RAPID PHOTO-OXIDATION OF UV-STABILIZED POLYPROPYLENE FIBER DUE TO AN EXTERNAL ANTAGONIST

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Abstract

Polypropylene fiber in an outdoor carpet exhibited unusual photo-oxidation behavior that occurred in some cases in as little as 3 months. Degradation rate and severity were shown to be dependent on exposure to materials the carpet came into contact with after manufacturing. Other causes of increased UV sensitivity were also identified. Since the failure manifested as a consistent change in color, colorimetry was used as a simple diagnostic tool. Mechanisms for accelerated degradation are discussed whereby the effectiveness of hindered amine light stabilizers (HALS) is disrupted by external antagonists.

Introduction

Polypropylene is well known to be sensitive to UV degradation. Polymer additives are routinely used to protect polypropylene from premature failure. Additive choice is dependent on the potential for UV exposure as well as end use requirements such as life expectancy, color requirements and cost constraints.

UV protection of polypropylene carpet products can be challenging due to increased surface exposure of vertically oriented fiber bundles presented in a tufted construction. For instance a 16 oz./SY carpet that has a pile height of ½ inch and that is produced from a 2400 denier polypropylene yarn bundle containing 120 filaments will have a fiber surface area of over 350,000 cm² in a square yard of carpet. Degradation initiates at filament tips where UV exposure is particularly severe.

Photo-oxidative degradation of polypropylene leads to chain scission reactions and results in fiber degradation. Photo-oxidation initiates with alkyl radical and subsequent peroxy radical formation at the tertiary carbon upon exposure to oxygen. The peroxy radicals participate in an intramolecular propagation reaction that leads to the formation of hydroperoxide pendant groups that are subsequently converted to ketones upon UV exposure. Norrish Type I cleavage and hydrogen extraction leads to chain scission of the polymer backbone, causing a rapid decrease in molecular weight.

There are several approaches used to protect polypropylene from photo-oxidation, including UV absorbers, quenchers, and radical scavengers. UV absorbers reduce radical formation by competing with vulnerable functionalities to absorb UV light. Carbon black for example absorbs UV light and converts it into infrared radiation. Carbon black is frequently used as an additive due to its low cost and ready availability; however, its black color limits the range of color possibilities. Common organic UV absorbers include benzophenones and benzotriazoles. Organic UV absorbers afford greater options for material coloration.

Nickel quenchers function to inhibit chain scission by quenching excited carbonyl functionality formed during photo-oxidation. Nickel quenchers are a versatile quencher, but the presence of a heavy metal and a characteristic color shift in the host material are both disadvantages.

Hindered amine light stabilizers (HALS) are widely used to scavenge free radicals, particularly the alkyl and peroxy radicals formed during the initial steps of photo-oxidation. HALS have the ability to regenerate to the active N-oxide species following radical neutralization. This process is referred to as the Denisov cycle (Figure 1) and makes HALS effective long term UV stabilizers.

Figure 1. Schematic of the Denisov Cycle.

The chemical structure of HALS includes the 2,2,6,6-tetramethylpiperidine functionality in which the piperidine amine can be either a secondary or tertiary amine or it can also be a functionalized as a N-alkoxide (NOR HALS). Each of these functionalities will have an effect on the susceptibility of the HALS to side reactions from potential antagonists. HALS selection is also based on molecular size and molecular mobility. Low molecular weight HALS are known to migrate, reducing effectiveness over time, whereas oligomeric or polymeric HALS exhibit minimal migration.
It is well known that HALS can be negatively affected by antagonistic materials. For instance, mineral or organic acids are well known to be HALS antagonists. Protonation of the piperidinyl amine (Figure 2) prevents initial oxidation of the amine to the amine oxide, thus disrupting the Denisov cycle.\(^7\)

![Figure 2. Schematic of protonation of the piperidinyl amine.](image)

Transition metals are also known to be antagonistic toward HALS, although the mechanism for disruption is less clear. For example, transition metals coordinated in phthalocyanine pigments, such as copper phthalocyanine (Figure 3), are known to have an antagonistic effect on HALS.\(^7,8,9,10\) Other forms of copper are also known to have prodegradant effects as are other metals such as iron, manganese and zinc.\(^1\)

![Figure 3. Chemical structure of copper phthalocyanine.](image)

This paper describes the photo-oxidative sensitivity of polypropylene carpet to chemical antagonists. Discoloration occurred in as few as 3 months of outdoor exposure in the presence of antagonists. The defective carpet exhibited unusual darkening that occurred in irregular and unpredictable patterns that were inconsistent with carpet construction patterns. At the same time, representative samples of fiber and carpet exposed to accelerated weathering and to standardized outdoor weathering tests without antagonists present did not display the same irregular discoloration and instead exhibited traditional degradation behavior. Probable antagonists are identified and their effects discussed.

