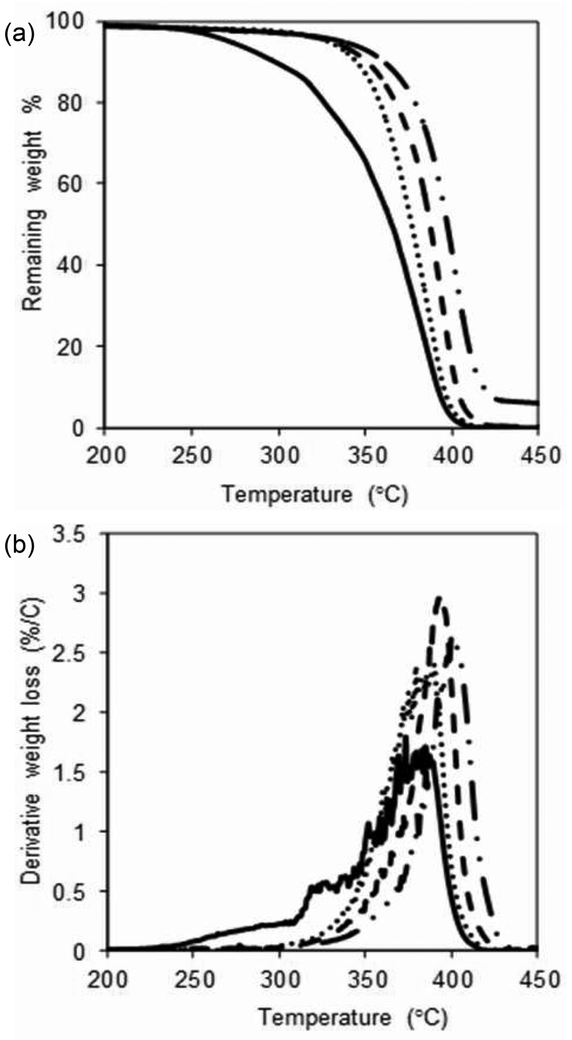

Figure 4. (a) Thermogravimetric analysis and (b) derivative thermogravimetric analysis plots of PMMA and PMMA—synthetic melanin blends in a nitrogen atmosphere: 0 wt % (solid line), 0.5 wt % (dotted line), 1 wt % (dashed line), and 5 wt % (dash-dotted line) synthetic melanin. All samples were heated in nitrogen at 2 °C/min. Similar results are observed for heating rates of 20 °C/min (see Supporting Information).

solubility issues. One efficient way to evaluate synthetic melanins for melanin-like properties is to determine their photoabsorbance behavior. Melanins are particularly known for their photoprotective functions in the body, largely absorbing ultraviolet and visible light and dissipating it as heat. Figure 2a shows the UV—vis absorbance of synthetic melanins. The broad-band monotonic absorbance of these synthetic melanins derived from oxidation of L-Dopa in the entire UV—vis range is essentially identical to that of natural melanins extracted from *Sepia Officinalis*. Like natural melanins, solutions of synthetic L-Dopa-derived melanins appear dark brown to black depending on concentration (Figure 2b,c). Further, the thermal degradation behavior of synthetic melanins is similar to that of natural melanins both in nitrogen and air atmosphere (Figure 3). Both display a multistep weight loss arising from chemical heterogeneity of these pigments and the presence of different volatile species. The low-temperature weight losses can be ascribed to loss of water since melanins are hygroscopic, containing as much as 10—30% water.[29−31] Sepia melanins have been reported to have a protein fraction that is very tightly bound to a chromatoporic component. Not much is known about the nature and binding of this protein component.[22] These proteins and other organic components may be responsible for the slight differences observed in decomposition behavior of Sepia melanins as compared to synthetic melanins. Here, synthetic melanins appear to be slightly more thermally stable than natural Sepia melanins, in contrast to a previous report; however, the preparation protocols of natural and synthetic melanins were not the same as in the present study.[30] Sepia melanin has more thermally stable residue at high temperatures compared to synthetic melanins in both air (Figure 3a) and nitrogen (Figure 3b). Perhaps this difference could result from significant metal ion content in natural melanins.[32]

