THEORETICAL CONSIDERATION AND LITERATURE REVIEW

2.1 Polyethylene

Polyethylene, $n(CH_2-CH_2)n$, is the most extensively used thermoplastic [1]. The ever-increasing demand for polyethylene is partly due to the availability of the monomer, ethylene, from the abundant raw material, associated gas, and naphtha. The ease of processing the polymer, its relative low cost, its resistance to chemicals, and its flexibility are also strong influences. All these and other factors lead to the strong market demand.

The two most widely used grades of polyethylene are low density polyethylene, LDPE, which has branched chains, and high density polyetylene, HDPE, which is predominantly linear. Low density polyethylene is produced by a free radical initiated polymerization at high pressures while high density polyethylene is produced by a low pressure process with a metallic oxide catalyst of the Ziegler type.

The main difference between the two grades of polyethylene is that LDPE is more flexible because of its lower crystallinity. This lower crystallinity is caused by the presence of branches of two or four carbons along the backbone of the polymer. HDPE is more closely packed because of the absence of branches and thus the molecules become closer and less permeable to gases.

2.1.1 Physical and chemical properties

Probably the most important property of the polyethylenes is the molecular weight and its distribution within

a sample. Methods used to determine molecular weights are numerous. A widely used one is by viscosity determination.

Polyethylene is to some extent permeable to most gases. The higher density polymers are less permeable than the lower density ones. Polyethylene, in general, has a low degree of water absorption and is not attacked by dilute acids and alkilis. However, it is attacked by concentrated acids. Its overall chemical resistance is excellent. Polyethylenes are affected by hydrocarbons and chlorinated hydrocarbons and swell slowly in these solvents. Tensile strength of polyethylenes is relatively low, but impact resistance is high. The use of polyethylenes in insulation is due to the excellent electrical resistance properties.

2.1.2 Production

The polymerization of ethylene is an exothermic reaction from which 850 calories are released for each gram of ethylene. For this reason, an adequate method of removing the heat of reaction is needed. Polyethylene decomposes at high temperatures, even in the absence of air. Explosions might take place if the temperature is not controlled. The decomposition products are methane, carbon, and hydrogen. Reactions that take place in the reactor are:

Polymerization

$$nC_2H_4 \longrightarrow 1/n \ (C_2H_4)n \qquad \Delta H = -22 \text{ kcal/mole} \qquad (2.1)$$

Decomposition

$$C_2H_4 \longrightarrow 2C + 2H_2 \qquad \Delta H = -11 \text{ kcal/mole} \qquad (2.2)$$

$$C_2H_4 \longrightarrow C + CH_4 \qquad \Delta H = -30 \text{ kcal/mole} \qquad (2.3)$$

2.1.3 Low density polyethylene

Most low density polyethylenes are made by high
pressure processes. Either tubular or stirred autoclave reactors
are used. In the stirred autoclave reactor, the heat of reaction
is absorbed by the cold ethylene feed which is mixed with the
reacting polymer. The stirring action keeps a uniform
temperature throughout the reaction vessel. The tubular reactor
consists of three zones-a heating zone, a reaction zone and a
cooling zone. A large amount of the reaction energy is removed
through the tube walls.

LDPE polymers produced using tube reactors are
better suited for film manufactrue, and products from the
stirred autoclave reactor are more suitable for coatings. The
autoclave will, in general, make all grades, but for film grades
lower conversions are used to minimize long chain branching.

2.1.4 High density polyethylene

All high density polyethlenes are made by a low
pressure process in a fluidized bed reactor. The catalyst is
either a Ziegler type catalyst which is a complex between an
aluminum alkyl and a transition metal halide, such as titanium
tetrachloride, or a catalyst of silica or silica alumina
impregnated with a small amount of metal oxide, usually either
chromium oxide or molybdenum oxide. Catalyst preparation and
activation are very important. They do not only determine the
activity or efficiency of the catalyst but also the properties of
the polymer. Molecular weight may be controlled by introducing
hydrogen to the circulating gas.

2.1.5 Application

Products made from polyethylene are numerous and range from building materials and electrical insulation to packing materials and sheets. It is an inexpensive plastic which can be molded into almost any shape, extruded into fiber or filament, and blown or precipitated into film or foil. Because it is more flexible and more transparent, the low density polymer is used in sheets, films, and injection molding. High density polyethylenes are extensively used in blow-molded containers. About 85 percent of the blow-molded bottles is produced from HDPE. Irrigation pipes made from polyvinyl chloride and high density polyethylene, HDPE, are widely used. Pipes made from HDPE are flexible, tough, and corrosion resistant. These pipes are used for carrying corrosive materials and/or abrasives, such as gypsum, slurry, and various chemicals. Corrosion resistant pipes are also used in well drilling and crude oil transfer. Spun-bonded polyethylenes are extremely fine fibers interconnected in a continuous network. Their uses include notebook and reference book covers, wall coverings, bags, labels, etc. The point-bonded, spun-bonded potyethylenes are used, for example, as laboratory coats, aprons, garments, and sleeping bag liners.

2.2 Processing

The blown film process has a scientific interest especially in the behaviour of the molten film as it is stretched in two directions while being simultaneously cooled between the die and the freeze line where the film becomes solid [2].

2.2.1 Extrusion

The extrusion process comprises the forcing of a plastic or molten material through a shaped die by means of pressure. In the modern process, however, screws are used to progress the polymer in the molten or rubbery state along the barrel of the machine. The most widely used type is the single screw machine and Figure 2.1 shows the main features of this type of extruder.

