Effect of UV blocking on lipid oxidation of heavy cream during short exposure to sunlight

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Abstract

This study focuses on exploring effect of UV light on photo oxidation of heavy cream, specifically exploring short time exposures to direct sunlight, which could happen during transportation. Heavy cream was exposed to various light conditions including ambient, windowsill, direct sun and simulated sun using UVA-10 365 nm transilluminator for short periods of time ranging from 30 to 90 min. Lipid oxidation was determined using the TBA test for oxidative rancidity. Experiments were conducted with and without UV blockers to determine whether UV blocking in the packaging can minimize or eliminate lipid oxidation during a short time exposure to direct sunlight. The results show that short-term exposure of just 10-15 min can cause degradation of heavy cream even under ambient conditions, and incorporating UV blocking into the packaging material could significantly reduce the degradation.

Introduction

Exposure to light results in degradation of milk and other dairy products, which is undesirable because of the decrease in nutrition as well as changes in color and taste that would make the products less appealing to consumers. There are many factors that contribute to rancidity and the resulting off-flavor of milk and other dairy products, one of which is lipid oxidation. Lipid oxidation generally begins with the formation of a free radical on an unsaturated fatty acid that reacts with oxygen and hydrogen to form an unstable fatty acid hydroperoxide and another free radical. The hydroperoxide decomposes to yield carbonyl compounds, one of which, malonaldehyde, can easily be detected using the Thiobarbituric Acid (TBA) test (Sattar *et al*. 1975)(O'Brien, 2011). After UV radiation initiates the reaction, the initiation products can react without additional energy entering the system (Schaich & Pryor, 1980). This means that it only takes a small amount of UV to start the reaction, so it is critical to block as much UV as possible.

For packaging of milk, consumers prefer translucent or clear white containers (White, 1985). Thus, milk is typically sold in a translucent high-density polyethylene (HDPE) jug in the United States, but it has a relatively short shelf life. Currently, cream products are sold in opaque containers, perhaps to prevent photo oxidation. If the majority of photo oxidation that occurs can be attributed to UV radiation, incorporating UV blocking into transparent packaging materials could potentially allow cream products to be sold in transparent containers while maintaining or even extending their shelf lives. A transparent plastic packaging could make the package more appealing and reduce the transportation costs due to the decrease in weight (Pilz et al., 2005).

Cladman *et al*. (1998) and Mestdagh (2005) explored effect of UV blocking on lipid oxidation in milk. Milk was kept in various packaging materials under fluorescent bulbs at 4° Celsius over several weeks. Both found that incorporating UV blocking feature in a polyethylene terephthalate (PET) container significantly decreased the lipid oxidation in milk over a long period of time. In addition, Van Aardt et al. (2001) found that blocking UV light over an 18-day period also decreased the oxidative off-flavor in whole milk. However, there can be situations in which milk and other dairy products are exposed to considerably more UV light for a shorter period of time, such as during transportation. This study examines the effect of short term UV light exposure on heavy cream. We consider various environments including direct exposure to sun outdoors, indirect exposure in a room and on a windowsill, and finally simulated exposure on a transilluminator. We also explore whether blocking UV light could eliminate or significantly decrease oxidation rates for heavy cream even if the sample is exposed to high intensity of visible light in presence of ample oxygen. It should also be noted that UV light has been known to degrade other components of milk, such as vitamin A and riboflavin, decreasing the nutritional value of the product (Sattar, 1975). While these are not tested in this paper, incorporating UV blocking particles into packaging could also protect these from the harmful radiation.

Methods and materials

Cream

Publix brand heavy whipping cream was bought and kept in a refrigerator at 4° Celsius for the entire duration of the experiment. Heavy cream was selected because of its higher lipid content, which was about 33% by mass, in relation to milk. This allows for the detection of lipid oxidation byproducts at an earlier time. Since cream has essentially the same composition as milk but with a higher concentration of fat globules (Kalab, 1985), the reactions observed in cream will likely be applicable to milk as well, though rates will likely vary.

