Polymer Degradation

Process which deteriorates polymer properties or their outward appearance

Any process which inhibit or retard the degradation process is called polymer stabilization

      Eg. Discolouration
      Stiffening etc

Factors Causing Degradation

- Heat
- Mechanical energy
- Radiation
- Ozone

Dissociation energy   C–Cl   65 kCal / mol
                            C-F   108 kCal / mol
                            C-C   75-85 kCal / mol

Heat – during processing, Mechanical energy during processing , grinding etc gives sufficient energy. Radiation (UV) with λ 300 A (~ 95 kCal / mol) also can cause breakage of bonds

Changes Due to Degradation

- Chains undergo scission
- Crosslinking
- Oxidation
- Other chemical reactions

Factors Affecting Polymer Stability

1. Chemical structure
2. Chemical composition (What kinds of bonds and what sort of arrangement)

    Eg. Bond energy are different or different bonding (different depending on the chemical groups to which that form belongs)

C2H5 – H	99 kCal/mol
C3H7 - H	98
C6H5-CH2-H	83
C3H7-CH3	83
C6H5-CH2-CH3	72

    Tertiary allylic bonds are weaker than primary. Their presence sweaken the molecule. The degradation always starts by the scission of the weakest
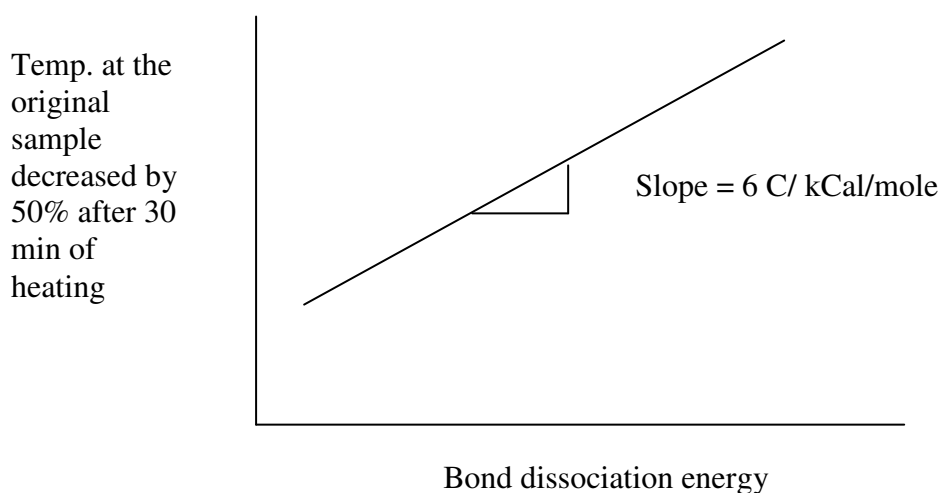
available bond or with an attack at this site and first step usually determines the further direction of the process

3. Other factors of chemical structure

- Steric facftors
- Resonance stabilization
- Tacticity
- Physical and morphological factors
- Internal mechanical stresses
- Contaminants

Bond dissociation of energy of groups CH3 – R bonds

-R	Energy
-CH3	88.4 k Cal/mol
-C2H5	84.5
-n C4H9	84.7
-t-C4H9	80.5
-n C3H7	84.9
-i-C3H7	83.8

Temp. at the original sample decreased by 50% after 30 min of heating

Slope = 6 C/ kCal/mole

Bond dissociation energy

Ie. An increase in dissociation energy of 5 kCal / mol causes approximately 30 C increase of the half weight loss temperature.

Tacticity

Syndiotactic PVC has increased stability than the ordinary (atactic) PVC

Physical and Morphology

Oxidation is initiated in the amorphous phase of semi crystalline polymers and propagates to crystalline regions – results in destruction of crystalline order

Diffusion

Incompact materials diffusion of oxygen is less. Hence they are more stable. But in PVC auto catalytic degradation is more in compact systems as HCl is not easily eliminated by diffusion. Ie. Less compact PVC is more stable.

Internal mechanical stress – stress as

   Sources of later mechanical deterioration
   Inititation of or assistants to various chemical attacks

Contaminants

Ingredients – forms radical – which may then attack the polymer
Additives – some undergo radical formation which may then attack polymer.