The zones in an extruder

Feed zone In the first zone, usually termed the "feed" zone, the function is to preheat the polymer and conver it to the subsequent zones. The screw depth is constant and the length of this zone is such as to ensure a correct rate of feed forward, neither starving it nor overfeeding. This varies somewhat for optimum performance with different polymers.

Compression zone The second zone has decreasing channel depth. There are several functions for this zone, usually called the "compression" or "transition" zone. Firstly, it expels air trapped between the original granules; secondly, heat transfer from the heated barrel walls is improved as the material thickness decreases; thirdly, the density change during melting is accommodated. Again, there is variation in the ideal design for each polymer type. For a polymer which melts gradually, e.g. low density polyethylene, a screw with the overall length roughly evenly divided between the three zones is appropriate. Screws of this type are often referred to as polyethylene screws.

Metering zone This zone is constant screw depth. The function is to homogenize the melt and hence to supply to the die region material which is of homogeneous quality at

constant temperature and pressure.

Die zone The final zone of an extruder is the die zone, which terminates in the die itself. Located in this region is the screen pack (Figure 2.1). This usually comprises a perforated steel plate called the breaker plate and a die be pack of two or three layers of wire gauze on its upstream (screw) side.

2.2.2 Tubular blown film

The extruder is fitted with an annular die, pointing (usually) upwards. The tube repoduced is inflate with air and at the same time is drawn upwards in a continuous process. The air inside is contained as a large bubble by a pair of collapsing rolls at the top (Figure 2.2). The polyethylene may be thought of as sliding over a pressurized gaseous internal sizing mandrel. It expands outwards to about three times its original diameter and at the same time is drawn in the other direction. The result is that it becomes biaxially orientated and this orientation is made permanent by the crystallization which freezes the orientation in place.
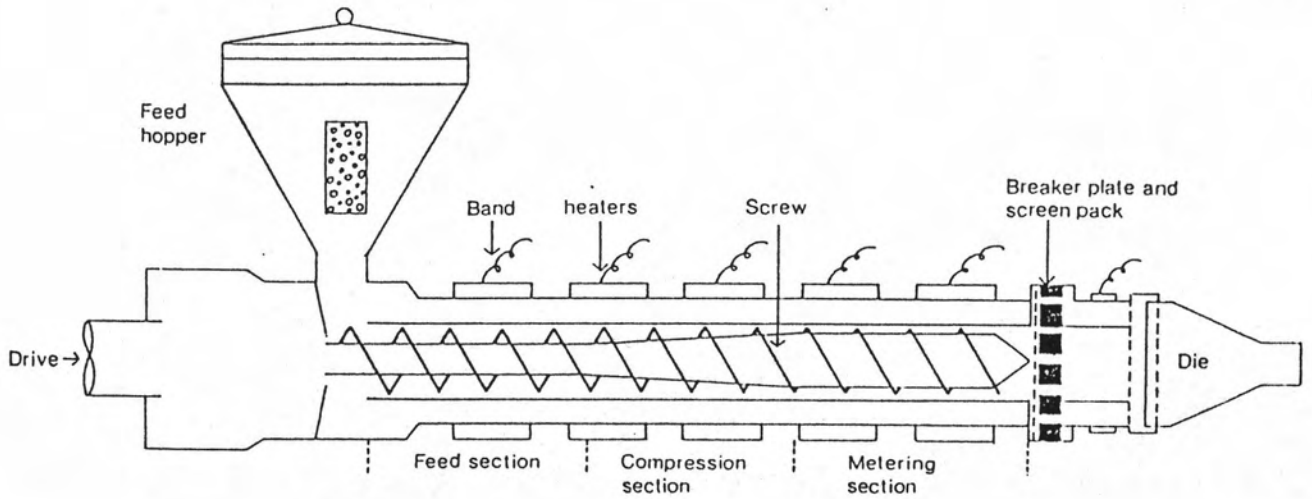
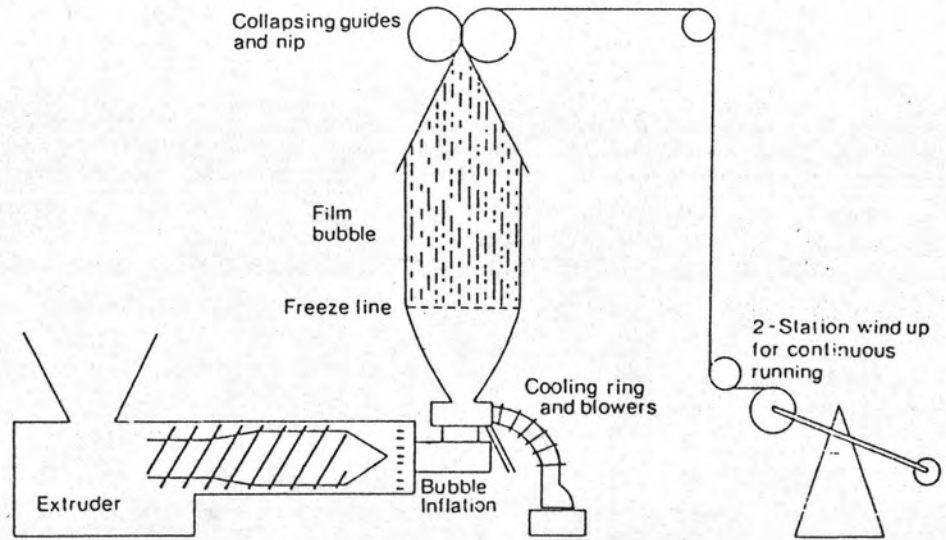Figure 2.1 Main features of a single sxrew extruder [2]

Figure 2.2 diagram of blown film process [2]

2.3 Theory of photodegradation

Sunlight was soon recognized as an important factor in the deteriorative ageing and weathering processes which occur in commercial polymers [3]. The reasons for this are readily understood. The wavelength of the radiation from the sun which reaches the earth's surface extends from the infra-red (>700 nm), through the visible spectrum (approximately 400-700 nm) into the ultra-violet (<400 nm) with a cut-off at approximately 300 nm depending upon atmospheric conditions. The energies of 700-400 and 300 nm photons are approximately 170, 300 and 390 kJ mol^{-1} respectively. The strengths of C-C and C-H bonds are approximately 420 and 340 kJ mol^{-1} respectively although they may be very much less in certain environments, for example in the neighbourhood of aromatic or unsaturated structures. Thus it is clear that the energy of the quanta of the UV and possibly of the visible components of sunlight is sufficient to break chemical bonds and that the shorter wavelengths will be the more effective.