Figure 4 shows the thermal degradation behavior of PMMA with and without addition of synthetic L-Dopa-derived melanin. PMMA is known to degrade under elevated temperature by radical-initiated chain scission followed by chain unzipping.[33−36] Hence, it was of interest to determine if the radical scavenging abilities of melanin could be used to enhance the thermal stability of PMMA. As seen in Figure 4, synthetic L-Dopa-derived melanin has a significant thermal stabilization effect on PMMA. While neat PMMA starts to degrade at ~230 °C (Figure 4b), the addition of as little as 0.5 wt % synthetic melanin shifts the onset decomposition temperature to ~300 °C. As the concentration of synthetic melanin is increased to 1 and 5 wt %, there is a further increase in the onset decomposition temperature of PMMA to about 320 °C. It is important to mention that the addition of 0.5—1 wt % melanin into PMMA still results in 100 μm thick films with greater than 80% light transmission from 350 to 800 nm as measured by UV—vis absorbance spectroscopy. The films appear slightly brownish in color, and no aggregates are visible to the eye, indicating the dispersion is reasonably good.

Thermal degradation of neat PMMA has been widely investigated.[33−37] Although it is well-accepted that the polymer degrades by chain-end unzipping and random chain scission events, structural differences arising from polymerization conditions lead to significant variation in PMMA decomposition behavior and kinetics. For example, anionically polymerized PMMA is typically more thermally stable than free radically polymerized PMMA (commercial PMMA such as that used in this study is typically free radically polymerized) due to the absence of molecular features introduced during free radical termination.[35] Kashiwagi et al.[35] reported a three-step weight loss for free radically polymerized PMMA. The low-temperature weight losses (around 160 and 270 °C) have been attributed to head-to-head repeat unit linkages from termination by combination and from unsaturated chain ends from termination by disproportionation, respectively, while the high-temperature weight loss step (>300 °C) is attributed to random main-chain scission events. Other studies[33] show a two-step weight loss arising from unsaturated chain-end scission followed by random main-chain scission at higher temperature. The presence of unsaturated chain ends causes the polymer to start unzipping at about 220—230 °C, producing smaller fragments resembling monomers. We also observed here (Figure 4b) a low-temperature weight loss beginning at ~230 °C for neat PMMA. However, incorporation of melanin eliminated the low-temperature weight losses in PMMA, and the onset of decomposition was shifted to 300—320 °C.