Preparation of Reagents

TBA Reagent was prepared using the method of Kohn and Liversedge (1944), excluding the decolorizing carbon and citrate buffer. 2N sodium hydroxide was prepared using solid sodium hydroxide (NaOH) from Acros Organics and deionized water. 2-thiobarbituric acid (TBA) was obtained from Sigma-Aldrich, and 1 N hydrochloric acid (HCl) was obtained from Fisher Chemical. The TBA reagent contained approximately 1% TBA, 1.4% HCl, and 3% NaOH. Deionized water, TBA, and sodium hydroxide were mixed and heated at 80° Celsius for 15 minutes. After cooling, HCl was added to acidify the solution. The reagent was then refrigerated for its entire lifetime. Trichloroacetic acid (TCA) was obtained from Fisher Chemical. 20% solution was made by adding 20% TCA by mass to deionized water. The acid was stored in a dark cabinet at room temperature.

Preparation of Samples

Cream samples were placed in Pyrex petri dishes and exposed to UV light by directly placing those in the sunlight. Open exposure to sun will result in a much higher exposure to both UV and visible light, compared to usual exposure when cream is in packaged in a container. Additionally, open exposure allows access to oxygen, further increasing the rates of oxidation. These exposure conditions were designed to test whether transparent or translucent oxygen permeable containers can be used for packaging cream if the UV light is blocked.

UV blocking with Sunscreen

For samples that were protected from UV light, Coppertone "Clearly Sheer" SPF 30 sunscreen was first weighed and spread evenly over the entire outer surface of the petri dish lid. 20 mL of cream were placed into each Pyrex 9 cm diameter petri dish, and the corresponding lids were immediately placed on top. Petri dishes were placed either on the windowsill of the lab or the roof of the building, keeping the lid on at all times. After 30, 90, or 120 minutes, the samples were taken out of the sunlight before removing the lid.

Without Sunscreen

For experiments that were conducted without UV blocking, 20 mL of cream were simply pipetted into separate petri dishes and left uncovered to maximize the exposure to sun. The samples were tested under different conditions: 1) under a 26W fluorescent light bulb in a room with ambient lighting, 2) on a windowsill exposed to indirect sunlight, and 3) on the roof of the building exposed to direct sunlight. After 30, 90, or 120 minutes, the samples were removed from their light source.

Transient Studies

Petri Dishes

30 mL of cream were micro-pipetted into two identical petri dishes. Approximately 0.5 g of SPF 30 Coppertone sunscreen was spread on the top and sides of the lid to one of the petri dishes to block UV light. Both samples with their lids were placed on the roof of a 4-story building. After 20, 40, and 60 minutes, a 3 mL sample was taken from each petri dish for testing.

Modified Milk Cartons

Publix brand milk was bought, and the empty cartons were washed and cut into smaller cubes in which to test the cream. The edges were taped closed using clear scotch tape, leaving a small space from which to take samples, then approximately 1 gram of sunscreen was spread on all surfaces of one of the containers except the bottom. The samples were placed on the rooftop and 3 mL samples were taken after 20, 40, and 60 minutes.

Analysis of Lipid Oxidation

0.6 mL of deionized water was added to each vial. 3 mL of cream from each sample were added to the appropriate vial. As quickly as possible, 2 mL of the TBA reagent were added to each vial followed by 1 mL of 20% TCA. All vials were then shaken to disperse reagents, placed in a boiling water bath for 15 minutes, and immediately cooled to room temperature in running deionized water. 5 mL from each vial were added to centrifuge tubes containing 1.67 mL chloroform from Sigma-Alrdrich. These were also shaken and immediately centrifuged for 10 minutes at 4750±50 RPM. The resulting supernatant fluid on top of the precipitated protein (Saffran and Denstedt, 1948) shown in figure 1 was tested for visible light absorbance using a Thermo Scientific Genesys 10S UV-Vis Spectrophotometer. Sample spectra of control and light-exposed samples are shown below in figure 2.

