Additives in Polymers: Focus on Polyethylene

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Agenda

(1) Examples of polymers in industry

(2) Background on polyethylene & copolymers

(3) Common additives in polyethylene

- Functions, issues, and future

(4) How additives are regulated

Polymers in Industry – some examples

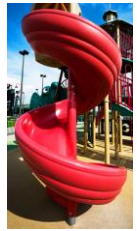
- **Thermoplastics**: melt-processable
  - Polyolefins: PE, PP, and their copolymers
  - PVC
  - Acrylics
  - Nylon
  - Polystyrene
  - Polyesters
  - PTFE

- **Thermosets:** irreversibly hardened after forming (via reaction, heat, UV, moisture)
  - Polyurethanes
  - Vulcanized rubber
  - Epoxies
  - Acrylics
  - Polyimides

Focus on Polyethylene and Copolymers

- Most types of plastic contain specialized additives adapted to the specific needs of the type of polymer
- **One of the most commonly used plastics is polyethylene**: 100 MM MT produced annually, ~34% of plastics market (as of 2017)
- Used for packaging, pipes, bottles, diapers, cables, roofing, etc…

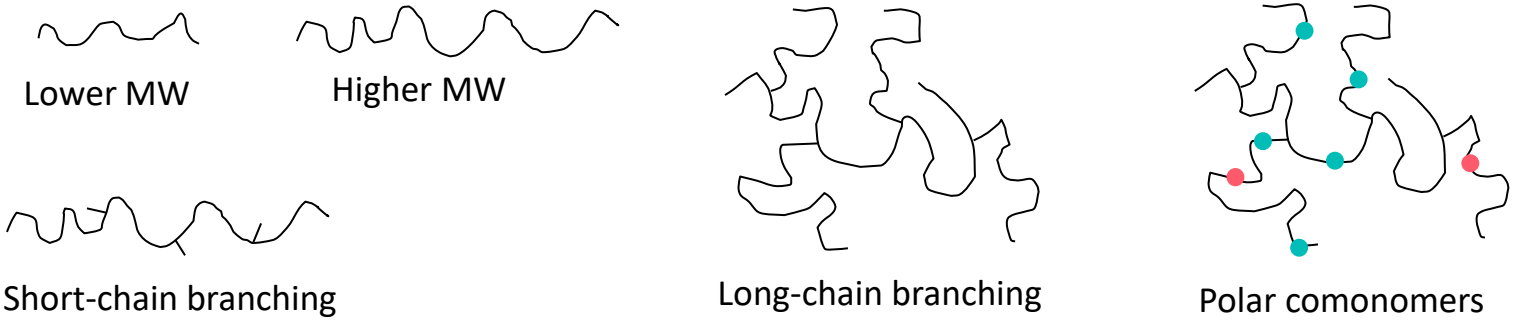






Polyethylene Types

- Mechanical, rheological, and chemical properties are highly versatile:
  - Molecular weight, and molecular weight distribution
  - Incorporation of propene, butene, hexene, or octene comonomers (“short-chain-branching”)
    - Amount of incorporation, and distribution of SCB across the MW range
  - Long-chain branching
  - Incorporation of polar comonomers (e.g. acid, acid-salt, ester, acetate, epoxide)



Why does Polyethylene need Additives?

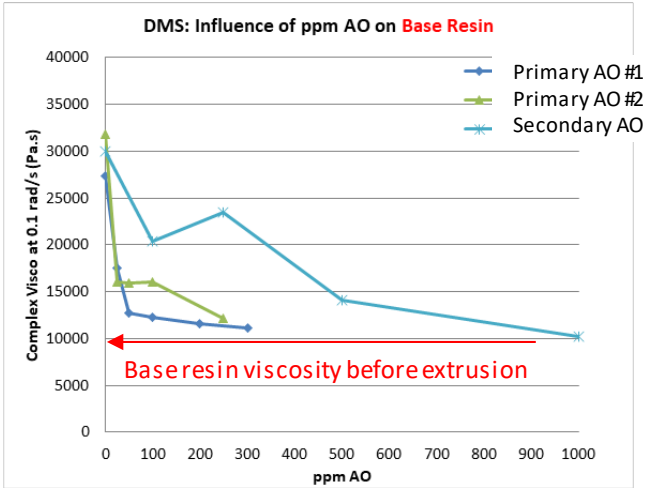
- Prevent oxidative degradation during processing, storage, and use
- Prevent degradation by exposure to sunlight
- Flame retardancy
- Improve barrier to water vapor
- Help make smooth-surfaced articles
- Improve balance between processability and toughness: allows downgauging
- Prevent films sticking together
- Allow films to glide over metal surfaces during manufacturing
- Provide lubrication for application and removal of bottle caps & closures
- Neutralize acids that can originate from catalysts
- Pigmentation

