New Solutions for Polyolefin Stabilization: Advanced UV Stabilizer for Molding Applications and a UV/Thermal Stabilizer for Building & Construction

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Abstract

Compounders, extruders, and molders are constantly demanding extended weatherability in polymer parts and looking for competitive advantages. New innovations are highlighted for two rapidly expanding market segments: molding and building & construction. A new stabilizer for molded products provides excellent color stability, long outdoor service life, and has broad food contact approvals. A new solution for building & construction provides outstanding UV weatherability and thermal stability for rugged applications. These new solutions deliver many advantages including the ability to meet extended warranties on roofing materials, and for molded articles, to look great and retain mechanical integrity for years.

Introduction

Polymers are inherently unstable when exposed to sunlight. Ultraviolet photons from the sun contain sufficient energy to homolytically cleave chemical bonds and form radical species. These radicals attack polymer chains, pigment, etc. in the presence of oxygen. The use of UV stabilizing chemistries is essential for outdoor polymer applications. For especially rugged applications, such as roofing materials, UV stabilizers must also factor in the ability to handle extended exposure to intense sunlight and heat, and must deliver commercial service lives in excess of 10 or more years.

As outdoor applications for polyolefins become more diverse, compounders, extruders, molders, as well as consumers, are demanding improvements in the stabilizer performance in polymer articles. For some applications, the manufacturer now guarantees the product against photobleaching and physical degradation by sunlight for a specified length of time. With minimal increases in the cost of a formulation, producers can realize the value of well-stabilized materials and products for their customers. Solvay, from the days of American Cyanamid and Cytec, is committed to delivering UV stabilizer innovations that enable customers to capture additional value from performance differentiated products.

Solvay is introducing stabilizers for different market segments: CYASORB CYNERGY SOLUTIONS® M535 Stabilizer for polyethylene injection and blow molding, and CYASORB CYNERGY SOLUTIONS® B878T Stabilizer for polyolefin construction materials that require long-term UV and heat stability for harsh conditions.

Injection Molding is the Future

From automotive interiors to packaging, injection molded parts are everywhere. The global injection molded plastic market is expected to reach 296 billion USD by 2020.[1] Much of this growth is driven by the replacement of metals and other materials with polymers, as well as precipitous general growth in Asia. The performance requirements for polyolefin injection molded articles vary drastically depending on application and producer – some products use no UV stabilizer and barely enough antioxidant to survive processing, and some high-end products require a decade or more of outdoor exposure. CYASORB CYNERGY SOLUTIONS® M535 stabilizer is a new solution recommended for general polyethylene molded articles to provide UV-8+ protection at modest loading levels.

CYASORB CYNERGY SOLUTIONS® M535 Stabilizer for UV-8+ PE Molding Applications

To test the performance of the new stabilizer, the material was extruded into HDPE along with phenolic/phosphite antioxidant and was injection molded into plaque test specimens and Type V tensile bars. All weathering in this section was performed in an Atlas Ci5000 Weatherometer using ASTM G155 Cycle 1 conditions.

In an HDPE containing 1% of a white pigment masterbatch, CYASORB CYNERGY SOLUTIONS® M535 stabilizer shows 10,000 hours of ASTM G155 weathering with 90% retention of strain at break (Figure 1). Compared to three popular competitive stabilizers, CYASORB CYNERGY SOLUTIONS® M535 stabilizer delivers equal performance at nearly half of the concentration.

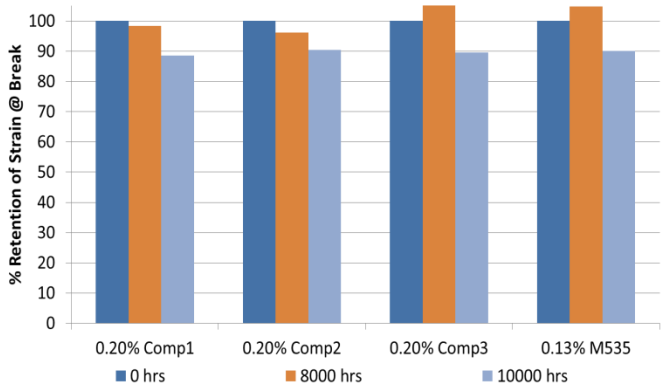

Figure 1 | Tensile data comparing CYASORB CYNERGY SOLUTIONS® M535 stabilizer *to popular competitive stabilizers in HDPE with 1% white pigment masterbatch and* CYANOX® *2777 antioxidant in ASTM G155 Cycle 1 Weathering*