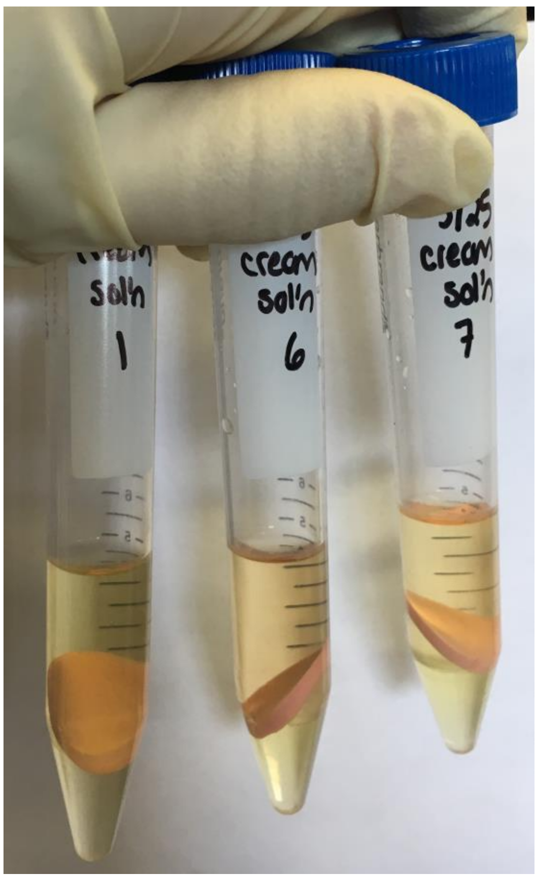

Figure 1: Samples after centrifuging. “1” is a control sample, “6” is a sample that was exposed to light directly (without sunscreen) on the roof for 60 minutes, and “7” is a sample that was exposed to light on the roof for 60 minutes, but the lid was coated with sunscreen.

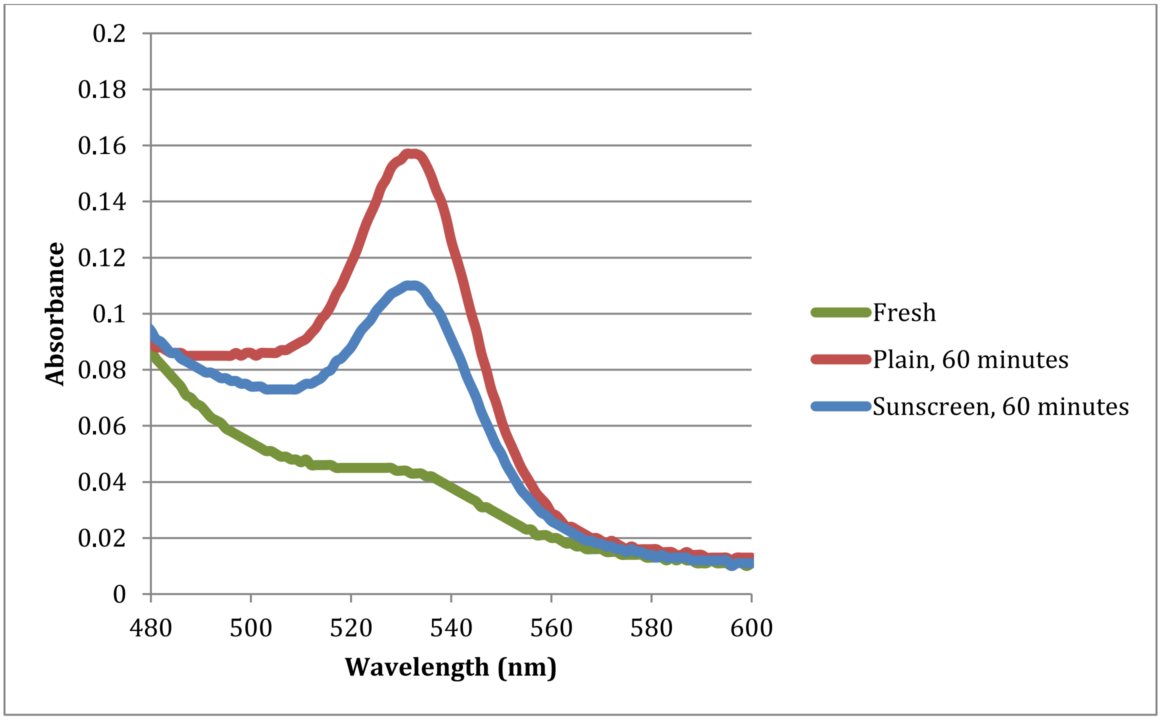

Figure 2: Absorbance spectra of supernatant fluid.

