Radiation Effects on Polymeric Systems

Crosslinking and Scission

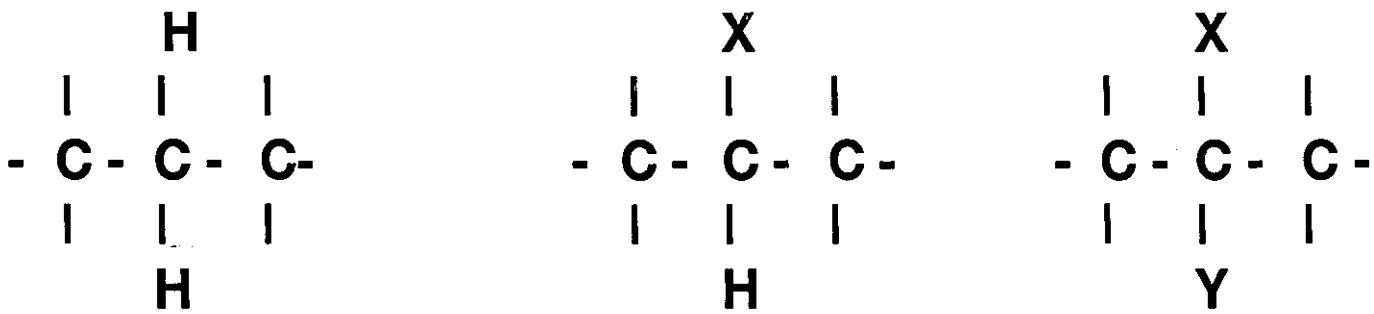
- Both crosslinking and scission occur on irradiation of polymers; however, their relative importance varies from polymer to polymer

Predominant Processes in Irradiated Polymers

Crosslinking	Scission
Polyethylene	Polyisobutylene
Polypropylene	Poly-α-methylstyrene
Polystyrene	Polymethacrylates
Polyacrylates	Polyvinylidene chloride
Polyamides	Cellulose
Polyesters	Cellulose acetate
Rubbers	Polytetrafluoroethylene
Polysiloxanes	Polytrifluorochloroethylene
Polyacrolein	Poly-α-methacrylonitrile
Polymethylene	Polyethylene terephthalate
Chlorinated polyethylene	
Polyacrylonitrile	
Polyethylene oxide	

Polymer Structure
Crosslinking vs Scission

- As the hydrogen in the backbone of an organic polymer is replaced with heavier substituents, its tendency to crosslink decreases and its tendency to scission increases



(a) (b) (c)

X and Y, heavier than H, e.g., CH_3, Cl

Crosslinking a>b>c; Scission a<b<c

Yields of Gaseous Products from Irradiated Polymers[a]

(γ- or electron irrad, room temp)

Polymer	Products G (product)(molecules/100 ev)
High-density PE	H_2 ~3; CH_4 ~0.002
Polypropylene	H_2 ~2.5; CH_4 ~0.1
Polyisobutylene	H_2 ~1.5; CH_4 ~0.5
Poly(vinyl chloride)	HCl ~2.7; H_2 ~0.15; CH_4 ~0.002
Poly(vinyl acetate)	H_2 ~0.6; CH_4 ~0.3; CO ~0.28; CO_2 ~0.06
Poly(methyl methacrylate)	CH_4 ~ 0.6; CO ~0.5; CO_2 ~0.4; H_2 ~0.2
Polystyrene	H_2 ~0.03; CH_4 ~ $1x10^{-5}$
Poly-α-methyl styrene	H_2 ~0.04; CH_4 ~0.003

[a] Woods and Pikaev (1994)

Free Radicals Formed on Irradiation of Polyethylene

$-CH_2-CH_2-(CH_2-CH_2)_n- \rightsquigarrow -CH_2-\dot{C}H-(CH_2-CH_2)_n-$

alkyl radical

$-CH_2-CH_2-(CH_2-CH_2)_n- \rightsquigarrow -\dot{C}H-CH=CH-(CH_2-CH_2)_{n-1}-$

allyl radical

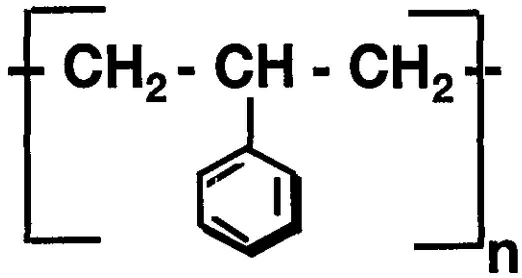
- At very high doses

$-CH_2-CH_2-(CH_2-CH_2)_n- \rightsquigarrow$

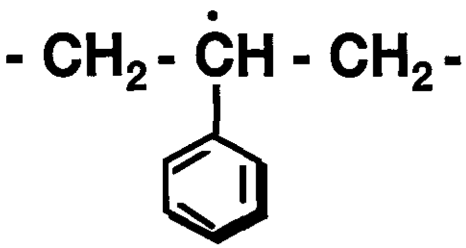
$-CH_2-\dot{C}H-(CH=CH)_x-(CH_2-CH)_{n-x}-$

