The Bright Science Behind Thermo-Oxidative Stability

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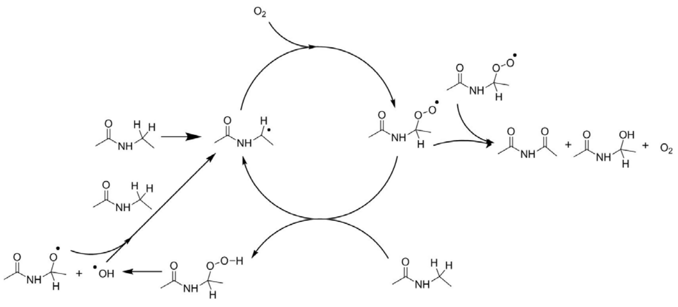
Engineering plastics that take the heat

Today's plastics need to perform in hotter environments than ever before. Numerous applications expose plastic parts to high air temperatures over long periods of time, particularly in car engine compartments. Temperatures under the hood have continued to rise due to smaller compartments with less air flow, increased use of turbo chargers, and air management systems that utilize exhaust gas return.

At DSM, studying the chemical and mechanical behavior of polyamide-based plastics in high-heat environments is one of our key areas of expertise. Once we understand the chemical mechanism of thermo-oxidation, we can determine methods to slow down the process.

The concept of stabilization focuses on breaking the reaction chain, for example, by including components that will react with the radicals formed during the oxidation process. While this approach is widely used, the improvements are limited to an increase in continuous use temperature of around 10-20°C, as these solutions slow down the degradation reactions rather than preventing them. To meet the demands of today's under-the-hood applications, we need to achieve a larger improvement in the continuous use temperature materials can withstand.



Source: P. Gijsman, D. Tummers, K. Janssen, Polymer Degradation & Stability 49 (1995) 121-125.

Figure 1 — Thermo-oxidative degradation mechanism in polymers

Understanding thermo-oxidative aging

Thermo-oxidative aging is best described as slow, controlled burning of the material. This means we can apply the same approaches used in firefighting:

Remove the Heat	Remove the Fuel	Remove the Oxygen

Figure 2 — Controlled burning: O_2+Polyamide › CO, CO_2, C, H_2O, N_2...

Remove the heat

Removing the heat is possible through the car design, rather than through the material itself. This approach includes moving parts away from heat sources or including heat shields, however it is not necessarily possible based on the complexity of current car designs. At DSM, we have worked the problem from this fundamental approach to gain major strides in the thermo-oxidative stability of our materials.

Remove the fuel – Arnitel TPE

On the surface, this seems like an invalid approach, since the plastic is the fuel. Yet our material scientists dug deeper, and discovered some interesting things.

We took a close look at the thermo-oxidation behavior of Arnitel®, a polyester-based thermoplastic elastomer (TPC) commonly used to replace rubber in under-the-hood applications. This class of materials is generally limited to continuous use temperatures of 125°C after stabilization.

What we discovered was that one part of the polymer chain – a polyether block – was oxidizing faster than the rest of the polymer. By slightly modifying the chemistry of the polyether block – or redesigning the polymer backbone – we could make the polymer considerably less sensitive to oxidation. This made it possible to achieve a significant improvement in the stability of the material.

This new chemistry is used in our Arnitel C and Arnitel HT grades, suitable for applications with a continuous use temperature over 150°C. These applications include hot charged air ducts, high temperature vacuum brake tubing, and headlamp cable jacketing.

When we compare a number of grades in the 63 Shore D hardness range on an Arrhenius plot, we can clearly see the increase in performance from the standard polyether chemistry (Arnitel EM630), the heat-stabilized material (Arnitel EM630-H), and the material with an optimized polymer backbone (Arnitel CM622). Stabilization increases the continuous use temperature by around 15°C, however modifying the polymer backbone gained an improvement of almost 60°C – much more effective than using stabilizers.

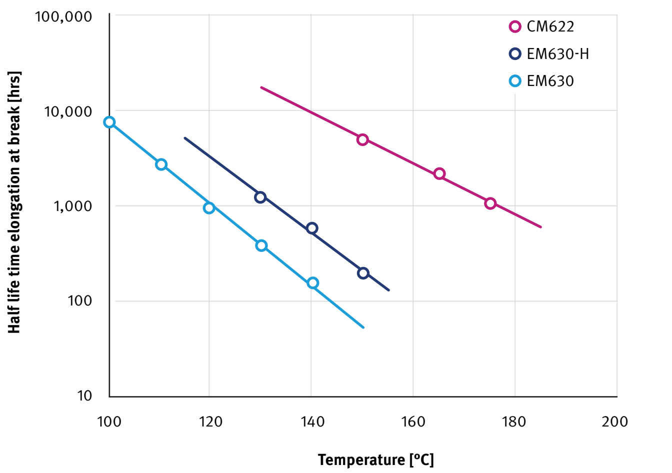


Figure 3 — Comparing the effect of adding a stabilizer and improving the intrinsic stability of the polymer backbone on retention of properties