Data Analysis

A more intense pink color after the TBA-TCA reaction corresponds to a higher level of oxidation. Thus, to achieve numerical values for oxidation, the difference between the absorbance values at 532 nm (the pink color and peak of the spectra) and 572 nm (to account for background absorption) were determined (Lapenna, 2001).

Results and Discussion

UV Radiation in Sunlight

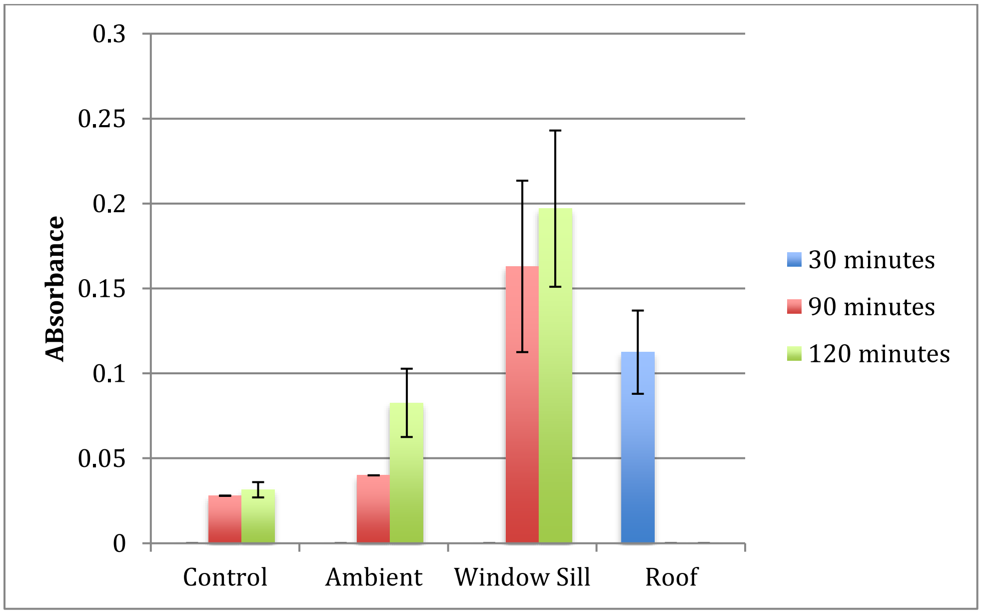

Figure 3: Degradation of cream exposed to visible light (ambient lab conditions), sunlight through a window, and sunlight on the roof compared to a control of fresh cream.

Figure 3 compares the photodegradation under various light conditions for times ranging from 30-90 min. Under ambient conditions, there was negligible degradation in the first 90 min, but significant degradation was apparent at 120 min. Near the window, the degradation rates were higher, with significant degradation apparent at 90 min. The degradation under direct sunlight was considerably higher as clear signs of degradation were apparent at 30 min. These results show the expected increase in photodegradation with increasing intensity of light, which includes both visible and UV. These results also show that an open cream container will not lead to significant degradation inside a house unless it is left open for times longer than an hour.

