Chapter 10
Gowariker.

Polymer Degradation.

Deterioration in properties of polymers is characterized by an uncontrolled change in the molecular weight or constitution of the polymer.

Conventionally, the term 'degradation' is taken to mean a reduction in the molecular weight of the polymer.

Polymer can suffer degradation at two stages of its life

① During the fabrication process
- extrusion/molding etc involve heating which if polymer is unable to endure, can degrade

② During daily usage. - During usage, it faces - mechanical stresses, solar radiations, atmospheric oxygen, moisture, etc.

Useful Advantageous use of degradation -
Use of Heat shield on spacecraft. During re-entry into the atmosphere the polymer shield chars on heating & by degrading protects metal by taking away the severe heat.

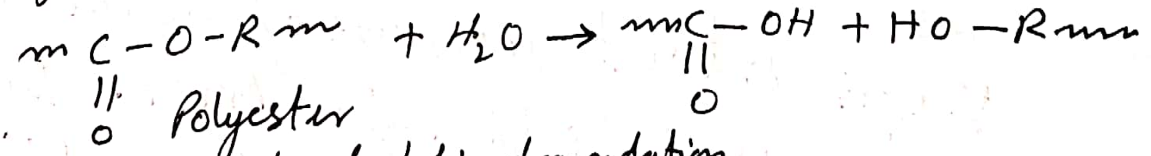
Types of degradation

① Chain end degradation

- starts from chain ends, resulting in the successive release of monomeric units.
- reperse of propagation in chain polymerization
- also called depolymerization or unzipping
  $M_n^* = M_{n-1}^* + M \rightarrow M_{n-2}^* + 2M$ and so on
- example = ~~Ist~~ Poly α methystyrene is ~~punt~~ put into a solvent - anhydrous tetrahydrofuran & heated from -70°c to 60°c. At 60°c; the entire polymer is converted ~~back~~ into the monomer.

② Random degradation.

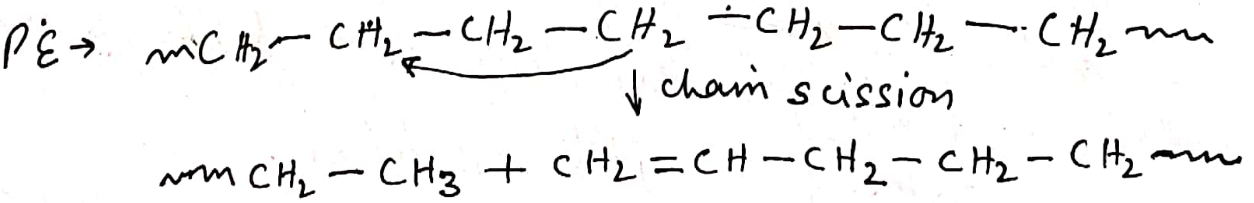
- occurs at any random point along the polymer chain - Reverse of polycondensation:-
  $M_n \rightarrow M_x + M_y$
- Polymer degrades to lower molecular wt fragments but no monomer is liberated.



$$\sim C(=O)-O-R\sim + H_2O \rightarrow \sim C(=O)-OH + HO-R\sim$$

Polyester

hydrolytic degradation.



$$PE \rightarrow \sim CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2\sim$$

↓ chain scission

$$\sim CH_2-CH_3 + CH_2=CH-CH_2-CH_2-CH_2\sim$$

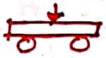
The polymer molecule breaks up while degrading ~~Ir~~ In chain end degradation, the molecular weight drops very slowly and a large quantity of the monomer is released; in random degradation, there is a sudden drop in the molecular weight with little or no release of the monomer.

Degradation of polymers may be brought about either by physical factors such as heat, light or mechanical stress ~~&~~ or by chemical agents such as oxygen, ozone, acids or alkalies.

