Compounding Solutions

STABLIZERS IN MEDICAL PLASTICS FOR EXTRUSION

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SCOPE AND PURPOSE

- Medical plastics today are being pressed further than ever before
- Extruded tubing is being challenged dimensionally and chemically
- The demands on materials are not decreasing
- Thin walled applications are increasingly common
- Issues have been present and are exacerbated by processing
- Solutions are under review – quantify stabilizer effect/impact

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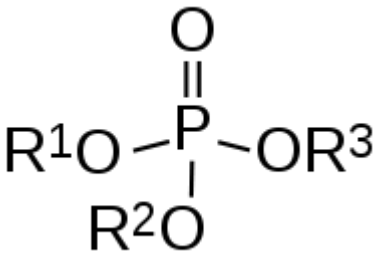
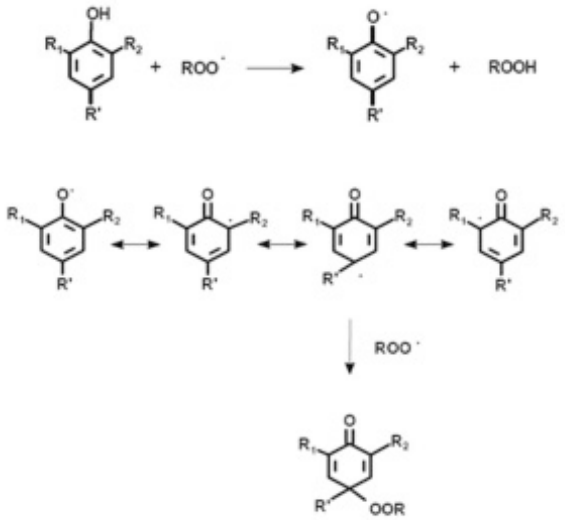
HEAT STABILIZERS

Thermal degradation of polymers is molecular deterioration as a result of overheating. At high temperatures the components of the long chain backbone of the polymer can begin to be broken (chain scission) and react with one another to change the properties of the polymer. Thermal degradation can present an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss. Indeed unless correctly prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include reduced ductility and embrittlement, chalking, color changes, cracking, general reduction in most other desirable physical properties.

Thermal Degradation of Polymers - The Zeus Polymer Minute

HEAT STABILIZERS





Mode of action of primary antioxidants

The physical appearance of polymers and their strength, ability to withstand deformation, general durability and overall consistency and performance can be preserved via heat stabilizers.
Two broad categories exist. Organophosphites and phenolic antioxidants. The first helps to protect materials during the manufacturing process or early stage processing as it relates to the medical device industry. The second helps to preserve the material in later stages of its usage.
Many brands exist in both categories. We have focused on a handful for this review however their common purpose is to trap free radicals released by heat processing in the presence of oxygen which creates the issues of note.

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Multiple Heat Histories

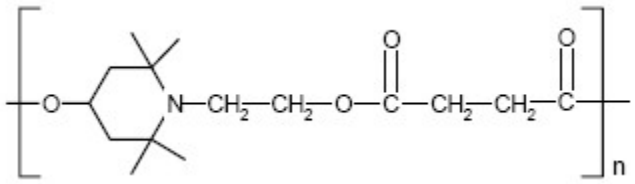
- Anecdotal issues have been tossed around for many years. Cracking, stress lines, discoloration, flaking, straight line fractures usually simply blamed on “bad material” or “over processed material” or “over compounded” are often discussed.
- Environmental issues such as humidity during the summer months which causes “bubbling” during secondary processing or extrusion or molding are usually seen as a material failure when the environment has a major impact. Desiccant coffins and dryers for materials or parts that will experience multiple processing steps is critical for high yield. Moisture analysis is critical especially for TPU materials and other hygroscopic materials.
- Heat splash from tipping processes can cause critical failure when associated with long tapers or long resonance time in a heated die.
- Compounding, Extrusion, Reflow and/or Tipping, Sterilization, Aging both accelerated and real time impacts on materials.
- Actual issues have been increasing over the past 5-7 years which can now be linked to the multiple processes steps required in the medical device industry especially where multilayer catheter construction is in use and are very common in wall thicknesses at or below .005”.

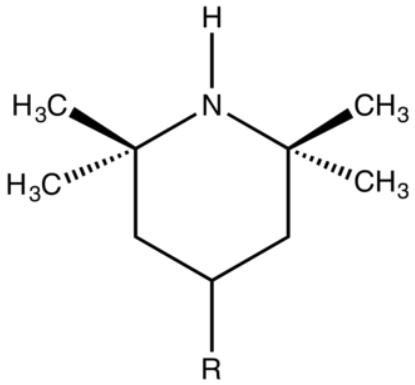
AMBIENT LIGHT-UV EXPOSURE/OXIDATION

Photo-oxidation is the degradation of a polymer surface in the presence of oxygen or ozone. The effect is facilitated by radiant energy such as UV or artificial light. This process is the most significant factor in weathering of polymers. Photo-oxidation is a chemical change that reduces the polymer's molecular weight. As a consequence of this change the material becomes more brittle, with a reduction in its tensile, impact and elongation strength. Discoloration and loss of surface smoothness accompany photo-oxidation. High temperature and localized stress concentrations are factors that significantly increase the effect of photo-oxidation.