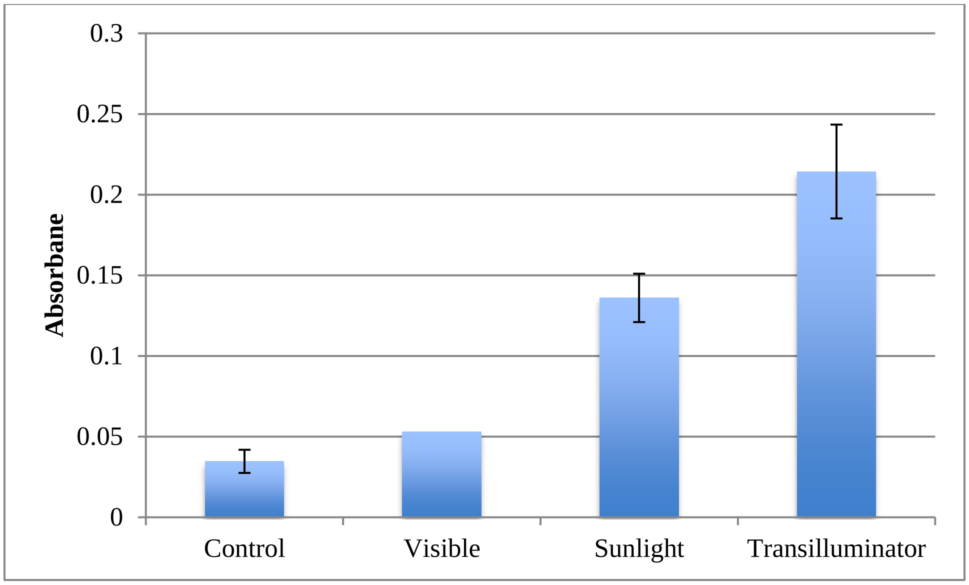

Figure 4: Absorbance values for 20g of cream left under varying high-intensity conditions for 120 minutes.

Figure 4 compares fresh cream to the photodegradation of cream under 3 different light conditions: high-intensity visible, sun, and UV light. The cream under the transilluminator was consistently more degraded than any of the other samples with the sunlight causing the only comparable degradation. These results support the suggestion that UV light in sunlight is causing more photodegradation than visible light.

Sunscreen Experiments

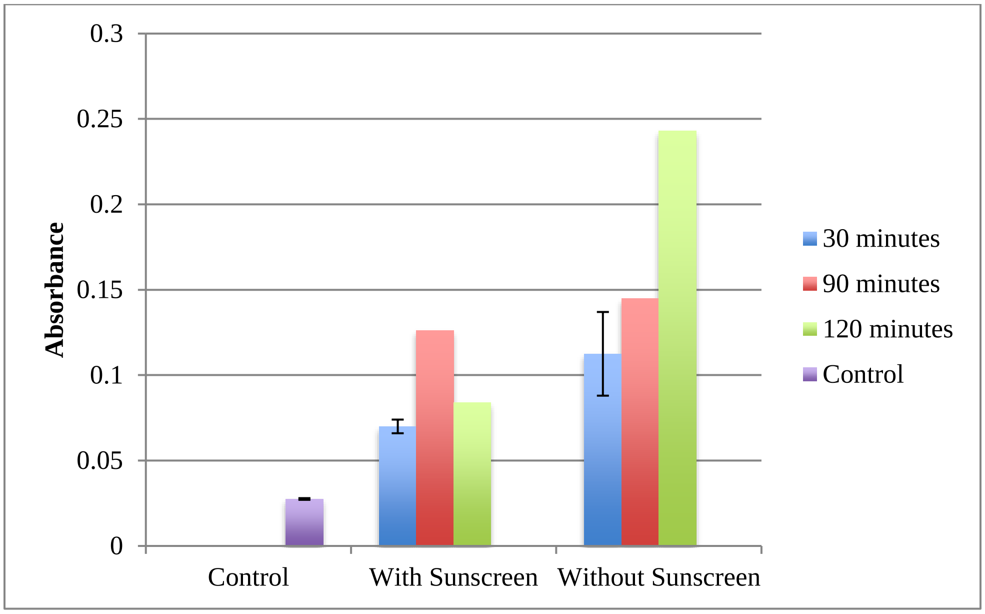

Figure 5a: Absorbance values for samples in petri dishes covered with sunscreen vs. without sunscreen when exposed to sunlight.

As demonstrated in figure 5a, samples that were covered with sunscreen showed significantly less degradation than those without sunscreen. The degradation in the systems with the sunblock showed less degradation at 120 min compared to that in the exposed systems at just 30 min. Note that the samples exposed for 120 and 90 minutes were placed on the windowsill of the lab during the winter and, thus, received less UV exposure per unit time than the samples exposed for only 30 minutes, which were placed on the rooftop during spring.

Transient experiment using petri dishes

After it was determined that cream that has been protected from most UV light degraded less than cream that was not protected, it was desired to determine how much it would oxidize over time. Thus, a transient experiment was done, first in petri dishes.

