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Proximal effects of ultraviolet light absorbers and polymer matrix in the photostability of β-carotene

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ABSTRACT

β-Carotene was used as a probe to investigate the protection offered by 2-ethylhexyl 4-methoxycinnamate, a photostabilizer, upon ultraviolet-A photodegradation. β-Carotene and 2-ethylhexyl 4-methoxycinnamate were arranged in two distinct macroscopic configurations (core/shell and homogenous) in solution with tandem and single cuvettes. 2-Ethylhexyl 4-methoxycinnamate was also combined with poly(methyl methacrylate) in solution to investigate the protective synergy between the photostabilizer and the polymer matrix. The choice of configuration played a more dominant role than the concentration of 2-ethylhexyl 4-methoxycinnamate in the degradation of β-carotene, with β-carotene remaining more stable in the homogeneous configuration. Changing configurations yielded different proximities of 2-ethylhexyl 4-methoxycinnamate to β-carotene; closing the proximity increased the potential close interactions (<1 nm) where transfer of excited state energy from β-carotene to 2-ethylhexyl 4-methoxycinnamate could occur resulting in increased photostability. The addition of poly(methyl methacrylate) had a negligible impact on the decay of β-carotene in both configurations.

1. Introduction

Approximately 40% of the solar energy which reaches Earth is allowed to pass through the atmosphere to reach the surface. The atmosphere allows visible light to pass through while blocking hazardous light, by use of stratospheric oxygen and ozone molecules which absorb 97–99% of the sun's high frequency ultraviolet radiation (wavelengths of 150–300 nm). The ultraviolet light that successfully reaches the earth's surface is predominantly ultraviolet-A (UVA) radiation (wavelengths of 320–400 nm), with a smaller component of ultraviolet-B (UVB) radiation (wavelengths of 280–320 nm). UVA radiation is of particular interest because of its prevalence in sunlight and being of relatively high energy it is important to investigate the harmful effects of UVA radiation [1]. Among fillers and other inactive ingredients, traditional sunscreens are comprised of primary UV absorbers and additional UV absorbers dedicated to protect the primary UV absorber, which serve as photostabilizers [2,3].

Many structural and spectroscopic studies [4,5] have been performed in order to understand the specific interactions such as hydrogen bonding, solvent–solute complexation, changes in the electronic charge distribution following photoexcitation, and excited state reactions. Several studies have been performed to understand the influence of polymer matrices on photophysical properties of intermolecular hydrogen bridged UV absorbers [6,7]. In these UV absorbers an excited state intramolecular proton transfer in the excited singlet state opens a pathway for the transformation of harmful ultraviolet radiation into thermal energy [8]. The migration of UV absorber molecules out of the polymer matrix is influenced by the free volume of the polymer as well as by the size and shape of the diffusing molecules [9]. The systematic investigation on the photophysical properties of molecules in the condensed phase and their molecular structure provides insight into the impact of interactions between the solvent and solute [10]. For example, the proximity of the carbonyl and hydroxyl groups in UV absorbers can allow for the formation of intra- and intermolecular hydrogen bonds. The interaction of UV light and UV absorber begins when a photon of UV light interacts with a ground state molecule of the UV absorber by encountering a pair of electrons. The photon energy is transferred to one of the electrons promoting it to the singlet excited state. This singlet state electron intersystem crosses to a less energetic triplet excited state. In the triplet excited state, the absorbed energy is dissipated as heat before the electron returns to its ground state pairing. Once in the ground state, the molecule is free to repeat the

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absorption process which is of the order of a few milliseconds. As the cycle of absorption and dissipation progresses, molecules may be damaged by photochemical reactions and no longer able to repeat the cycle. This typically occurs in the triplet excited state, where a competition exists between the excited state electrons fighting to return to ground state and reactive oxygen species searching for donor electrons. With prolonged exposure to UV light, more UV absorber molecules become damaged and the overall effectiveness, or photostability, of the absorber decreases. Photostabilizers are added to maintain the photostability of the UV absorber. They are able to quench and dissipate the excited state energy of the UV absorber before any damaging photochemical reactions occur [11,12].

Recently, polymer nanocomposites have been formulated to achieve increased photostability and UV protection [13–21]. These studies showed the significance of UV absorbing activity in zinc oxide (ZnO) treated matrices and ZnO-polyethylene terephthalate (PET) nanocomposites. In addition, photo-oxidation studies on polyethylene containing nanoparticle and pigmentary grade titanium dioxide pigments showed that in general the former are more photoactive. It was argued that the proximity of nanoparticle pigments induces oxidation of the polymer during processing and the formation of hydroperoxide and carbonyl groups. Similarly, composites of titanium oxides and silicon dioxide hybrid capsules showed good UV protective properties. Although these studies showed the role of the proximity of metal oxides on UV protection, there are almost no systematic studies performed which delineate the proximity of absorbers and matrices.

Most previous studies used small concentrations of UV absorber paired with a weak UV absorbing polymer. In this paper high concentrations of absorber were paired with a strongly absorbing dye. A new experimental method was introduced to understand the proximal effects of high levels of UV absorbers and polymer matrices. The relationship between molecule proximity and photostability was examined. Additionally, a polymer matrix was added to consider the photoprotective synergy between absorber and polymer. Overall, the role of the proximity of absorbers and polymer matrix in the protection against UVA radiation was investigated.