Of course it is not enough that sufficiently energetic quanta are available. Chromophoric groups are necessary to absorb the incident radiation. In polymers, these are usually unsaturated structures such as carbonyl, ethylenic or aromatic groups. The absorption of energy and its transfer to the bond to broken may be described as the photophysical aspect of photodegradation. This is a very large subject in its own right and beyond the scope of the present treatment, which will be concerned only with the chemical processes which occur from the time at which the initial bond scission occurs.

Because absorption of radiation is an essential first step to photo-degradation, strongly absorbed radiation will be attenuated as it passes through the polymer and reaction will be concentrated in the surface layers. It is for this reason

that a "skin effect" is frequently observed in photo-initiated reactions.

The first chemical step in photo-degradation is usually homolytic bond scission to form free radicals. These radicals will normally react rapidly with any oxygen present. In this way, visible and especially UV radiation are particularly effective initiators of oxidation.

Polymers have different photodegradative sensitivities to UV light of different wavelengths [4]. The varying sensitivities result from differences in the chemical structure. As shown in Table 2.1, the maximum sensivity of several polymers (as determined by the bond dissociation energies) is in the range of 290 and 400 nm. Although the atmosphere of the earth filters out the UV part of solar radiation, the above (so-called actinic) range of solar ultraviolet radiation is about 6 % of the total radiation of the sun which reaches the earth's surface. In many applications of plastics, sunlight is a significant source of degradative energy; hence, the study and understanding of the physical and chemical processes caused by light are of great practical importance.

2.4 Photophysical processes

The physical processes involved in photodegradation include absorption of light by the material, electronic excitation of the molecules, and deactivation by radiative or radiationless energy transitions, of by energy transfer to some acceptor [4]. When the lifetime of the excited state is sufficiently long, the species can participate in various chemical transformations.

Phenomenologically, the absorption of light can be described by Beer-Lambert's law. The intensity of the incident

Table 2.1 Wavelength of UV radiation (energy of a photon) at
which various polymers have maximum sensitivity [4]

Polymer	nm	kcal/mol
Styrene-acrylonitrile copolymer	290,325	99,88
Polycarbonate	295,345	97,83
Polyethylene	300	96
Polystyrene	318	90
Polyvinyl chloride	320	89
Polyester	325	88
Vinyl chloride-vinyl acetate copolymer	327,364	87,79
Polypropylene	370	77

radiation (I_o) will be only partly transmitted (I) through
the material; the logarithm of the transmittance ($T=I/I_o$), is
proportional to the thickness of the layer (l) and to the
concentration of the absorbing component (c):

$$A = -\log T = \log I_o/I = \varepsilon lc \qquad (2.4)$$

where the proportionality factor is the absorption coefficient
(ε). A (also known as the extinction, E) is dimensionless; i.e.,
when l is given in cm and c in mol/liter, then the dimension of
ε is liter mol^{-1} cm^{-1} (molar absorption or extinction-coefficient).

The absorption of light results in an electronic
transition between two energy levels in the absorbing molecule;
this absorbing molecule; this absorbed energy is exactly equal
to the energy of a light quantum:

$$\Delta E = h\nu \qquad (2.5)$$

where h is Planck's constant and ν is the frequency of the absorbed light:

$$\nu = c^*/\lambda = c^*\nu^* \tag{2.6}$$

where c^* is the velocity, λ is the wavelength, and ν^* is the wave number of the absorbed light (a possible set of values and dimensions: $h = 6.62 \times 10^{-27}$ erg sec, ν sec^{-1}, $c^* = 3 \times 10^{10}$ cm sec^{-1}, λ cm, ν^* cm^{-1}).

The energy absorption produces an excited state of the molecule, two types of which can be distinguished. In a single state (S) the spins of the electrons are (remain) paired, in a triplet state (T) they are unpaired. The ground state is almost always a singlet state (S_o). An excitation of a molecule from the ground state to the first excited singlet state ($S_o \longrightarrow S_1$) is shown in Figure 2.3. Here, the curves represent the potential energies of the corresponding states and the horizontal lines are the various vibrational energy levels. The excited molecule can lose its excess energy by vibrational relaxation and emission (fluorescence). Radiationless transitions (internal conversion) from higher excited singlet states (S_2, S_3, etc.) to the S_1 state, or from S_1 to the S_o state are also possible.

