

CHAPTER II

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

2.1 Introduction of Photodegradation

Sunlight was soon recognized as an important factor in the deteriorative aging and weathering processes which occur in commercial polymers [4]. The reasons for this are readily understood. The wavelength of the radiation from the sun which reaches the earth's surface extends from infrared (> 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 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 be broken may be described as 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 photodegradation, 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 photodegradation is usually homolytic bond scission to form free radicals. These radicals will normally react rapidly with any oxygen present. In this way, visible and UV radiation are particularly effective initiators of oxidation.

Polymers have different photodegradative sensitivities of UV light at different wavelengths [5]. The varying sensitivities result from differences in the chemical structure. As shown in Table 2.1, the maximum sensitivity of several polymers (as determined by the bond dissociation energies) is in the range of 290 and 400 nm. 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.

Table 2.1 Wavelength of UV radiation (energy of a photon) at which various polymers have maximum sensitivity [5].

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

2.2 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, or by energy transfer to some acceptor. 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 radiation (I_0) will be only partly transmitted (I) through the material; the logarithm of the transmittance ($T=I/I_0$), is proportional to the thickness of the layer (l) and to the

concentration of the absorbing component (C) ;

$$A = -\log T = \log I_0/I = \epsilon l C \quad (2.1)$$

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 molecules ; this absorbed energy is exactly equal to the energy of a light quantum:

$$\Delta E = h\nu \quad (2.2)$$

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

$$\nu = c^* / \lambda = c^* \nu^* \quad (2.3)$$

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).

2.3 Photochemical Processes

The chemical processes of photodegradation include isomerization, dissociation, and decomposition of a molecule.

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 decomposition :

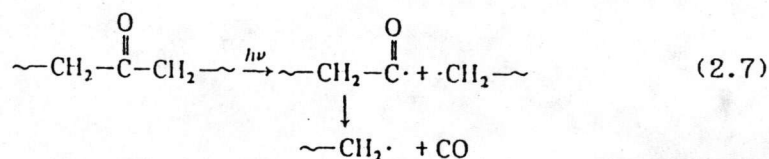


Dissociation of the O-H bond is less facile :

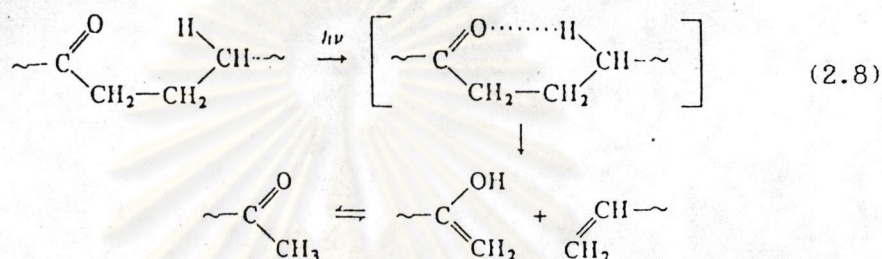


Because of low bond dissociation energy, decomposition according to reaction (2.4) is predominant in polymer photooxidation.

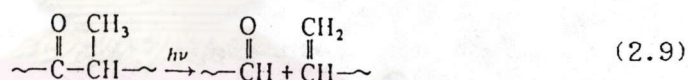
The role of carbonyl groups in polymer photooxidation is of great importance because once they have been formed they absorb UV light readily, hence, excitation to singlet and triplet states is easy. The excited carbonyl groups decompose via Norrish reactions of types I, II and III. The Norrish-I reaction is a radical cleavage of the bond between the carbonyl group and the α -carbon atom (α -scission), and is usually followed by the formation of carbon monoxide:



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 δ -carbon atom results in decomposition by β -scission to an olefin and an alcohol or ketone. For example, in the case of polyethylene, a terminal double bond and an enol/ketone end group are formed:



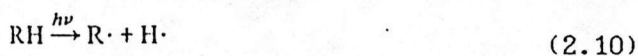
The Norrish-III reaction is also a nonradical chain scission; however, it involves the transfer of a β -hydrogen atom and leads to the formation of an olefin and an aldehyde:



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 temperature.