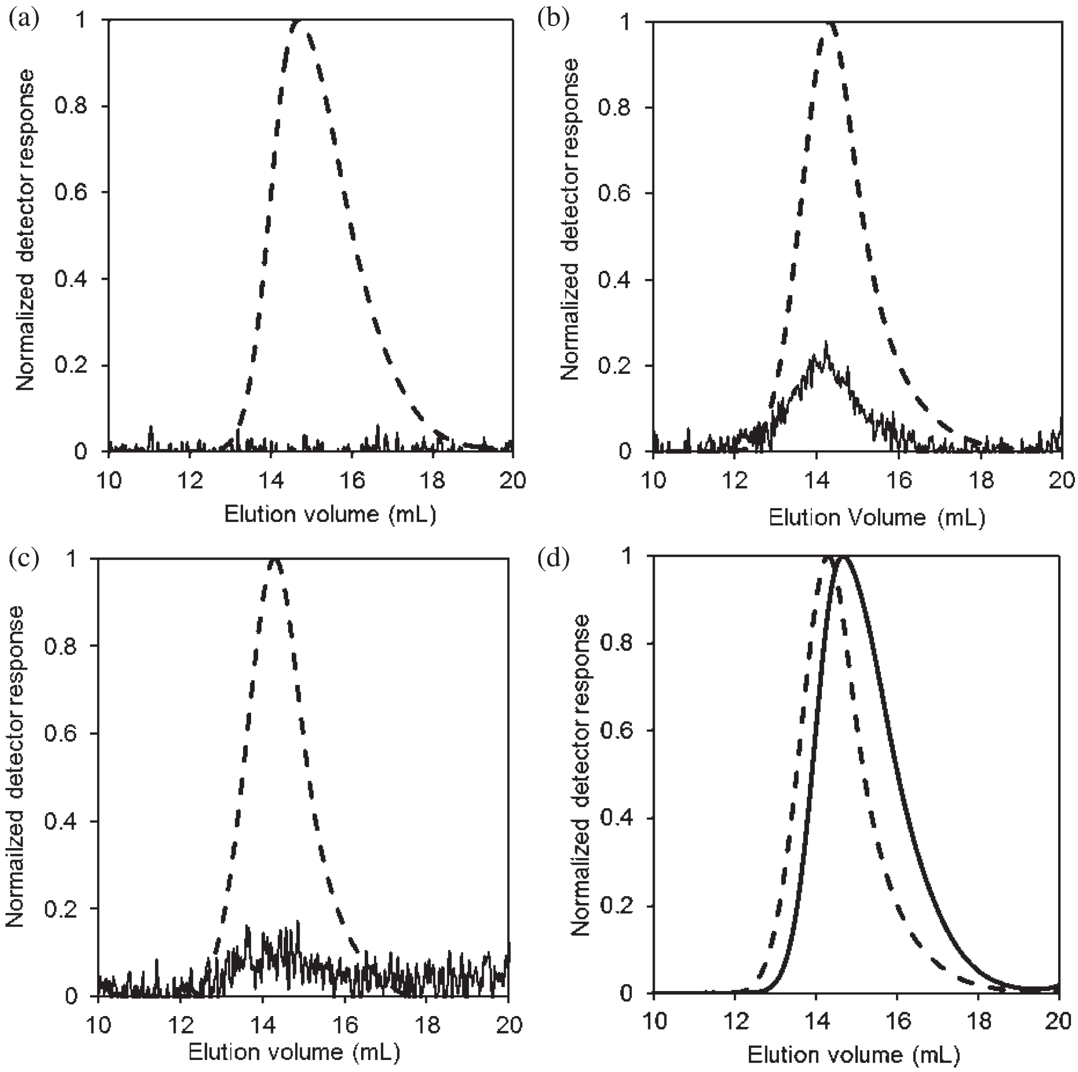

Figure 5. Gel permeation chromatograms of (a) PMMA, (b) PMMA−5% synthetic melanin heated to 320 °C in TGA in nitrogen, and (c) melt compounded PMMA−5% synthetic melanin composite not run in the TGA. Refractive index signal (dashed line), photoabsorbance signal (solid line). (d) Comparison plot of chromatogram of PMMA (solid line) and PMMA−5% synthetic melanin composite (dashed line), indicating the higher molecular weight of the composite in comparison to neat PMMA after heating the samples to 320 °C in nitrogen.

It has been shown by other researchers that melanins can interact with a range of oxidizing and reducing free radicals where the radical scavenging properties depend on the lifetime of radicals, their redox potential, and electric charge.[11] Melanins can react with radicals either by a simple one-electron-transfer process or by radical addition. The fact that the low-temperature weight loss of PMMA is eliminated by incorporation of melanin suggests that melanin scavenges the radicals arising at the unsaturated chain end and exerts a blocking effect on the unzipping depolymerization mechanism. Therefore, degradation of PMMA containing melanin proceeds mostly via main-chain random scission at temperatures above 300 °C. Other research has shown that similar thermal stability, where low-temperature degradation at 230 °C is eliminated and degradation processes above 300 °C dominate,[34] has been imparted to PMMA synthesized with thiol end-groups instead of unsaturated chain ends.