A direct excitation from S_o to an excited triplet state is not allowed. This transition is, however, possible by intersystem crossing, an example of which is shown in Figure 2.4. The condition of such a transition is that the potential curves of S_1 and T_1 have a common (crossing) point with identical nuclear configuration so that a vibrational transmission ($S_1 \longrightarrow T_1$) is possible. The radiative deactivation $T_1 \longrightarrow S_o$ is also forbidden; therefore, the T_1 excited triplet state has a much longer lifetime than the S_1 state. The emission of light by $T_1 \longrightarrow S_o$ transition is called phosphorescence.
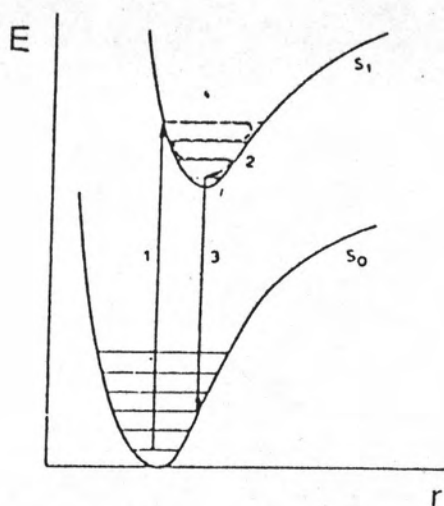
Figure 2.3 Potential energy curves of a molecule (S_o=
ground state, S_1=first excited singlet state):
(1) absorption; (2) vibrational relaxation;
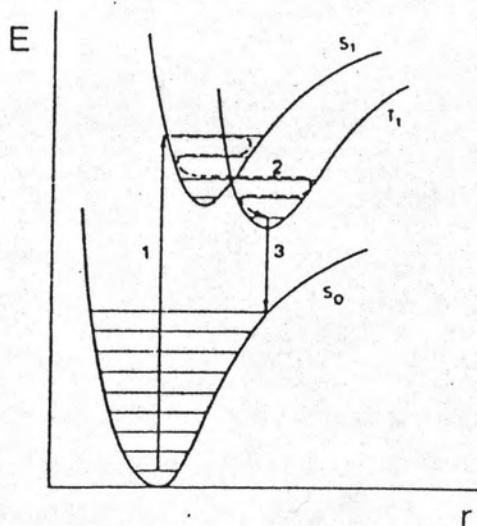(3) fluorescence [4]

Figure 2.4 Potential energy curves of a molecule (T_1 =
first excited triplet state): (1) absorption;
(2) vibrational relaxation; (3) phosphorescence
[4]

When the lifetimes are sufficiently long, a bimolecular deactivation of the excited states (deactivation by collision) is also possible. This is very important because it makes the application of deactivators (suitable energy acceptors) possible. This kind of energy transfer is called quenching; the addition of quencher molecules to the polymer is a common method of photostabilization.

There are, however, also other possibilities for energy transfer from an excited species, e.g., radiative transfer in which the light emitted during deactivation is absorbed by another molecule, or nonradiative transfer occurring over quite large distances (50-100 A°; so-called resonance excitation transfer) or over shorter distances without a real collision but by overlapping of the electron clouds of the participating species (10-15 A°; referred to as exchange energy transfer).

2.5 Photochemical processes

The chemical processes of photodegradation include isomerization, dissociation, and decomposition of a molecule as a direct consequence of its photophysical excitation, as well as those nonunimolecular chemical reactions which are facilitated by the absorbed energy [4]. Obviously, a photochemical reaction can take place only during the lifetime of the excited state; such a reaction must compete with the physical modes of deactivation.

Photodissociation occurs when the excitation reaches a point above the dissociation limit of the excited potential curve, as illustrated in Figure 2.5a, or when a dissociative excited state is formed (Figure 2.5b) in which repelling of the atoms occurs at any seperation distance. Dissociation can also occur after intersystem crossing to an excited triplet state above the dissociation limit (Figure 2.6a) or to a dissociative potential curve (Figure 2.6b).
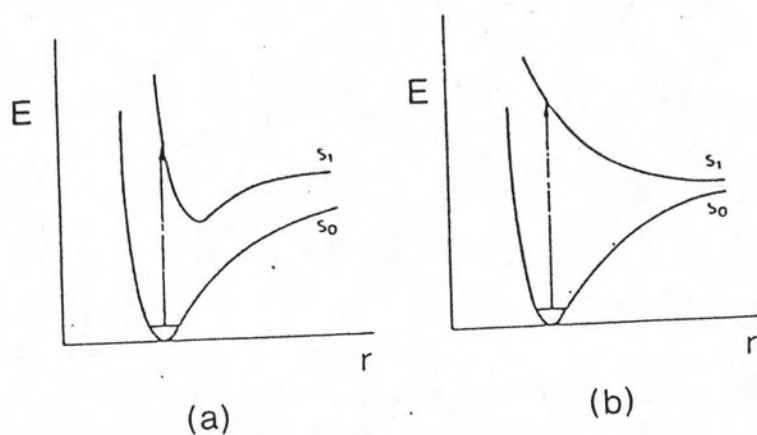
Figure 2.5 Photodissociation of a molecule: (a) by excitation above the dissociation limit of the S_1 potential curve; (b) by formation of a dissociative excited state [4]
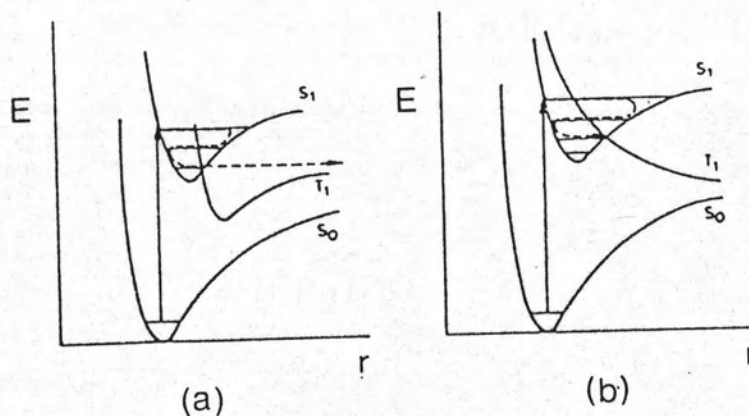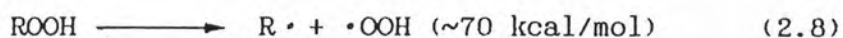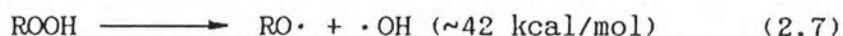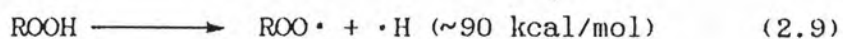