https://en.wikipedia.org/wiki/Photo-oxidation_of_polymers

UV Stabilizers





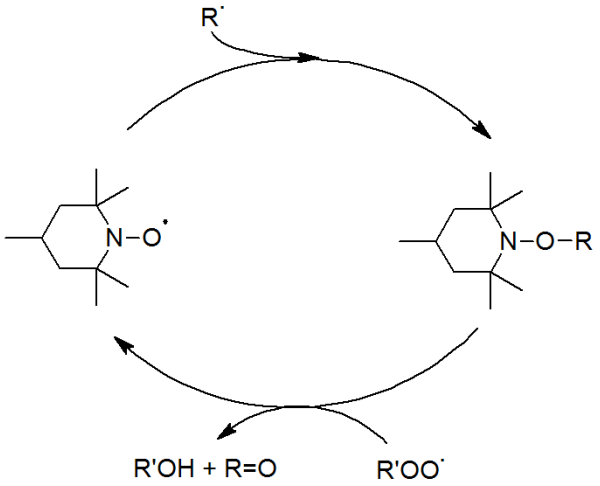


Photo degradation in plastics can occur from exposure to any UV source including office lighting. Stabilizers have been developed to inhibit the initiation process from occurring. As with heat stabilizers a UV stabilizer can help to preserve the physical appearance of polymers and their strength, ability to withstand deformation, general durability and overall consistency and longevity.

HALS (Hindered Amine Light Stabilizers (left images)), UV Absorbers and Quenchers are the most common. We are choosing to focus on HALS in this review which remove free radicals as opposed to absorbing them through the Denisov cycle (image on right).

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LIGHT EXPOSURE PROBLEMS

- The ambient light of your office space can cause polymers to degrade.
- COLOR SHIFT – “bleaching”
- CRACKING – surface fracturing
- LEACHING – tacky or gooey surface, trace elements of the base constituents of a polymer.
- TOTAL DEGREDATION – complete breakdown that is exhibited as anything from chunks of material falling away to them turning into a gum like material.
- TIO2 ENHANCEMENT OF ISSUES – PC is well known to react harshly with TiO2, Nylon and PEBA materials can also react with a variety of TiO2 grades.
- ANY EXTRUDED MATERIAL SHOULD ALWAYS BE KEPT IN OPAQUE BAGS UNTIL THE TIME OF USE.

STERILIZATION – IMPACTS?

- Ebeam sterilization has an impact on PEBA materials as shown in a recent study - PROGRESS in MEDICAL PHYSICS Vol. 25, No. 4, December, 2014 http://dx.doi.org/10.14316/pmp.2014.25.4.205
- The following tables are from pages 50-52 of The Handbook of Polymer Applications in Medicine and Medical Devices table 3.4.

Polymer	Polymer Abbreviation	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	Electron Beam
Polyolefins						
High-density polyethylene	HDPE	Poor	Poor	Good	Good	Good
Low-density polyethylene	LDPE	Poor	Poor	Good	Good	Good
Acrylonitrile butadiene styrene copolymer (Abs)	ABS	Poor	Poor	Good	Good	Good
Polycarbonates[a,b]		Fair	Fair	Good	Good	Good
Polyurethanes		Poor	Poor	Good	Good	Good
Acetals	POM	Good	Good	Good	Poor	Poor
Nylon 12, 6/12	PA12	Poor	Poor	Good	Fair	Fair
Urethane thermoplastic elastomer	TPU	Poor	Fair	Good	Good	Good

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COMPOUNDING SOLUTIONS STUDY PROPOSAL

Over the course of the next 6 months to 1 year a range of studies will be conducted to assess the effectiveness of different stabilizer combinations and loading levels (both antioxidants and UV stabilizers) at minimizing the degradation of polymers with multiple heat histories, sterilization steps, and aging.

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FORMULATIONS TO BE TESTED

- Pebax 5533 SA01 MED, Natural
- Pebax 5533, 0.2% Stabilizer Total (AO + UV)
- Pebax 5533, 0.5% Stabilizer Total (AO + UV)
- Pebax 5533, 0.5% Stabilizer Total (AO1 + AO2 + UV)
- Pebax 5533, 0.5% Stabilizer Total (AO1 + AO2 + UV1 + UV2)

- Pellethane 2363-55D, Natural
- Pellethane 2363-55D, 0.2% Stabilizer Total (AO + UV)
- Pellethane 2363-55D 0.5% Stabilizer Total (AO + UV)

- Tungsten loaded materials - ?

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TESTING AND AGING STUDY

- **Testing:**
- Tensile Strength, Elongation, and microscopic observations for stabilizer blooming will be made several time increments throughout the study.
- **Aging Study:**
- Day 0 properties measured followed by the simulated equivalent of 1 month, 3 months, 6 months, 12 months, 18 months, 24 months
- Testing for each sample, at each time interval after the following processes:
- Control tubing extrusion
- After sterilization
- After Re-flow
- After annealing
- After annealing, re-flow, sterilization in sequence

ONGOING REPORTING

- **Compounding Solutions will be making regular updates at each phase of the review.**
- **All data will be available on our website for download**
- **Scope will expand a bit over time to include additional materials and/or fillers/radiopacifiers.**

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STAY TUNED FOR UPDATES AT THE FOLLOWING

2nd Annual
MPC 2017
Medical Plastics & Compounding Conference
Organized & Presented by
Compounding Solutions

MPC 2017
December 5,2017
San Jose, CA

BIOMEDevice San Jose
Booth 302
December 6-7, 2017
San Jose, CA

M&M WEST

MD&M West
February 6-8,2017
Anaheim, CA

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