To gain further insight into this mechanism, both PMMA and PMMA−melanin samples were heated in the TGA to 320 °C (the temperature where 10% weight loss is observed in neat PMMA and where main-chain scission events have just started emerging) at 20 °C/min in nitrogen and immediately cooled. They were dissolved in DMF (concentration of ~3 mg/mL) and injected into a GPC with a DMF mobile phase and analyzed using both refractive index and diode array absorbance detectors. While melanins absorb broadly in the UV and visible wavelengths (Figure 2), PMMA does not have a characteristic photoabsorbance in this regime.

As can be seen in Figure 5a, neat PMMA heated to 320 °C in the TGA displays only a refractive index signal with no characteristic absorbance at the visible wavelength of 650 nm. However, PMMA−5% synthetic melanin composite heated to 320 °C in the TGA shows both refractive index and photoabsorbance peaks at the same elution volume (Figure 5b), suggesting that melanin becomes covalently linked to PMMA chains during the heating process. This is supporting evidence for the hypothesis that melanins covalently attach to the radical end of the PMMA chain and hinder chain unzipping following chain-end scission. It should be noted here that the PMMA used in this study is a

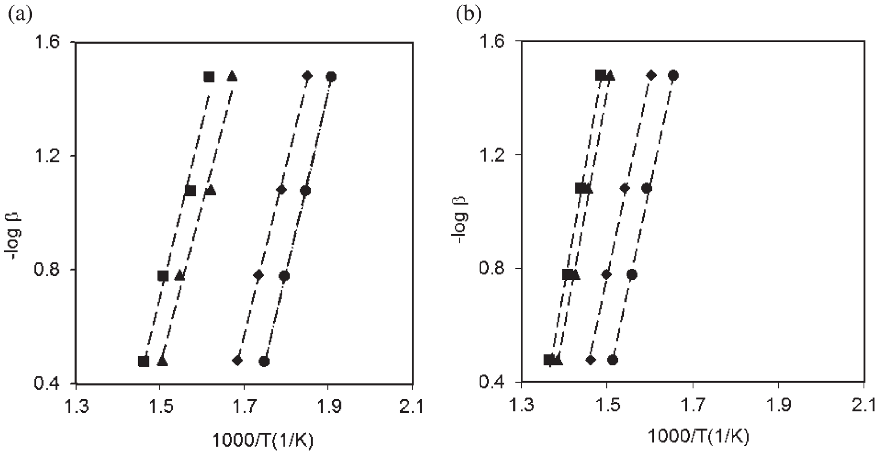

Figure 6. Isoconversion plots used to determine the activation energy based on the thermal decomposition data of (a) PMMA and (b) PMMA−5% synthetic melanin blends run at different heating rates (β). Each symbol represents a particular weight loss condition: 5% weight loss (solid circles), 10% weight loss (solid diamond), 50% weight loss (solid triangles), 70% weight loss (solid squares). The dashed line connecting a set of symbols represents the temperature at which a given degree of weight loss occurs at various heating rates (β). Activation energies determined from the slope of the dashed lines using eq 1 are listed in Table 1.

Table 1. Activation Energies for Thermal Decomposition of PMMA and PMMA−5% Synthetic Melanin Blends Determined by the Flynn−Wall−Ozawa Method[a]

	activation energy (E), kJ/mol	
conversion (%)	PMMA	PMMA−5% synthetic melanin
5	114	129
10	109	128
50	103	150
70	112	154

[a] The expected standard error in the determination of activation energies by this method has been reported to be ±10%.[37]

commercial sample of high molecular weight ($M_w \sim 350\,000$ g/mol). While the molecular weight characterization of melanins still remains a major challenge owing to its structural heterogeneities, the solvent soluble synthetic melanin in this study appears in our chromatograms at elution volumes greater than 20 mL. As a control experiment, the chromatogram of PMMA−5% synthetic melanin immediately following melt compounding shown in Figure 5c exhibits a small photoabsorbance peak that is barely distinguishable from the instrument baseline at the same elution volume of the refractive index peak. This is likely due to the same attachment mechanism of melanin onto the PMMA chain which occurs to a lesser extent during melt compounding of melanin with PMMA at 220 °C for 10 min. We also observe from Figure 5d that PMMA−5% synthetic melanin composite heated to 320 °C in the TGA elutes much earlier than neat PMMA heated to similar conditions, indicating melanin can prevent significant molecular weight loss. This suggests that melanin, by its radical scavenging action, can stabilize PMMA such that it retains its molecular weight during thermal processing at elevated temperatures. Since molecular weight is a structural parameter which has significant influence on the mechanical and flow properties of polymers, this could be particularly advantageous in polymer processing and demanding thermal applications.