Remove the oxygen – DSM Diablo technology

While this seems even less possible than removing the fuel, our bright scientists have pushed their thinking further to find an incredibly effective solution. We built our approach on the idea that while oxygen is present outside the part, that does not necessarily mean that oxygen is present inside the part.

Consider the case of rust (another controlled burning process) on steel. Standard steel oxidizes very rapidly, much like stabilized polyamides. With stainless steel, the outer layer reacts with the environment to form a very thin, stable film on the surface that protects the core within. Our Diablo technology is modelled after this.

Recognizing that we cannot prevent the oxidation of the outer layer, Diablo is designed so that when the outer layer oxidizes, it creates a film that has high barrier properties to oxygen. This removes the oxygen from reacting with the core of the material and vastly improves the upper temperature limit where the material can be used. Our Diablo technology is used in components for applications including air management systems, and other parts that are close to heat sources.

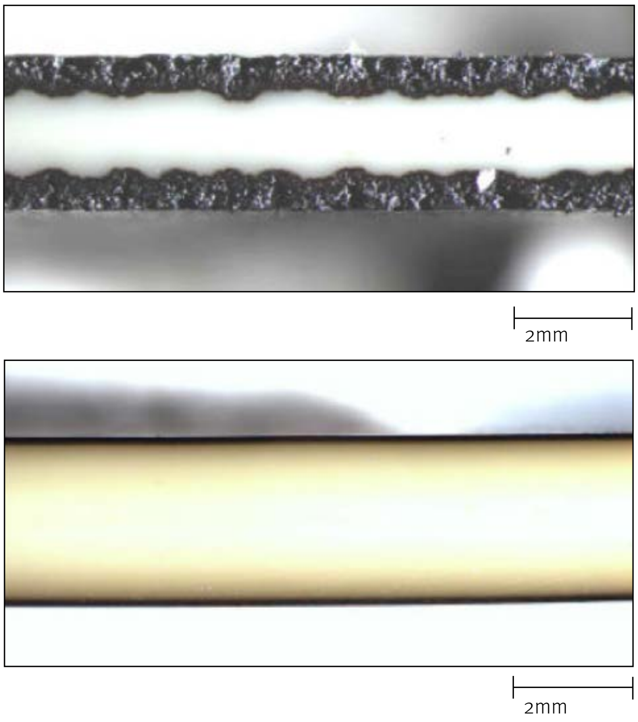


Figure 4 — Parts based on materials with (R) and without (L) the Diablo solution after aging at high temperatures

The difference is clear – Diablo forms a strong barrier that strongly reduces oxidation of the core of the material.

When we compare the long-term heat performance at 210°C of one of our Diablo grades (Stanyl® OCD2100) with a heat stabilized PA66, a heat stabilized PPA, and two different PPS grades (which is an intrinsically heat stable material), our Diablo technology substantially outperforms the competition.

These examples demonstrate how we like to work at DSM – using science to understand the fundamental issues in a problem. This approach enables us to think far beyond what is currently available to develop next-generation solutions that meet the industry's biggest challenges – today, tomorrow, and in the future.

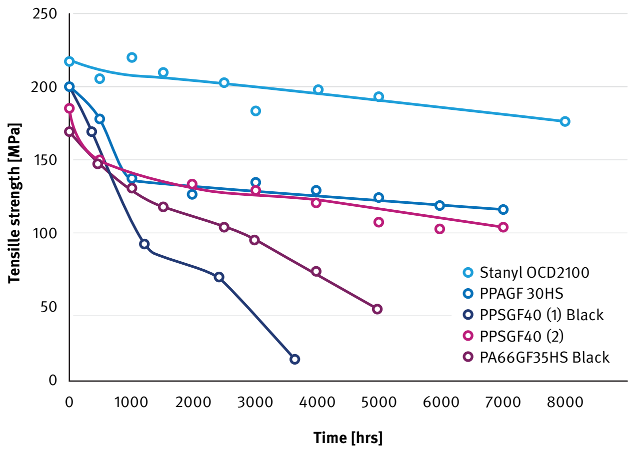


Figure 5 — Tensile strength retention of Stanyl Diablo versus other materials

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