Figure 2.6 Photodissociation of a molecule after intersystem crossing: (a) to above the dissociation limit of the T_1 potential curve; (b) to the dissociative excited triplet state [4]

An especially important case of photodecomposition is the radiation-induced decomposition of hydroperoxides formed during polymer oxidation. The energy of UV light is sufficient to cause both of the following decompositions:
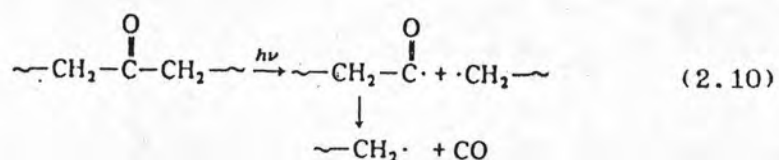
$$ROOH \longrightarrow RO\cdot + \cdot OH \quad (\sim 42 \text{ kcal/mol}) \qquad (2.7)$$

$$ROOH \longrightarrow R\cdot + \cdot OOH \quad (\sim 70 \text{ kcal/mol}) \qquad (2.8)$$

Dissociation of the O-H bond is less facile:

$$ROOH \longrightarrow ROO\cdot + \cdot H \quad (\sim 90 \text{ kcal/mol}) \qquad (2.9)$$

Because of low bond dissociation energy, decomposition according to reaction (2.7) is predominant in polymer photooxidation.

The role of carbonyl groups in polymer photooxidation is of great importance because once they have been formed the absorb UV readily, hence excitation to singlet and triplet states is easy. The excited carbonyl groups decompose cleavage of the bond between the carbonyl group and the α-carbon atom (α-scission) and is usually followed by the formation of carbonmonoxide:

$$\sim CH_2 - \overset{\overset{\textstyle O}{\|}}{C} - CH_2 \sim \;\xrightarrow{h\nu}\; \sim CH_2 - \overset{\overset{\textstyle O}{\|}}{C}\cdot + \cdot CH_2 \sim \qquad (2.10)$$
$$\downarrow$$
$$\sim CH_2\cdot + CO$$

The Norrish-II reaction is a nonradical scission which occurs through the formation of a six-membered cyclic intermediate. Abstraction of a hydrogen from the γ-carbon atom results in decomposition by β-scission to an olefin and an alcohol or ketone. For example, in the cake of polyethylene, a terminal double bond and an enol/ketone end group are formed:

$$\underset{\substack{\\ CH_2-CH_2}}{\sim C{=}O} \quad \underset{\substack{\\ }}{\overset{H}{\underset{}{\diagdown}}}CH\sim \xrightarrow{h\nu} \left[\sim C \overset{O\cdots\cdots H}{\underset{CH_2-CH_2}{\diagdown\diagup}} CH\sim \right] \tag{2.11}$$

$$\downarrow$$

$$\underset{CH_3}{\sim C{=}O} \; \rightleftharpoons \; \underset{CH_2}{\sim C}\overset{OH}{\diagup} + \; \underset{CH_2}{CH}\sim$$

The Norrish-III reaction is also a nonradical chain scission; however, it involves the transfer of a β–hydrogen atom and leads to the formation of an olefin and an aldehyde:

$$\underset{\sim C-CH\sim}{\overset{O \;\; CH_3}{| \quad |}} \xrightarrow{h\nu} \underset{\sim CH}{\overset{O}{|}} + \underset{CH\sim}{\overset{CH_2}{|}} \tag{2.12}$$

The activation energies of the Norrish reactions are different; the probability of Norrish-II ($E_a = 0.85$ kcal/mol) is higher at room temperature than that of Norrish-I ($E_a = 4.8$ kcal/mol); the latter is, however, more probable at higher tempertures.

2.6 Photooxidation

Polymer photooxidation is very similar to thermal oxidation of polymers [4]. Significant differences exist with respect to the photochemical decomposition of the hydroperoxide and carbonyl groups, as well as with regard to the initiation reaction. The formation of polymer radicals

$$RH \longrightarrow R\bullet + H\bullet \tag{2.13}$$

by scission of a C–H bond is a possible consequence of UV irradiation. The probability of reaction (2.13) is higher than that of the direct reaction between molecular oxygen and a polymer, although the probability of the latter reaction may be increased due to UV excitation.

Not only can the polymer be in an excited state, but the oxygen as well. There are two types of excited singlet oxygen ($^1O_2$) having different excitation energies above their ground state. The lower (more stable) excited singlet state ($^1\Delta_g$) has an energy excess of 22.5 kcal/mol; the higher ($^1\Sigma_g$), 37.5 kcal/mol. Singlet oxygen can be formed by direct irradiation of O_2; although this excitation is unfavorable, it is possible in the upper layers of the atmosphere. Ozone photolysis, which is very rapid in the upper atmosphere, leads to the formation of singlet oxygen. Singlet oxygen also forms easily in polluted (urban) atmospheres. This may cause the rapid deterioration of polymers in urban areas. Molecular oxygen can act as a deactivator of various excited species present in the polymer. Quenching usually results in formation of singlet oxygen. The lifetime of singlet oxygen in solution strongly depends on the solvent; for example, the lifetime of $^1O_2$ ($^1\Delta_g$) in methanol is 2 μsec, in benzene 24 μsec, and in carbon tetrachloride 700 μsec. Besides initiation of oxidation by hydrogen abstraction from a saturated hydrocarbon

$$RH + {}^1O_2 \ ({}^1\Delta_g) \longrightarrow R\cdot + HO_2\cdot \qquad (2.14)$$
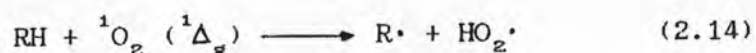
initiation may occur by the addition of singlet oxygen to unsaturated bonds present in polymers.