2. Materials & methods

2.1. Sensor molecule

β-Carotene ($M_w = 536.8$ g/mol), was selected as a UVA sensitive probe molecule to investigate the proximal effect on photostability when paired with other absorbers and a polymer matrix. β-Carotene is not typically used as a sunscreen active ingredient, but it serves as an ideal probe molecule because it absorbs UVA light, photodegrades and undergoes a fluorescence shift. As shown in Fig. 1, the β-carotene molecule contains a long conjugated hydrocarbon chain, consisting of many C=C bonds which serve as a chromophore for the molecule. This chromophore is responsible for the light absorption and gives β-carotene its deep orange color. Based upon the Planck–Einstein equation, $E = hc/\lambda$, UV light has more energy than visible light. When exposed to an abundant UVA light source, the C=C and C–C bonds of the hydrocarbon chain break, the molecule degrades and loses its deep orange color, becoming transparent [22].

2.2. Photostabilizer molecule

The known UV absorber 2-ethylhexyl 4-methoxycinnamate (EHMC) ($M_w = 290.3$ g/mol) was selected to serve as a photostabilizer (structure shown in Fig. 1). Its peak absorption when dissolved in acetone was between 325 and 375 nm, thus validating its use as a UVA absorber. The photoprotective effects of

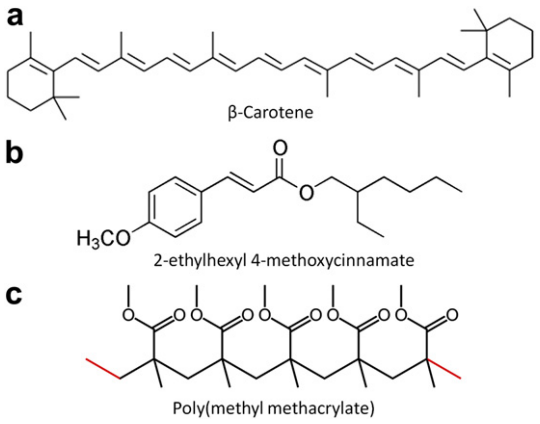

Fig. 1. (a) β-Carotene molecule. (b) 2-ethylhexyl 4-methoxycinnamate. (c) Poly(methyl methacrylate).

2-ethylhexyl 4-methoxycinnamate when mixed with β-carotene in two distinct configurations were investigated. These two configurations are shown in Fig. 2.

2.3. Polymer matrix

Poly(methyl methacrylate) is often used as a polymer matrix for producing microparticles. It is important to evaluate its effect (structure shown in Fig. 1) on the overall photostability of each configuration tested. Poly(methyl methacrylate) of $M_w = 120{,}000$ (Sigma Aldrich) was dissolved in acetone and was mixed with 2-ethylhexyl 4-methoxycinnamate in a ratio of 2-ethylhexyl 4-methoxycinnamate: poly(methyl methacrylate) (4:1).

2.4. Macroscopic configurations

β-Carotene solutions were mixed with each dilution of 2-ethylhexyl 4-methoxycinnamate in two distinct configurations using a standard or tandem cuvette cell (NSG Precision Cells Inc., Farmingdale NY). The tandem cell uses a quartz divider which has no effect on the fluorescence signal. The cuvette cells were chosen to macroscopically replicate the physical orientation of microparticles containing the UV sensitive molecule (β-carotene) and the photostabilizer (2-ethylhexyl 4-methoxycinnamate). For

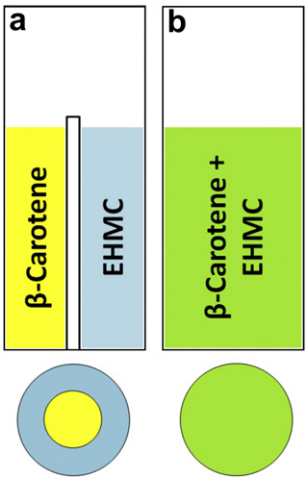

Fig. 2. (a) Core/shell configuration of β-carotene and 2-ethylhexyl 4-methoxycinnamate in tandem cuvette cell. (b) Homogenous configuration of β-carotene solution and 2-ethylhexyl 4-methoxycinnamate in standard cell.

both configurations the total concentration (i.e. no tandem divider) of β-carotene equaled 16.65 uM and the total concentration of 2-ethylhexyl 4-methoxycinnamate was equal to one of 868 mM, 434 mM, 217 mM or 108 mM. The total sample volume equaled 2 mL. It is important to note that the homogeneous configuration used a single well cuvette, rather than a tandem well cuvette. By eliminating the divider, the free motion of β-carotene and 2-ethylhexyl 4-methoxycinnamate throughout the entire 2 mL sample occurs. This is analogous to a completely homogenous microparticle of the same radius as the core/shell configuration, rather than a core–shell particle. Each mixture of 2-ethylhexyl 4-methoxycinnamate/poly(methyl methacrylate) was configured with β-carotene in the two configurations shown in Fig. 2. The overall β-carotene, 2-ethylhexyl 4-methoxycinnamate and poly(methyl methacrylate) concentrations for each configuration were fixed at 16.65 uM, 217 mM, and 1.67 mM respectively.

2.5. Experimental device

Fluorescence was measured for 30 s using QuantaMaster UV VIS fluorimeter (PTI, Birmingham NJ) shown in Fig. 3(a). For consistency and optimal fluorescence, the right well of the cuvette (tandem only) was adjacent to the light source. After fluorescence was recorded, the sample was removed from the fluorimeter and placed 18.5 mm from UVA light ($\lambda = 365$ nm, I = 1900 μW/cm^3) for 10 min using a Pen Ray Mercury lamp (UVP, Upland CA) as shown in Fig. 3(b). The right well of the cuvette (tandem only), representing the outer surface of a particle was always adjacent to the lamp. The entire apparatus was enclosed in a black box to minimize any background radiation and reflection. After exposure the cuvette was returned to the fluorimeter and the fluorescence was measured again for 30 s. This cycle was repeated for a total exposure time of 60 min.

