Photodegradation & Photostabilization of Polymers.

Dr. Ahmed A. Ahmed

Lec.4

Different Types of Degradation

- Chemical Degradation
- Thermal Degradation
- Biodegradation
- Radiolytic Degradation
- Mechanical Degradation
- Photodegradation

Photodegradation

Photodegradation is degradation of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, such as infrared radiation, visible light, and ultraviolet light.

Factors Causing Photodegradation

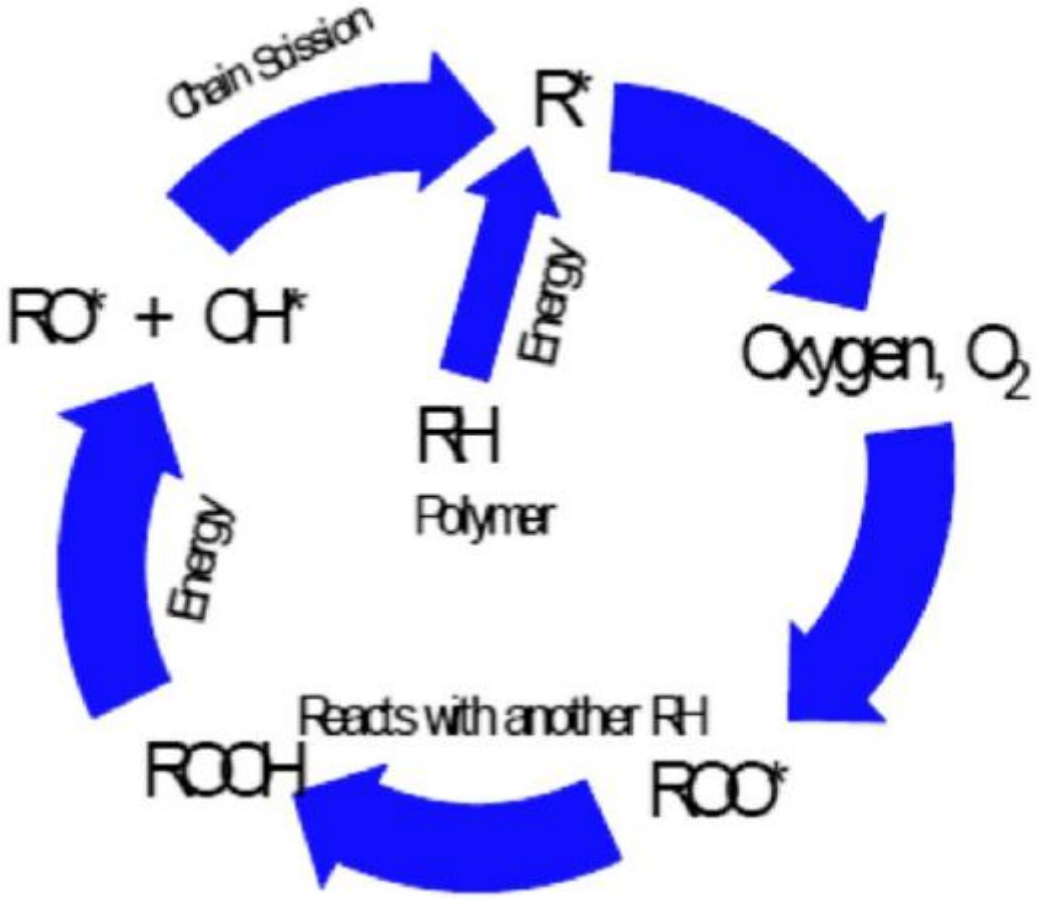
INTERNAL IMPURITIES

- Hydroperoxide
- Carbonyl
- Unsaturated bonds
- Catalyst residue
- Change transfer (CT) complexes with oxygen

EXTERNAL IMPURITIES •

- Traces of solvent, catalyst,etc.
- Compounds from a polluted urban atmosphere and smog
- Additives
- Traces of metal & metal oxides from processing equipments & containers, such as Fe, Ni or Cr.

Reaction Cycle



Effects of Photodegradation & Need for Photostabilization

1-Loss in physical properties

2-Discolouration

3-Hence in order to avoid such problems in the service life of any product we give photostabilization effect to the polymer.

Photostabilization

Photostabilization is the retardation or elimination of the photodegradation of any polymer.

Stablizers are classified as:

- Light screeners
- UV absorbers
- Excited state quenchers
- Peroxide decomposers
- Radical scavengers

Factors affecting thickness of absorber coating

The amount of the absorber required to provide economical protection in a polymer depends on:

1-Thickness of the polymer product

2-Tolerance of colour

3-Effect of high concentration of absorbers on it

4-Compatibility of the absorber with it

Mode of action of UV absorbers

- It interacts with the first step of the photo-oxidation process.
- It absorbs the harmful UV radiation before it reaches to the photo active chromophoric species in the polymer molecule (300-400nm).
- Hence, energy dissipates in the manner that does not lead to photosensitization.
- A UV absorber should be light stable.

Light Screeners

- Application of a coat of material on the polymer to screen it from photodegradation.
- Some examples are pigments, carbon black, etc.
- The energy that attacks the chromophoric group is absorbed and dissipated in a manner that it does not affect the polymer.

Pigments

- Pigments are insoluble inorganic or mineral and organic compounds of complex structure.
- Powdered metal Aluminium is an excellent reflector to UV light.
- Fe_2O_3, Fe_3O_4, ZnO, TiO_2 are inorganic pigment excellent UV screener.
- Organic pigments such as azo and anthraquenone display good UV light absorption.