polyenyl radical

Radiation Effect on Polystyrene



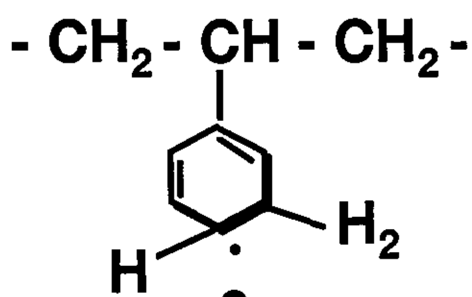
- Ions and radicals formed on irradiation
- Shows thermoluminescence on irradiation at - 196°C and subsequent warming
- G(free radicals) low, ~0.2



1

Radiation stable in inert atmosphere

and



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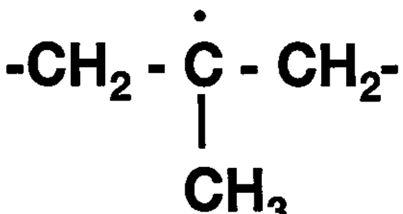
Radiation-induced oxidation in air

Radiation Effect on Polypropylene

- On irradiation, long-lived free radicals formed

Low temperature (-196°C)



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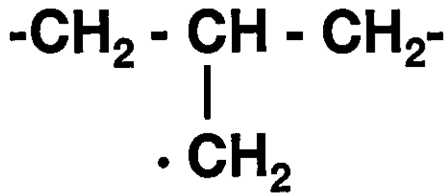

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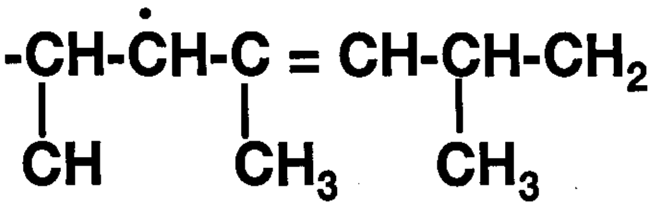
Room temperature



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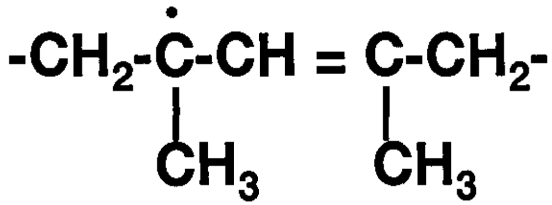


(4)

- Overall effect of irradiation: loss of mechanical strength

Dole (1973); Bradley (1984)

Chemical Basis of Oxidative Degradation

- ***Initiation***

$$RH \rightsquigarrow R\cdot + H\cdot$$

$$H\cdot + RH \longrightarrow R\cdot + H_2$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

- ***Crosslinking***

$$R\cdot + R\cdot \longrightarrow R\text{-}R$$

(not favoured in air/oxygen)

- ***Degradation***

$RO_2\cdot$, ROOH ⟶ Chain scission, degradation, alcohols, ketones

Propagation, Chain Reaction and Post-Irradiation Degradation of Polymers

- Oxidative degradation of polymers reduces strength and flexibility, causes cracking, increases moisture uptake and degrades electrical insulation properties