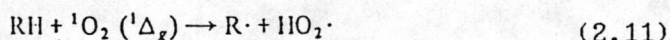
2.4 Photooxidation

Polymer photooxidation is very similar to thermal oxidation of polymers. 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 by scission of a



C-H bond is a possible consequence of UV irradiation. The probability of reaction (2.10) 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. Besides initiation of oxidation by hydrogen abstraction from a saturated hydrocarbon, initiation may occur by the addition of singlet oxygen to unsaturated bonds present in polymers.

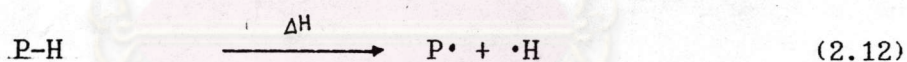


In photooxidation the sample thickness is even more important than in thermal degradation. The extent of oxidation mainly occurs in a very surface layer of the material. The molecular weight of the polyolefins rapidly decreases during photooxidation.

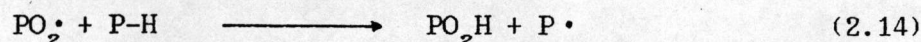
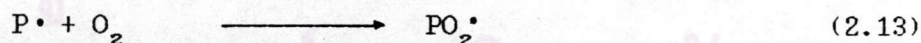
Various chromophores originally present in the polymer, accumulated during processing and storage, or added intentionally to the polymer may have an important effect on photostability. Metallic impurities, e.g., residues of Ziegler-Natta catalysts or metallic traces originating from processing equipment,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

Therefore, hydroperoxide groups are capable of absorbing (albeit very weakly) sunlight wavelengths photochemically harmful to the polyolefins. It is believed that the hydroperoxide groups are formed during the manufacture and/or melt processing of the polyolefin by the Bolland-Gee autooxidation mechanism thus [6]

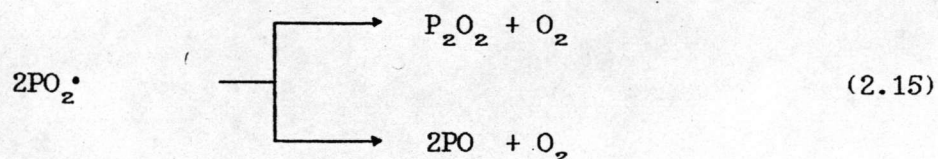
Initiation



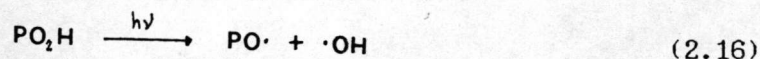
Propagation



Termination



On exposure to light, the hydroperoxides dissociate in the excited state to give alkoxy and hydroxyl radicals thus



The radicals $\text{PO}\cdot$ and $\cdot\text{OH}$ can then start the free-radical chain process.

2.5 Photodegradable Plastic

Photodegradable plastics are used for applications where materials are used out-of-doors for a limited time only and it is not economically desirable to collect the residual materials after use [7]. Examples are agricultural cordage and films, packaging films and drinking cups. Thus, sensitized photodegradation is mainly restricted to the bulk plastics such as polyolefins, poly (vinyl chloride) (PVC) and polystyrene.

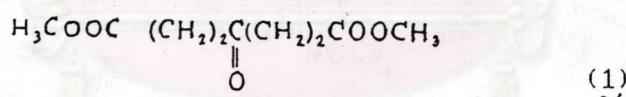
Although many unstabilized plastics such as polypropylene and polystyrene are themselves light-sensitive, if ultraviolet deterioration by sunlight exposure is desirable then it is important to be able to control and, indeed, monitor this effect. At present there are two ways of achieving this aim: one is the use of specially prepared photosensitive plastics, and the other, appropriate selection of photoactive additives which are incorporated in the commercial plastic during processing.

