Chapter 6. Degradation, Stability and Environmental Issues

Polymers are susceptible to attack by a wide variety of agents

TABLE 6.1 EFFECTS OF ENVIRONMENTAL AGENTS ON POLYMERS

Agent	Susceptible Polymers	Examples
Organic liquids and vapors	Amorphous polymers	Polystyrene, Poly(methyl methacrylate)
Moisture	Heterochain polymers	Polyesters Polyamides Polyurethanes
Ozone	Unsaturated elastomers	Polyisoprene Polybutadiene
Sunlight	Photosensitive polymers	Polyacetals Polycarbonate
Biodegradation	Short-chain polymers, nitrogen-containing polymers, polyesters	Polyurethanes Polyether–polyurethane
Ionizing radiation	Aliphatic polymers having quaternary carbon atoms	Poly(methyl methacrylate) Polyisobutylene polypropylene

For tires, UV & ozone resistances are provided by adding fillers & stabilizers.
In some cases, degradation may be a desirable goal.

6.1 Polymer degradation & stability

Degradation occurs

by exposure to high T, O_2 & O_3, UV, moisture, radiation, & chemical agents.

. *weathering* : deterioration of plastics to normal environmental conditions

6.1.1 Thermal degradation

Vinyl polymers are particularly susceptible to thermal degradation.

. chain scission (breakage of backbone bonds to yield free-radical segments)

. nonchain scission (elimination of a small molecule from a substituent group)

(See Fig. 6.1)

* Chain scission (PE, PP)

Mechanism of depolymerization

$$M_n^* \underset{k_p}{\overset{k_d}{\rightleftharpoons}} M_{n-1}^* + M$$

where k_p : propagation constant

k_d : depropagation constant

M^* : active chain

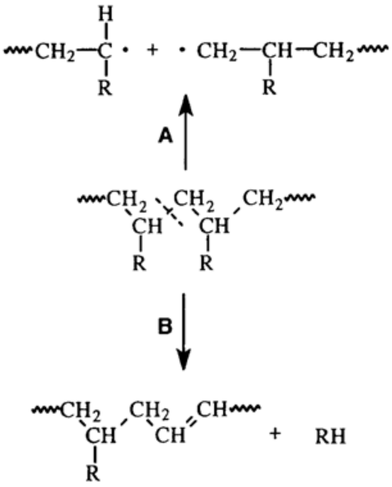


Figure 6.1. Illustration of thermal degradation of a vinyl polymer by random chain scission (**A**) and by nonchain scission (**B**) mechanisms.

At ceiling temperature, T_c : $k_d[M_n^*] = k_p[M_{n-1}^*][M]$

If MW is high (i.e., n>>1), $M_{n-1} \approx M_n$

$$\therefore k_d = k_p[M]$$

Expressing the rate constant, k, in Arrhenius form,

$$A_d \exp\left(\frac{-E_d}{RT_c}\right) = A_p \exp\left(\frac{-E_p}{RT_c}\right)[M]$$

$$\Rightarrow T_c = \frac{E_p - E_d}{R \ln(A_p[M]/A_d)}$$

where A : collision frequency factor
E : activation energy
(See Table 6.2)

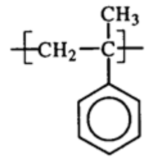
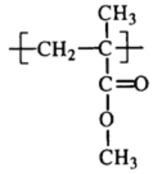
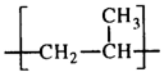
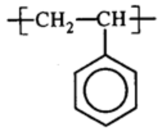
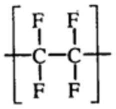
* Nonchain scission (PVC, PVAL, PAN)
Dehydrohalogenation of PVC (See Fig. 6.2)
PAN --- good gas-barrier properties suitable for packaging film
cannot be melt-processed
∵ nitrile groups undergo a cyclization rxn
(See Fig. 6.3)

* Strategies for thermally stable polymers
Flame-retardant additives
---> improve fire resistance of polymers but thermally unstable.
Polymers with highly aromatic structures
---> good at high T for extended periods of time