2.6. FTIR analysis of β-Carotene degradation

A 2 mL solution of β-carotene [16.650 uM] in a standard cuvette was exposed to UVA light for 60 min. At the beginning and end of exposure a Spectrum One FTIR (PerkinElmer, Waltham MA) was used to measure the absorption bands associated with C=C and C–C bonds, which range from 1600 to 1680 cm^{-1}.

2.7. UV–Vis analysis of β-Carotene degradation

A 2 mL solution of β-carotene [16.650 uM] in a standard cuvette was exposed to UVA light for 60 min. At the beginning and end of the exposure time, the absorbance of the solution was measured using a NanoDrop 1000 UV–Vis Spectrophotometer (Wilmington, DE).

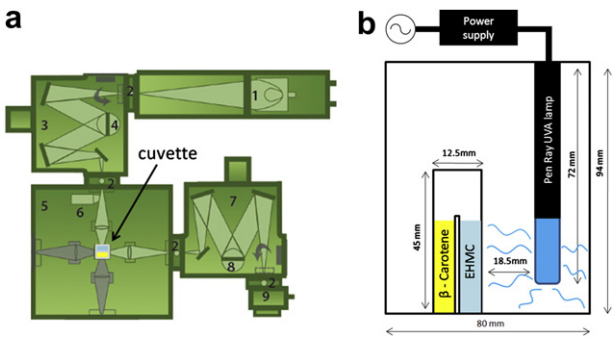

Fig. 3. (a) QuantaMaster UV VIS fluorimeter. (b) UVA exposure chamber.

2.8. UV–Vis analysis of 2-ethylhexyl 4-methoxycinnamate degradation

A 2 mL solution of 2-ethylhexyl 4-methoxycinnamate [868 mM] in a standard cuvette was exposed to UVA light for 60 min. At the beginning and end of the exposure time, the absorbance of the solution was measured using a NanoDrop 1000 UV–Vis Spectrophotometer (Wilmington, DE).

3. Results & discussion

β-Carotene solution excitation and emission spectra were determined. β-Carotene dissolved in acetone showed a maximum excitation at 350 nm and a maximum emission at 525 nm. The 2-ethylhexyl 4-methoxycinnamate solution excitation and emission spectra were also determined; a maximum excitation at 380 nm and a maximum emission at 413 nm, although it had a fairly broad emission spectrum. Because of this broad emission, it was important to compare the emission spectra of both 2-ethylhexyl 4-methoxycinnamate and β-carotene to ensure that 2-ethylhexyl 4-methoxycinnamate did not interfere with the fluorescence signal of β-carotene. A comparison of 2-ethylhexyl 4-methoxycinnamate and β-carotene emission spectra, when excited with 350 nm light, revealed that the 2-ethylhexyl 4-methoxycinnamate fluorescence was insignificant when compared to β-carotene fluorescence. This ensured that 2-ethylhexyl 4-methoxycinnamate fluorescence did not interfere with measuring β-carotene fluorescence.

3.1. β-Carotene degradation

The solution of β-carotene contained in a single well cuvette was bleached when exposed to the UVA light source in 10 min intervals for a total of 60 min Fig. 4(a) illustrates the decay of the fluorescence signal, measured in photons/sec. The data was normalized by dividing each data point in a set by its initial data point at time- = 0 min. As the concentration of β-carotene was reduced, a higher percentage of β-carotene molecules were interacting with a fixed number of UVA photons which caused more rapid photodegradation, thus a less photostable sample. Conversely if the concentration of β-carotene increased, a smaller percentage of β-carotene molecules were interacting with a fixed number of UVA photons resulting in greater photostability. This is analogous to sunscreen manufacturers increasing the concentration of active ingredient (UV absorber) in a formulation to increase the photostability of the sunscreen.

The photoreaction of β-carotene (A) is often described by the following equation [2]

$$A \overset{hc/\lambda}{\rightarrow} P \tag{1}$$

where P refers to product(s) formed. Assuming instant mixing of samples, the rate of photodegradation can be described by

$$-\frac{d[A]}{dt} = \varphi_A I_A = \varphi_A I_0 (1 - \exp(-\chi[A]d)) \tag{2}$$

where $[A]$ is the concentration of β-carotene at after UV exposure time t, φ_A is the quantum yield for excitation of A, I_0 is the lamp intensity, I_A is the absorbed intensity, χ is the molar excitation coefficient and d is the optical path length. The general solution of this equation is

$$\frac{[A]}{[A_0]} = \frac{1}{[A_0]\chi d} \ln\{1 + \exp([A_0]\chi d - \varphi_A I_0 \chi dt) - \exp(-\varphi_A I_0 \chi dt)\} \tag{3}$$

where $[A_0]$ is the known initial concentration of β-carotene. With $d = 1.25$ cm in our experiments, $[A]$ can be evaluated given the values