$$RO_2\cdot + RH \longrightarrow R\cdot + ROOH$$

$$ROOH \xrightarrow[\text{Light}]{\text{Heat}} RO\cdot + \cdot OH$$

$$RO\cdot + RH \longrightarrow R\cdot + ROH$$

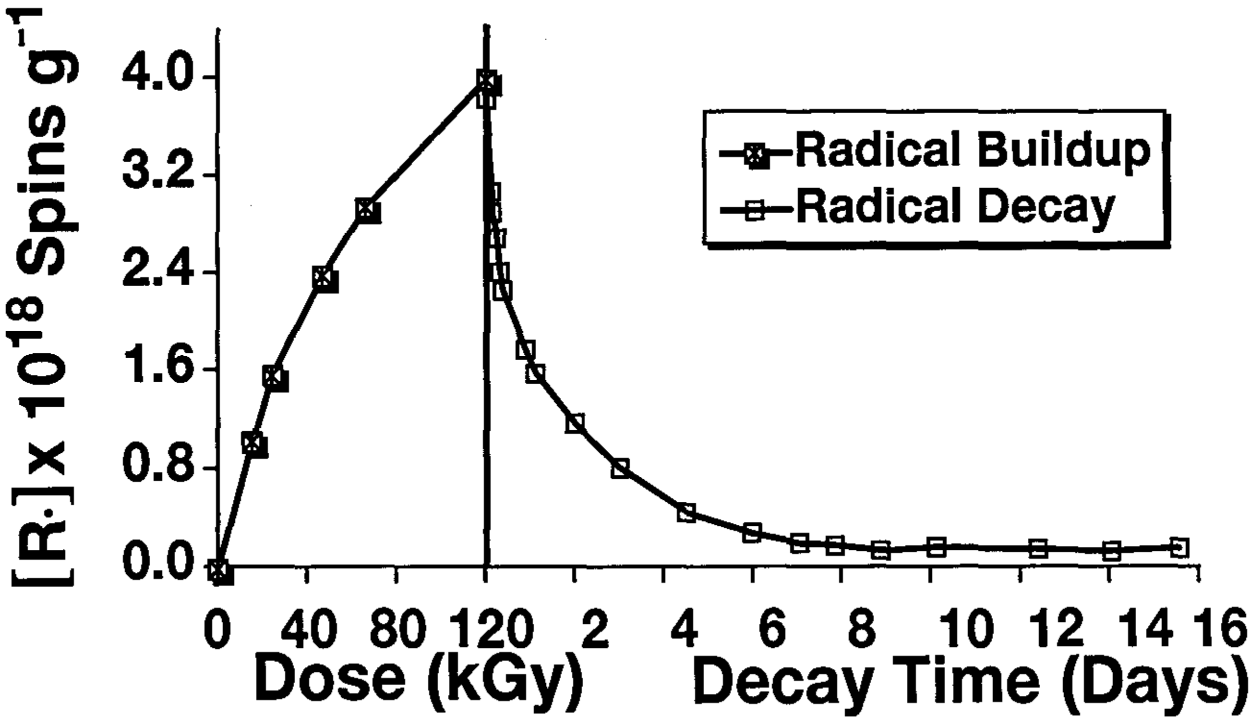
$$\cdot OH + RH \longrightarrow R\cdot + H_2O$$

- Oxidative degradation usually continues for months after irradiation, e.g., initiated by the reactions of ROOH

Radiation Effects on Polyethylene

- Known products on irradiation in air include H_2O, CO, CO_2, alcohols, ketones, hydroperoxides, peroxides and carboxylic acids
- Free radicals (alkyl and allyl) usually considered precursors of crosslinks
- Free radical migration form crystalline to amorphous regions
- Unsaturation in PE participates in crosslinking reactions
- Oxygen and additives excluded from the crystalline regions
- Roles of excited states and ionic reactions not well understood

Radical Buildup and Decay in Gamma Irradiated Polypropylene in Air



Kashiwabara and Seguchi, 1992

Radiation-Induced Oxidation of Polymers

G-Value of Oxygen Consumption at Room Temperature under ~ 70 kPa Oxygen (Kashiwabara and Seguchi, 1992)

Polymer	Dose (kGy)	Dose Rate (kGy/h)	$G(-O_2)$
Low-density polyethylene	500-1000	10	14
High-density polyethylene	500-1000	10	18
Medium-density polyethylene	500-1000	10	18
Ethylene propylene rubber	100-500	2	8
Isotactic polypropylene	100-200	10	50
Polyvinyl chloride	100-200	10	29
Polyvinyl chloride (stabilized)	100-200	10	11

Polymer Degradation by Irradiation

- Radiation degradation can be used to reduce the molecular weight of commercial polymers, e.g., polypropylene and polyethylene oxide
    - PP-vis-breaking, a patented process
- Teflon: scrap or waste Teflon is converted into useful powder and low MW products by irradiation (500 kGy), e.g., for producing lubricants and coated non-stick pans