2.5.1 Photosensitive Plastics

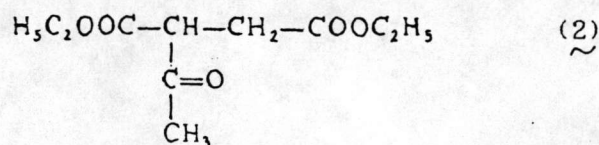
One effective method of preparing photosensitive plastics is to copolymerize the monomer with variable amounts of

carbon monoxide or a vinyl ketone monomer. The plastics will degrade when exposed to outdoor sunlight but will remain intact if kept indoors, i.e., behind window glass. This is because the ketonic groups introduced into the plastics do not absorb light of wavelengths greater than about 330 nm which is the cut-off point for soda glass. On exposure out-of-doors, where the light also contains radiation in the region 290-330 nm, the same ketonic groups are photoactive and can initiate degradation of polymer by the Norrish type II process. Control of photodegradation is achieved by varying the concentration of carbon monoxide gas or ketone monomer during polymerization.

Photodegradable poly(ethyleneterephthalate) has been prepared by using a keto-diester such as dimethyl- δ -ketopimelate of structure (1). The polyester degrades

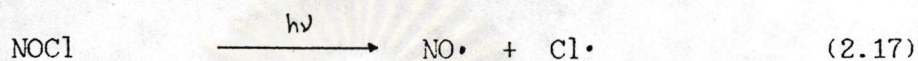


by a Norrish type I process. Using diethyl acetyl succinate of structure (2), the diester did not produce a photodegradable polyester since the ketone group on the side-chain does not directly cause scission of the polymer backbone.

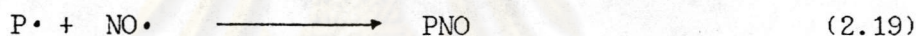
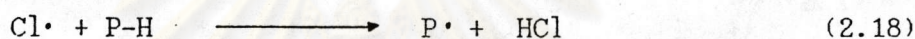


A recent modification of the above processes involves the introduction of photosensitive carbonyl groups into the polymer backbone by a photooxidation process. Polyethylene,

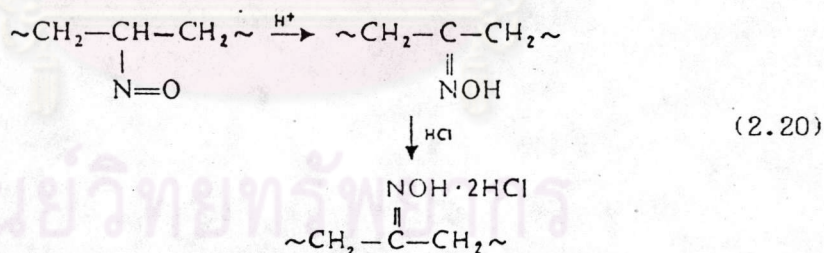
for example, is treated with nitrosyl chloride (NOCl) and hydrogen chloride gases. During the treatment process, the polymer is irradiated with visible light (wavelengths > 400 nm). This process generates nitroxyl and chlorine radicals by the following process



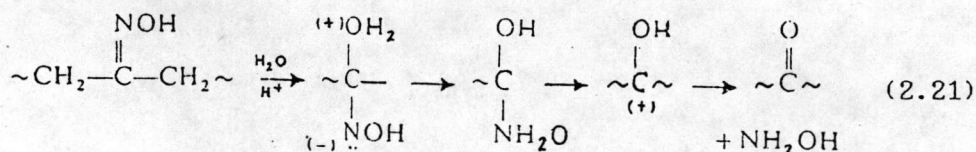
The photooxidation reaction then follows a non-chain radical mechanism to give a nitroso derivative



The presence of HCl causes the intermediate nitroso derivative to isomerize to the oxime and stabilization as the hydrochloride.