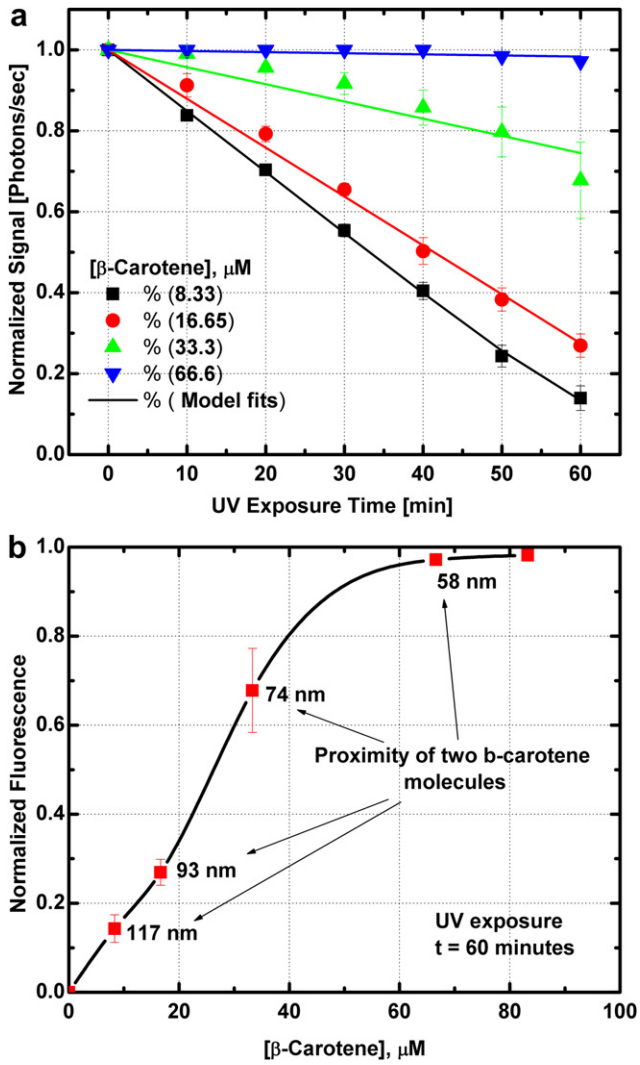

Fig. 4. (a) Fluorescence decay of β-carotene. (b) Fluorescence based upon concentration of β-carotene at time = 60 min.

of χ and $\varphi_A I_0$. The fits of this equation are plotted in Fig. 4(a). For $\chi = 8.6 \times 10^8$ cm^2/mole and $\varphi_A I_0 = 2.09 \times 10^{-12}$ mole/cm^{3}s, the fluorescence data for $[A_0] = 8.33$ μM fits very well with the model. However, the model does not accurately capture the entire experimentally observed decay profiles for concentrations higher than $[A_0] = 8.33$ μM. It is likely that at high concentrations, the interactions between molecules protected β-carotene degradation from UV exposure. To understand this behavior of β-carotene fluorescence, an average distance between β-carotene molecules can be evaluated. Fig. 4(b) shows that when the average proximity of individual β-carotene molecules was less than approximately 60 nm, the fluorescence stabilized. This corresponds to β-carotene solutions with a concentration greater than 67 uM. The normalized fluorescence of β-carotene after 60 min of exposure is plotted in Fig. 4(b).

Fig. 5(a) shows an FTIR spectrum of 16.65 uM β-carotene solution before and after 60 min UVA exposure. The FTIR spectra obtained after degrading β-carotene solution with UVA light for 1 h showed a significant decrease in absorbance (red ovals) associated with C=C and C–C bonds (1600–1680 cm^{-1}) indicating color loss and degradation of the hydrocarbon chain chromophore. However, the spectrum showed no significant decrease in absorbance for aromatic C–H bonds (3070 cm^{-1}).

Fig. 5(b) shows a UV–Vis Spectra of 16.65 uM β-carotene solution before and after UV exposure. The UV–Vis spectrum before irradiation (time = 0 min) for β-carotene showed absorbance in the UV range as well as in the visible spectrum. The UV–Vis spectrum after irradiation (time = 60 min) showed only absorbance in the UV range. The red oval region corresponds to loss of absorbance in the visible spectrum after 60 min. This was supported by FTIR results and verified by pre and post UV exposure visual observation.

3.2. Effect of 2-ethylhexyl 4-methoxycinnamate on β-carotene degradation

Next, we attempted to understand the varying photostability of β-carotene and 2-ethylhexyl 4-methoxycinnamate molecular configurations. 2-Ethylhexyl 4-methoxycinnamate 98% by volume [3.47 M], stabilized with 0.05–0.1% butylated hydroxytoluene (Acros Organics, Morris Plains NJ) was diluted in acetone to four concentrations: 868 mM, 434 mM, 217 mM and 108 mM. Preliminary experiments confirmed that butylated hydroxytoluene had no stabilizing effect on β-carotene. The 24.5% by volume [868 mM] solution of 2-ethylhexyl 4-methoxycinnamate was comparable to the 20% maximum concentration by volume regulated in Japanese sunscreen formulations. The 12.25% by volume [434 mM] solution was comparable to the 10% maximum concentration by volume regulated in European and Australian sunscreen formulations. The 6.125% by volume [217 mM] solution was comparable to the 7.5%maximum concentration by volume regulated in the USA. The 3% by volume [108 mM] fell below any maximum concentration regulation. The UV–Vis spectrum before irradiation (time = 0 min) for 2-ethylhexyl 4-methoxycinnamate showed absorbance in the UV range. The UV–Vis spectrum after irradiation (time = 60 min) also showed absorbance in the UV range. Fig. 5(c) shows UV–Vis spectra of 2-ethylhexyl 4-methoxycinnamate solution before and after UV exposure. The maximum absorbance was between 325 and 375 nm, suggesting its use as an effective UVA absorber.