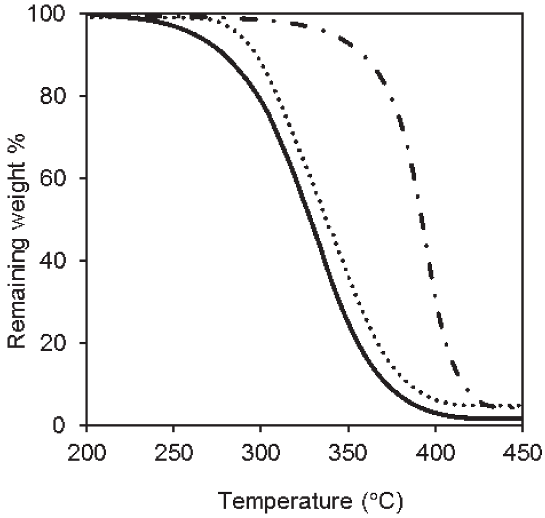

Figure 7. Thermogravimetric analysis plots of PMMA blends in air at a heating rate of 20 °C/min: PMMA−5 wt % synthetic melanin composite (dash-dotted line) showing significant increase in the onset decomposition temperature as compared to neat PMMA (solid line) or PMMA−5 wt % montmorillonite composite (dotted line).

In order to quantitate the activity of melanin on the thermal degradation of PMMA, the activation energy for decomposition of PMMA and the melanin blends was determined using the Flynn−Wall−Ozawa method.[38,39] In this method the kinetics of thermal decomposition of polymers is evaluated based on an isoconversion principle. When a sample is decomposed at different heating rates, the temperature (T) for a given conversion or percentage weight loss changes with heating rate (β) due to the interplay of heating rate with decomposition kinetics. By plotting log β against $1/T$ for a given conversion, the activation energy can be determined from the slope of the line fitting the data (Figure 6) using the equation

$$\frac{\mathrm{d}(\log \beta)}{\mathrm{d}(1/T)} = -0.4567\,\frac{E}{R} \tag{1}$$

where T is temperature (in K), β is the heating rate (K/min), E is activation energy (kJ/mol), and R is the universal gas constant (kJ/(mol K)).

The activation energy for the thermal decomposition of neat PMMA was between 103 and 114 kJ/mol, falling within the broad range of values (60−320 kJ/mol) found in the literature.[33] This wide variation can be attributed to structural differences in PMMA arising out of different polymerization conditions and also the use of a wide variety of methods to determine this activation energy. While the activation energy of PMMA reported here remained closely similar across different degrees of conversion, the activation energy of PMMA−5% melanin increased slightly with higher degrees of conversion but was always higher than neat PMMA. This indicates the superior thermal resistance of PMMA−melanin blends originates from enlarged activation energy for decomposition, likely by diverting the primary degradation mechanism to main-chain scission events which only take place at higher sample temperatures.

More significantly, synthetic melanin also enhances the thermal stability of PMMA in air, a far more oxidative environment. As can be seen in Figure 7, incorporation of 5 wt % synthetic melanin in PMMA enhances the onset decomposition temperature from 230 to 300 °C when PMMA is heated in air. The 70−80 °C shift in decomposition temperature of PMMA in an air atmosphere represents a significant thermooxidative stabilization effect that could be potentially useful in extending the thermal processing and use temperature of this commercially relevant polymer. In comparison, montmorillonite, which is widely used to enhance mechanical and flame-retardant properties of polymers, does not have a significant effect on the thermal stability of PMMA (Figure 7).