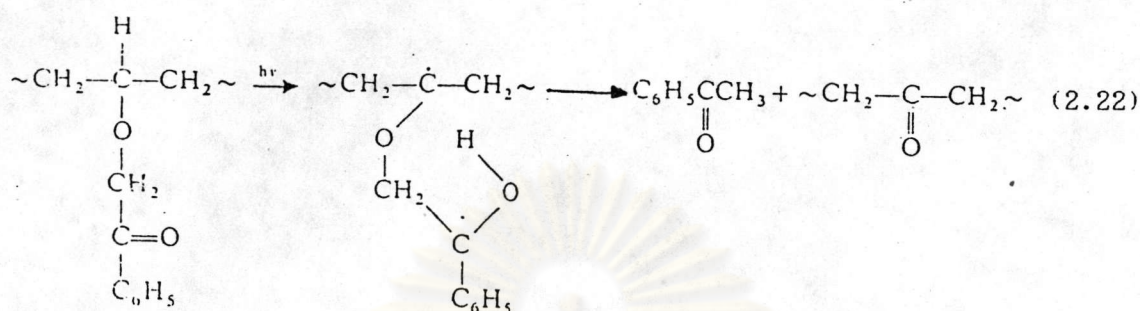


The carbonyl group is then obtained by hydrolysis of the oxime.



Another process involves the grafting of diazoacetophenones onto an ethylene-vinyl alcohol copolymer to give a photodegradable polyethylene. During irradiation, and intramolecular hydrogen-abstraction process gives rise to free

alkyl aryl ketone (acetophenone) and in-chain ketone groups.



Sensitized photodegradation is then believed to occur predominantly by the Norrish type I and II processes involving the "in-chain" ketone groups. The free alkyl aryl ketone may also sensitize the photodegradation of the polymer by a hydrogen atom abstraction process, but to a much lesser extent than the "in-chain" ketone.

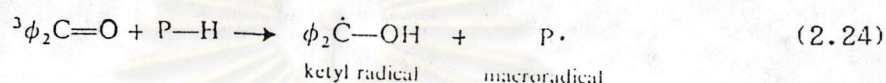
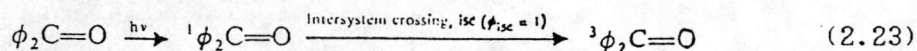
2.5.2 Photoactive additives (Photosensitizers or Prodegradants)

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). A good sensitizer should be easily admixed with the polymer and must not decompose thermally or in the dark.

Carbonyl compounds

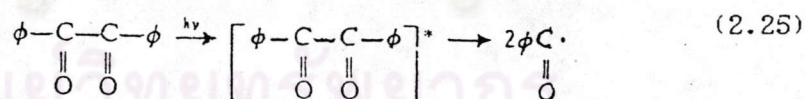
A wide range of derivatives of aromatic aldehydes, ketones and quinones effectively sensitize the photodegradation of plastics. The most effectively studied group of compounds is benzophenone and its derivatives. These compounds sensitize,

through a primary photochemical process of hydrogen atom abstraction from the polymer involving the photoexcited triplet state of the carbonyl group.



The macroradical, P·, then initiates the oxidative chain process.

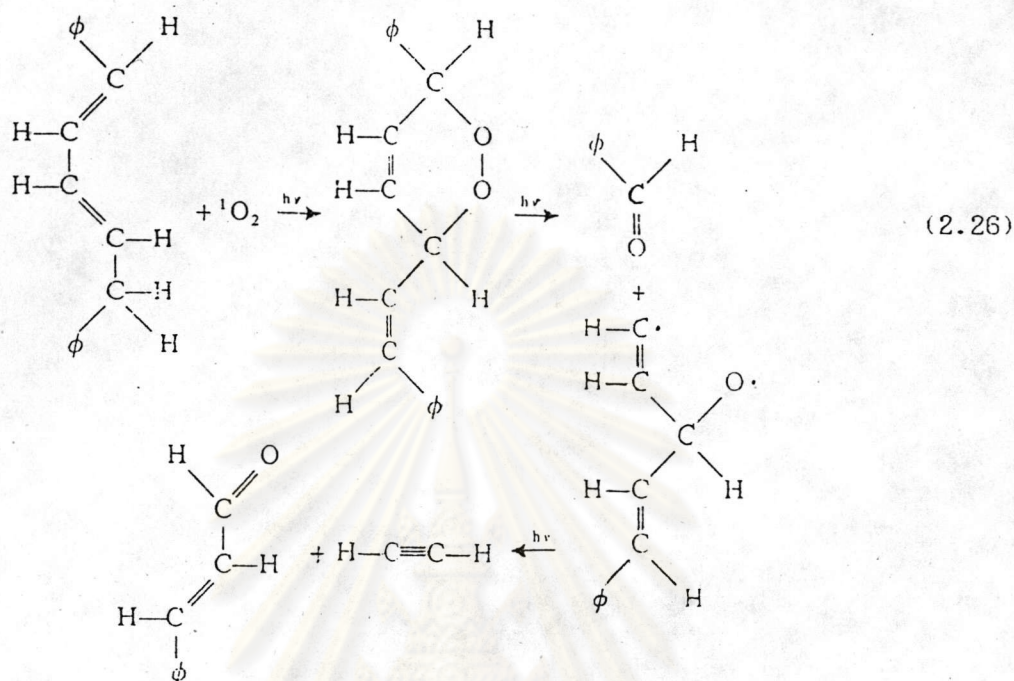
Aromatic diketones are also very effective photosensitizers for plastics. One of the most extensively studied aromatic α -diketones is benzil. When photolysed this compound gives benzoyl radicals by the following mechanism.



