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Equistar Technical Tip

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Additives: Antioxidants

Polypropylene (PP) and some polyethylene (PE) resins in their natural state (without additives) are inherently unstable and degrade when exposed to oxygen. The degradation is similar to the rusting (or oxidation) of untreated iron in that the polymers change color to yellow-brown and begin to flake away until the material becomes useless.

When PP or PE degrades, chain scission, or the breaking up of the polymer chains into smaller pieces, takes place. The physical properties of the polymer deteriorate and its average molecular weight (chain length) decreases, melt flow rate increases and a powdery surface eventually forms.

Polymer degradation is a natural phenomenon that cannot be totally stopped. Instead, resin producers seek to stabilize the color and physical properties of their polymers for a reasonable life span, which varies depending on the end use requirements.

The degradation of these polyolefin resins follows an autoxidation process (Figure 1). Energy, in the form of heat or light or the presence of reactive metals such as catalyst residues, causes a hydrogen atom to escape the polymer chain. The result is a polymer radical [R*] and a free hydrogen [*H]. The polymer radical [R*] reacts with a molecule of oxygen [O_2] to form a peroxy radical [ROO*]. The peroxy radical then removes another hydrogen atom from the polymer chain, forming unstable hydroperoxides [ROOH], alcohols [ROH] and new hydrocarbon free radicals [R*]. Autoxidation continues unless countermeasures are taken to halt the process.

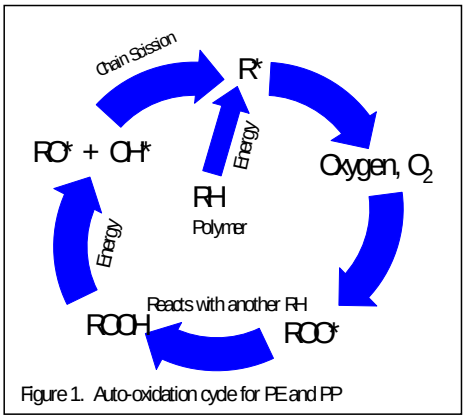

Figure 1. Auto-oxidation cycle for PE and PP

One way to terminate autoxidation is by adding various antioxidants to the resin. Antioxidants (A/O) are a class of chemicals with varying chemical compositions and methods of terminating autoxidatic Antioxidants are generally classified into three types:

Primary A/O: organic molecules consisting of hindered phenol and amine derivatives; generally, the higher the molecular weight of the additive, the better the performance.

Secondary A/O: organic molecules consisting of phosphates and lower molecular weight hindered phenols; generally, the lower the molecular weight, the better the performance.

Thioesters: organic molecules containing sulfur which have a cooperating (synergistic or additive) effect when added with a primary A/O.

Primary antioxidants [AH] work as radical scavengers [R*] by the following mechanism:

$$R^* + AH \longrightarrow RH + A^*$$

[Continued on Page 2]

Equistar Technical Tip

tech.topic

Additives: Antioxidants *(Continued)*

The phenol radical [A*] can cause polymer degradation but is kept from doing so by the hindered physical structure of the primary A/O. Primary antioxidants are added to the polymer to protect against degradation during the service life of the finished product.

Secondary antioxidants are added to the resin to reduce color formation and to provide processing stability during the pelletization and extrusion/molding processes. Secondary A/Os [$P(OR)_3$] decompose hydroperoxides [ROOH] to form stable alcohols [ROH] by the following mechanism:

$$ROOH + P(OR)_3 \longrightarrow ROH + O = P(OR)_3$$

Thioesters perform a role similar to that of secondary A/Os in that they decompose the hydroperoxides [ROOH] into alcohols and other non-reactive species. But they also have a synergistic effect with primary A/Os, especially with the high molecular weight, hindered phenol type of primary A/O. The particular method by which the thioesters decompose hydroperoxide radicals is not well known but is theorized to be similar to that of the secondary A/Os.

Thioesters are usually used in end products with requirements that include long-term exposure to high temperatures, such as under-the-hood automotive applications and home appliances. Thioesters have been shown to be quite effective at temperatures greater than 122°F (50°C). Even at these high temperatures, these A/Os can deactivate up to 55 molecules of hydroperoxide for every molecule of thioester.

A certain minimum amount of antioxidant is necessary to stabilize and protect polyoleins from autoxidative degradation. Primary antioxidants and thioesters are added to the polymer to provide end use product stability while secondary antioxidants are added to provide color and processing stability during pelletization and extrusion/molding. As the temperatures of the finished part must withstand rise, so must the level of antioxidants in the polymers to prevent long-term degradation.

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