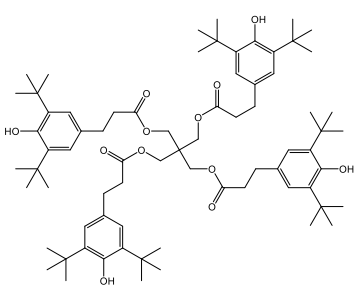
- Additives generally help with manufacturability, processability, increase the lifetime of the finished article, and sometimes improve its properties

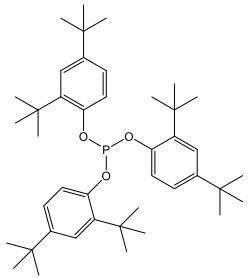
Antioxidants

- Antioxidants (AO) are very commonly used in PE
- Prevent oxidative degradation during processing, storage, and use: interruption of thermo-oxidative cycle
- Hindered phenols (primary AO) and phosphites (secondary AO) are often used together
  - Hindered phenols capture oxygen centered radicals
  - Phosphites break up hydroperoxides
- Without these AO's, viscosity / gels increase rapidly during processing

After extrusion of LLDPE in air at 215°C



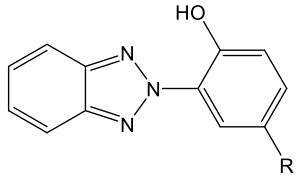


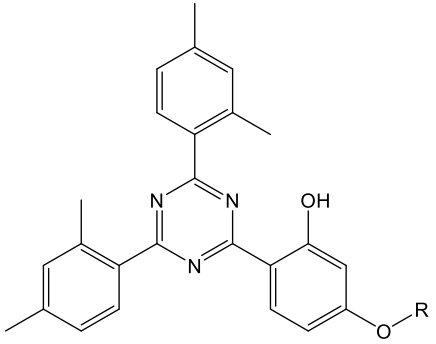


UV Stabilizers

UV Absorbers

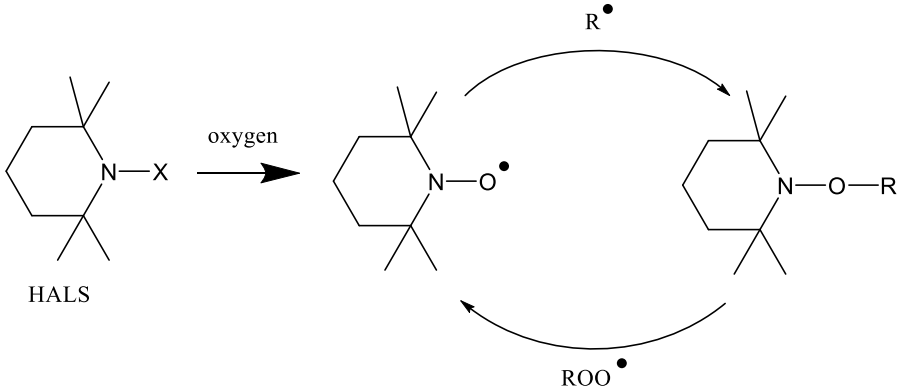
- Absorb UV light and dissipate as heat before it can interact with resin





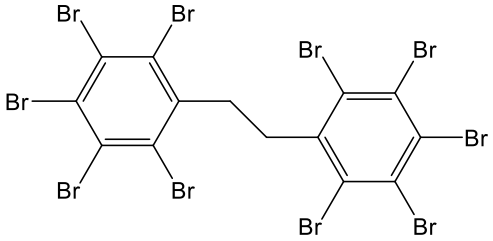
Hindered amine light stabilizers (HALS)

- Scavenge radicals generated by UV exposure before they can damage resin (Denisov cycle)
- Usually polymeric



