How Light Impacts Recycled Polyethylene Terephthalate (rPET) Characteristics

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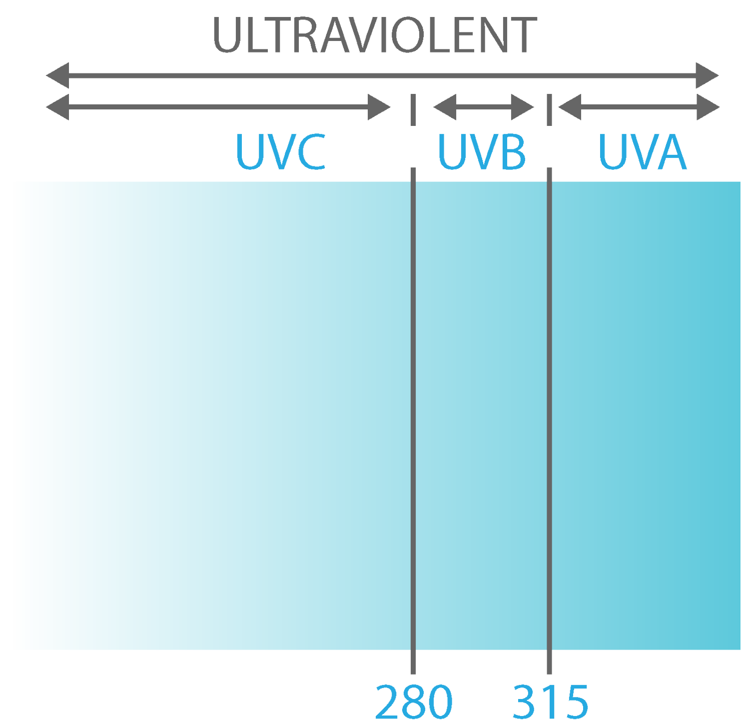


One of the problems that limits the amount of recycled PET (rPET) used in rigid packaging applications is the degree of yellowness that it can cause. The more rPET that is added to virgin PET during bottle manufacture, the more yellow the resulting bottle tends to become.

The source of the rPET used has a great influence on yellowing. Deposit-grade materials are in the greatest demand as they result in less yellowing than do curbside-grade material. Even virgin PET will discolor and yellow with each additional melting cycle.

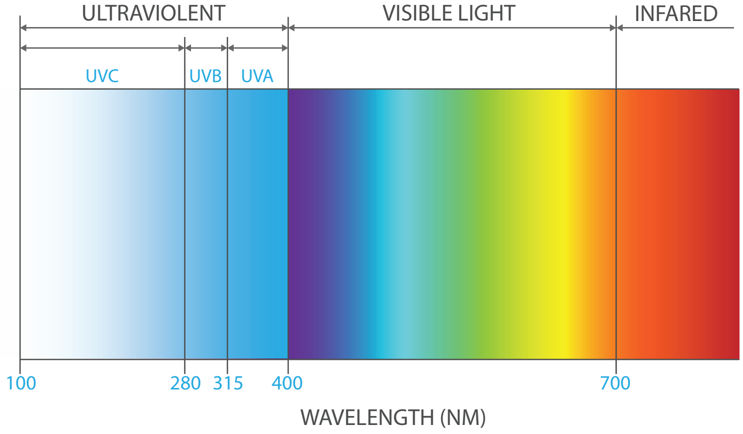
But there are many other causes that contribute to this problem. For example, it is known that low levels of nylon coming from multilayer bottles can remain trapped in the PET flake after washing and cleaning. This residual nylon will cause considerable yellowing when the rPET is extruded. The presence of additives such as ultraviolet (UV) light blockers, acetaldehyde and oxygen scavengers, and slip agents can all contribute to yellowing as the rPET is subjected to additional melt histories.

A study performed by Phoenix Technologies, LLC looked at the effects that adhesives used to adhere labels to bottles had on yellowing. The results showed that these could be a significant contributor when not washed away from the PET flake during the cleaning process[1].

But one cause of yellowing that has not been widely addressed is the effect that UV radiation from the sun, as well as that emitted by artificial sources, such as fluorescent lighting, can have on PET. PET is sensitive to UV light especially at elevated temperatures, under high humidity, and in the presence of oxygen—all of which are present when PET bottles are exposed to the weather.

UV radiation is part of the electromagnetic spectrum that occurs from below 100 to 400 nanometers (nm). Long wavelength UV radiation occurs in the UVA part of the spectrum. The UVA portion of the spectrum represents the greatest amount of UV radiation that penetrates the atmosphere and reaches the earth. This type of radiation is strong enough that it can cause chemical reactions to occur and it is responsible for the damage that plastics experience when exposed to the elements.