To ensure good long-term quality control, color matching is essential whenever anything is added to a polymer/pigment system, especially UV stabilizers. CYASORB CYNERGY SOLUTIONS® M535 stabilizer imparts a very low initial color in natural HDPE (Figure 2). Because CYASORB CYNERGY SOLUTIONS® M535 can be used at lower loadings than competitive solutions, a color concentrate producer could add more pigment or other additives to the formulation in lieu of stabilizer, allowing for formulation flexibility and helping to maximize value.

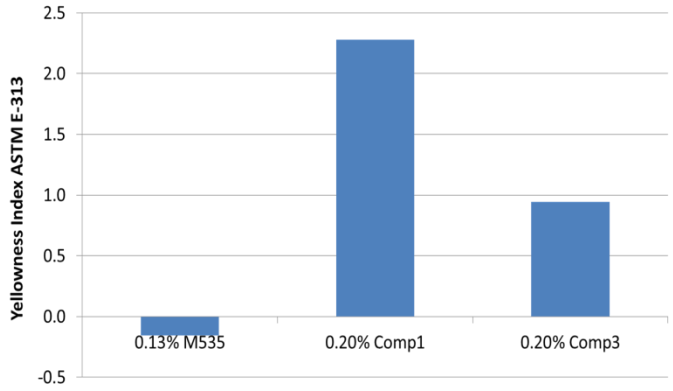

Figure 2 | Initial color of HDPE containing various stabilizers and CYANOX® 2777

In addition to low initial color, the retention of the intended initial color of a polymer article during outdoor exposure/field use is critical. CYASORB CYNERGY SOLUTIONS® M535 stabilizer demonstrates good color stability in natural HDPE (Figure 3), staying below ΔE of 2.0 after 10,000 hours of Xenon weathering.

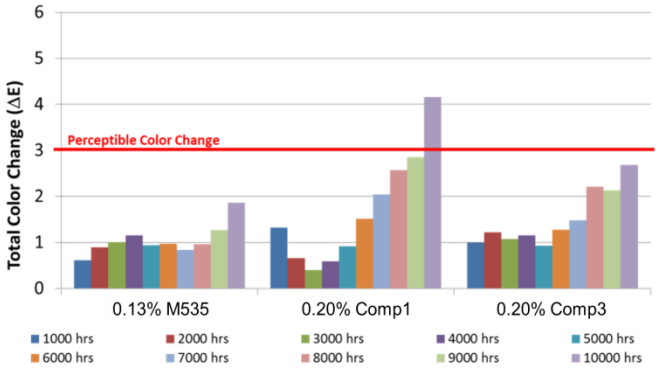

Figure 3 | Total color change in natural HDPE after 10k hours G155 weathering. Samples contain CYANOX® 2777 *antioxidant.*

CYASORB CYNERGY SOLUTIONS® M535 stabilizer is especially effective in preventing photo-induced color change and surface degradation (as measured by loss of gloss) in pigmented systems – color data is shown for HDPE with a phthalocyanine green-based pigment masterbatch (Figure 4), demonstrating a ΔE of 3.0 after 10,000 hours of weathering. Gloss data further demonstrates excellent surface protection (Figure 5). Again, the new stabilizer outperforms competitive systems at nearly half the loading level.