Fig. 6(a) shows the results of the core/shell configuration. The data was normalized by dividing each data point in a set by its initial data point at time = 0 min. Increasing the concentration of 2-ethylhexyl 4-methoxycinnamate had a minor effect on the photostability of β-carotene in the core/shell configuration. The limiting factor of photostability in this configuration was that an interface existed, preventing close interactions between β-carotene and 2-ethylhexyl 4-methoxycinnamate molecules. Fig. 6(b) shows the results of the homogeneous configuration; in which all of the β-carotene and 2-ethylhexyl 4-methoxycinnamate molecules are in close contact, a feature which resulted in optimal quenching and dissipating of excited state energy and the most photostable configuration. 390 uM and 790 uM concentrations of 2-ethylhexyl 4-methoxycinnamate were also included to show that increasing the concentration of 2-ethylhexyl 4-methoxycinnamate resulted in greater photostability of β-carotene in this configuration. However, the fluorescence results showed that for the same overall concentration of 2-ethylhexyl 4-methoxycinnamate in the core/shell and homogenous configurations, the homogenous configuration offered much more effective photoprotection. Therefore the proximity of 2-ethylhexyl 4-methoxycinnamate to β-carotene had a greater impact than the concentration of 2-ethylhexyl 4-methoxycinnamate on the photostability, whereby closing the proximity of 2-ethylhexyl 4-methoxycinnamate and β-Carotene yielded substantial benefits to photostability.

β-Carotene retained the most fluorescence when mixed with the highest concentration of 2-ethylhexyl 4-methoxycinnamate and it retained the least fluorescence when mixed with the lowest concentration of 2-ethylhexyl 4-methoxycinnamate in both molecular configurations. Comparing the two configurations to one another for

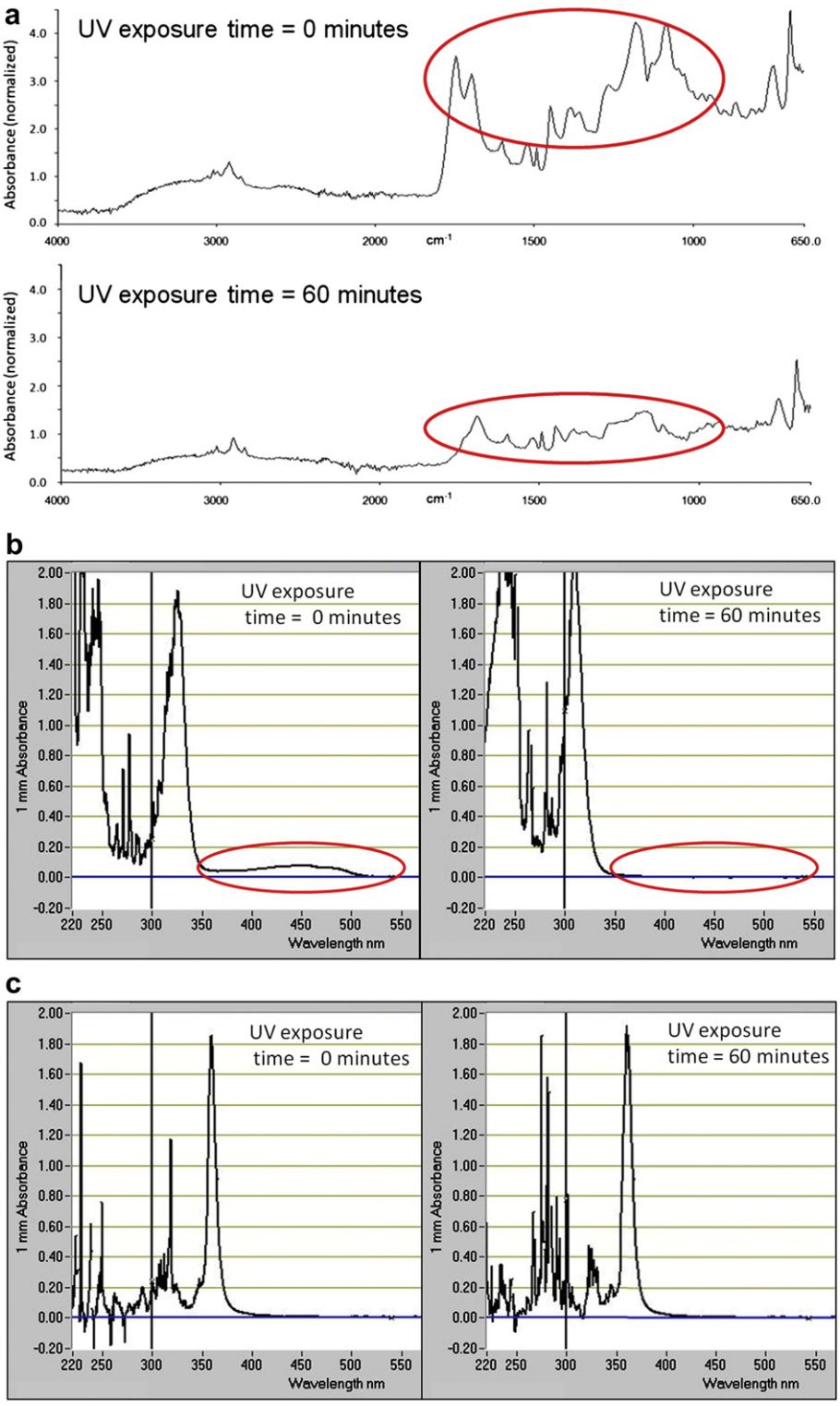

Fig. 5. (a) FTIR spectrum of 16.65 uM β-carotene solution before and after 60 min UVA exposure. (b) UV–Vis Spectra of 16.65 uM β-carotene solution before and after UV exposure. (c) UV–Vis Spectra of 2-ethylhexyl 4-methoxycinnamate solution before and after UV exposure.