These radicals are highly reactive and can abstract hydrogen atoms from the polymer. The high photochemical activity of aromatic diketones has led to their use as photosensitizers for photopolymerization and photografting processes.

Aromatic carbonyl compounds have also been introduced into polyolefins as photosensitizers by an indirect process. Aromatic dienes such as 1,6-diphenyl-1,3,5-hexatriene

have been formed to give benzaldehyde and cinnamic aldehyde during photooxidation by the following process



The singlet oxygen is formed initially by quenching of the photoexcited triplet state of the diene by ground state molecular oxygen.

Quinones behave similar to benzophenone: their excited state has biradical character, the biradical abstracts hydrogen from the polymer the hydroquinone forms. For example, the addition of various quinones sensitizes the photodegradation of polyisoprene solutions. The sensitizing effect is drastic, especially with anthraquinone.

Transition - metal compounds

Apart from the carbonyl-based photosensitizers, certain types of transition-metal complexes and salts have also been found to be effective as photosensitizers for plastics. Of the transition-metal salts, the chlorides have been widely studied as photosensitizers. The effect of different

transition-metal halides on the rate of photooxidation of polypropylene is shown in Figure 2.1.

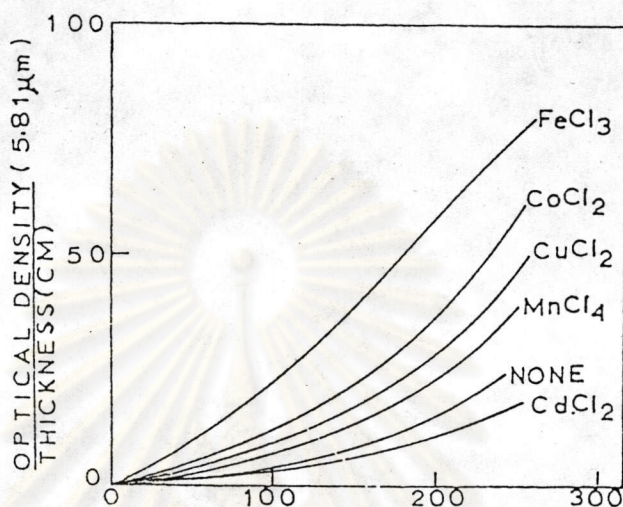
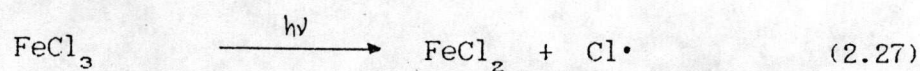
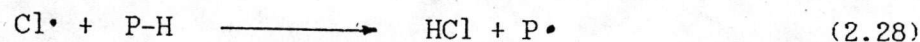


Fig. 2.1 Effect of metal chlorides in accelerated ultraviolet degradation of polypropylene as indicated by carbonyl formation [6].