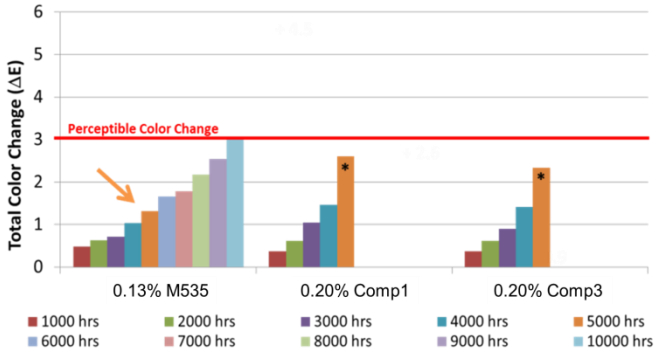

Figure 4 | Total color change in green HDPE after 10k hours G155 weathering. The (*) denotes surface crazing.

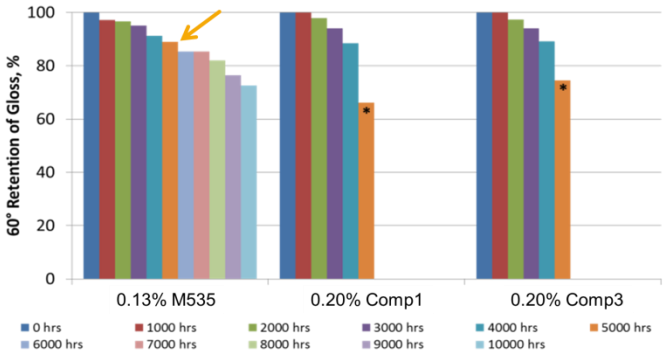

Figure 5 | 60° retention of gloss in green HDPE after 10k hours G155 weathering. The (*) denotes surface crazing.

Unique Challenges in Stabilizing Building & Construction Polymers

Polyolefins, especially TPO, TPV and TPE, are replacing other materials in construction for reasons including: their physical properties, ease of fabrication, barrier properties, relative cost effectiveness, lower weight, and recyclability. For some building applications, including roofing membranes, the performance requirements are even more demanding, with some manufacturers looking to meet and even exceed the current long-term heat aging and weather resistance specifications set forward by the ASTM (Table 1). A product that far surpasses the current long-term heat aging standards could help a producer find new markets in desert regions or in equatorial locations; at the extremes, a roof could be hotter than 90°C due to location, design, materials and radiant heat from surrounding surfaces. In addition to the aforementioned environmental stresses on roofing sheets, they will often be in contact with tar and other building materials that could contain stabilizer-inactivating chemicals.

North America ASTM D6878 Standard for Thermoplastic Based Sheet Roofing			
Test	ASTM Test Method	Test conditions	Passing requirements
Heat Aging	ASTM D573	5,376 hours at 116 °C/240 °F	>90% retained elongation and breaking strength
Weather Resistance	ASTM G155	10,080 kJ/m² at 340 nm and 80 °C, BPT, 50 °C air temperature	7x magnification No cracks/crazing

Table 1 | Various standards for thermoplastic polyolefin sheet roofing.

CYASORB CYNERGY SOLUTIONS® B878T Stabilizer for Building & Construction Applications

The samples described in this section were prepared as follows:

- TPO resin, $Mg(OH)_2$, TiO_2, stabilizers
- 27 mil (~0.7mm) TPO roofing sheet for single ply membranes
- Specimens testing according to ASTM D6878 + ASTM D573
- ASTM D6878 Xenon conditions: 0.70W/m^2 @ 340nm, 80°C
- ASTM D573: Oven aging at 116°C and 138°C
- Tensile testing according to ASTM D751
- Color measurements according to ASTM E313

As shown in Table 1, the current UV specification for TPO sheet roofing is no cracking/crazing on a mandrel after 10,080 kJ/(m^2·nm) radiant exposure @ 340nm, and the oven specification calls for 5,376 hours @ 116°C. CYASORB CYNERGY SOLUTIONS® B878T stabilizer shows no cracking or crazing over a mandrel at 3x the radiant energy of the ASTM UV specification (Figure 6). The commercial formulation failed after ~27,500 kJ/m^2.

ASTM UV Requirement

kJ/m²	2520	5040	7560	10080	20160	25200	27470	30240
B878T	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Commercial Reference	Pass	Pass	Pass	Pass	Pass	Pass	Failed	Failed

Figure 6 | Results of mandrel testing after UV exposure. The (**) denotes the starting of cracking.