14-6
p.533

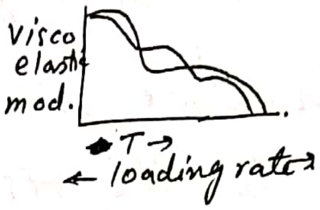
Service performance of polymers

Polymers are rigid below ~~#~~ their Tg. As the temperature is raised beyond the glassy range and into the viscoelastic range ~~&~~ creep and distortion begin to be significant under applied loads. The rate of strain is of course, dependent on the temperature and the nature of the polymer. For this reason, standardized "heat-distortion" tests have been devised.

eg ASTM D648 heats a sample bar, 5 in x 0.5 in x 0.5 in, at the rate  of 2°C/minute while the bar is loaded in flexure. The temperature at which a deflection of 0.25 mm develops is called the heat-distortion temperature. Of course, this temp. varies with the load. Therefore, a calculated "outer fibre" stress of either ~~66~~ 0.455 MPa or 1.82 MPa is commonly chosen. This value gives a reproducible distortion temperature for any given polymer that [illegible], as expected, ~~varies~~ varies significantly among products, even those of the same type, because fillers, plasticizers, molecular weight, and so on are additional factors.

Stress relaxation.

In the discussion of fig



we assumed constant stress and increasing strain. In other situations, ~~to~~ strain is constant, and since viscous flow proceeds, the stress is reduced.

~~You h~~ [eg. Observe a stretched rubber band removed from a bundle of papers after an extended period: The rubber band does not return to its original length. That is why it has not been holding the papers as tightly as it did initially. Some of the stress has disappeared.]

The stress decreases in a viscoelastic material that is under constant strain because the molecules can gradually flow by one another. The rate of stress decreases (−ds/dt) is proportional to the stress level, s*.

$\left(\frac{-ds}{dt}\right)\tau = s$. [τ = (relaxation time) ↳ proportionality constant.]

Here s = shear stress

Rearranging

$$\frac{ds}{s} = -\frac{dt}{\tau}$$

Integrating

$$\ln s/s_0 = -t/\tau$$

$$\boxed{s = s_0 e^{-t/\tau}.}$$

The stress ratio s/s_0 relates the stress at time t to the original stress s_0 at t_0. The proportionality constant τ must have the units of time. It is called the "relaxation time"

When $t = \tau$, $s/s_0 = 1/e = 0.37$

Stress relaxation is a result of molecular movements; therefore we find that temperature affects stress relaxation in much the same manner as it affects diffusion. $D = D_0 e^{-E/kT}$ $D \rightarrow \frac{\text{atoms}}{m^2 \cdot sec}$

Since relaxation time is the reciprocal of a rate : $1/\tau \propto e^{-E/kT}$

$1/\tau = \frac{1}{\tau_0} e^{-E/kT}$

or $\ln 1/\tau = \ln 1/\tau_0 - E/[(13.8 \times 10^{-24} J/K)(T)]$

Degradation

Although viscoelastic deformation is accelerated as the Temp. exceeds T_g, this softening does not break the primary covalent bonds ~~of~~ within the molecule.

Under more severe conditions, however, these bonds may be ruptured. Of course, any resulting change in structure affects the properties. Extreme heat can degrade a polymer by breaking of bonds and by oxidation ①.

The most obvious "degradation" of polymers is "charring". If the side groups or the hydrogen atoms of a vinyl polymer are literally torn loose by thermal agitation, only the backbone of carbon atoms remains. (e.g. ① carbohydrates of bread toast – brown/black. ② charred wood)

~~Thus~~ charring is generally avoided in a commercial product. ~~Carboni~~ [Under controlled conditions, a graphite fiber can be formed from a polymer fiber. Such fibers hold considerable promise as a high-temperature reinforcement for composites.] Carbonization is accelerated in the presence of air, because oxygen reacts with the hydrogen atoms along the side of the polymer chain.

The degradation ~~descr~~ just described is (increased) accentuated by oxygen. In addition, oxygen ~~has~~ can have other effects. eg. many rubbers are vulcanized with only 5 to 20~~%~~% of the possible positions anchored by sulfur cross-links. This permits the rubber to remain deformable and "elastic". Over a period of time, the rubber may undergo further cross-linking by oxygen of the air.

The result is identical to cross-linking by sulfur, except that oxygen rather than sulfur is the connecting link. Naturally, the rubber becomes harder and less deformable with an increased number of cross-links.