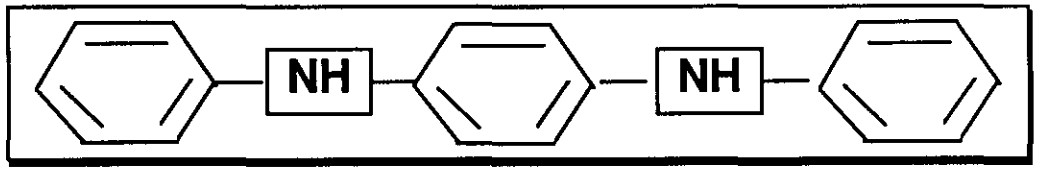
Effect of Additives

There are four main types of additives whose effect on irradiation of polymeric systems needs to be considered

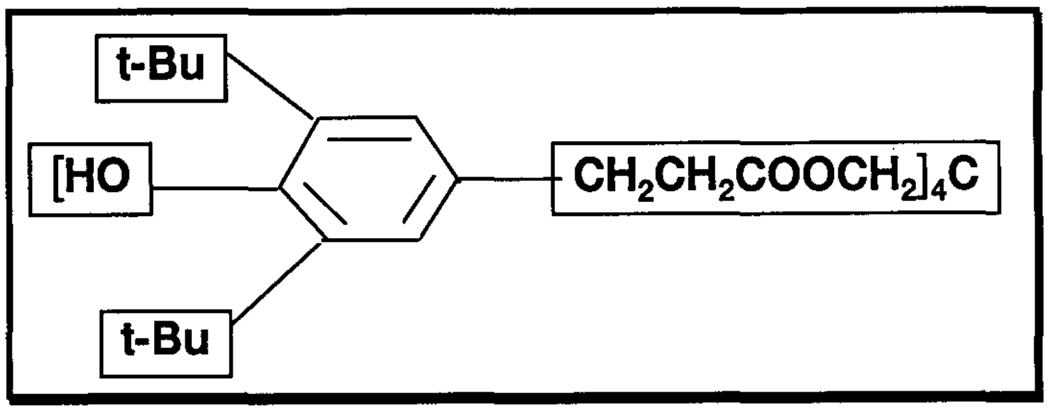
1. Crosslinking agents: these are typically multifunctional monomers (such as di-and triacrylates) that reduce the dose required for crosslinking
2. Degradation agents: primarily oxygen; it degrades polymers via the formation of peroxy radicals
3. Protective agents: basically, there are two types of protectors- the anti-rads, which act as energy acceptors (such as pyrene and other aromatic hydrocarbons), and free radical scavengers or anti-oxidants, e.g., phenols, which protect the polymer via peroxy or carbon centred radical reactions
4. Neutral additives: frequently, mineral powders or fibres are added to polymers; many of these have no effect on irradiation of polymers

Chemical Formulae of Some Antioxidants
(Kashiwabara and Seguchi, 1992)

Symbol	Name and formula
DPPD	N,N'-Diphenyl-p-phenylenediamine



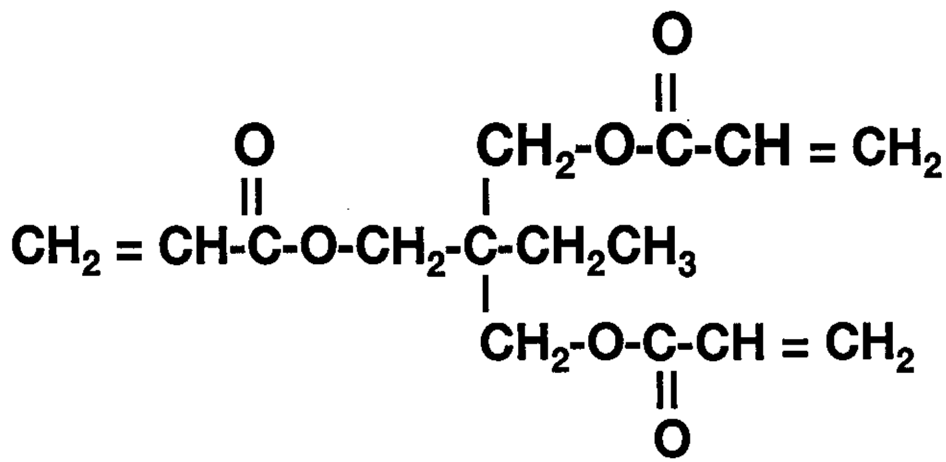
Symbol	Name and formula
Irganox 1010	Tetrakis[methylene-3(3,5-di-t-butyl-4-hydroxyphenyl) propionate]methane



