UNIVERSITI MALAYSIA TERENGGANU

Polymer and Environment
KEJ4604
Semester II 2015/2016

GROUP 3

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18 April 2016

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Recap

Environmental Stability

- The ability of a polymer to remain unchanged over time in the influence of environmental agents.

Environmental Agents:

1. Heat
2. Light
3. Moisture, oxygen and other aggressive gases
4. Bio-active organism

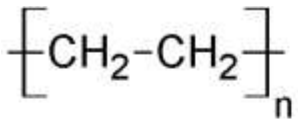
Heat

- Polymer may decomposed when heated.

Light

- The energy of the UV component of natural light is sufficient to break chemical bonds in polymer.

Industrial Polymer



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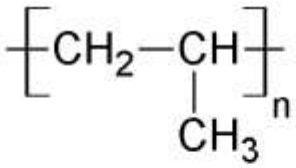
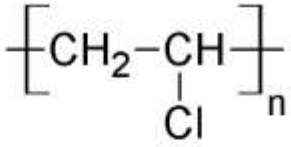
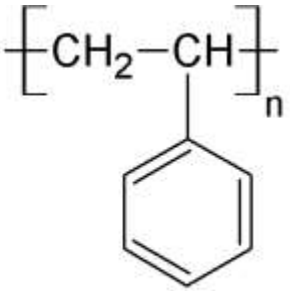


PP



PVC



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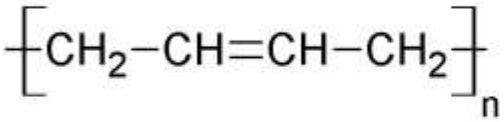

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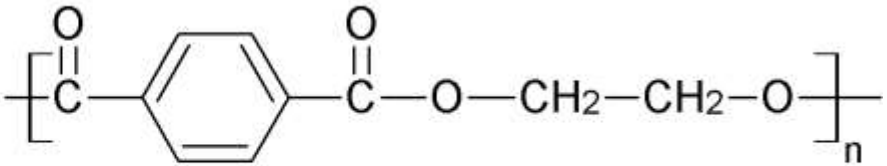

PET

Harmful effects in the production, processing and application of polymers:

- Light – Photo degradation
- Oxygen – Oxidative degradation
- Heat – Thermal degradation

What is Stabilizer?

The term stabilizer is the comprehensive technological term used to describe the inhibition (prevention) of polymer degradation.

- Stabilizer is the key component of an additive system.

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Why to use stabilizer in polymer?

- Improve processing conditions
- Obtain better impact resistance
- Increase or decrease hardness
- Control surface tension
- Control blocking
- Increase flame resistance

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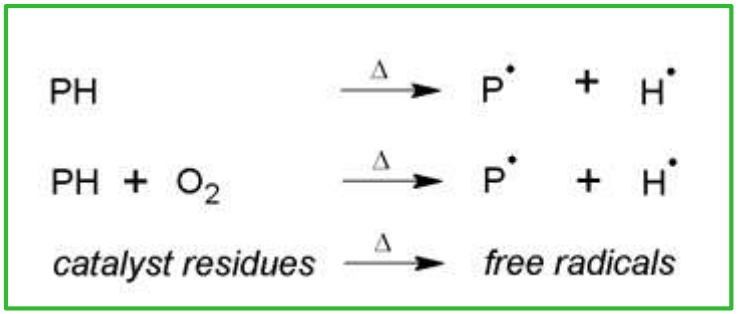
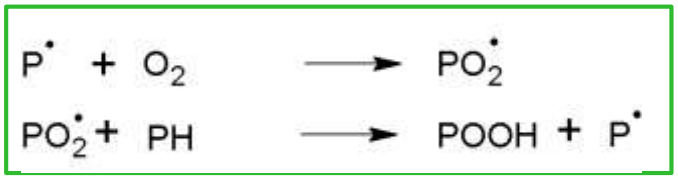
HEAT STABILIZER