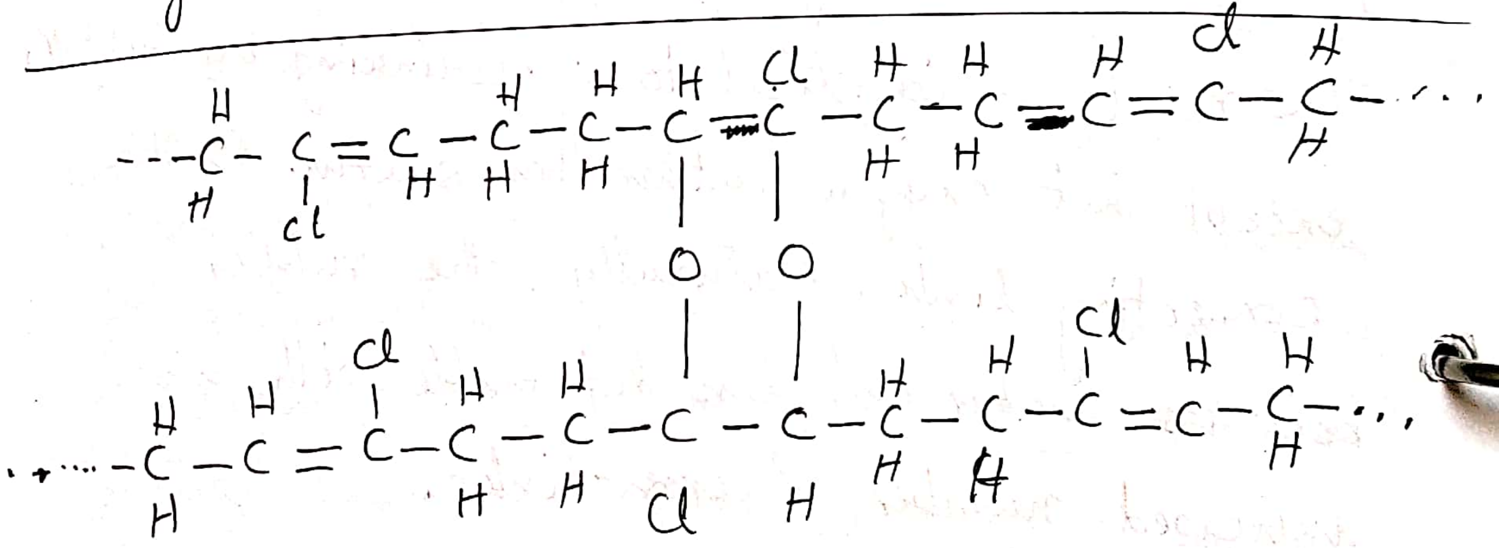
Several factors accelerate the oxidation reaction just described:-

① Oxygen in the form of ozone, O_3 is much more reactive than is normal O_2.

② Ultraviolet light can provide the energy to break existing bonds, so that the oxidation reaction can proceed.

③ The existing bonds are broken more readily when the molecules are stressed.

Because of these features, tyres commonly contain carbon black or similiar light abserbers to decrease the oxidation rate. Applying the same principle, accelerated testing procedures for product stability commonly expose the polymer to ozone &/or ultraviolet light.



Vulcanization of rubber in the presence of oxygen. Like sulfur, oxygen from air can cross link rubber molecules (chloroprene), which hardens the rubber. Still further oxidation would degrade the chloroprene to micromolecules.

Swelling

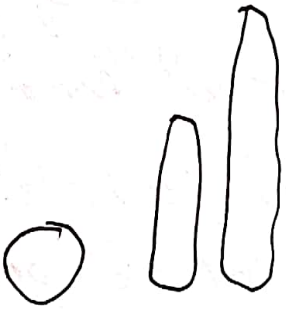
Micromolecules are intentionally added to polymeric materials to make the latter more flexible. However, this is not always desirable. Consider a polyvinyl alcohol, $-\!\left(C_2H_3R\right)\!-_n$, with the R being $-OH$

Water molecules can be absorbed among the vinyl chains. The absorption leads to a weakening and a swelling of the polymer. Likewise, unless the necessary structural adaptations are made, petroleum molecules can be absorbed into the rubber of a gasoline hose, which produces swelling and reduces the usefulness of the hose.

Swelling is not compatible with enggineering specifications. One should try to prevent it.

Cross-linking reduces swelling, since the molecules are linked together. Crystallized plastics have more closely intermeshed molecular structures, and hence are less prone to swelling them amorphous polymers. Finally, the engineer can choose among a number of polymers in order to avoid swelling.

Swelling: Micromolecules of benzene are absorbed between large molecules of isoprene ~~in the~~ rubber in the sample at the right, expanding it 60%. Rubber, if it is not sufficiently cross-linked is particularly subject to this type of deterioration.