Free radicals form within the plastic that cause subsequent degradation. The degradation effects seen are also compounded by the presence of oxygen in the air. The free radicals created by the UV radiation react with this oxygen to form hydroperoxides that can result in polymer chain breakage. Thus the end result in many plastics, including PET exposed to an outdoor sunny environment, is that they will discolor, embrittle, and crack over time. While antioxidant and UV absorbers can be added to the plastic to help stabilize and prolong the material's useful life, PET bottles normally do not contain significant amounts of these additives.



The Association of Postconsumer Plastic Recyclers (APR) notes in their model bale specification for PET bottles, that bales should not be stored outdoors uncovered for a period exceeding two weeks to prevent UV degradation. There have been many papers published that describe the degradation effects that UV light has on PET3-5. But these papers have primarily focused on the degradation seen on the actual PET article being studied and not what happens to the properties of PET when it is recycled.

The life of a PET bottle is one that is not usually exposed to direct sunlight. UV radiation will begin to pass through PET that does not contain UV absorbers above 320 nm. Products packaged in PET that need UV protection will either have a UV blocking full-sleeve label covering the bottle or will have UV absorbers added to the PET during the bottle manufacturing process. However only a small number of PET bottles in the market contain these UV absorbers. The majority of bottles do not.

While PET bottles and their contents do not experience significant exposure to sunlight, bottles under storage after manufacture as well as product-filled bottles sitting on a store shelf can be exposed to artificial light sources that can also emit low levels of ultraviolet light. But the most probable time that PET bottles might see significant exposure to the elements occurs when bales of PET bottles are stored outside while waiting to be brought into a reclamation facility to be ground into flakes, washed and re-pelletized for sale back into the industry.

This study was undertaken to understand the effects weathering would have on PET bottles exposed to Toledo, Ohio weather for one year. Two-liter PET bottles produced using a commercial grade of PET were used for this study. This resin did not contain any ultraviolet absorbing additives. These virgin bottles were crushed, stacked five to six deep, and placed in uncovered open sided crates to afford maximum exposure to the elements.

These crates of bottles were then placed on the roof of the PTI building in early January. Every three months, the bottles in the crates were agitated so that those on the bottom had a chance over time to move to the top or outside edges.

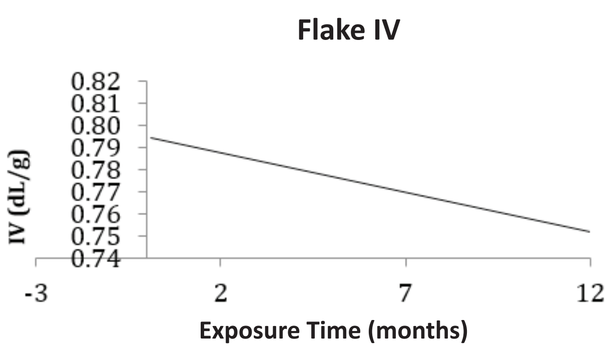
Another set of bottles was stored indoors approximately 18-inches under a fluorescent light source. This light source was left on continuously, exposing the bottles for two months. A third set of bottles was stored and protected from light exposure for one year for use as a control.

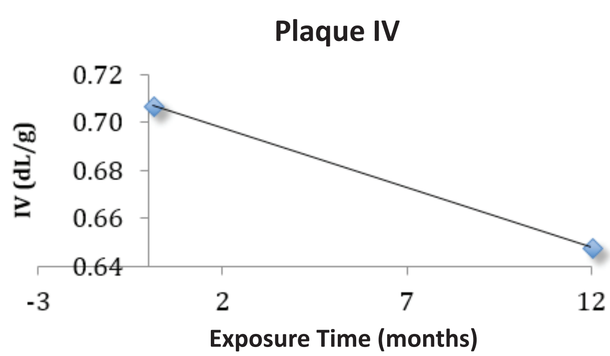
Periodically bottles were taken off the roof to study the effects of sunlight and weathering over the course of 12 months. Each aged set of bottles was ground through a 3/8" screen into flake. The flake was then aggressively washed to remove accumulated surface dirt at 88°C for 15 minutes using a wash composition of 0.3% by weight Triton X-100 and 1.0% caustic (NaOH). Following the hot caustic wash, the flake was rinsed twice with fresh water, dried to less than 50 ppm moisture and injection molded into 3mm thick plaques.

Samples of flake from each of the exposure time periods was measured for IV to determine if the ultraviolet light from the sun's radiation caused any loss in molecular weight. The plaques molded from this flake were also measured for IV, color and haze. The IV results are quite interesting but not surprising in that the data clearly shows that exposure to ultraviolet radiation was very damaging to the PET material.

Sample flake was also measured for color before and after the one year exposure to determine if any obvious yellowing occurred. Surprisingly there was not a significant amount of yellowing seen in the color of the bottle flake. The yellowing only became significant after the weather exposed PET has been subjected to melting required for molding the plaques.