a given concentration of 2-ethylhexyl 4-methoxycinnamate we found that the homogeneous configuration retained the most fluorescence when exposed to UVA light for the duration of one hour for all concentrations of 2-ethylhexyl 4-methoxycinnamate. This result was most apparent for the 2-ethylhexyl 4-methoxycinnamate of concentration 217 mM shown in Fig. 7. Here we added a hybrid configuration which used 2-ethylhexyl 4-methoxycinnamate in both wells of the tandem cuvette. Note that the total amount of 2-ethylhexyl 4-methoxycinnamate in the system was equal for all three configurations, but the 2-ethylhexyl 4-methoxycinnamate was distributed differently among the compartments in each configuration. In the core/shell configuration all of the 2-ethylhexyl 4-methoxycinnamate was in front of the β-carotene and should reduce the UV irradiation level for all the β-carotene molecules according to Beer's law. In the

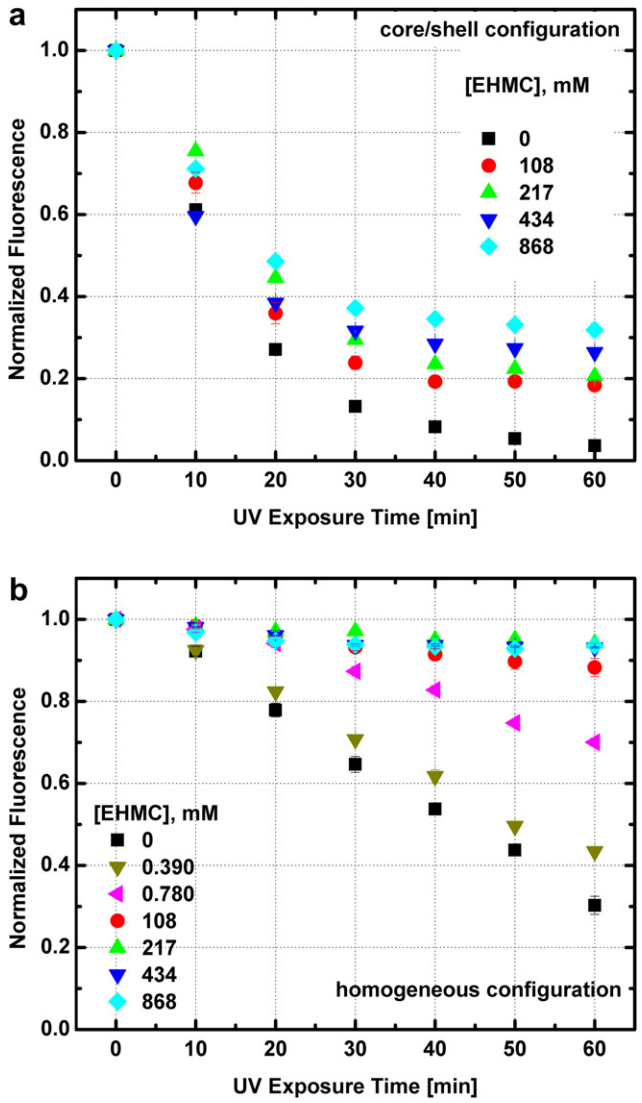

Fig. 6. (a) β-Carotene decay at 16.65 uM fixed concentration mixed with varying 2-ethylhexyl 4-methoxycinnamate concentrations in the core/shell configuration. (b) β-Carotene decay at 16.65 uM fixed concentration mixed with varying 2-ethylhexyl 4-methoxycinnamate concentrations in the homogenous configuration.

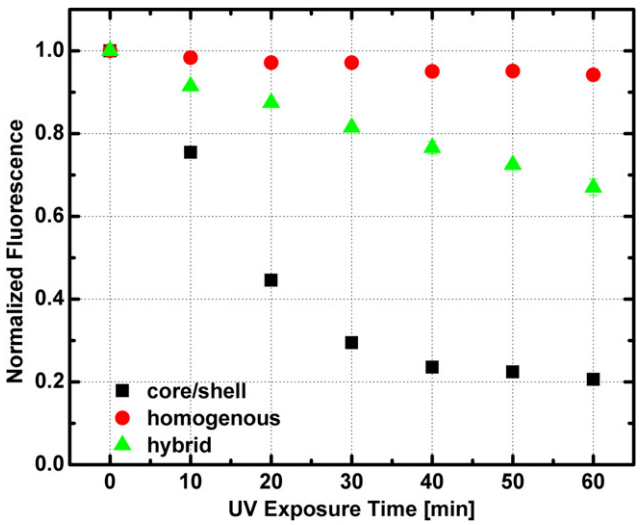

Fig. 7. β-Carotene decay at 16.65 uM fixed concentration mixed with 2-ethylhexyl 4-methoxycinnamate [217 mM] for all three configurations.

homogenous configuration, with conditions constant, one would expect less stability (Beer's law) because half of the 2-ethylhexyl 4-methoxycinnamate molecules were behind the β-carotene and only half were in front, while in the core/shell configuration all 2-ethylhexyl 4-methoxycinnamate molecules were in front of β-carotene molecules. However the homogenous configuration showed greater stability than the core/shell, which is strong evidence for a proximity effect between β-carotene and 2-ethylhexyl 4-methoxycinnamate.