Flame Retardants

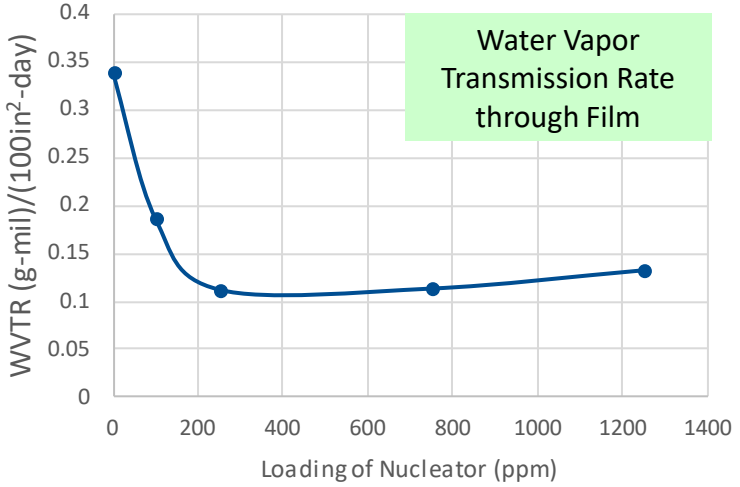
- Often used in Wire and Cable resins
- To prevent short-circuits igniting cable jacketing, propagating flames along wires, generating smoke, failure of emergency lighting
- Halogen containing molecules

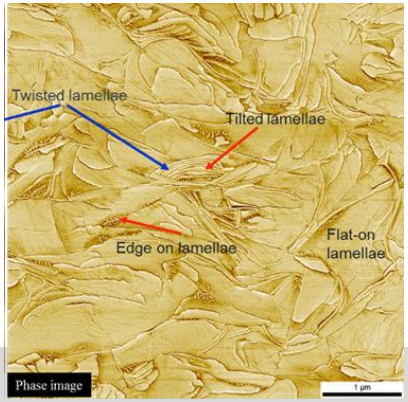


- …or halogen-free, such as $Mg(OH)_2$, $Al(OH)_3$, ZnO, $CaCO_3$
- Note W&C resins often contain multiple other additives such as UV stabilizers, antioxidants, synergists, and curing catalysts

Nucleators for Improved Water Vapor Barrier

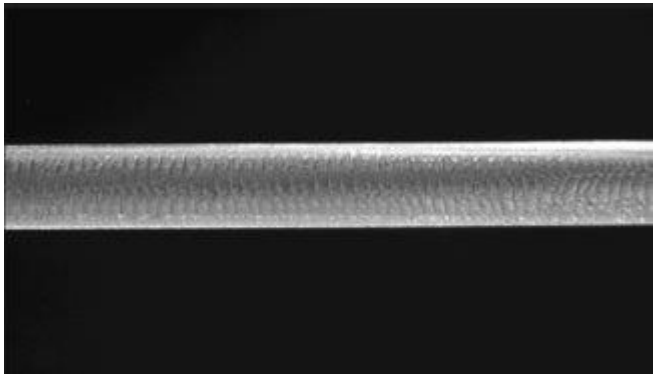
- Dry-food packaging
- Oriented organic salt crystals with specific morphology and surface chemistry.
- As the melt cools, polyethylene crystals nucleate rapidly on their surface, and orientation is controlled
- More PE crystals (lamellae) oriented parallel with the plane of the film → better barrier to water molecules

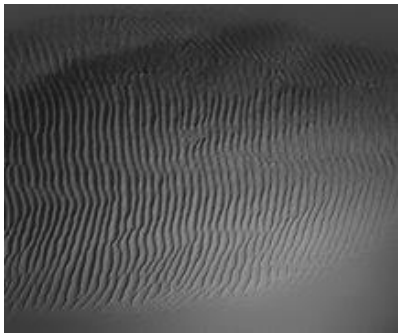




Melt-Fracture and Die Build-Up Reduction

- When certain tough, high MW PE resins are extruded at high rates, extrudate surface-distortion can occur: “melt-fracture” (e.g. for trash bags, pipes)
- PPA’s (polymer processing aids) are typically used to lubricate interface between polymer melt and extrusion dies, to give smooth articles
- Traditional PPA’s are often fluoropolymers: concerns about persistence in the environment
- Industry moving to other types of PPA



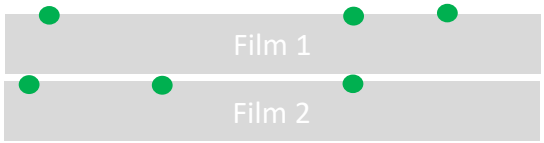


Processability / Toughness Balance

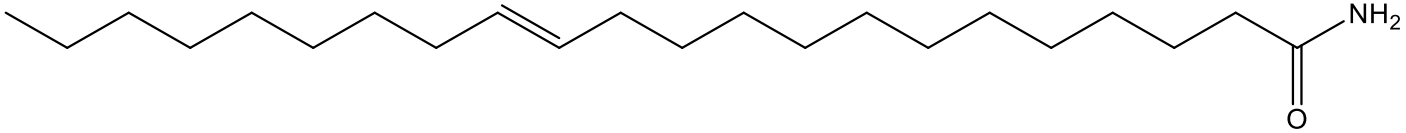
- Reactive additives (free radical generators) can impart low levels of cross-linking to PE during extrusion
- This greatly improves rheological properties / processability
- This allows adjustment of PE blends (LDPE/LLDPE ratio) which can afford much tougher films
- Tougher films can be down-gauged, saving on material use

