Oxidationof polymers

Degradation taking place in the presence of oxygen and temperature

It is auto catalytic in nature with a stabilizing effect at higher level of temperature
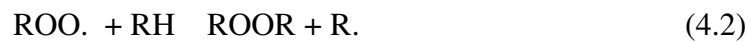
Ie. The rate gradually accelaerate to a constant value

It is possible because of the diradical nature of oxygen. O2 exists as

$$O - O$$

(low activation energy process being a radical forming process)

These can get attached to polymer radical

$$R. + O2 \quad RO2. \tag{4.1}$$

$$ROO. + RH \quad ROOR + R. \tag{4.2}$$

It requires breaking of C-H bond, hence higher activation energy except in case where the R. radical formed is stabilized.

$$C= CH - CH2 - CH = C$$

$$C = CH - CH - CH = C$$

$$C - CH = CH - CH = C$$

In most cases the rate of this step determines the overall rate of the reaction

Termination

$$2R. \quad R-R \tag{4.3}$$

$$R. + ROO. \quad ROOR \tag{4.4}$$

$$2ROO. \quad ROR + O2 \tag{4.5} \text{ major part}$$

(since the alkyl peroxyl radicals are the dominant radical species present in autoxidation)

4.3 and 4.4are important in cases where oxygen access is limited by diffusion.

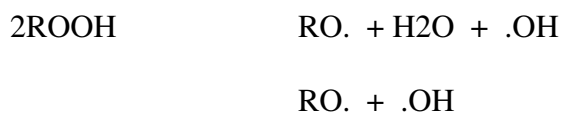At ambient pressures, the rate of oxidation:

.ri is the rate of initiation
Ie. The rate is independent of O2 pressure.

For higly oxidisable hydrocarbons, or at low O2 pressures, the equation is
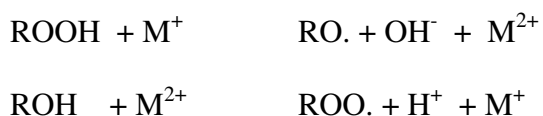
Ie. The rate is O2 dependent

Initiation

The initiation normally occurs by thermolysis or photlysis of hydroperixides formed

$$2ROOH \qquad RO. + H_2O + .OH$$

$$RO. + .OH$$

RO. And .OH are efficient H abstracting agents.

RO.   ROH + R.
Or   .OH H_2O

Transition metal ions like Co, Fe, Mn and Cuar important catalysts for hydroperoxides decomposition

$$ROOH + M^{+} \qquad RO. + OH^{-} + M^{2+}$$
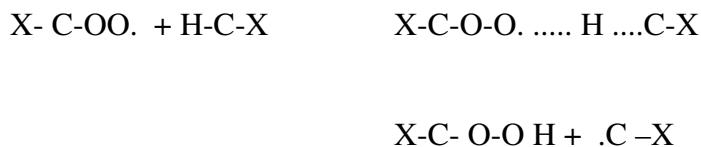
$$ROH + M^{2+} \qquad ROO. + H^{+} + M^{+}$$

Ie. The action of metal ions is to reduce the activation energy of hydroperoxide decomposition.

Effect of chemical structure on oxidation rate

Resistnace to oxidation vary markedly with chemical structure.

The rate constant k4.2 (the abstraction of H by a peroxide radical) depends on the energy of the transition state

$$X- C-OO. + H-C-X \qquad X-C-O-O. ..... H ....C-X$$

$$X-C- O-O H + .C –X$$

In hydrocarbon polymers in soltion the rate of oxidation increases in the series:

$-CH_2$ < $-CH-$ < $-CH$ < $-CH_2-CH=CH-CH_2$ < $-C=CH-CH_2$

Primarily due to electron delocalising effect of attached group. Polar effects are also super imposed.

In polymers containing hetero atoms polarity normally predominates

The rate of oxidation decreases

-CH2- > -CH2-NHCO-CH2- > CH2 –O-CO- Φ > –CH- > -CH -   > -C - > -CH- >

This is not necessarily the order of thermal stability eg. PAN undergoes cyclisation, PVC eliminates HCl etc.

PTFE is the most resistant to thermal oxidation. No autoxidation as there is not labile H.