More quantitatively, tensile testing was used to probe the physical properties of the sheets after Xenon weathering; retention of stress at break (Figure 7) and retention of strain at break (Figure 8) are shown. The CYASORB CYNERGY SOLUTIONS® B878T-containing formulation had minimal loss of stress or strain at break after the prescribed 10,080 kJ/m^2, whereas the commercial reference exhibited a steady loss of stress at break over time, finally reaching ~80% retention at the ASTM minimum exposure.

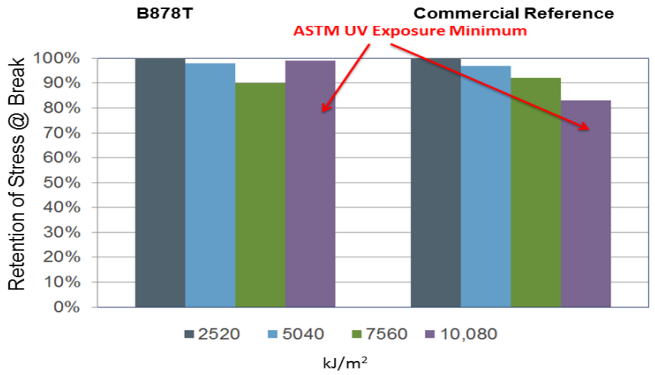

Figure 7 | TPO roofing sheet – retention of stress at break after 10,080 kJ/(m^2·nm) radiant energy in an ASTM D6878 weatherometer

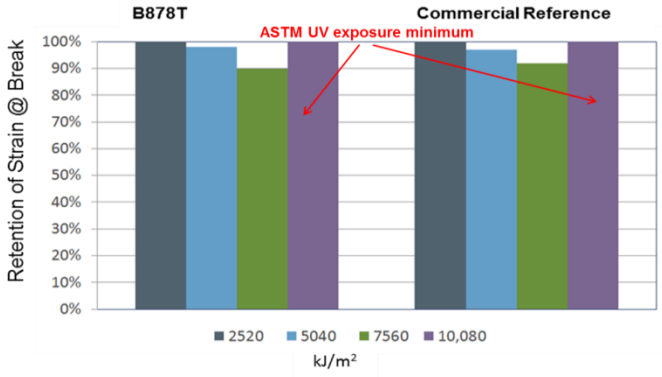

Figure 8 | TPO roofing sheet – retention of strain at break after 10,080 kJ/(m^2·nm) radiant energy in an ASTM D6878 weatherometer

With respect to thermal performance, CYASORB CYNERGY SOLUTIONS® B878T stabilizer maintains over 70% retention of stress at break (Figure 9) and strain at break (Figure 10) after 7,500 hours of thermal aging at 116°C, compared to a commercial formulation that loses both properties after 3,000 hours. Tensile data from a more extreme, supplementary 138°C oven aging test shows CYASORB CYNERGY SOLUTIONS® B878T maintaining 90% retention of stress at break (Figure 11) and 70% retention of strain at break (Figure 12) after 4,000 hours compared to two competitive samples that show loss of physical properties after 2000 hours. Note that in the aforementioned studies, single ply TPO roofing sheets were used; multilayer constructions are used in most applications.