Increasing the concentration of 2-ethylhexyl 4-methoxycinnamate did increase the photostability, but the configuration played a more dominant role in the photostability. With the concentrations of β-carotene and 2-ethylhexyl 4-methoxycinnamate fixed, changing from core/shell to hybrid to homogeneous yielded very significant improvements in the overall photostability. The homogeneous configuration was approximately 1.5 times more stable than the hybrid configuration and 5 times more stable than the core/shell configuration based upon β-carotene fluorescence after 60 min of UVA exposure.

We also attempted to understand the proximal effect of β-carotene and 2-ethylhexyl 4-methoxycinnamate in the homogeneous configuration. When β-carotene molecules and 2-ethylhexyl 4-methoxycinnamate molecules were freely allowed to mix, the highest level of fluorescence was retained over an exposure period of 60 min. This led to the hypothesis that a proximal relationship existed at the molecular level between the β-carotene and 2-ethylhexyl 4-methoxycinnamate with regard to the photostability of β-carotene. Since the β-carotene concentration was constant [16.65 uM], the distance between one β-carotene molecule to an adjacent 2-ethylhexyl 4-methoxycinnamate molecule could be approximated using a body centered cubic unit cell. There were exceedingly more 2-ethylhexyl 4-methoxycinnamate molecules than β-carotene molecules present; therefore we assumed that one unit cell containing a β-carotene molecule would also contain eight 2-ethylhexyl 4-methoxycinnamate molecules. This assumption was valid for our data since the number of molecules in solution from the lowest concentration of 2-ethylhexyl 4-methoxycinnamate used [390 uM] far exceeded the number of β-carotene molecules in solution, by over a factor of 23. This model would be valid for solutions with 2-ethylhexyl 4-methoxycinnamate concentration of less than approximately 133 uM for the given β-carotene concentration of 16.65 uM. As the concentration of 2-ethylhexyl 4-methoxycinnamate increased, the average distance between 2-ethylhexyl 4-methoxycinnamate and β-carotene decreased, hence the probability of 2-ethylhexyl 4-methoxycinnamate closely interacting with β-carotene increased. More relevant was the relationship between fluorescence and proximity. Fig. 8 shows that increasing the distance between the β-carotene/2-ethylhexyl 4-methoxycinnamate molecules resulted in a decrease in fluorescence after the 60 min exposure. By closing the proximity between 2-ethylhexyl 4-methoxycinnamate and β-carotene, we effectively increased the probability of close interactions ($<$1 nm) between 2-ethylhexyl 4-methoxycinnamate and β-carotene. These close interactions allow for effective energy transfer, i.e. quenching of excited state molecules. Interpolating the data, there appears to be a threshold value on the magnitude of 15 nm. For molecules spaced closer than this value, fluorescence was maintained, while for molecules spaced further than this value, there was considerable decay in the fluorescence. The proximity of β-carotene/2-ethylhexyl 4-methoxycinnamate in the core/shell configuration was fixed because of the divider in the tandem cuvette. In its microparticle analog, β-carotene and 2-ethylhexyl 4-methoxycinnamate would only physically interact minimally at the core–shell interface.

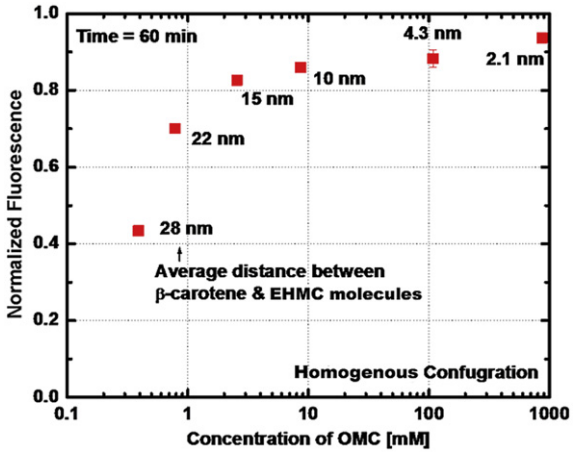

Fig. 8. Fluorescence of β-carotene 16.65 uM after 60 min exposure in the homogeneous configuration vs. concentration of 2-ethylhexyl 4-methoxycinnamate.

The proximal effect, fluorescence versus proximity, could be calculated for the hybrid configuration, but only for the core (left well of the cuvette).

An additional UV–Vis analysis was performed for the homogeneous configuration (2-ethylhexyl 4-methoxycinnamate = 434 mM, β-carotene = 16.65 uM) to compare the absorbance before and after UV exposure. Both pre and post exposure spectra showed strong peaks from 350 nm to 400 nm resulting from the absorbance of 2-ethylhexyl 4-methoxycinnamate as shown in Fig. 9. There was also a faint absorbance band from 400 nm to 500 nm due to the absorbance of β-carotene. UV–Vis results from Fig. 5(b) clearly showed that absorbance in the visible light region of β-carotene decreased with exposure to UVA radiation. This corresponds with the visible observation of the orange colored solution decaying to a clear solution after one hour of exposure to UVA radiation. However, Fig. 9 shows that when β-carotene was homogenously mixed with 2-ethylhexyl 4-methoxycinnamate [434 mM], absorbance in the visible light region of β-carotene was maintained throughout the 60 min of UV exposure (red ovals). This is verified by visual observation of the orange colored solution remained orange throughout the duration of exposure and this further supports that the homogeneous configuration effectively maintained photostability.

The fluorescence decay of β-carotene was compared when using 2-ethylhexyl 4-methoxycinnamate alone as the UV photostabilizer versus using 2-ethylhexyl 4-methoxycinnamate mixed with poly(methyl methacrylate). Fig. 10(a) and (b) show this comparison. The addition of poly(methyl methacrylate) appeared to have only a minor inhibitory or synergistic effect on the fluorescence decay of β-carotene in our three configurations, without a clear trend.