Benefits of using Pigments

- Cost reduction
- Reinforcement
- Hardening
- Improving slip and skid resistance
- Colour effect
- Storage stability

Pigment as a Light Screener

- Pigment as a light screener should be:
- Light stable for long term performance without fading.
- Heat stable to withstand polymer processing conditions.
- Migration resistant.
- Low cost.
- Non-toxic.

Radical Scavengers

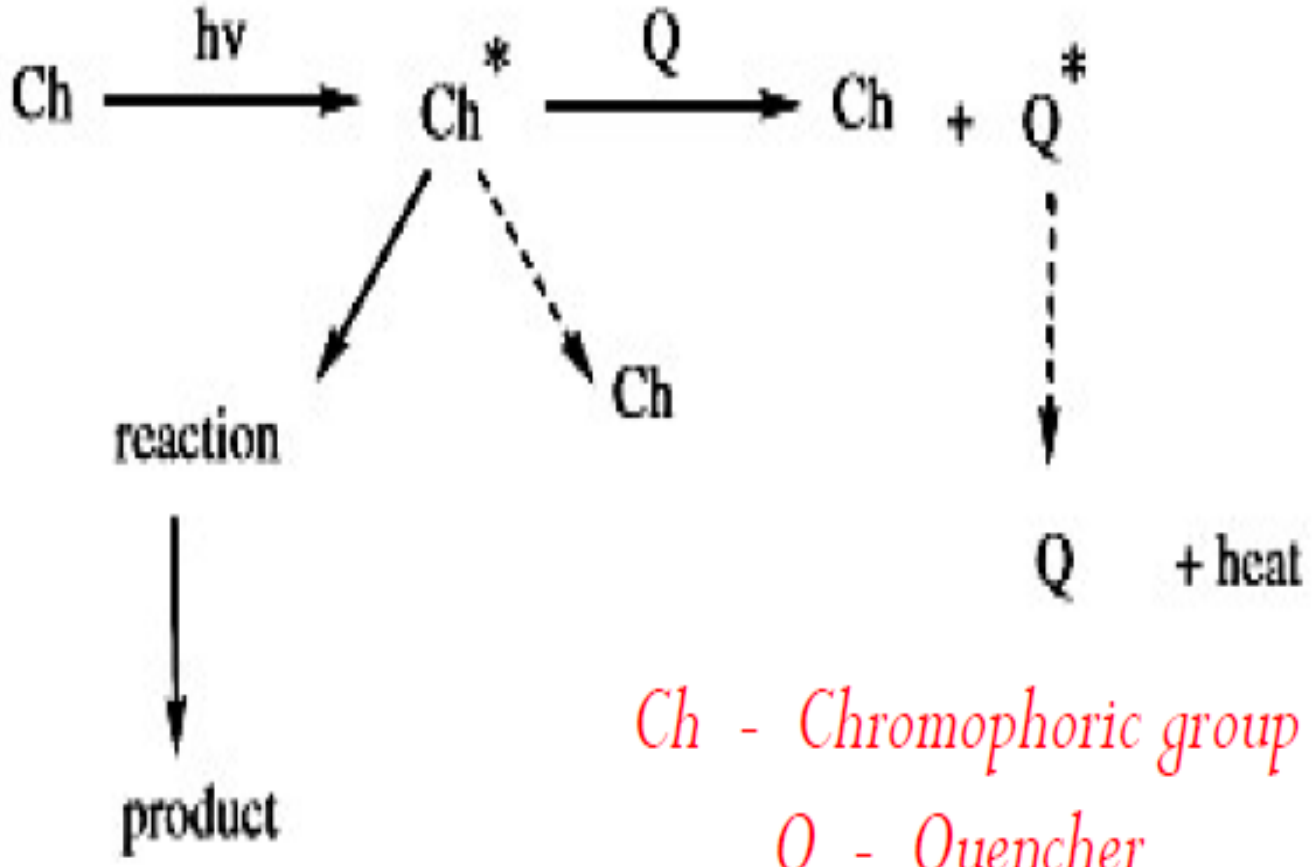
- The radical scavengers operate by interfering with the propagating step in the oxidative chain and this can be achieved by two routes:
- Reaction with propagating radicals (R., RO., ROO.).
- Reaction with resulting hydroperoxides which are the source of chain branching through the propagating process.
- Quinones react with alkyl radicals to form radicals that do not initiate polymer oxidation.

Quenchers

- Quenchers deactivate excited states of chromophoric groups in polymers before bond scission can occur by two mechanisms:
- Energy Transfer Process
- Intermolecular Energy Transfer
- Intramolecular Energy Transfer
- Chemical and / or Physical Deactivation

Quenching Mechanism

- There are two mechanisms:
- Long range Energy Transfer
- Contact (Collisional) Energy Transfer



Ch - Chromophoric group

Q - Quencher

Carbon Black

- Acts as an UV absorber as well as a radical scavenger.
- Carbon black absorbs UV radiation more efficiently than conventional coloured pigments.
- Carbon black consists of functional groups such as carbonyl, hydroxyl, quinone, ether, etc. that as a radical scavenger.

Conclusion

- Complete stabilization of polymers against photodegradatoin is not possible, hence the additives must decompose –OOH, and acts as quenchers of some excited state in the early stages of photodegradation.
- The "hydroperoxide" (POOH) is the most important initiator in the photooxidative process. Hence it must be quenched.

Innovative Stabilizations

- Use of PTFE (teflon) as a light screener due to its high bond dissociation enthalpy.
- Application of coatings with high refractive index difference with air will lead to better stabilizing effect. (Concept of Rubber paints).