SUNLIGHT EXPOSURE EFFECTS ON THE INTRISNIC VISCOSITY OF PET

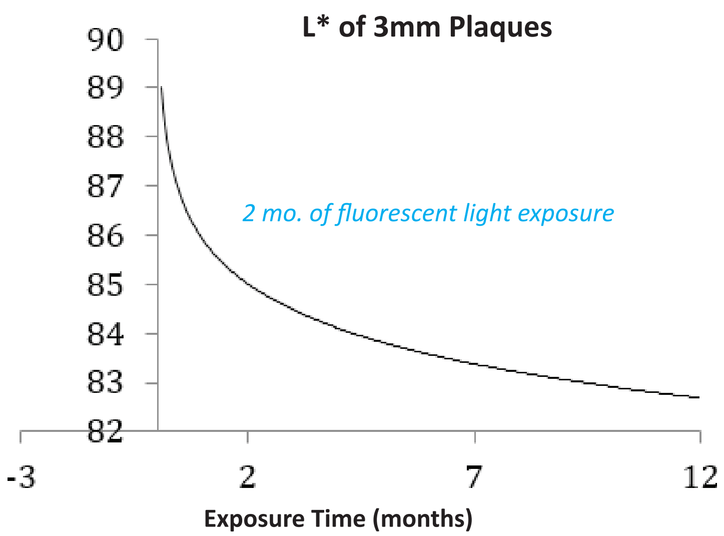


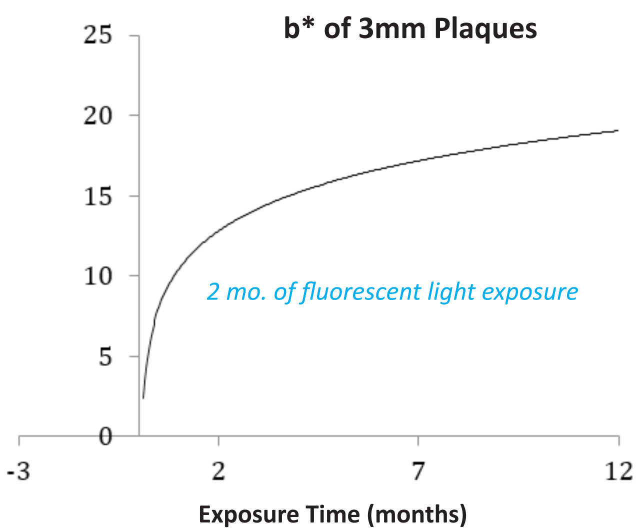


Intrinsic viscosity measurements are used to relate the measured value to the molecular weight of PET. The cleaned and washed flake samples were all measured to determine if there was any loss due to the effects of sunlight. The results showed a definite trend downward with an apparent loss in IV of about 0.04 dL/g over 12 months. This same molecular weight loss was seen when the weathered flake was injection molded into the 3mm thick plaques. While the loss due to exposure of the flake to ultraviolet radiation was ~0.04 dL/g, the degree of IV loss increased to ~0.06 dL/g when this flake was melt processed into 3mm plaques.

PET reclaimers will take washed and cleaned flake and extrude it into pellets (not plaques). Thus if their bottles have been exposed to similar levels of ultraviolet radiation from being stored outside, there would be an expected increase in yellowness resulting from the extrusion process. Further yellowing will then result when this extruded pelletized rPET is blended with virgin PET resin and melted yet again during preform manufacture. Thus the bottle production process will only further exacerbate the yellowing seen when this rPET is used.

Effects of Sunlight Exposure on PET Color and Haze





L* indicates the lightness of the sample with 100 being very white and 0 being very dark or black. The injection molded plaques made from these weathered bottles show a definite trend with a reduction in L* over time. Typical bottles made from PET today will have L* values ranging from the high 80s to the low 90s. Recycle content bottles made with this weather exposed recycled PET would show a reduction in their L* values resulting in bottles that are less clear to the eye and more dull in appearance. The diamonds on the graphs show the effect that fluorescent light had after the bottles had been exposed to two months of fluorescent light when molded into plaques. While there was a measureable decrease in L* seen on plaques molded from bottles exposed to the fluorescent light, direct sunlight had a much more significant and pronounced effect.

b* denotes the degree of chromaticity from yellow (+b*) to blue (-b*). The effect that the ultraviolet radiation exposure had on the molded plaque b* values is even more noticeable than was L*. The increase in yellowness on molded plaques was very significant even after only one month of exposure. Beyond 4 months, the effects of the ultraviolet radiation, while still significant, were not as dramatic as what was seen during the initial months. As was the case with L*, yellowness development was not as significant from the fluorescent light exposed PET compared to the effect seen from direct sunlight.

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