**Materials**

The carpet is constructed of 2400 denier bulk continuous filament (BCF) fiber grade polypropylene such as SABIC PP 518P (24 g/10 min melt flow index @ 2.16 kg and 230 °C, ASTM D1238) and has a typical face weight of 16 oz./SY. Individual filaments have a delta cross section and are approximately 20 denier per filament (dpf). The carpet tuft fibers are multicored, consisting of both light colored and black fibers. The carpet colors that are the most problematic have high contrast. In one case, a portion of the filaments are pigmented black using carbon black. Another portion of the filaments is pigmented light gray. The light colored ends may include phthalocyanine pigments, which will be the source of discussion below.

The carpet fibers are stabilized with a common secondary amine HALS along with conventional primary and secondary antioxidants. The black fibers are stabilized with HALS, primary antioxidant and secondary antioxidant and pigmented with carbon black thus offering an added degree of UV protection. The light fibers contain the same HALS, primary antioxidant and secondary antioxidant stabilizers, but they contain a different mix of inorganic and organic pigments.

The primary antioxidant is typically a hindered phenol. The secondary antioxidant is typically a phosphite. A typical HALS is poly[[6-{(1,1,3,3-tetramethylbutyl)amino}-1,3,5-triazine-2,4-diyl][2,2,6,6-tetramethyl-4-piperidinyl]imino]-1,6-hexanediyl][2,2,6,6-tetramethyl-4-piperidinyl]imino]).

Discolored carpet samples from the field were examined by optical microscopy to establish the mode of failure. Damaged carpets were also examined for backing integrity and for potential contamination of other substances.

Accelerated UV testing was performed with a Q-LAB Q-SUN Xe-1 or Xe-3. Test conditions were per ISO 4892-2 with an irradiance of 0.5 W/m\(^2\)/nm or 0.6 W/m\(^2\)/nm at 340 nm. Black panel temperature was 36 °C. Ambient air temperature was 37 °C.

Colorimetry was performed with a X-rite Ci7x00 series spectrophotometer.

**Discussion**

Initial examination of carpet confirmed preferential degradation of light colored fibers. Degradation began at the fiber tips and progressed vertically down the length of the tufts, resulting in material loss. Once tip degradation removed 1-2 mm of light fiber tips, black fiber visually dominated the surface affording a noticeable darkening to the carpet. However, the darkening pattern was not uniform across the carpet, but instead occurred in splotches. In many cases, the discoloration did not cross the carpet seam even though the seamed carpet sections were cut from the same production role. These odd discoloration patterns could not be fully explained by exposure or shading patterns.
In addition to the above observations we were able to discern patterns that correlated with materials that were underneath the carpet. In some cases a light colored outline could be clearly seen in the carpet face within a dark background. The light outline corresponds with the exact location of tape that covers a treated plywood sub-flooring. The treated wood contains copper arsenate which is hypothesized to interact with HALS at the fiber surface after migrating to the carpet face. The tape appears to block this migration. The mechanism of migration has not been established but could be from wicking that occurs after the carpet is wet from rain or other sources.

In an attempt to further understand the failure mechanism, carpet retains were exposed to accelerated UV testing. The samples were evaluated over time using a colorimeter utilizing CIE color space L*a*b* notation (“Lab”). Light colored tip deterioration principally led to a darkening of the carpet, with very little color shift in the “a” (green-magenta) or “b” (blue-yellow) coordinates. Delta L, as will be reported, is the difference in L (lightness) values between the carpet after UV exposure and the carpet before UV exposure.

It was possible to follow the progression of UV degradation by measuring delta L. Thus, colorimetry can be used as a diagnostic tool. An example is shown below where carpet was exposed to UV radiation for 2000 hours. A significant increase in delta L (lighter) is seen after 500 hours (Figure 4). This corresponds to a typical life cycle pattern experienced with this carpet. In this example, light color discoloration is evident, but actual material loss has not yet occurred and the carpet has not yet turned dark. It is hypothesized that the increase in delta L is actually the precursor to a decrease in delta L after light colored tip degradation and material loss begins. This hypothesis fits with anecdotal observations of the carpet turning lighter (increasing L values) prior to noticeable tip deterioration and is believed to be due to crazing and micro-cracking of light colored filaments as evidenced by optical microscopy.

Another important observation is that certain colors are more stable than others. As can be seen in Figure 5, carpet color affects how the carpet responds to UV radiation. Carpet color 2 (combination of light gray and black filaments) contains only inorganic pigments, namely carbon black and titanium dioxide, whereas Carpet color 1 (combination of light gray and black filaments) contains organic pigments in addition to carbon black and titanium dioxide. It can be seen that Color 2 maintains a stable L value over the course of 2000 hours suggesting improved stability over Color 1. A likely cause for the performance difference in Colors 1 and 2 is the presence of copper phthalocyanine pigments in Color 1, a known HALS antagonist.