Minor impurities like branching and double bonds etc largely determine their oxidative stability

Eg. with increasing branching the oxygen uptake increases
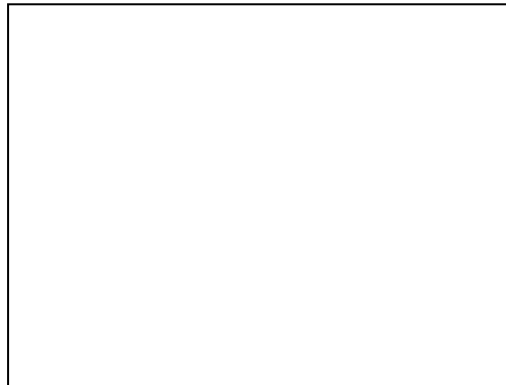
EP copolymer (10.7 Me group / 1000 Carbon),
EP   (21.0)
EP   (35.)
PP   (333)

PS is extremely readily oxidised in solution but in solid form it is relatively stable to thermal oxidation (being below Tg, O2 diffusion is low as segmental motion is restricted)

In HIPS and ABS, the diffusion is easier through rubber domains and these are more susceptible to oxidation.

Degradation during melt processing

Processing – shearing and temperature - polymer undergoes homolytic scission at C-C bonds - formation of macroalkylradicals. These species can initiate radical chain reaction.

Proof

1. Radical scavengers have a profound effect on the reaction
2. In the absence of oxygen there is not appreciable change in molecular weight. With oxygen, the degradation is immediate.
3. Without oxygen these R. radicals can recombine .
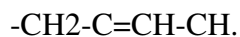4. In Nitrogen atmosphere, 1% benzoquinone causes rapid degradation

NR in nitrogen
NR + 1% benzoquinone in nitrogen
NR + 1% benzoquinone in air.

In NR the bond usually broken is the one between the isoprene units.

-CH2-C=CH-CH.

And this radical is not so reactive and they tend to recombine.

For saturated chains, they tend to abstract H.

In the absence of O2, and in the presence of vinyl monomer, a block copolymer is formed

- CH - =CH –CH2. + =   -C=CH-CH2 [-CH2-C-]n

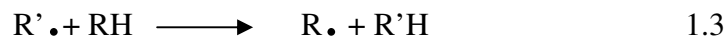-CH = CH- CH2 –OOH
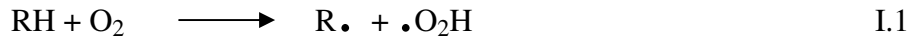
Melt degradation of polymer olefins

Different hydrocarbon polymer behave differently during processing

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A – PP at 180 C closed mixed
B – LDPE at 150 C closed mixer
C – PP & PE in closed mixer after purging with Ar.
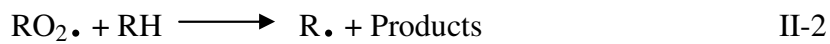
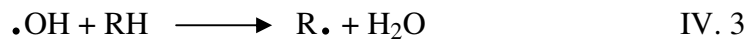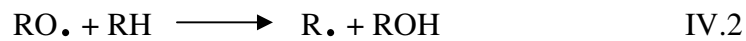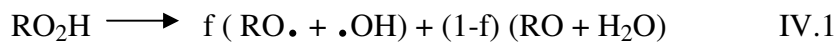## Simplified general mechanism of polymer oxidation

Initiation

$$RH + O_2 \longrightarrow R\bullet + \bullet O_2H \qquad\qquad I.1$$

$$Initiator \longrightarrow {}_2f\ R'\bullet \qquad\qquad 1.2$$

$$R'\bullet + RH \longrightarrow R\bullet + R'H \qquad\qquad 1.3$$

$$\bullet O_2H + RH \longrightarrow R\bullet + H_2O_2 \qquad\qquad 1.4$$

Radical conversion (stabilization)

$$R\bullet + O_2 \longrightarrow RO_2\bullet \qquad\qquad II$$

Chain propagation

$$RO_2\bullet + RH \longrightarrow R\bullet + ROOH \qquad\qquad III\text{-}1$$

$$RO_2\bullet + RH \longrightarrow R\bullet + Products \qquad\qquad II\text{-}2$$

Degenerate chain branching

$$RO_2H \longrightarrow f\,(RO\bullet + \bullet OH) + (1\text{-}f)\,(RO + H_2O) \qquad\qquad IV.1$$

$$RO\bullet + RH \longrightarrow R\bullet + ROH \qquad\qquad IV.2$$

$$\bullet OH + RH \longrightarrow R\bullet + H_2O \qquad\qquad IV.3$$

Termination

$R\bullet$

$2\,RO_2\bullet$

$2R\bullet$

$R\bullet + RO_2\bullet$

$RO_2\bullet + RO_2\bullet$

$\Bigg\}\longrightarrow$ products.

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