Mechanism of thermal oxidation of polymers

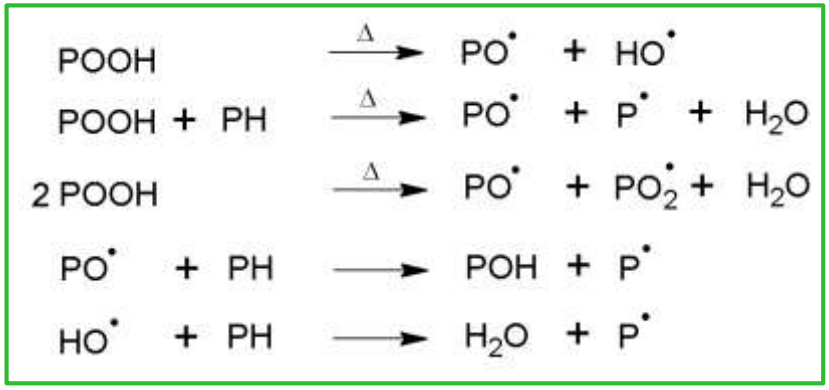
1) Chain initiation



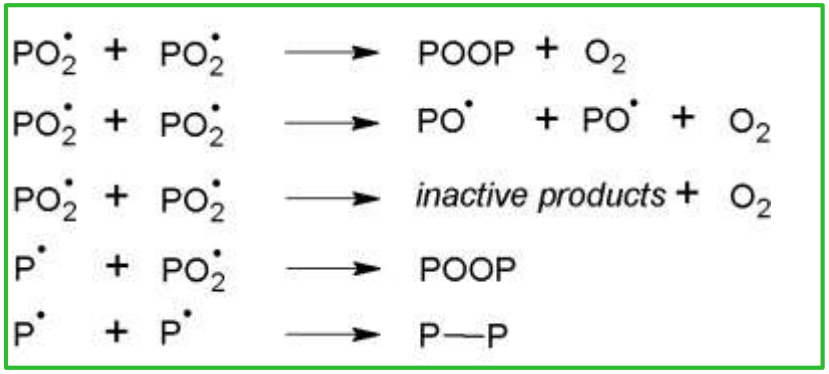
2) Chain propagation



3) Chain branching



4) Chain termination



Methods to Prevent Thermal Degradation

Method #1

Primary (chain breaking)

- Interfere with the chain propagation step

Method #2

Secondary (preventive)

- Destroy hydroperoxide groups

Stabilization by chain-breaking antioxidants

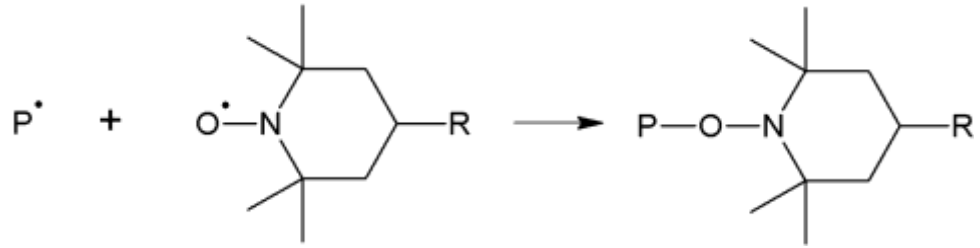
Two reaction mechanisms by which antioxidants interfere with chain-carrying radicals:

- Chain-breaking donor mechanism (CB-D)