In photooxidation the sample thickness is even more important than in thermal degradation. The extent of oxidation mainly occurs in a very thin surface: layer of the material. The molecular weight of the polyolefins rapidly decreases during photooxidation. The average number of chain scissions (s) in a polypropylene sample as a function of irradiation time is shown in Figure 2.7. After longer UV irradiation, microcracks appear and the sample becomes opaque and brittle.

Various chromophores originally present in the polymer, accumulated during processing and storage, or added intentionally to the polymer may have an important effect on photostability. Metallic impurities, e.g., residues of Ziegler-Natta catalysts of metallic traces originating from processing equipment, may have a catastrophic effect because they can participate in various steps of photooxidation. Metal compounds can, however, be useful in some functioning as UV absorbers.
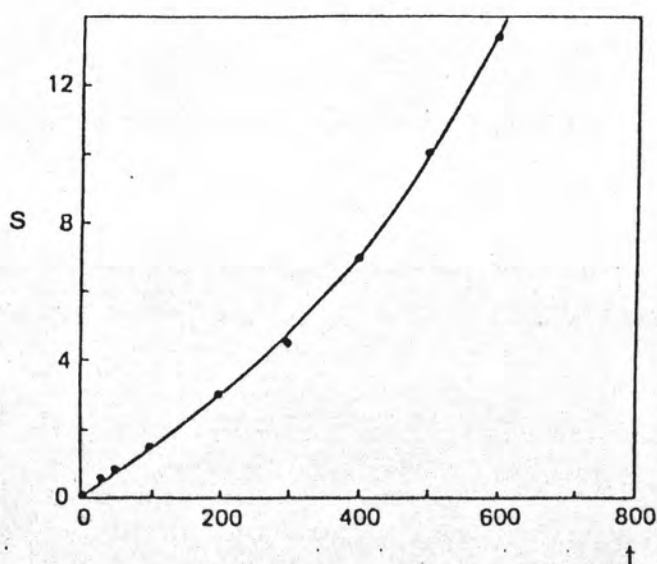

Figure 2.7 Average number of chain scissions $(s = P_{n,o}/P_n - 1)$ in one original macromolecule as a function of time [4]

2.7 Sensitized photodegradation

A photosensitizer usually has a high absorption coefficient for UV light; the excited compound either decomposes into free radicals and initiates degradation or oxidation of the polymer, or it transfers the excitation energy to the polymer (or to oxygen) [4]. A good sensitizer should be easily admixed with the polymer and must not decompose thermally or in the dark.

Polycyclic aromatic compounds, e.g., naphthalene, anthracene, pyrene, etc., are assumed to generate singlet oxygen by energy transfer to ground state oxygen molecules. Aromatic ketones and diketones abstract hydrogen or decompose after excitation and cause the initiation of photochemical processes. For example, excited benzophenone can abstract hydrogen from the polymer, or the radical formed from benzophenone can react with oxygen and form a $HO_2^{\cdot}$ radical and regenerate a benzophenone molecule:

$$+ \ O_2 \rightarrow \qquad + \ HO_2^{\cdot} \qquad (2.15)$$
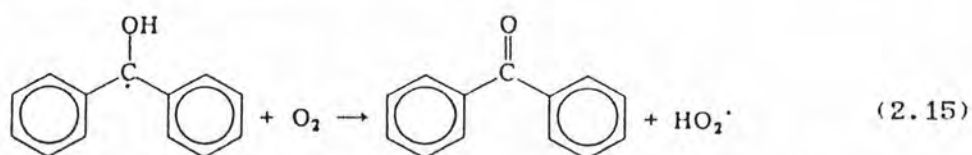
Quinones behave similarly: their excited state has biradical character, the biradical abstracts hydrogen from the polymer and hydroquinone forms. for example, the addition of various quinones sensitizes the photodegradation of polyisoprene solutions. The sensitizing effect is drastic, especially with anthraquinone.

Various nitrogen containing chromophores, e.g., azo, nitroso, and aromatic amino compounds, decompose to radicals when excited by UV light. For example, 2-chloro-2-nitroso-propane was found to sensitize photodegradation of polyisoprene even more effectively than anthraquinone. Some N-halides are also active sensitizers, e.g., trichlorosuccinimide. Organic disulfides, like peroxides, photodecompose to form radicals, hence causing initiation of the degradation process. Dyes can also be applied for sensitizing polymer photodegradation. For example, the photodegradation of cis-1,4-polyisoprene can be significantly accelerated by the addition of a small amount of methylene blue.

Both organic and inorganic metal compounds can sensitize photodegradation. Especially interesting is the fact the certain iron complexes, e.g., Fe(II) and Fe(III) complexes of

dithiocarbamates and 2-hydroxyacetophenone oximes, exhibit a delayed action as UV sensitizers. Fe(III) acetylacetonate (A) has an immediate effect; however, the effect of the Fe(III) complex of 2-hydroxy-4-methylacetophenone (B), as shown in Figure 2.8, can be observed only after an induction period of significant lenght. Ferrocene derivates such as benzoylferrocene (C) can act as photosensitizers.