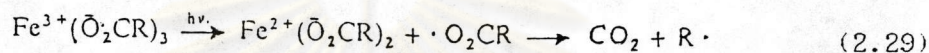
It is interesting to note that only the transition-metal salts are photosensitizers. Ferric chloride, which is the most effective, has been shown to give ferrous chloride and chlorine radicals during irradiation.



The chlorine radicals may then abstract hydrogen atoms from the polymer substrate to give hydrogen chloride and a macroradical center.



Of the many transition-metal complexes, iron complexes are particularly favoured because of their cheapness and low toxicity. Ferric stearate has been intensively studied and is believed to sensitize by first absorbing light, then undergoing electron transfer to give a carboxylic acid free radical. This species then decarboxylates to give an alkyl radical, which initiates polymer degradation.



Another photoactive additives such as 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 radicals sensitized 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 addition of a small amount of methylene blue.

2.6 Literature Review

There are many reports investigating the degradation of polymers in different ways. Some reports have investigated the changes in artificial weathering and natural weathering with and/or without introducing photosensitizers into the polymer. The physical and chemical properties of photodegradable plastics were observed. Some works were summarized as follow.

Torikai et al [7] studied photodegradation of polyethylene. Four kinds of annealed polyethylene films with varying densities as shown in Table 2.2, were photo-irradiated with medium pressure mercury lamp. Photodegradation processes were followed by ultraviolet and fourier transform intrared spectroscopic techniques and by gel and mechanical porperty measurements.

Table 2.2 Characteristics of polyethylene [7]

Sample	Commercial name	Density (g/cm ³)	Melt index (g/10 min)
I	Hizex 2200J (HD)	0.970	5
II	Hizex 5100B (HD)	0.945	0.25
III	Neozex 4060B (MD)	0.945	7
IV	Neozex 2015H (LLD)	0.922	1.2

Oxygenated products build-up such as carbonyl and hydroperoxide was more favoured in LLDPE and the rate of formation increased in the reverse order of polymer density. A

similar trend was seen in gel formation. Measurements of elongation at break (%) showed that the embrittled time of photo-irradiated PE increased with the decrease of polymer density (see Figure 2.2). Elongation at break of annealed HDPE was very small both before and after photo-irradiation. The experimental results on unquenched samples were compared with those of quenched samples. It was found that the photostability of quenched LLDPE is superior to annealed LLDPE because of the density (or crystallinity) and crystal size of PE play important roles in determining photostability.

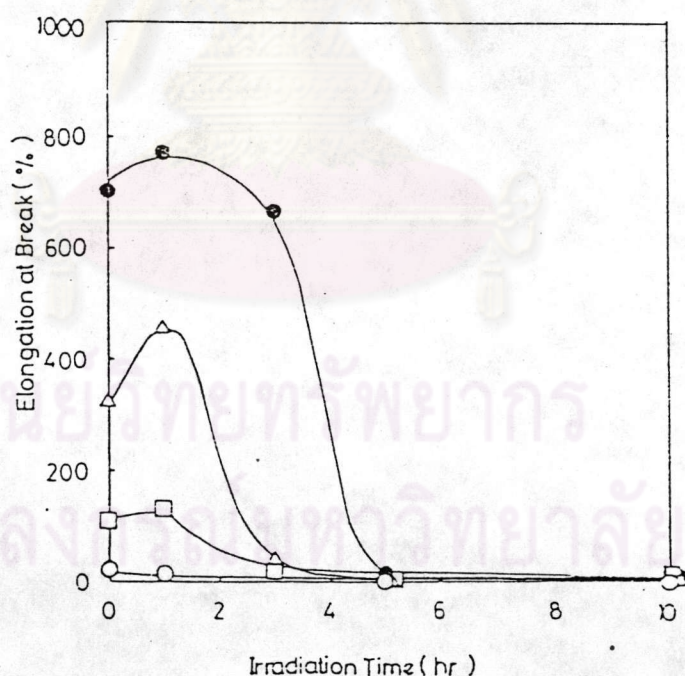


Fig. 2.2. Changes in elongation at break (%) with irradiation time of PE samples photo-irradiated in air at 30°C: sample I(○), II(△), III(◻), and IV(●) [7].