  phenols, disubstituated phenols,
  secondary aromatic amines

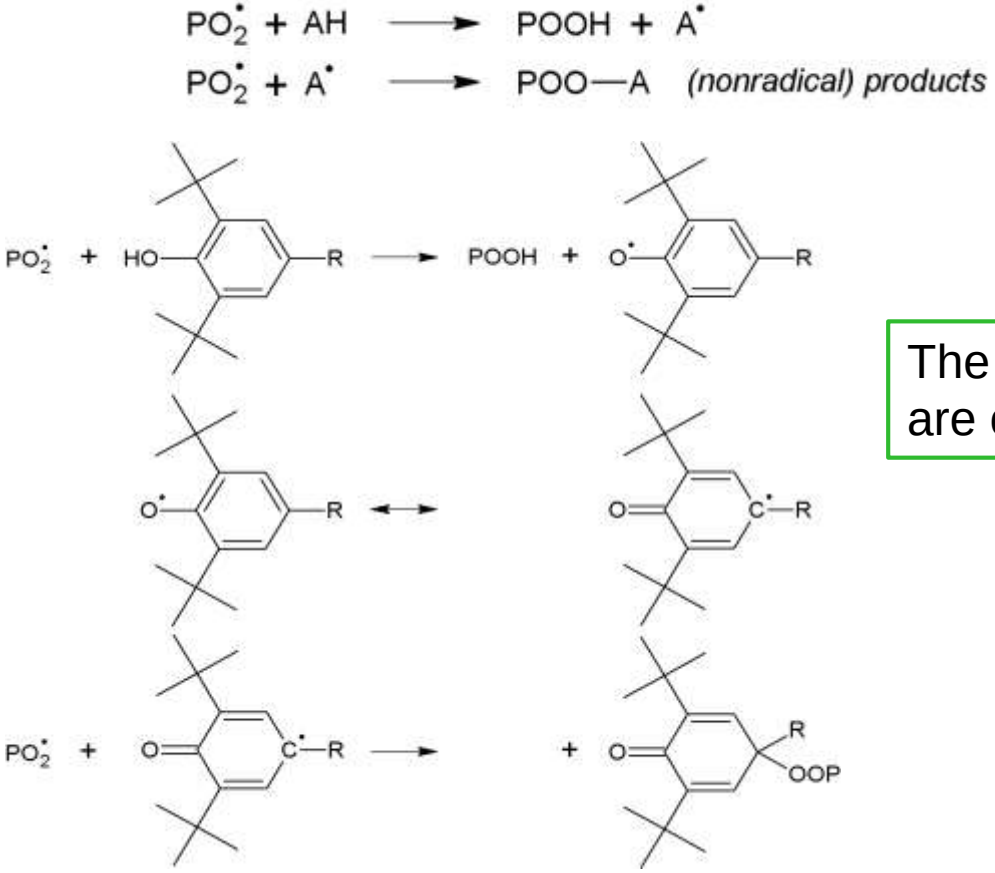
- Chain-breaking acceptor mechanism (CB-A)

  quinone-type compounds
  stable free radicals: e.g. piperidinoxyl-compounds



Chain-breaking donor mechanism (CB-D)

The radical abstract a H atom from the inhibitor (AH) which is transformed into the radical (A•) which can interact with another peroxy radical:



The most widely used antioxidants are ortho-disubstituated phenols.

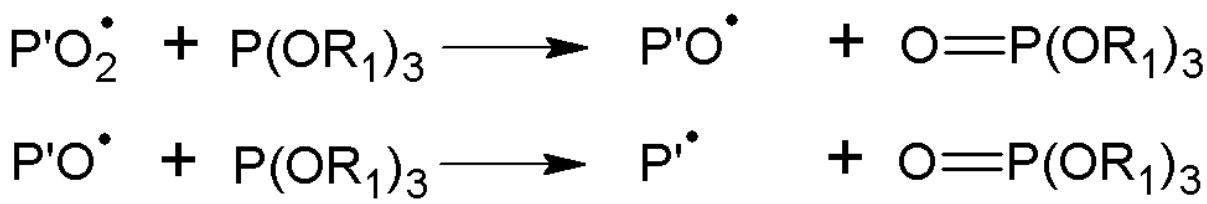
Stabilization by secondary (preventive) antioxidants

By decompose hydroperoxides without intermediate formation of free radicals.