∵ resonance stabilization & high main-chain bond strength
(See Table 6.3)

Polymers having high T stability & high performance properties
---> difficult to process by usual methods
∴ compromise betw. thermal properties & processibility

TABLE 6.2 CEILING TEMPERATURES OF SOME COMMON VINYL POLYMERS

Polymer	Structure	T_c (°C)
Poly(α-methylstyrene)		61
Poly(methyl methacrylate)		220
Polypropylene	 $-\!\left[CH_2-CH(CH_3)\right]\!-$	300
Polystyrene		310
Polyethylene	$-\!\left[CH_2-CH_2\right]\!-$	400
Polytetrafluoroethylene	 $-\!\left[CF_2-CF_2\right]\!-$	580

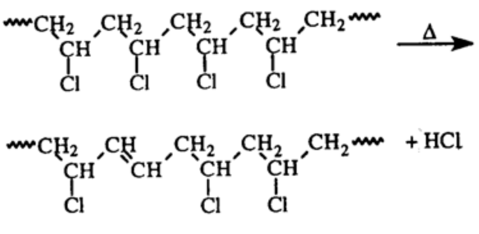


Figure 6.2. Partial dehydrochlorination of a repeating unit of PVC resultng in double-bond formation and the liberation of hydrogen chloride.

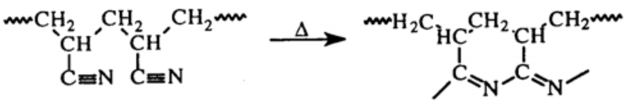
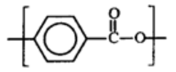
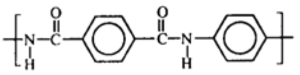
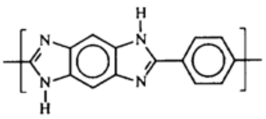
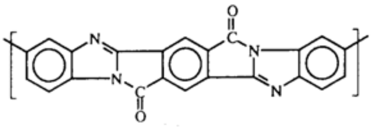
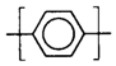


Figure 6.3. Cyclization of polyacrylonitrile at melt temperatures.

TABLE 6.3 EXAMPLES OF THERMALLY STABLE POLYMERS

Polymer	Structure	Decomp. T (°C)[a]
Aromatic polyester		480
Polybenzamide		500
Polybenzimidazole		650
Polypyrrole		660
Poly(p-phenylene)		660

[a] Temperature at onset of weight loss in an inert atmosphere as determined by TGA.

6.1.2 Oxidative & UV stability

---> increasing brittleness & deterioration in strength

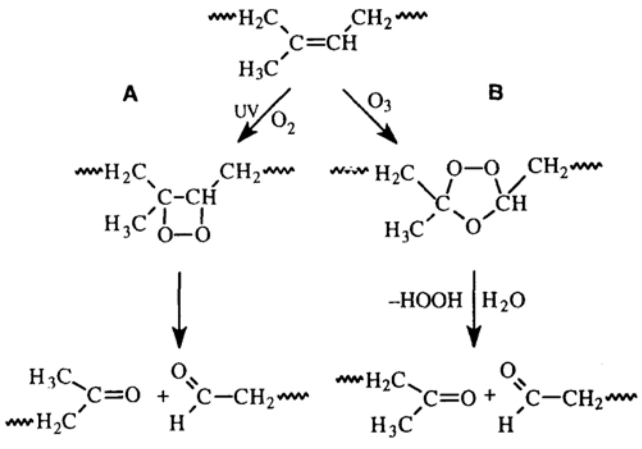


Figure 6.4. Degradation of polyisoprene by photolysis (**A**) and ozonolysis (**B**).

Polystyrene --- susceptible to photooxidative degradation
UV is absorbed by phenyl group --->
Energy is transferred to polymer chain --->
Cleavage of main chain & phenyl ring --->
Yellowing & embrittlement of the plastic.