(2.16)
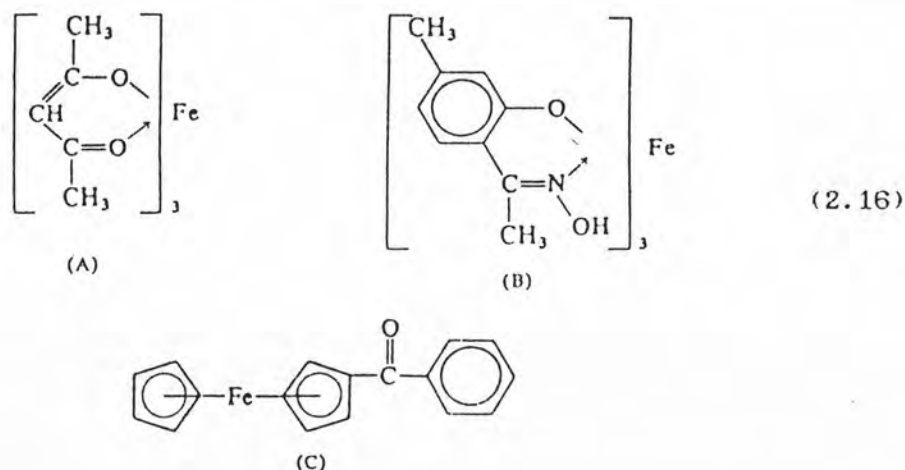
Inorganic metal oxides and salts, e.g., ZnO, TiO_2, and $FeCl_3$ accelerate photodegradation. It is assumed that free radicals are formed from these compounds during irradiation.

Another type of photosensitized polymer contains the sensitiser in the form of chromophores chemically bound to the polymer or incorporated as comonomer units into its backbone. Such photodegradable polymers have been prepared by copolymerization of ethylene with carbon monoxide, of methyl methacrylate with methyl vinyl ketone, and of styrene with phenyl vinyl ketone. Among the copolymers containing carbonyl groups, the yield of photolytic scission is small when CO is in the backbone and relatively high when CO is in a pendant group. Vinyl polymers and polyamides have been prepared with pyridine or pyrazine rings in the backbone. Polymers with unsaturated bonds in the main chain are sensitive to photodegradation.
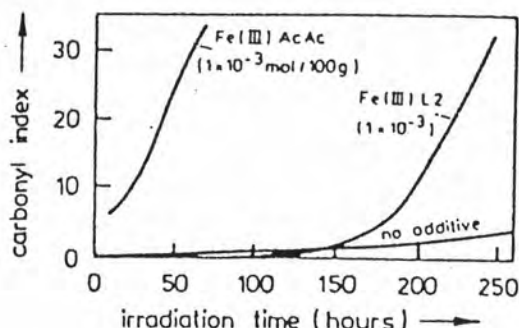
Figure 2.8   Carbonyl index (IR absorbance due to =CO groups
related to a reference absorbance) as a function
of time during UV irradiation of low density
polyethylene samples: Fe(III)AcAc =
Fe(III) acetylacetonate; Fe(III)L2=
Fe(III) 2-hydroxy-4methylacetophenone [4]

2.8   Ultraviolet light

An important thing to know is that ultraviolet is not a
single entity, but is a wide band of wavelengths [5]. This fact
is not often realized. The chief natural source of UV is the sun.
In fact, about 9% of all energy emitted by the sun is UV. Most of
which is in the region between 300-400 nm. Artificial sources of
UV include incandescent, gas discharge, low pressure mercury,
medium pressure mercury metal halide, electrodeless and xenon
lamps.

An interesting characteristic of UV radiation occurs
when it falls upon certain substances known as phosphors, where
it causes the phosphors to emit specific radiation. This
phenomenon is known as fluorescence. Everyday fluorescent
lighting is basically a UV lamp constructed of a type of glass
bulb that blocks UV rays. The inside of the bulb is coated with

a thin layer of fluorescent material that receives UV generated by the lamp and in turn emits a visible light in return.

Scientifically speaking, ultraviolet light is electromagnetic radiation in the part of spectrum between X-rays and visible light. It differs from light only in that its wavelength are too short to be seen by the human eye. The boundary between visible light and UV light is usually taken to be radiation with a wavelength of 400 nanometers (4000 angstroms). It is customary to divide the UV spectrum into near UV (300-380 nm) and for UV (200-280 nm), the adjectives near and far indicating the relative distance from visible light.

One effect of UV energy upon certain substances is a phenomenon that takes place at the atomic level. UV energy affects the charge carried by the proton orbiting the nucleus of an atom. This forces the proton into a different orbit and produces the gloves we call ultraviolet fluorescence. Fluorescence, then, is produced by the material itself when its atoms are excited by UV energy the material is the light source. When the UV energy is turned off, the proton resumes its natural orbit and we no longer see it glow.

On some materials the fluroescence lingers and disappears slowing after the UV source is removed. Here, the protons return slowly diminishing fluorescence called phosphorescence. These unique properties of UV fluorescence and phosphorescence are but two of the many ultraviolet radiation phenomena that make it vital to science and industry alike.

2.9 Identification and selection of degradation sensitizing additive

In order to have maximum utility in practical applications, on additive or additive systems for polyethylene

one should have the following characteristics [6]:

1. Effective sensitization of photo-oxidative degradation of the polymer.

2. No adverse effect on the thermal-oxidative stability of polyethylene, so that the additive can be in corporated prior to melt processing.