- Phosphites

  reduce hydroperoxides to the corresponding alcohol and are transformed into phospates:

  can react with peroxy and alkoxy radicals:

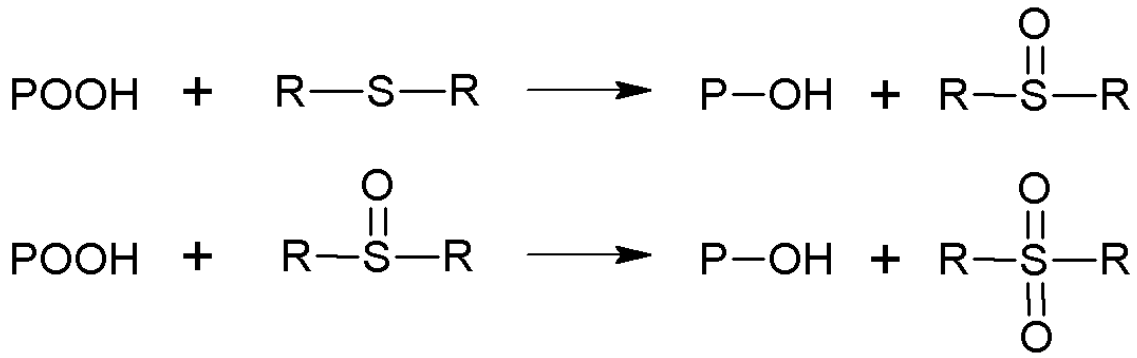


Stabilization by secondary (preventive) antioxidants

Decompose hydroperoxides without intermediate formation of free radicals.

- Organic sulfides

  transform two molecules of hydroperoxide into alcohols:

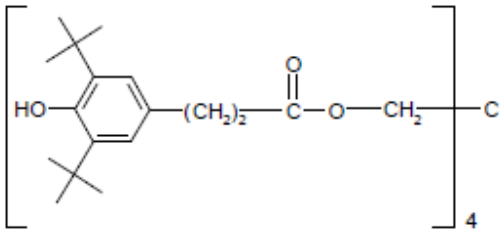


Commercially used antioxidant

- Depending upon the type of oxidation , various heat stabilizers :

I. Metallic salts (stabilize PVC) – barium cadmium, barium zinc
II. Organometallic compounds – based on tin
III. Non metallic organic stabilizer -phosphites
IV. Epoxies – derivatives of soya bean oil

- Phenolic antioxidant are typically added to the polymer(**plastics, synthetic fibers, elastomers, adhesives, waxes, oils and fats**) to ensure good melt processing stability and long term thermal stability.
- The role of phenol based antioxidants is to donate hydrogen atoms to quench free radicals, as well as to generate phenoxy groups which can also scavenge free radicals.



- Mostly stabilizer used contained heavy metals (e.g. lead carbonate, cadmium and barium carboxylates)
- Due to their potential toxicological effects in the human environment it has been replaced by Zn and Ca which is less toxic and give very transparent PVC for bottles.
- Heat stabilizers as additives for polymers increase the overall ability of the plastic to withstand the negative effects of exposure to heat/high temperatures.

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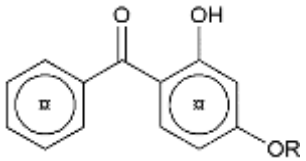
LIGHT STABILIZER

What is Light Stabilizers?

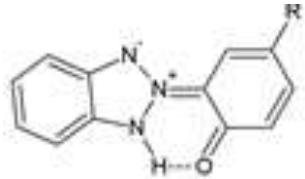
- Light stabilizer are chemical compounds capable of interfering with the physical and chemical processes of light-induced degradation.

Types of Light Stabilizers

- **UV absorbers:** absorption of harmful UV radiation and it dissipation that does not form heat. Need a thickness.

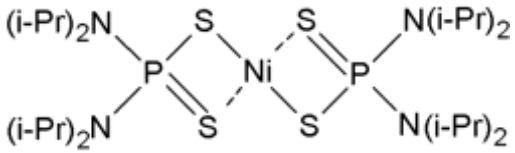


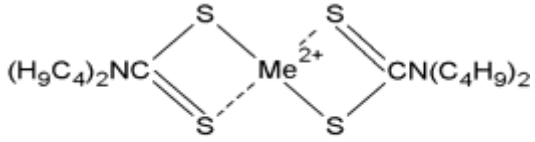
dihydroxybenzophenones



Hydroxyphenyl benzotriazoles

- **Quenchers of excited states:** light stabilizers able to take over energy absorbed by the chromophores present in the plastic and to dispose of it efficiently to prevent degradation.
- **Hydroperoxide decomposers:** metal complexes of sulfur-containing compounds such as dialkyldithiocarbamates, dialkyldithiophosphates and thiobisphenolates.