Types of polymer degradation

- Thermal
- Thermooxidative
- Photo
- Photooxidative
- Mechanical
- Hydrolytic
- Chemical
- Biological
- Degradation by irradiation
- Pyrolysis
- Oxidative pyrolysis

Various reactions undergone by polymers

- Random chain scission
- Depolymerization
- Crosslinking
- Side group elimination
- Substitution
- Reactions of side groups among themselves

Depolymerization

Essentially a reversal of polymerization process

Ie. It consists of
   Initiation at chain ends
   Depropagation
   Termination

Other reactions like chain scission etc also do occur in a predominantly depolymerization reaction

    Eg. PMMA - depolymerization occurs at   250 C
                            Random chain scission   300 C
                            Loose methanol   320 C

Depolymerization is favoured if

- Initiation by main chain scission is possible
- Intermediates of the process are stable
- The unzipping of monomers requires a relatively small activation energy

Initiation at the chain end is preferred as this avoids other reactions. For this chain end must be weak. (eg end double bond formed by disproportionation)

The radicals formed must be stable enough not to participate in side reactions

Steric factors also affect

Monomer yield 0.7%   Monomer yield >90%

Under these favourable conditions only depropagation steps occur.

Energy

Activation energy of depropagation = activation energy of polymerization propagation + heat of polymerization ΔH_p

Lower the ΔH_p higher is the probability of depolymerization.

Polymer	ΔH_p
PS	16.7
PMMA	13.3
α-methyl styrene	8.4

Any modification of a polymer which would prevent the initiation step of depropagation would stabilize the polymer eg. methylation or acetylation of terminal Oh of polyformaldehyde raises degradation temperature.

Degradation

Loss of desirable properties with time in the presence of external agencies like Oxygen, ozone heat , light nad radiation.

In 1861 Hoffman demonstrated that oxygen is involved in the degradation of rubber

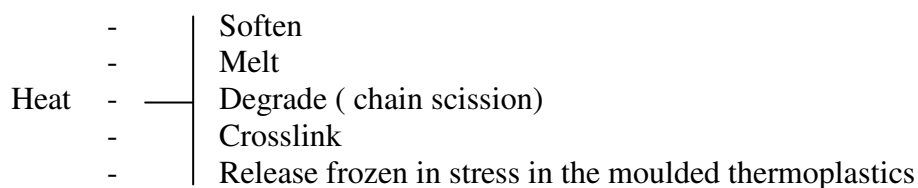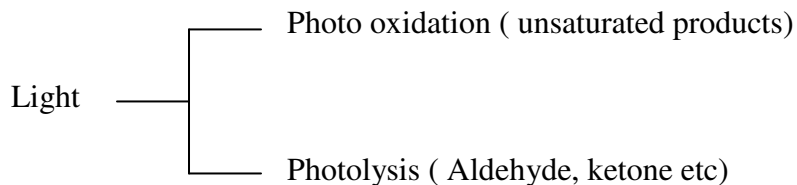Polymer can be destroyed by a variety of environmental agents.l

Eg. Condensation polymers undergo chain scission (by hydrolysis eg. amides, esters and urethanes,)
2. in the absence of light most polymers are stable for long periods at ambient temp.
3. eg. PP is sensitive to phototoxidation. Sun light accelerates the rate of oxidation which may be accelerated by atmospheric pollutants capable of being activated to free radiacal species. Eg N and S oxides.