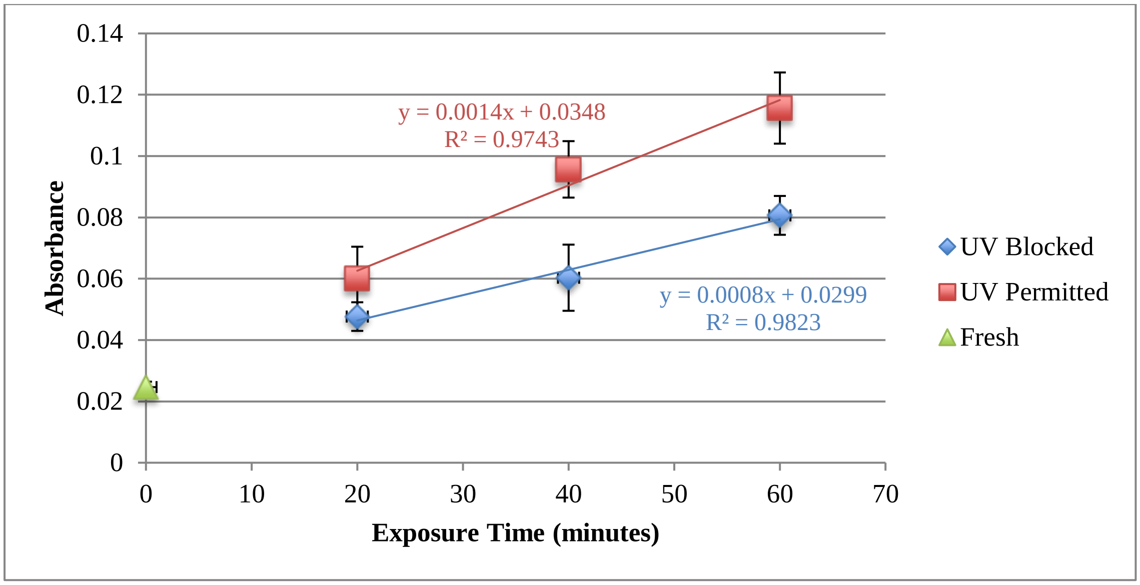

Figure 5b: Average values for lipid oxidation over time in petri dishes with and without sunscreen to block UV light.

The results clearly show that there is a linear increase in oxidation with time and that the rates of oxidation are reduced by about 40%. Furthermore, this data also shows that after only 20 minutes of exposure to the sun, cream degrades significantly compared to the fresh cream, which had a normalized value of 0.

Dependency of Degradation on Packaging Material

In an attempt to create a more realistic environment in which lipid oxidation would occur, milk cartons were modified to create containers similar in size to the petri dishes. Figure 6 demonstrates that the degradation in the glass petri dishes vs. the milk jug is comparable, and thus the results obtained in petri dishes could be applicable to more realistic packaging. The comparable degradation in the petri dish and the milk jug suggests that the jug material (PTFE) is transparent to both oxygen and UV light (Cladman, 1998)(Figure 7). The UV transmittance spectrum shows significant broad transmittance from the milk jug material. Additionally, it is noted that the UV-Vis Spectrophotometer (without integrating sphere) does not take UV light that is scattered by the material into account, so the actual transmittance of light may be higher than suggested by the spectrum. This explains why there is not a significant difference between degradation in the two different materials and supports the idea that current packaging materials do not block sufficient UV radiation.