. Antioxidants
--- free-radical scavengers

. UV protector :
carbon black in tire manufacture --- screen UV wavelengths (300-400nm)
benzophenone derivatives into PC --- convert absorbed radiation into heat

6.1.3 Chemical & hydrolytic stability

* Solvent crazing & cracking
Organic liquids & vapors -- develop crazes or cracks inside polymer
(due to localized plasticization)
Solvents with solubility parameters close to that of the polymer
---> minimum critical-strains.

* Hydrolysis
: degradation due to effect of water
Susceptible polymers : polysaccharides, proteins,
condensation polymers (polyesters & PA)

6.1.4 Radiation effects

<---- γ-radiation, electron beam, X-ray, . . .
Plastics in space vehicles, nuclear power plant
--- must have good resistance to radiation.
Thermosets(epoxies, phenolics & urethanes), polymer with aromatic ring(PS, PA, PSF)
---- extremely radiation resistant
PMMA --- susceptible to chain scission when radiating

6.1.5 Mechanodegradation

<---- results from high shear deformation.
comminition (grinding, milling, or crushing), machining, stretching, fatigue, tearing, abrasion or wear --- severe for high MW polymers
Mastication : softening of natural rubber & dispersing of filler and additives
(additives : accelerators, vulcanizers, antioxidants)

6.2 Management of plastics in the environment

In US, plastic wastes --- 25 vol% of all solid wastes cf.) paper --- 40%

==> landfills, recycling, incineration & biodegradation

6.2.1 Recycling

In US, 36% of plastic soda bottles are recycled.

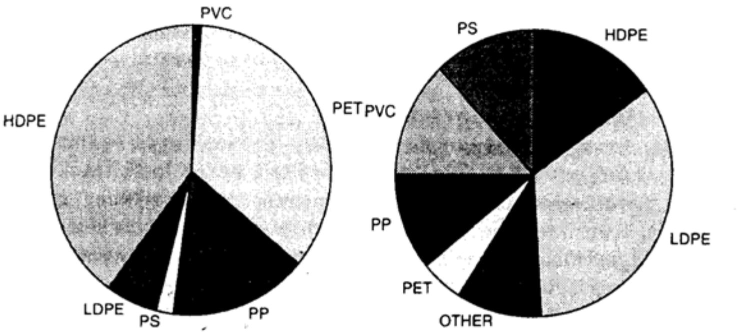


Figure 6.6. Comparison of the compositions of plastic wastes recyled in the United States (left) and Europe (right) during 1991. Source, *Chemical Engineering*, July 1992.

* Two approaches to recycling

i) Reprocessing of waste plastics

ex) manufacture of insulation board by waste PET

waste PET --> washing --> shredding, grinding into 5mm particles --> drying --> mixing with nucleating agent & additive --> processing in foam extruder --> injecting Freon gas --> insulation boards ($T_m = 260℃$)

. Advantage over EPS ($T_g = 100℃$) :

lower smoke emission during burning

suitable for the use of hot-melt adhesives in laminate preparation

ii) feedstock recycling

: chemical or thermal treatment to transform waste plastics into their monomers

. Condensation polymers (polyesters, nylon, PUR)

--- depolymerized by glycolysis, methanolysis & hydrolysis

. Addition polymers (PE, PP, acrylics, fluoroplastics)

--- thermal or catalytic cracking

ex) waste polyester resin (bottles, fibers, film)

--> heating with methanol & catalyst under pressure

--> depolymerization of PET into ethylene glycol & DMT

ex) worn carpets (nylon-6) ---> caprolactam at 536 - 752°F

* Recycling of tires

미국에서의 폐타이어 발생량 : 대략 1년에 1인당 1개 (즉, 2억개 이상)

대부분은 매립, 용지부족 현상 발생

Solutions:

i) extending the life of tires (source reduction)

ii) recycling of tires :

retreads

grinding into crumb (pads, mats, carpet backing, asphalt, sport tracks, etc.)

iii) production of syn gas (H_2 & CO) by waste tires

tires --> mixing with waste oil --> liquefaction (700^{o}F) --> removing steel --> liquid hydrocarbon mixture --> syn gas & inert slag

* 물질들의 recycle 정도

plastics : 3%, glass : 20%, paper : 29%, steel : 16%, aluminum : 39%

플라스틱의 경우 recycle이 낮은 이유 :

collecting & recycling 비용이 virgin resin보다 20% 고가.