So PP without a proper stabilizer is a poor choice for out door application

Photolysis gives unsaturated product at broken chain ends.
Photo oxidation gives aldehydes , ketones and acids either along or at the end of the polymer chain.

```
                    ──────  Photo oxidation ( unsaturated products)
                  ┌─
Light   ─────────┤
                  └─
                    ──────  Photolysis ( Aldehyde, ketone etc)
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        -  │  Soften
        -  │  Melt
Heat    -  ───  Degrade ( chain scission)
        -  │  Crosslink
        -  │  Release frozen in stress in the moulded thermoplastics
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Stabilizers are used to counter the various types of degradation processes
Eg. Flame retardants are used to fight flammability. Antioxidants are used to reduce oxidation etc.

Antidegradant is used to encompass heat stabilizer, anti fatigue agents and antiozonants.

Degradation reaction can be studied by monitoring the mol wt by using thermal analysis, spectroscopy and chromatography etc,.

Eg.   viscometry
        Osmometry
        Light scattering
        Ultracentrifuging
        GPC
        TGA
        DSC
        Thermal Volatalization Analysis

Since most polymers degrade by oxidation, the kinetics of degradation (of the formation of functional groups) can be studied by following eg. by IR studies.

Thermal Degradation

Degradation reactions that occur in the presence of thermal energy – classiefied into two:

- Depolymerisation (main chain reactions)
- Substituent reactions

Depolymerisation reaction is characterized by the breaking of the main polymer chain backbone so that at any intermediate stages the products are similar to the parent material in the sense that the monomer units are still distinguishable. The ultimate product may be the monomer. Eg. PMMA. This is called Unzipping.

Volatile chain fragments like the range of short- chain alkanes and alkenes from PE are formed in certain cases. This is called unbuttoning.

In the substituent reactions the substituent attached to the main chain undergoes reaction so that the chemical nature of the repeat unit is changed although the chain structure may remain intact. Volatile products if at all formed will be different from the monomers

Eg.

Polyacrylonitrile   cyclisation of PAN

Elimination of HCl from PVC.

Thermal degradation reaction maily proceeds via free radical reaction

Some of the typical radical depolymerization reactions are given below

<u>PMMA</u>

Simplest depolmerization reaction is that of PMMA in which monomer is obtained in tantitative yield.

The degradation in the region of 300 – 400 C is associated with scission of polymer chain at random along its length to form radicals.

The olefinic double bonds at the chain ends formed due to disproportionation reaction during polymerization reaction during polymerization (FR) weakens the adjacent singma bond and is probably the most common reason for instability in polymers

This makes the bond weaker because of the stability of the allylic radical formed.

The active chain end thus formed can further unzip to give MMA

Polystyrene

The PS degrades in a single step and the monomeric styrene is the principal volatile component formed (Thermal Analysis). Other are benzene, toluene etc. Some oligomers are also formed by intramolecular transfer reactions

Oligomers are formed

These are called unbuttoning. This takes place due to the presence of α - H atom.
When α - H is replaced by methyl group, the transfer is completely eliminated

| Polymer	% Monomer
Styrene	42
MMA	100
Methacrylonitrile	100
α–deuterostyrene	70

PE

- Degradation produces hydrocarbons with 1-70 carbon atoms.
- Depropagation is not significant, as little monomer is produced. But large proportion of monoolefins   is mormed b intramolecular transfer process.

A portion of the larger fragments are formed by the inter molecular transfer reactions.
Propene and 1-hexene are most abundant volatile products.

This is because of favourable transition state involving a six member ring

In PE the molecular weight decreases to a limited extent even at much lower
temperature than those at volatile products appear. This is attributed to the presence
of weaker link in PE. These are peroxides, carbonyls, chain branches and unsaturated
structures. One double bond appears for each chain scission. The double bonds may
be of 3 types.

 R-CH=CH=R' > R   C=CH2   R-CH=CH2
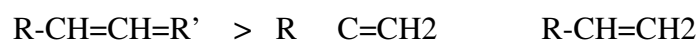
The peroxides may abstract one H in unbrached parts fo the molecules or at near
chain braches.

General mechanism of radical depolymerization

It involves:

1. Random initiation
2. Terninal initiation