Small molecules distribute themselves ~~mo~~ more readily when the two types are chemically similiar. ~~e~~ eg. PVA C_2H_3-OH and water $H-OH$, are closely related. ∴ water is readily absorbed among these vinyl molecules. Likewise, hydrocarbon petroleum fluids are absorbed into hydrocarbon rubbers. Where swelling is critical, such similiarities should be avoided through judicious selection of polymers.

Example 14-6.1

A stress of 11 MPa is required to stretch a 100 mm rubber band to 140 mm. After 42 days at 20°C in the same stretched position, the band exerts a stress of only 5.5 MPa.

ⓐ What is the relaxation time?

ⓑ What stress would be exerted by the band in the same stretched position after 90 days?

Procedure :- ⓐ The stress drops to 50% of its initial value. Therefore, $42/\tau = \ln 2.0$.

ⓑ Here, $90/\tau = \ln(S_{90}/S_0)$ or use $\boxed{\ln S/S_0 = -t/\tau}$

Calculation

ⓐ $\ln \frac{S}{S_0} = -\frac{t}{\tau} \Rightarrow \ln \frac{5.5}{11} = -\frac{42}{\tau}$

$\underline{\tau = 61 \text{ days}}$

ⓑ $\ln \frac{S_{90}}{S_0} = -\frac{t}{\tau} \Rightarrow \ln \frac{S_{90}}{11} = \frac{-90}{61}$

$S_{90} = 11 e^{-90/61} = 2.5 \text{ MPa}.$

alternative answer → with 48 additional days

$S_{48} = 5.5 e^{-48/61} = 2.5 \text{ MPa}$

Example 14-6.2

The relaxation time at 25°C ~~to~~ is 50 days for the rubber band, in the above example. ~~#~~ What will be the stress ratio ~~a~~ S/S_0 after 38 days at 30°C?

Procedure :- Observe ~~in~~ in the above example that $\tau_{20^\circ} = 61$ days. With this and $\tau_{25^\circ} = 50$ days, we use eqn to solve simultaneously for E & $\ln(1/\tau_0)$. With these values, we can calculate τ_{30°, and hence the remaining stress.

$$\ln \frac{1}{\tau} = \ln \frac{1}{\tau_0} - \frac{E}{(13.8 \times 10^{-24}\ \mathrm{J/K})(T)}$$

Calculation

At 20°C

$$\ln \frac{1}{\tau_0} = \ln \frac{1}{61} + \frac{E}{(\checkmark)(293)\,\mathrm{K}}$$

At 25°C

$$\ln \frac{1}{\tau_0} = \ln \frac{1}{50} + \frac{E}{(\checkmark)(298)\,\mathrm{K}}$$

Solving simultaneously

$E = 4.8 \times 10^{-20}\ \mathrm{J}$

$\ln \frac{1}{\tau_0} = 7.76.$

At 30°C

$$\ln \frac{1}{\tau} = \cancel{\ln \frac{1}{\ }}\ 7.76 - \frac{4.8 \times 10^{-20}\ \mathrm{J}}{(13.8 \times 10^{-24}\ \mathrm{J/K})(303\ \mathrm{K})}$$

~~$\ln \frac{1}{\tau} =$~~ $\tau = 41$ days

$S_{38} = S_0\, e^{-38/41}$

$\frac{S_{38}}{S_0} = 0.4$

<u>Comments</u> : The relaxation time shortens at higher temperatures.

A rubber is more subject to oxidation when it is under stress. When this occurs, the structure is modified, and we observe other changes, such as hardening & cracking.

Example 14-6.3

A nylon absorbs 1.66 w/o water (dry basis). Because of differences in density, this means that 100 cm^3 of dry nylon absorbs 1.9 cm^3 of H_2O to produce 101.5 cm^3 of saturated nylon. Account for the missing 0.4 cm^3.

Solution :- In this case, ~~the~~ where absorption occurs, the attraction between unlike molecules is greater than is the attraction between like molecules, that is the nylon water attractions are greater than are the average of ~~nn~~ nylon-nylon and water-water attractions. A contraction of volume results.

Comments :- If the attraction between like molecules had been greater than that between unlike nylon-water pairs, the water and nylon would have become segregated and absorption would have been limited.