Anti-Blocks and Slips

- **Anti-blocks**, typically inorganic particles such as talc or silica, are used to prevent films sticking together, via presenting less surface contact

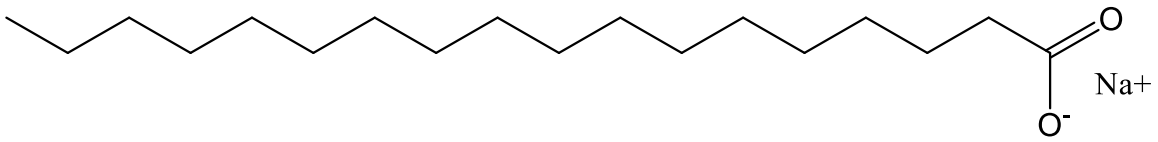


- **Slips**, typically aliphatic amides, are used to allow film webs to glide over metal surfaces during manufacturing, or to provide lubrication for application and removal of bottle caps
- Additive migrates to surfaces and forms thin layers of waxy crystals



Neutralizers

- Some common catalysts used to make polyethylene (Ziegler-Natta) generate residual acid when they are quenched with water
- Additives are used to neutralize the residual acid, to prevent corrosion at manufacturing plants and customers' equipment
  - Metal soaps



  - Dihydrotalcites, $Mg_6Al_2CO_3(OH)_{16}$, via anion exchange
  - Metal oxides, such as ZnO

Additive Side-Effects

- **Discoloration**: pellets or fabricated articles can become yellow (or pink) due to phenolic antioxidants
  - During storage: O_2 or NOx
  - During melt-processing: O_2
- **Migration out of resin**: some metal soaps, some antioxidants
  - Build up on surface of PE articles: haziness, or lamination issues
  - Deposit on equipment (plate-out): messy
- New tech. available to mitigate these issues

Conclusion & Future Directions of Additives in PE

- Additives are essential for plastics to realize their full potential: manufacturability, processability, longevity, performance

- The industry is continuously improving performance of additives
  - Higher efficiency, less side-effects
  - Design for recycling: minimize gels and discoloration, last longer

- Continuous evolution to even **safer additives**
  - Eliminate additives with potential future health and safety concerns, and perceptions, example: fluoropolymer PPAs

How are chemical additives regulated?

UN GHS - Globally Harmonized System of Classification and Labelling of Chemicals

- Framework to identify and classify potential hazards using an unified system for governments and industries around the world.
- The chemical industry encourages countries to adopt UN GHS to enhancing chemical safety regulations.

EU CLP = European adaptation of UN GHS

Hazard Identification and Communication Frameworks

Chemical Management Regulatory Frameworks

Additives are regulated for safety under:

- Chemical management regulatory frameworks:
--Risk assessment of product safety and toxicological data to determine the entry of each substance into a country;
--Cover the all life-cycle of the substance;
--Can lead to reporting requirements, restriction or prohibition.
→e.g. US TSCA, Canada CEPA, EU REACH, Korea K-REACH, Japan CSCL, Australia AICIS…

- Global environment agreements:
Multilateral environment agreements that evaluate substances based on the overall hazard and risks.
→e.g. Stockholm Convention…

Use of Specific Regulatory Frameworks

Plastics and its additives are regulated in specific uses. E.g.:

Food contact packaging
- **Regulatory frameworks**: e,g. European Food Safety Authority (EFSA), US Food and Drug Administration (US FDA).
- **Objective** - Protect the safety and integrity of the food for human consumption.
- **How** - Evaluation of the levels of substances in the food packaging and its migration into food.
- **Scope** - Cover all materials, beyond plastics; Broad coverage; Require pre-market approval; Considers exposure; Set a high standard for safety; Ongoing risk assessments and updates.

Medical and pharmaceutical uses

Children's products

Source: ICCA white paper – Annex III – Overview on major chemical management regulatory frameworks covering Additives