Figure 8 shows that the thermooxidative stabilization effect from adding synthetic melanin to PMMA can also be attained with melanins derived from natural sources. Melanins isolated from the ink sacs of *Sepia officinalis* (cuttlefish) are commonly accepted as a standard for natural eumelanins.[22] Mild and generally applicable protocols for isolating melanins from Sepia ink without altering their native composition have been established previously.[21,22] Using this procedure, we obtained a black powder of natural eumelanin and melt compounded them with the same PMMA. As shown in Figure 8, natural Sepia melanin also has a significant thermooxidative stabilization effect in PMMA, but the amount of enhancement in the onset temperature of the degradation (~50 °C) is slightly less compared to synthetic melanin. This could be due to several reasons. Natural melanin has a significant amount of bound protein that is probably easy to degrade and which cannot be removed during extraction even after several washing cycles. Natural melanin is also not as dispersible in PMMA or simple organic solvents as compared to synthetic melanins due to its more particulate nature, possibly from metal ions which participate in inter- and intramolecular ionic bonds. In fact, the natural melanin in Figure 2c was made into a suspension using Soluene, a special solvent from Perkin-Elmer which contains surfactants and other dispersing aids.

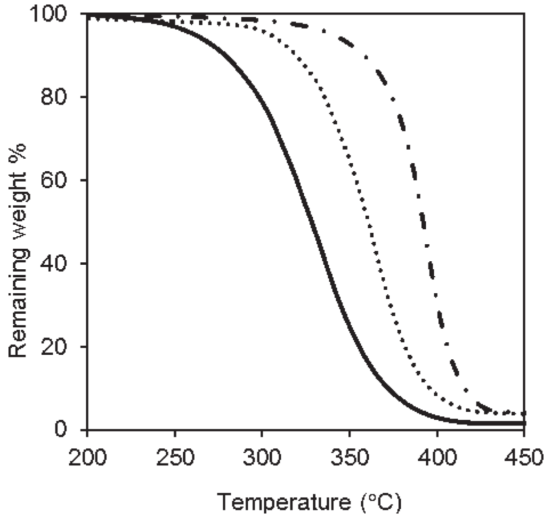

Figure 8. Thermogravimetric analysis plots of PMMA−natural melanin blends in air at a heating rate of 20 °C/min. Natural Sepia melanin also significantly enhances the thermooxidative stability of PMMA, but the effect is less compared to synthetic melanin: PMMA (solid line), PMMA−5 wt % natural sepia melanin (dotted line), PMMA−5 wt % synthetic melanin (dash-dotted line).