14 – P61

A stress relaxes from a 0.7 MPa to 0.5 MPa in 123 days (a) What is the relaxation time?
(b) How long would it take to relax to 0.3 MPa

$\boxed{+0.03\,°C}$

(a) $S_0 = 0.7\,MPa$

$S_{123} = 0.5\,MPa$ $S_{123} = S_0 \, e^{-t/\tau}$

$$\frac{0.5}{0.7} = e^{-123/\tau} \quad \text{or} \quad -0.33687 = -123/\tau$$

$$\tau = \frac{123}{0.3369} = 365.1 \text{ days}$$

or 366 days

(b) $S = 0.3\,MPa$ $S_0 = 0.7\,MPa$

$$\cancel{\frac{0.3}{0.7}} \quad \frac{0.3}{0.7} = e^{-t/365.1} = 0.42857$$

$$\cancel{-}t/365.1 = \cancel{-}0.8473 \qquad \boxed{t = 309.35 \text{ days}}$$

or 310 days

or 187 additional days.

$$\begin{array}{r} 310 \\ -123 \\ \hline 187 \end{array}$$

14-P62 An initial stress of 10.4 MPa ~~(1500~~ is required to strain a piece of rubber 50%. After the strain has been maintained constant for 40 days, the stress required is only 5.2 MPa. What would be the stress required to maintain the strain after 80 days?
(Solve this problem without using a calculator)

$S_0 = 10.4 \text{ MPa}$ strain $= 50\%$.

$t = 40$ days . $s = 5.2 \text{ MPa}$

stress = ? $t = 80$ days.

$$\cdot \quad \cancel{\$}\ \frac{\cancel{5.2}}{\cancel{10.4}_2} = e^{-t/\tau} = e^{-40/\tau} = \frac{1}{2}$$

$$\ln\frac{1}{2} = -40/\tau = \ln 0.5$$

$$\frac{-40}{\ln 0.5} = \tau$$

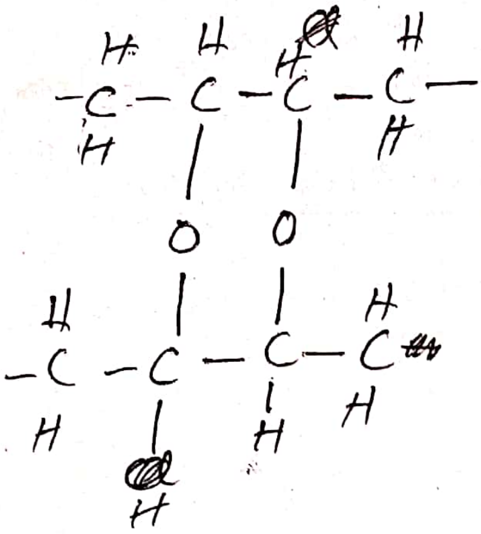
$$\frac{s}{10.4} = \cancel{\ln}\, e^{-80/\tau} = e^{\cancel{-40/\tau}} \cdot e^{-40/\tau}$$

$$\boxed{\frac{s}{10.4} = \frac{1}{2}\cdot\frac{1}{2}}$$

$$s = \frac{10.4}{4} = 2.6 \text{ MPa}$$

$s = 2.6$ MPa.

14-P63 Raw polyisoprene (i.e. nonvulcanized natural rubber) gains 2.3 w/o by becoming cross-linked by oxygen in the air. What fraction of possible cross links are established? (In this case, assume that the O_2 cleaves and then each cross-link involves a single oxygen.)



C H

$8 \times 12 + 12 \times 1 + \cancel{35.5 \times 2}$

$96 + 12 \cancel{+ 71.0}$

$2O \rightarrow 2 \times 16$

$= 32$

96
12
~~71~~
~~177~~
$\boxed{108}$

$108 \; \cancel{177} + 32 = \cancel{209} \; \boxed{140}$

$\cancel{\frac{32}{209}}$ $\frac{32}{140} = 22.86$ w% Oxygen

~~$\frac{\cancel{32}^{\,16\,8}}{\cancel{108}_{\,54\;27}} \times 100\% = 29.63$ w%~~

~~29.63 ~~100%~~ —— 100%~~

~~1 —— $\frac{100\%}{29.63} \times 2.3 = 3.375 \times 2.3$~~

~~2.3~~

~~$= 7.76\%$~~

22.86w% <u>oxygen</u> —— 100% fraction of possible cross links

1 —— $\frac{100}{22.86} \times 2.3 = 10.06\%$ ✓