Andrady [8] studied weathering of polyethylene (LDPE) and enhanced photodegradable polyethylene in the marine environment. The outdoor weathering of polyethylene homopolymer and enhanced polyethylene (1% CO copolymer) under exposure in air and in sea water were studied. 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 in sea water, compared to those exposed in air, as shown in Figure 2.3. The slower rates of degradation in sea water were possibly due to the samples being maintained at a relatively lower temperature.

The enhanced photodegradable polyethylene was found to undergo rapid loss in ultimate tensile extension, even where the samples were exposed floating in sea water. The rate of degradation marginally slower in sea water than in air, but the samples were embrittled in both cases.

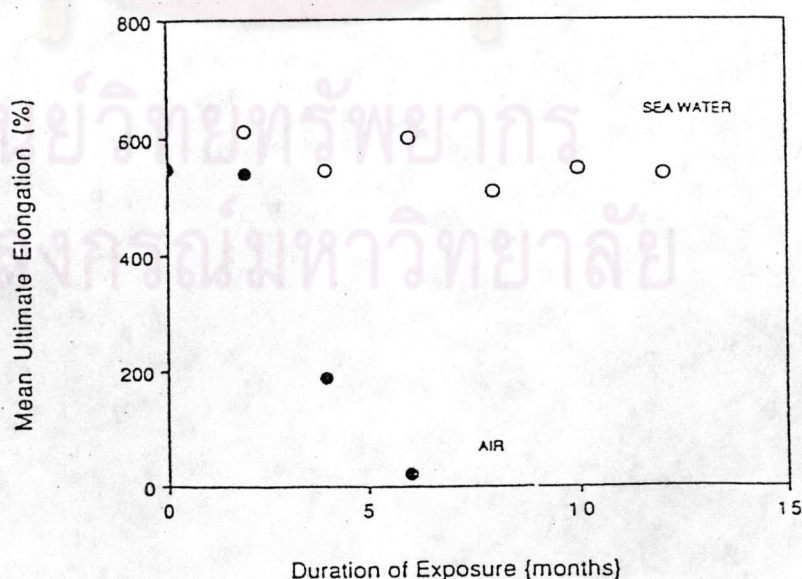


Fig. 2.3. The variation in the mean ultimate elongation of polyethylene samples with the duration of exposure [8].

Li and Guillet [9] studied the photochemistry of ethylene copolymers with carbon monoxide (CO), methyl vinyl ketone (MVK), and methyl isopropenyl ketone (MIPK) in solid films, the thickness of films was 0.10-0.15 mm. Infrared evidence is presented to show that a variety of unexpected ketone structures is presented in these polymers as a result of 1,5-hydrogen transfer or "back-biting" via a six-membered ring during free radical polymerization. The overall quantum yield for carbonyl disappearance which increases from 0.074 to 0.24 to 0.26 in the series PE-1% CO, PE-2% MVK and PE -2% MIVK which reflects the increasing stability of alkyl radicals produced from Norrish type I process in the respective ketone structures. In this work medium pressure mercury lamp was used.

It has been found that ketone groups located in side chains of polyethylene are photochemically much more reactive. Ketone groups located in the backbone of a polymer, as in the 1% CO copolymer, are important in polymer photodegradation primarily because of the Norrish type II chain scission process. Ketone groups bonded as a side chain to the polymer backbone are efficient in type II photo-scission and as free radical sources via the Norrish type I reaction. Studies of the gaseous products from extensive photodegradation under nitrogen show that in all three cases carbon monoxide is the major product (46-65% of the total). Acetaldehyde and methane, expected from the Norrish type I reaction, are major products only for the MVK and MIPK copolymers.