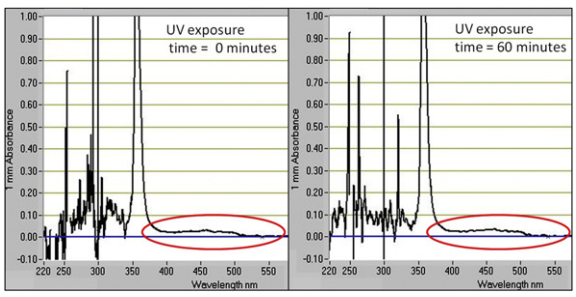

Fig. 9. UV–Vis spectra of 16.65 uM β-carotene when mixed with 434 mM 2-ethylhexyl 4-methoxycinnamate in the homogeneous configuration, before and after 60 min UVA exposure.

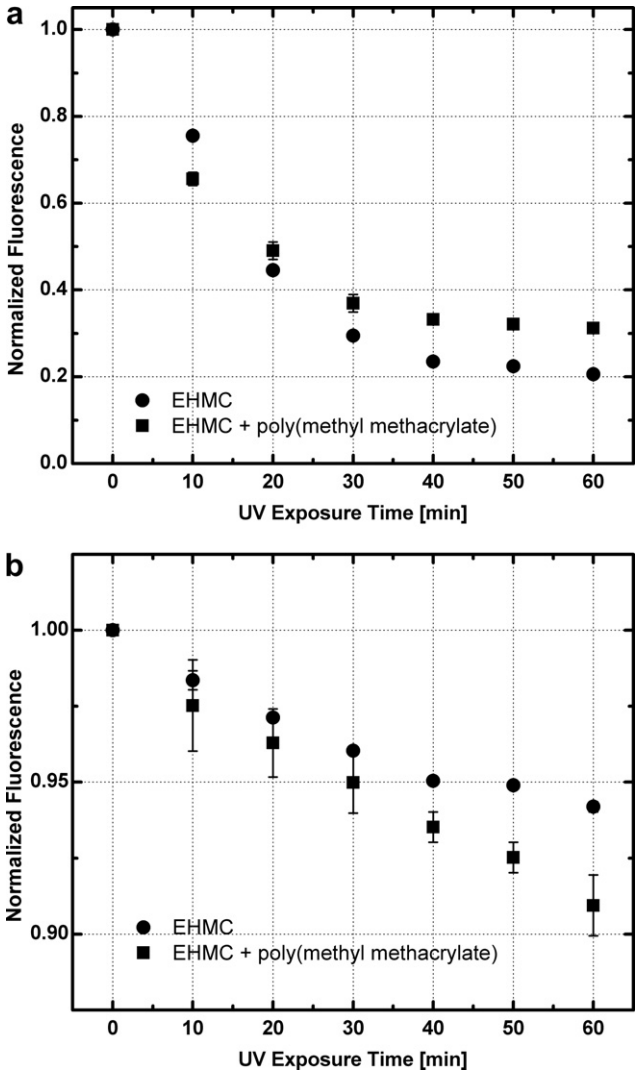

Fig. 10. (a) β-Carotene [16.65 uM] decay when mixed with 2-ethylhexyl 4-methoxycinnamate [217 mM] alone versus β-carotene decay when mixed with 2-ethylhexyl 4-methoxycinnamate and poly(methyl methacrylate) [1.67 mM] in the core/shell configuration. (b) β-Carotene [16.65 uM] decay when mixed with 2-ethylhexyl 4-methoxycinnamate [217 mM] alone versus β-carotene decay when mixed with 2-ethylhexyl 4-methoxycinnamate and poly(methyl methacrylate) [1.67 mM] in the homogeneous configuration.

In future assays we plan to use several different concentrations of poly(methyl methacrylate), thus affecting the overall viscosities of our formulations. We would like to elucidate the effect of viscosity on the proximal interactions between β-carotene and 2-ethylhexyl 4-methoxycinnamate in our system.

4. Conclusion

The proximity of the 2-ethylhexyl 4-methoxycinnamate to β-carotene played a significant role in the photostability of β-carotene exposed to UVA irradiation. Closing the proximity increased β-carotene photostability. This was achieved by first homogenously mixing β-carotene and 2-ethylhexyl 4-methoxycinnamate and then increasing the concentration of 2-ethylhexyl 4-methoxycinnamate. The body centered cubic cell model effectively showed that by increasing the concentration of 2-ethylhexyl 4-methoxycinnamate in the homogeneous configuration, we effectively decreased the average spacing between 2-ethylhexyl 4-methoxycinnamate and

β-carotene molecules in solution thus increasing the probability of 2-ethylhexyl 4-methoxycinnamate and β-carotene molecules having close interactions in solution where photostabilizing energy transfers could occur. Based upon our model there appeared to be a threshold separation of 15 nm, where below this average distance greater photostability was achieved. Furthermore, changing the proximity of 2-ethylhexyl 4-methoxycinnamate to β-carotene yielded very different fluorescence decay profiles for the same given concentration of 2-ethylhexyl 4-methoxycinnamate in the core/shell, homogenous and hybrid configurations, in which the homogenous configuration offered the best photoprotection. The addition of poly(methyl methacrylate) showed no clear trend with regard to the photostability of the configurations in this study. Moving forward, we may incorporate 2-ethylhexyl 4-methoxycinnamate with other UVA absorbers to explore synergistic effects.

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