3. Depropagation
4. Intramolecular transfer and scission

   Inter molecular transfer
   Scission

5. Termination

   n= chain length of the starting material
   Mi^*, Mj^* are long chian radicals
   Mi, Mj long chain 'dead' polymer molecules.

Non – radical depolymerization reactions

Eg. Polyesters

The maor initial step in all cases where β H atoms are available is invariably alkyl – oxygen scission involving six membered ring transition stage resulting in vinyl and carbonyl end groups.

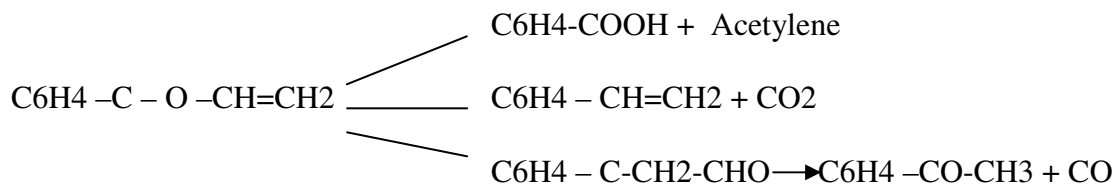Difference in the ultimate pattern of degradation products are due to differences in the structure of the end groups.

For aliphatic polyesters

   CO_2
   Cyclic ketones
   Cyclic aldehydes
   Water

Aldehydes ⎤
Dienes ⎬
Cyclic ethers ⎦   (from vinyl group)

Terephthalic acid, acetaldehyde and CO are the principal volatile products. The overall reaction is complex and

Anhydride
Benzoic acid
p- acetyl benzoic acid
acetophenone
vinylbenzoate
ketones
water
methan
ethylene
acetylene etc have been detected

$$C_6H_4-C-O-CH=CH_2$$

⎧ C_6H_4-COOH + Acetylene

── $C_6H_4 - CH=CH_2 + CO_2$

⎩ $C_6H_4 - C-CH_2-CHO \longrightarrow C_6H_4 -CO-CH_3 + CO$

Substitent reactions

In higher polmermethacrylates degradation of the ester groups may occur with the evolution of corresponding olefins.

P(tert-butyl methacrylates)

The ester decomposition mainly becomes important when the monomer unit incorporates at least five hydrogen atoms on the beta carbons.

Eg.
Methyl methacrylates   0 (mainly depolymerization)
Tert-butyl methacrylates   7 (ester decomposition)
Isobutylmethacrylates   1 (depolymerization)

In polymethylacetate

The reaction is facilitated by electron attracting groups in the vicinity. That is why the bond formed causes reactant to pass from unit to unit along the chain by:

The colour gradually passes from yellow to orange to red with evolution of HOAC.

PVC

With very fine powder samples the formation of HCl is linear with time. With larger samples, the reactionbecomes autocatalytic   if HCl is allowed to accumulate in the gas phase above the degrading polymer.

HCl elimination associated with more than one type of weak link in the chain. (like chain ends, tertiary structure etc).

The polyee sequence length does not extend ten.

The initiation involves liberation of Cl atom from a labile centre.

The Cl is believed to react with the most adjacent methylene H atoms thus leading to conjugated unsaturation. Occasionally they may escape and attack another chain.

The effect of HCl is assumed to involve cyclic transition state.

Polyurethanes

Methylene bus – (4-phenyliisocyate)

The products formed are (volatile products from thermovolatile analysis, TVA)

Carbondioxide
Butadiene
Tetrahydrofuran
Dihydrofuran
Water

Scheme

At about 210 C all methane linkage disappears without any other products being formed.

Effect of polymer properties on oxidation

Crystallinity -

Rate of oxidation is inversely proportional to degree of crystallinity. Crystallinity increases with degree of oxidation (due to chain breaking and chain orientation)

Tacticity

Stereoregular polymers are more crystalline and are more resistant to oxidation (PP is an exception)

Molecular weight

In solid polymers there no significant effect as both the rate of initiation and rate of termination are reduced.
In solution, rate decreases with molecular weight

Chemical structure.

Higher branching leads to higher rate of oxidation due to the presence of more number of tertiary H atoms and slow termination of tertiary peroxy radicals.

Presence of double bonds results in more allylic positions which are inherently more reactive and hence increases oxidation rate.

Film Thickness

Generally rate of oxidation decreases with increase in thickness as the reaction becomes diffusion controlled

Additives

Many ingredients eg. catalyst residues , processing aids, metallic impurities etc increase oxidation rate.

Oxidation products

First oxidation products are more easily oxidised than the parent polymer. Eg. Hydroperoxides are potentially powerful initiators of further degradation. They decompose thermally , photochemicaly oar catalytically to form free radicals.

Photodegradation

It is the photo –initiated oxidation. Primary effect of light is the generation of free radicals. It has relatively little effect on the propagating steps of the radical chain reactions.

To absorb energy (hv) chromophoric groups must be present. A variety of oxygen – containing groups are formed during the processing of polymers even under normally oxygten – free conditions due to O2 dissolved in the polymer.
Eg. Ketonic, ethylenic and aromatic groups