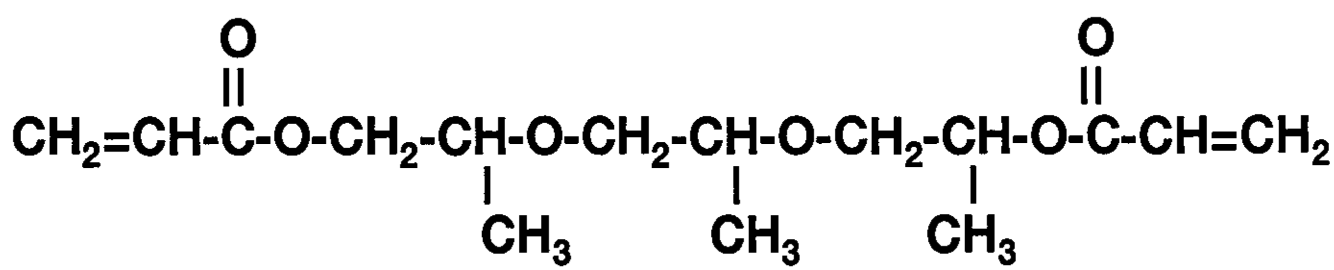
- Use of antioxidants, and mobilizers (e.g. mineral oils), reduces radiation-induced damage to most polymers

Multifunctional Monomers

Trimethylolpropane triacrylate (TMPTA)



Tripropylene glycol diacrylate (TPGDA)