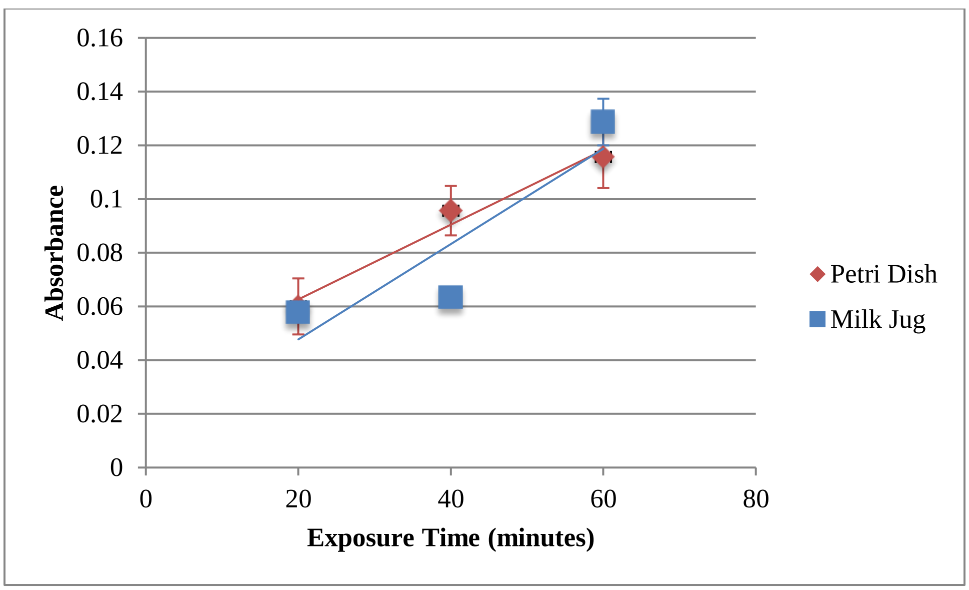

Figure 6: Degradation of cream in petri dishes vs. milk jugs over time for UV-permitting samples (without sunscreen).

To test whether a coating of UV blocking material could significantly reduce UV transmittance and photodegradation, a thin layer of the sunblock totaling 1 gram was coated on the milk jug container. The spectra of the coated and the uncoated PTFE jug material are compared in Figure 7, which shows that the coating virtually eliminates all UV light below 380 nm in wavelength. The coated milk PTFE container was then used to measure the photodegradation of the heavy cream (Figure 8). The results in figure 8 again suggest that UV blocking reduced photodegradation but the effect seems less compared to the 2-fold decrease observed in Figure 5b. The most likely reason for this discrepancy is the difficulty in uniformly spreading the sunscreen on the surface of the milk jug. For example, the milk carton has a surface area roughly twice that of the petri dish lid. Although the amount of sunscreen used was doubled, there was more room for error when spreading the sunscreen and more area through which UV light could penetrate the material. Since light transmission decreases exponentially with thickness, small variations in thickness of the coatings can lead to significant differences in light transmission.

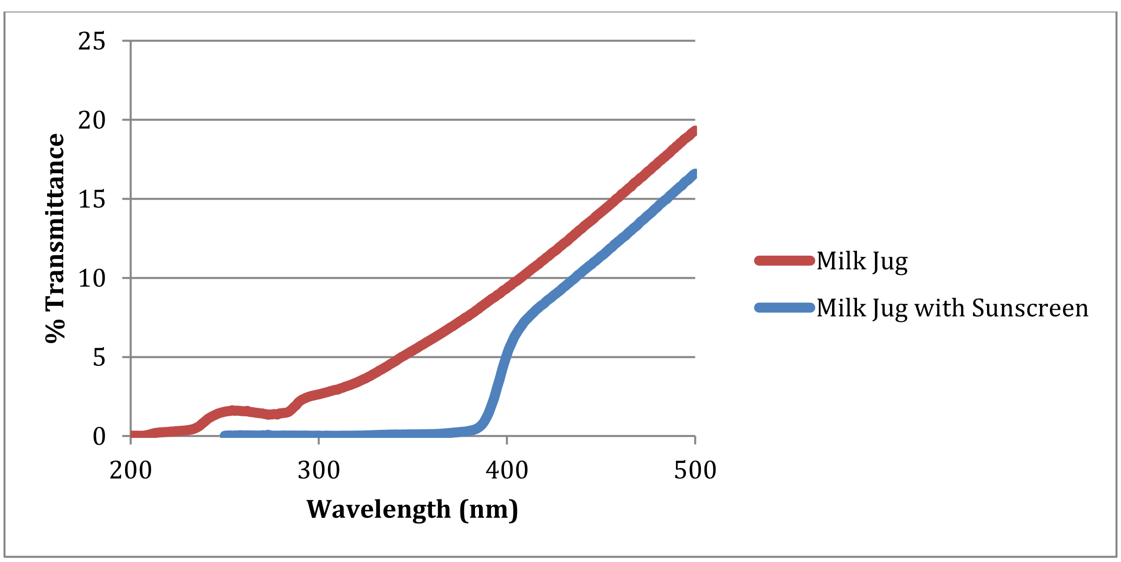

Figure 7: Transmittance spectra for HDPE milk jug and HDPE milk jug with sunscreen