These data explain the premature UV degradation of color-specific fibers, but they do not explain the unusual carpet discoloration patterns. The carpet discoloration patterns were hypothesized to likely be due to external contaminates. Therefore, additional accelerated UV testing and colorimetry measurements were employed to test retain carpet samples upon exposure to various suspect materials that were known to come into contact with the carpet during use.
Carpet was exposed to 0.4% w/w aluminum dust from a plasma cutting operation, 0.4% w/w copper sulfate, and a hydrocarbon solvent cleaning solvent (mineral spirits). The aluminum dust and copper sulfate were added as dry powders on top of the carpet, after which water was sprayed on the carpet. The water spray dissolved the copper sulfate and circulated the solution to be reapplied to the sample. Addition levels were intentionally high to force a response. The sample was exposed to UV light and color data collected at intervals of 250 hours. A stable delta L near the control would be a strong “no-effect” indicator. Data for the samples can be seen in Figure 6.

![Figure 6. Effect of chemical exposure on the change in L over time.](image)

The carpet samples treated with aluminum and with copper both show a large increase in delta L in less than 250 hours with a corresponding increase in the rate of discoloration. This indicates the initial stages of polypropylene degradation. In addition, the copper samples show a drop in delta L after reaching a maximum at 500 hours. The copper treated samples also showed fiber tip deterioration in the light-colored fibers that is characteristic of the field failures. However, the black fibers appeared unaffected. The sample treated with hydrocarbon solvent behaved similarly to the control sample (Color 1) and is judged to have no significant effect.

These data suggest accelerated UV degradation is a result of exposure to aluminum dust and copper salts, conclusions that are preliminary at this stage. Although copper salts are known to have an antagonistic effect on HALS, literature on aluminum catalyzed degradation of polypropylene or aluminum antagonization of HALS is minimal.\(^\text{12}\) Further investigation is needed to establish effects at more realistic concentrations. In addition, because there is no obvious diffusion pathway for particulate penetration into fiber, further investigation is needed to understand mode of attack.

Similar tests were also performed with a cured vinyl ester resin, which is a common material used underneath outdoor carpet installations for this application. The carpet sample was mounted on the cured resin and exposed to UV light. Color data was collected at intervals of 250 hours. A control sample that was isolated from the vinyl ester resin was prepared and exposed to the same conditions. The results are seen in Figure 7.

![Figure 7. Effect of vinyl ester resin contact on the change in L over time.](image)

The delta L response was dramatic, with strong increases (lighter) in delta L up to 500 hours and decreases (darker) between 500 and 1000 hours. After 2000 hours, the deterioration of fibers had progressed beyond the fiber tips to the base of the tufts, which were completely deteriorated. The black fibers were affected as well. While the mode of deterioration progressed similarly to what is seen during actual use, the severity was significantly worse. Although not seen in the field to date, we surmise that such a severe response may be possible under the right conditions.

Very little is mentioned in the literature of an antagonistic effect of vinyl ester resins with HALS. Wright mentions an antagonistic effect with ethylene vinyl acetate but offers little elaboration.\(^\text{13}\) A plausible hypothesis is that residual carboxylic acid from hydrolysis of monomer or resin is available to react with the HALS. This needs to be investigated further.

**Conclusions**

UV degradation of polypropylene is complex. In this case photodegradation is affected by outdoor exposure but also by color pattern, pigment choice, and external HALS antagonists.
The unusual patterns of carpet darkening lead to the conclusion that a combination of causes is required to produce the objectionable appearance. Carpet that contains both black and light colored fiber, even when both contain UV stabilizers, photodegrade at different rates. This is likely due to the added presence of carbon black in the black fibers acting as a UV absorber. The faster deterioration of the light fibers leaves black fibers at the carpet surface and creates an objectionable dark appearance.

Potential HALS antagonists have been identified. Copper is a known HALS antagonist and shows a rapid increase in the rate of photodegradation when it is in contact with carpet. This was apparent in the fiber containing copper pigments as well as in the copper sulfate exposure. During use, we hypothesize that the source of copper is treated plywood from the sub-flooring material used in some installations. It is suspected that copper may potentially leach from the treated wood and interact at the fiber surface to deactivate the HALS.

Aluminum plasma dust was identified as another potential antagonist. It can also be present in some installations and can be deposited on the carpet during the carpet installation process. It is uncertain if the aluminum is behaving as a HALS antagonist or simply as a polypropylene prodegradant. Mode of attack is also uncertain.

Finally, vinyl ester resins were shown to be another, potentially more severe HALS antagonist. These resins are present in the sub-flooring of some carpet installations. It is conceivable that carboxylic acid could be made available from hydrolysis of residual monomer or resin. It is suspected that migration of residual acid to the carpet face may enable interaction with HALS at the fiber surface. The presence of residual acid has not been established.

Potential causes for premature failure of carpet due to photo-oxidative degradation have been identified. Additional work is needed to further isolate and understand modes of attack failure pathways and modes of attack.

References