Me= Zn, Ni

- **Free radical scavengers:**

✓ analogous to that used in prevention of thermal degradation

  - ➢ some phenolic antioxidant can improve the light stability

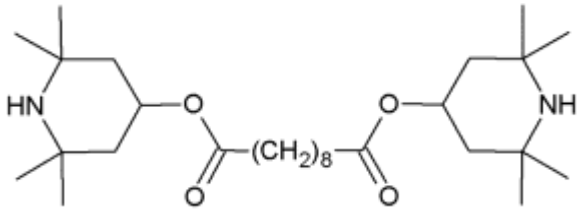
- Polymer will be unstable when exposed to UV light with wavelength 280-400nm.

Carbon Black

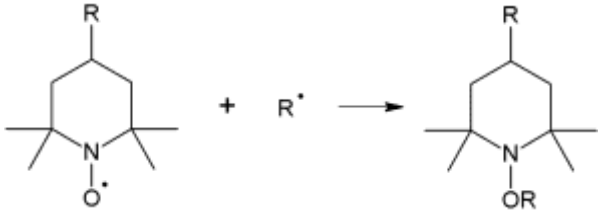
- Carbon black is the most effective light absorber, it also contain antioxidant groups (phenolic and quinonoid) as part of the polycyclic ring system.
- Carbon black normally unacceptable for aesthetic reasons except for specialized applications such as piping.
- Although not as effective as carbon black, titanium dioxide (a white pigment) is widely used to 'screen' plastics from the effects of UV light for example PVC window profiles.

*Hindered Amine Light Stabilizers (HALS)

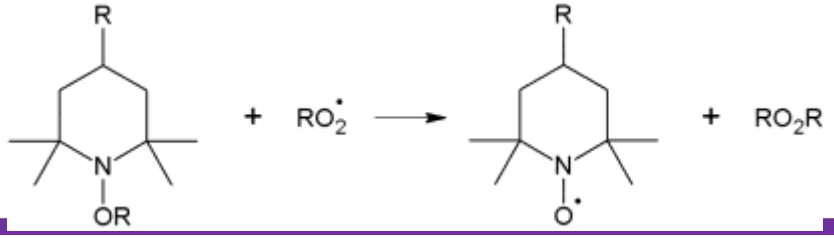
- **Free radical scavenger**
- **Does not absorb any light above 250 nm**



- **Mechanism (*„Denisov cycle"*):**
  - under photooxidative conditions sterically hindered amines are converted to the corresponding nitroxyl radicals
  - nitroxyl radicals combines with alkyl radicals and hydroxylamine ethers form in this reaction



  - peroxy radicals can react very quickly with hydroxylamine ethers and regenerate nitroxy radicals



Conclusion

Advantages

- To increase polymer's
  - ✓ appearance
  - ✓ strength,
  - ✓ elasticity,
  - ✓ durability
  - ✓ performance characteristics

Disadvantages

- Further functionalization reactions, which are often expensive and time consuming.

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References

1. Kasza, G. 2013. Thermal, antioxidative and photochemical stabilization of polymers: low molecular weight versus macromolecular stabilizers. *Advanced bio-friendly polymers.*
2. Yousif, E., El- Hiti, G. A., Haddad, R. and Balakit, A.A. 2015. Photochemical Stability and Photostabilizing Efficiency of Poly(methyl methacrylate) Based on 2-(6-Methoxynaphthalen-2-yl)propanoate Metal Ion Complexes). *Polymers*. 7, 1005-1019.
3. Scott. G. 1999. Polymer and The Environment.
4. Lambert. S. 2013. Environmental Risk of Polymers and Their Degradation Products. *Environment Department.*
5. Markarian J. 2005. Advances in PVC Heat and Light Stabilization. *Plastics Additives and Compounding.*
6. Platzer, N.A.J. 1968. Stabilization of Polymers and Stabilizer Processes. *American Chemical Society*, 85.