11%정도 차지하는 thermosets은 recycle이 안됨 (--> 점차 FRP의 filler로 사용)

6.2.2 Incineration

1lb of plastics : 16,000Btu (more than twice the energy of coal)

배출 gas : CO_2, NO_x, H_2O...

소각로에 독성물질 잔류, 독성 gas 배출

PVC 소각시엔 발암물질인 dioxin 배출

==> 환경적 문제 심각.

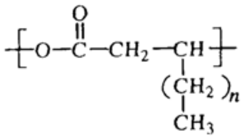
6.2.3 Biodegradation

* Biodegradable polymers

PUR, aliphatic polyesters -- potentially biodegradable

. poly(β-hydroxyalkanoates) -- naturally occurring polyester

: disposable plastic packaging materials



$$-\!\!\left[O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\underset{\underset{\underset{\displaystyle CH_3}{|}}{(CH_2)_n}}{\underset{|}{CH}} \right]\!\!-$$

poly(β-hydroxybutyrate) (PHB), (n=0) -- synthesized by bacteria

: brittle, 100% isotactic, highly crystalline, $T_g = 5-10$℃, $T_m = 175$℃,

decomposition T=200℃

poly(β-hydroxyvalerate) (PHV) , (n=1)

PHB & PP -- similar mechanical properties except extension-to-break

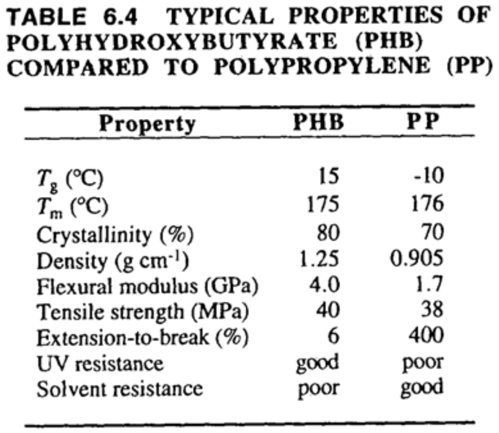


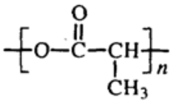
TABLE 6.4 TYPICAL PROPERTIES OF POLYHYDROXYBUTYRATE (PHB) COMPARED TO POLYPROPYLENE (PP)

Property	PHB	PP
T_g (°C)	15	-10
T_m (°C)	175	176
Crystallinity (%)	80	70
Density (g cm^{-1})	1.25	0.905
Flexural modulus (GPa)	4.0	1.7
Tensile strength (MPa)	40	38
Extension-to-break (%)	6	400
UV resistance	good	poor
Solvent resistance	poor	good

HB-HV copolymers (improved toughness) -- totally degradable

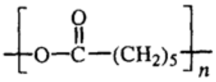
용도: matrices for controlled release of drugs

. poly(lactic acid) (PLA) : sutures, drug-delivery systems, wound clips, timed-release coatings for fertilizers & pesticides, mulch films for moisture & heat retention



$$\left[O - \overset{\overset{O}{\|}}{C} - \underset{\underset{CH_3}{|}}{CH} \right]_n$$

. polyester polycaprolactone (PCL)



$$\left[O - \overset{\overset{O}{\|}}{C} - (CH_2)_5 \right]_n$$

. poly(vinyl alcohol) (PVAL)
. cellulose & cellulose derivatives

. Starch additives

Blend or graft of PE with starch(5%) for plastic bags
Starch -- eaten by soil microorganisms
Plastic matrix -- broken down into smaller particles
Cornstarch -- inexpensive($0.10/lb)
6-20% moisture, stable up to 250℃
tensile strength of 20-30MPa at 10-15% elongation