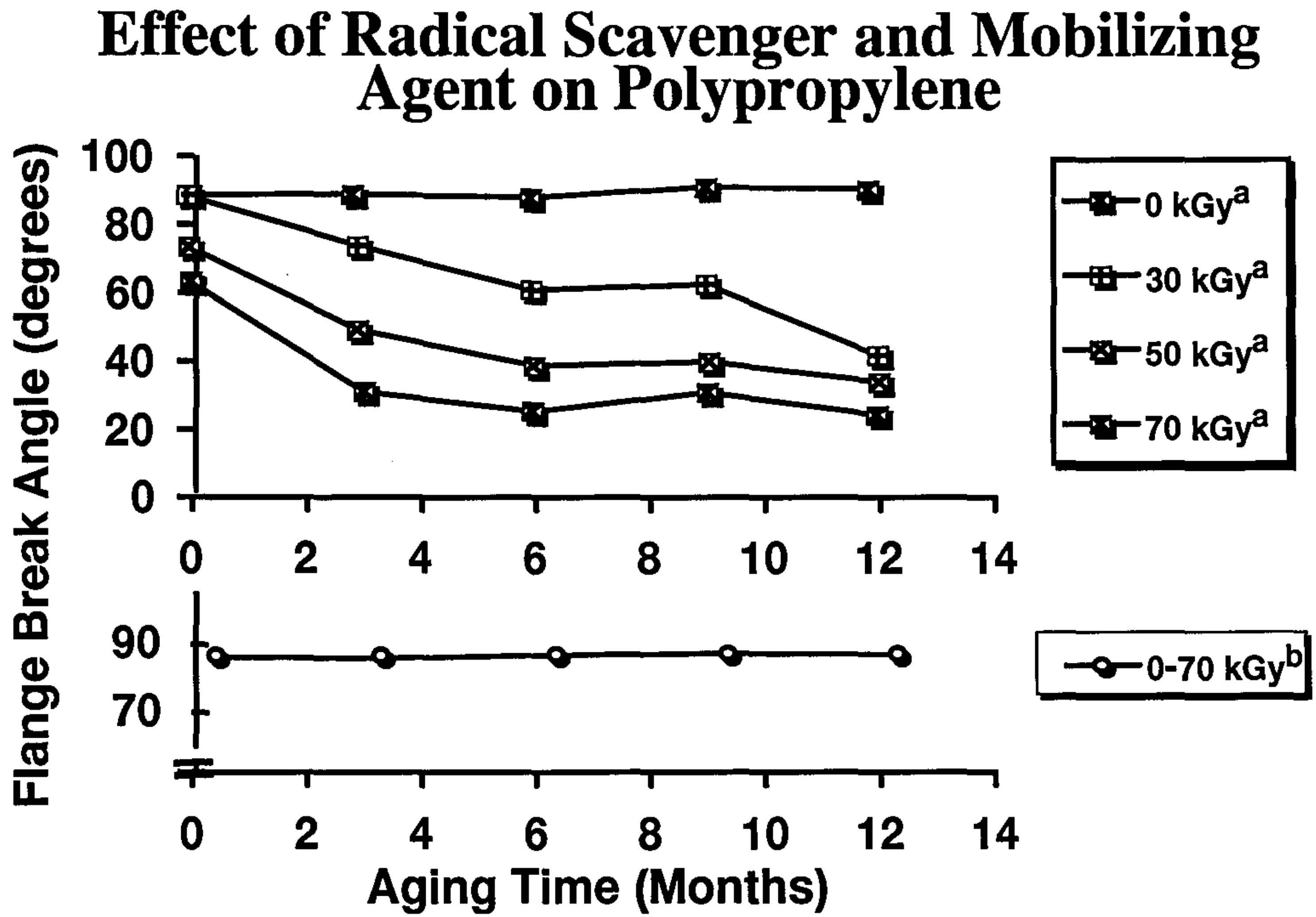


- These enhance crosslinking and grafting reactions

Effect of Electron and Gamma Irradiation on the Colour of Polycarbonate Resin

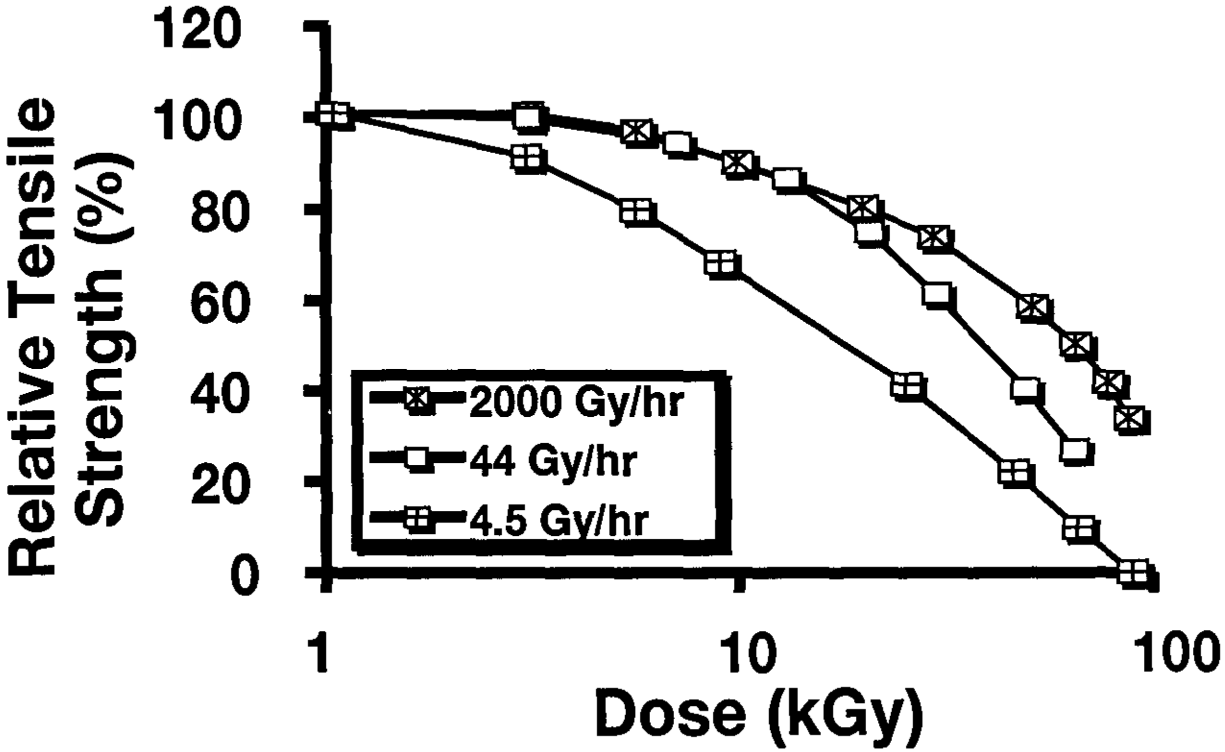
Dose (kGy)	Electron Yellowness Index	Gamma Yellowness Index
0	-	1.2
10	1.0	8.4
40	1.6	26.4

- The level of colour developed varies from polymer to polymer, and also depends on the stabilizers used



a. Radical scavenger, b. Radical scavenger + mobilizing agent

Effect of Dose and Dose Rate on the Tensile Strength of Polypropylene



- In general, the mechanical properties of polymers are less adversely affected on electron irradiation, as compared to gamma irradiation
- Satisfactory stabilized polymers for both types of irradiations are available