3. Minimal effect on color and transparency of the polymer.

4. Preferably, the wavelength of maximum photosensitivity should be in the range 300 to 330 nanometers, so that degradation would be rapid in sunlight but slow under normal indoor illumination.

5. The additive(s) should be readily incorporated in molten polyethylene, and should remain well dispersed in the polymer as the melt solidifies.

2.10 Literature review

Many investigators studied the degradation of plastics in different ways. The works reported on the changes of artificial weathering and natural weathering with and/or without introducing photosensitizers into the plastic. The physical, chemical porperties and character of degradable plastics were observed. Some works were summerized as follow.

Raab, M., et al. [7] studied the degradation of LDPE film containing quinoid sensitizers, anthraquinone, α-butylanthraquinone and 2-octanovloxyanthraquinone. LDPE films were exposed to the UV light from a fluorescent tube. The changes in strain at break, Young's modulus, yield stress and IR absorptions were recorded during irradiation to control the undergoing processes in the

LDPE films. The effect of UV exposure time on the mechanics of all samples was studied and infrared-spectra of undoped and doped LDPE samples with irradiation time were investigated by following the 1715 cm^{-1} band with corresponding to the presence of the carbonyl group in the PE chain and the 1675 cm^{-1} band corresponding to the carbonyl group in the molecule of anthraquinone or of its 2-substituted derivatives.

Taylor, L.J. and Tobias, J.W. [8] studied the accelerated photo-oxidation of polyethylene. A number of additives observed to promote photo-oxidative degradation of PE films had been evaluated with respect to their relative photo-initiating effectiveness at wavelengths near 300 nm. Depending on the nature of the additive, the photo-oxidation process may display autoretarding or autoaccelerating behavior. Thermomechanical analyses and gel content measurements on UV exposed films containing substituted anthraquinones suggest that at short exposure times, photo-oxidative degradation was accompanied by photochemical crosslinking.

Czekaj, T. [9] studied the activity of Schiff's bases of cinnamic aldehyde and aromatic amines in the controlled photodegradation of PE. N-cinnamylidene anilines containing different substituents in the amine ring (methyl group, halogen, or amine group) and N-cinnamylidene-naphthyl amine were synthesized and introduced into the polyethylene film by compression molding or extrusion and they were exposed to the filtered UV light produced by mercury lamp. The changes in molecular weight, tensile strength, and characteristic IR absorptions were followed during irradiation to control the processes undergoing in the polymer films. It was discovered that N-cinnamylidene anilines containing methyl or halogen substuents and N-cinnamylidene amine accelerated the photodegradation of PE. Their sensitizing activity increased when the mixtures of Schiff's bases and stannous laurate were introduced into the

polymer. PE films containing these additives become brittle after 600 hours exposure to artificial UV light which was the equivalent of 1.5-2.0 years exposure to natural sunlight in the medium geographic latitudes.

Kapko, J. [10] examined the sensitizing role of two-component system consisting of N,N',N"-triphenylguanidine (TPG) and metal laurates in LDPE films. The first step made fast selection of the optimal sensitizer concentration possible. In the second step, changes of molecular weight and tensile strength of PE were determined. The tensile strength decrease (in %) was almost proportional to the deterioration of PE, caused by irradiation.

Qureshi, F.S, Amin, M.B., Maadhah, A.G. and Hamid, S.H. [11] investigated the weather-induced degradation of LLDPE. It was shown that a characteristic feature of the ultimate mechanical properties was their sensivity to the presence of flaws in the bulk of the material, which facilitated the use of ultimate properties in the detection of processes that occurred at localized sites. Dimensionless tensile strength and percent elongation of LLDPE were studied with weathering time. There was a sudden loss in both these properties soon after exposure. Within 3 months of exposure almost 50% of the value of these properties was lost.

Kubota,H.,Takahashi, K. and Ogiwara, Y. [12] investigated the effects of benzophenone on the photodegradation of polyethylene by analyzing the ESR and infrared spectra of the irradiated samples. Infrared spectra of the irradiated PE showed that benzophenone strongly accelerates the formation of double bonds. It is believed that benzophenone acted in the photodegradation of polyethylene to enhance the formation of allyl and polyenyl radicals, which starts at the double bonds in the sample.

Kapko, J., Czekaj, T. and Huczkowski, P. [13] studied the sensitized photodegradation of polyethylene. PE films was irradiated in the Weather Ometer with Pyrex filter. When filter was used, one hour of irradiation in the cabinet corresponded with one hour exposure to summer sunlight in Poland. The change of physical properties of some sensitized LDPE films was studied. It was concluded that dialkoxybenzophenone was the most active photosensitizer but did not stabilize LDPE during processing.

Andrady, A.L. [14] studied the outdoor weathering of polyethylene homopolymer under exposure in air and in sea water. Photooxidative degradation of polyethylene films as monitored by changes in the tensile properties, particularly the mean ultimate extension, was markedly lower when the samples were exposed outdoors, floating on sea water, compared to those exposed in air. The slower rates of degradation in sea water were possibly due to the samples being maintained at a relatively lower and stable temperature in sea water compared to those exposed in air. A similar study on a commercially available enhanced photodegradable PE was found to undergo rapid loss in ultimate tensile extension, even where the samples were exposed floating in sea water. The rate of degradation was marginally slower in sea water than in air, but the samples were embrittled in both cases.

Cheeranee [15] investigated the photodegradation of HDPE by natural weathering and accelerated weathering. In order to increase the rate of photodegradation, 2-photosensitizers was added to HDPE sheets in various concentrations. The properties before and after irradiation was examined by physic and structure. It was seen that the difference in degradation rate of photosensitizing HDPE at various concentration was small.