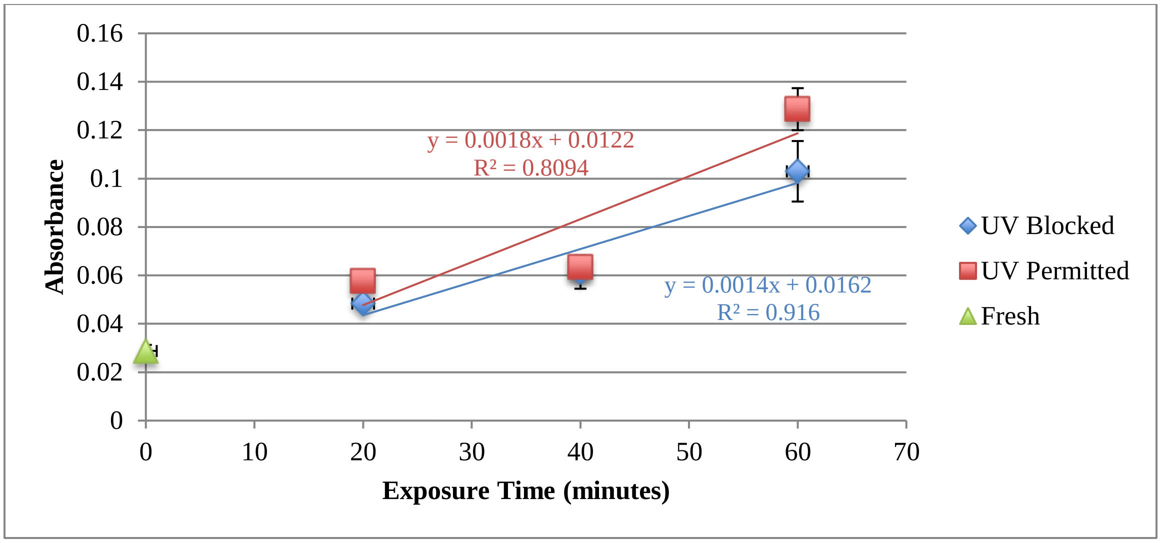

Figure 8: Average values for lipid oxidation in modified milk jugs with and without sunscreen to block UV light.

Inconsistencies in the data could be the result of a few different factors. Primarily, the results were highly dependent upon the weather. Unexpected intermittent cloud cover sometimes caused there to be non-constant UV exposure, leading to irregularities in the data. Additionally, when taking samples for the transient data, the petri dishes were uncovered for a short period of time. This resulted in increased UV exposure in those samples, lessening the gap between oxidation in the sunscreen covered and UV-permitting samples. Small differences in amount of reagent and time of addition could result in some samples showing more color than others. However, steps were taken to avoid this bias. For example, the TBA reagent was added to all vials before the TCA. The TCA was then placed in the vial that sat in an hour under sunscreen protection first, then the corresponding UV-permitting sample, and so on until finally it was added to the fresh cream sample. Therefore, if there were bias, it would result in the sunscreen-covered sample showing more oxidation than the UV-permitting sample. In the vast majority of runs, this was not the case, suggesting that the reaction did not go to a significant extent before heat was added.

Conclusion

This study shows that short-term direct exposure to UV light can cause significant degradation of heavy cream. Blocking UV light either by a thin surface film or direct incorporation of UV absorbers in the material can significantly reduce photo-oxidation, but it cannot eliminate it. Thus, while UV blocking will likely help in increasing shelf life, it will be difficult to package heavy cream in transparent or translucent containers. Indoors, degradation rates are significantly lower, and in fact one hour of exposure in a well-lit room does not cause significant degradation.

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