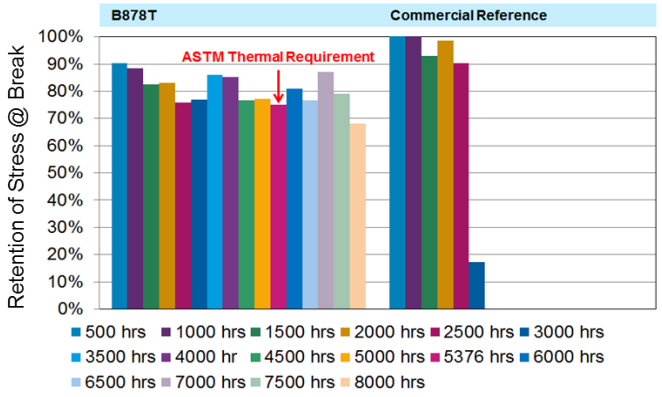

Figure 9 | 116°C oven aging of TPO roofing sheets – retention of stress at break

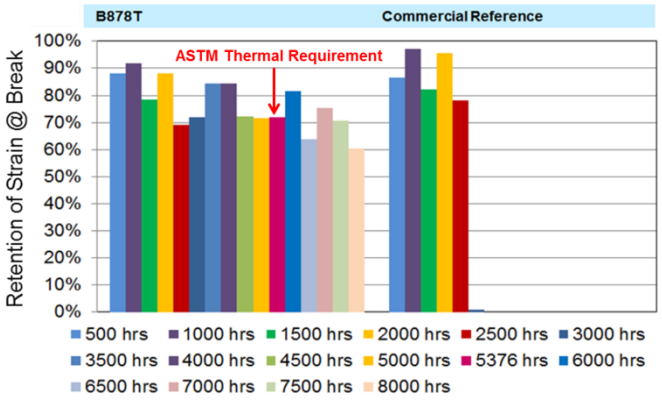

Figure 10 | 116°C oven aging of TPO roofing sheets – retention of strain at break

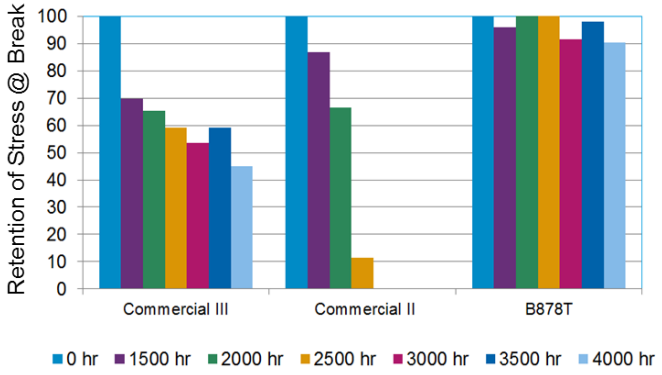

Figure 11 | 138°C oven aging of TPO roofing sheets – retention of stress at break

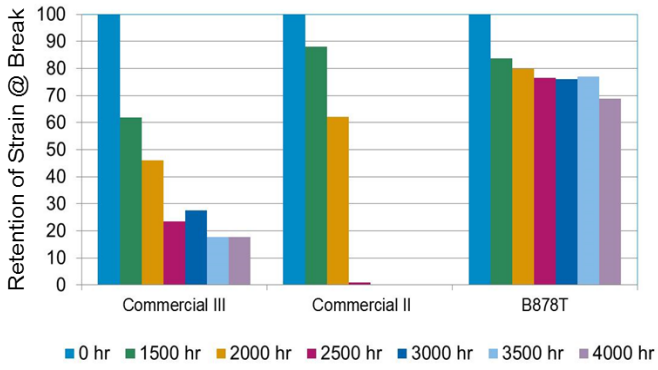

Figure 12 | 138°C oven aging of TPO roofing sheets – retention of strain at break

Conclusions

This paper highlights the UV and thermal performance of two new stabilizers: CYASORB CYNERGY SOLUTIONS® M535 stabilizer for injection and blow molding, and CYASORB CYNERGY SOLUTIONS® B878T stabilizer for demanding building & construction applications. In HDPE injection molded parts, modest levels of CYASORB CYNERGY SOLUTIONS® M535 have shown to deliver good surface protection, tensile property retention and colorfastness through various weathering experiments in an ASTM G155 Cycle 1 weatherometer. In TPO roofing materials, CYASORB CYNERGY SOLUTIONS® B878T demonstrated excellent retention of physical properties and strong resistance to cracking in both highly-intense ASTM D6878 Xenon weathering conditions and two high-temperature ovens. These new innovations in stabilizer technology and their corresponding improvements polyolefin performance highlight how Solvay is asking more from chemistry.

[1] Grand View Research Market Report, https://www.grandviewresearch.com/press-release/global-injection-molded-plastics-market

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