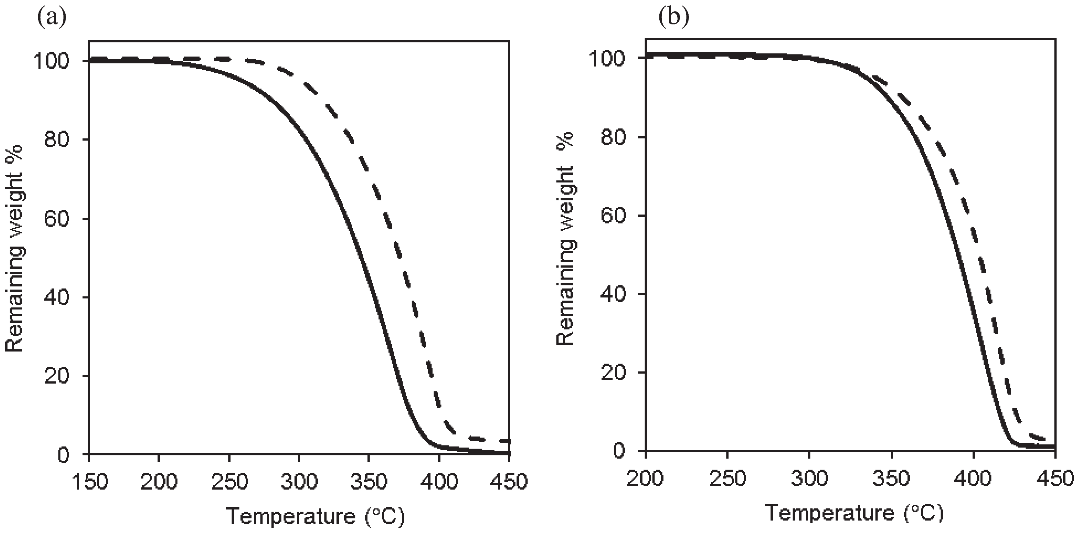

Figure 9. Thermogravimetric analysis plots of (a) PP (solid line) and PP−5 wt % natural sepia melanin composite (dashed line) and (b) PS (solid line) and PS−5 wt % natural sepia melanin composite (dashed line) in air at a heating rate of 20 °C/min.

Therefore, natural melanin added at similar loadings may be less effective in radical scavenging action due to its presence in larger aggregates rather than in a fully dispersible form as for synthetic melanins. It is also possible that synthetic melanin is not perfectly representative of natural Sepia melanin structure even though the same basic structural units are present. It has been very difficult to definitively establish these differences for reasons mentioned earlier, and more research is ongoing in this area in a number of research groups.

In order to establish generality of the thermal stabilization properties of melanins applied to other polymers as well, we incorporated 5 wt % natural Sepia melanin into PP and PS, two widely used polymers with very different chemistries and degradation pathways. PP is well-known for thermal degradation by radical attack due to the presence of tertiary hydrogens with low dissociation energy.[40] PS, on the other hand, is reported to undergo degradation via random chain scission followed by intra- and intermolecular radical transfer.

As seen in Figure 9, incorporation of melanin enhanced the onset decomposition temperature of PP by ∼50 °C, while the effect on the thermooxidative stability of PS was much less. It should be noted here that many polymers degrade at lower temperature in air than in nitrogen. In the presence of oxygen, the radicals produced by chain scission form peroxy radical intermediates and hydroperoxides. This appears to shift the rate-limiting step from random chain scission to decomposition of hydroperoxide radicals either during the early stages of degradation or throughout the process.[41] The effects of these on the radical scavenging role of melanin are not clear. The general radical scavenging action of melanin depends on several factors such as the reactivity and lifetime of radicals, steric hindrances, etc.,[10] which can be translated to some extent to melanin's stabilization activity in polymers. The fact that we observe less thermal stabilization effect of melanin on polystyrene could be due to the resonance stabilization of radicals by pendant aromatic groups or steric hindrance restricting the accessibility of melanin to these units. This is the subject of future investigations.

CONCLUSIONS

Melanin, a biomacromolecule well-known for its various functions in living systems, was investigated for its potential thermal stabilization capability in model synthetic polymers with well-known degradation pathways. Synthetic melanin derived from the oxidation of L-dopa significantly enhanced the thermal and thermooxidative stability of PMMA when incorporated even in very low amounts of 0.5 wt %. The low-temperature weight losses below 300 °C associated with chain-end scission arising from weak unsaturated ends in free radically polymerized PMMA were eliminated. The presence of melanin also delayed the onset of decomposition to above 300 °C. Combined thermal degradation and chromatography studies indicate that melanin scavenges the radical end of the chain and exerts a blocking effect on subsequent depolymerization. Natural melanin derived from the ink sac of *Sepia Officinalis* also exerts significant thermal stabilization behavior in PMMA and other polymers like PP and to a lesser extent in PS. Finally, this biopolymer can be harvested in large quantities from many natural sources like cuttlefish, chicken feathers, bacteria, etc., or synthesized from various indole precursors and could be used to enhance thermal and thermooxidative stability of commercial polymers, possibly without detrimental effects on the environment over traditional small molecule additives.

ASSOCIATED CONTENT

Supporting Information. TGA data of PMMA melanin composites (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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