The absorbed radiation will be attenueated as it passes through the polyumer and the reaction will be concentrated on the surface layers – skin effect.

Ketones are formed by processing at severe conditions and are formed by thermolysis of or photolysis of hydroperoxides.

Ketone can absorb energy and become a triplet state.

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        │              │              │

     Norish I       Norish II         RH
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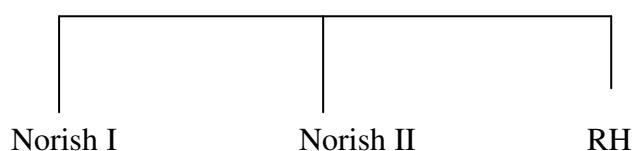
R ──O2──▶ ROO. Which can further react (the initiation).

In the absence of double bond in polyolefin they must be stable. However, the presence of small amounts of impurities or structural abnormalities in the macromoleclar structure;

In PE CO group is the most thermally labile structural entity

In PP the tertiary H is susceptible to oxidation during preparation, storage and processing. The carbonyl and hence, hydroperoxides are both decomposed by UV Vis forming radicals.

The Norrish I initiation of autoxidation does not occur to any significant extent during early stages of photoxidation

Norrish II leads to chain scission but it does not produce any free radicals and hence does not catalyse oxidative degradation.

Aromatic ketones have a higher quantum efficiency for radical formation than aliphatic ketones and photo sensitizers such as benzophenone may be deliberately added to polymers in order to increase their rate of photooxidation

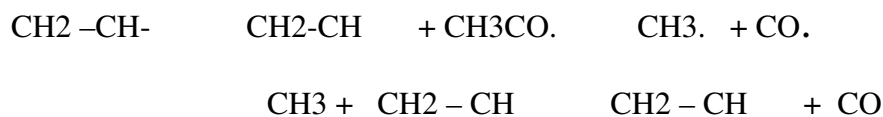It leads to rapid photodegradation of PP but it is ineffective in PE.

Polyketones

Poly(methylvinylketone)

Poly(methylisopropylketone)

Poly(phenylvinylketone)

For (1)   methane, acetaldehyde and CO are the main volatile products.

   CH2 –CH-   CH2-CH   + CH3CO.   CH3. + CO.

                   CH3 + CH2 – CH   CH2 – CH   + CO

CH3. and CH3 CO. abstracts H and CH4, CH3 CHO are formed.

For (2) Monomer is obtained in addition to the above type of reaction due to depropagation,

Norrish type II

Acrylates and Methacrylates

Becomes i Chain scission at atmbient temperature
Crosslinki leads to rapid decrease in molecular weight

But both have identical gaseous products formed eg. methyl formate, methanol, methane, hydrogen, CO and CO2 from the ester group.

Ie. UV reaction causes scission of ester groups leaving

While in solution, this does not happen as the radicals are separated by solvent.

In styrene tertiary hydrogen is removed as

The reaction proceed by the evolution of H2

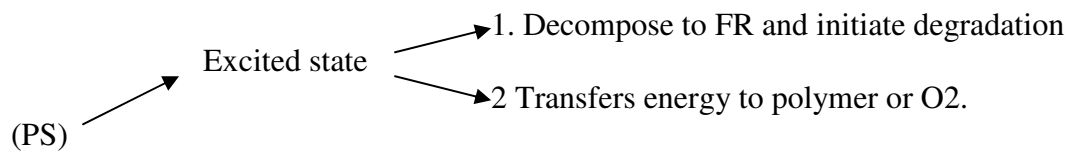Makes the alpha hydrogen more labile so that it will react more readily.

Sensitised photodegradation

Photodegradation is fast when chromophoric groups like C=O are present.

This can be used to facilitate easy degradation of otherwise useless plastic materials. (Controlled service life eg. of plastic film used for protection of plants)

These are sensitised for photodegradation bt also stabilised to an extent which ensures them preplanned service life.

Photosensitiser (PS) has high absorption coefft.

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                              →1. Decompose to FR and initiate degradation
            Excited state ⟨
        →                     →2 Transfers energy to polymer or O2.
(PS)
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Eg.,

Polycyclic aromatic compounds such as naphthalene, anthracene etc transfers energy to ground state O2.

Aromatic ketones either abstract hydrogen or decompose after excitation

Quinones behave similarly

Nitrogen containing chromophores eg. Azo, Nitroso and Aromatic amino compounds decomposite to radical by UV

Eg 2-chloro 2- nitroso propane sensitizes polyisoprene.

Trichlorosuccinimide
Dyes (methylene blue for cis 1,4 polyisoprene)
Org. disulfides

Inorganic: Iron complexes – Fe (II) and Fe (III) complexes of dithiocarbamates.

Fe(III acetyl acetone

Benzoyl ferocene

Inorganic metal oxides

ZnO, TiO2, FeCl3 etc. Free radicals are formed from these compounds during irradiation

Chromophores incorporated in polymer backbone as comonomer leads to photo-degradation of polymers

- Copolymers of ethylene with CO
- Methylamethacrylate with methylvinylketone
- Styrene with phenyl vinyl ketone

Carbon monoxide in the side chain is more effective

Polymers with unsatureated bonds in the main chain are sensitive to photodegradation

Bio degradation

Microorganisms generally cause degradation. However, they do not have polymer – specific enzymes. Polymers are to be initially broken down to smaller fractions

Biodegradability requires

- Low molecular weight.
- Presence of certain end groups
- Polarity
- Hydrophilicity

Eg polystyrene is stable but PS copolymerised with vinyl ketone is biodegradable.