Czekej [10] examined the activity of Schiff's bases of cinnamic aldehyde and aromatic amines in the controlled photodegradation of polyethylene. N-cinnamylidene anilines

containing different substituents in the amine ring (methyl group, halogen, or amine group) and N-cinnamylidene α -naphthyl amine were sensitized and introduced into the polyethylene films 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 into the polymer films. It was discovered that N-cinnamylidene anilines containing methyl or halogen substituents and N-cinnamylidene α -naphthyl amine accelerated the photodegradation of polyethylene. Their sensitizing activity increased when the mixtures of Schiff's bases and stannous laurate were introduced into the polymer. PE films containing these additives became brittle after 600 h exposure to the artificial UV light which was the equivalent of 1.5-2 years exposure to the natural sunlight in the medium geographic latitudes.

Taylor and Tobias [11] studied accelerated photo-oxidation of polyethylene. A number of additives observed to promote photo-oxidative degradation of LDPE films has been evaluated with respect to their relative photoinitiating effectiveness at wavelengths near 300 nm. Depending on the nature of the additive, the photo-oxidation process may display autoretarding or autoaccelerating behaviour.

Gonzalez and DeSaja [12] studied a durability index in the weathering of LDPE films. Degradation resulting from weathering in LDPE films used in agricultural applications was investigated by a series of mechanical and spectroscopic characterization techniques. An easy, sensitive and

nondestructive test, based on conventional microhardness measurement was presented and found that this technique can give very significant information on the durability of the LDPE films. Apart from the initial scission of LDPE chain and in the later exposure stage considered, probably simultaneously with the chain scissions, a predominant crosslink phenomenon, with a three dimensional network formation, may be the reason for the increase in the microhardness and deterioration in the properties of the degraded material.

Qureshi et al [13] investigated the weather-induced degradation of LLDPE. It was found that a characteristic feature of the ultimate mechanical properties was their sensitivity to the presence of flaws in the bulk of the materials. 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 of these properties soon after exposure. Within 3 months of exposure almost 50% of the value of these properties was lost.

Rabb et al [14] examined the effect of UV light on the mechanical properties of polyethylene and polypropylene films. It has been observed that photochemical degradation of polyethylene does not occur uniformly across the thickness of the material; a gradient of degraded material seems to exist. The damage is localized within a few micrometers of the surface and decreased quickly with depth. Such a gradient gives rise to internal stresses. In addition, the spherulitic boundaries, characterized by a high concentration of surface irregularities (including chromophores), result in weak center formation. These

defects eventually lead to stress concentration and microcracks. A schematic representation of the phenomenon is shown in Figure 2.4.

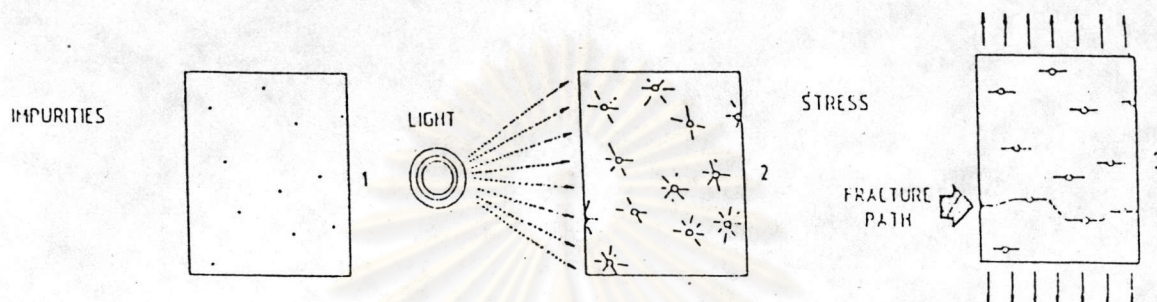


Fig. 2.4. Schematic diagram illustrating subsequent effects of UV radiation and mechanical stress on the formation of weak centers and microcracks in sites of initial chemical heterogeneities [14].

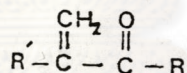
Bremer [15] investigated photodegradation of the ethylene-carbon monoxide (E-CO) copolymer. Four different polymers, containing nominal 0, 0.5, 1.0, and 1.5% carbon monoxide by weight were evaluated. These E-CO polymers were tested outdoor weathering and accelerated weathering. Photodegradation processes were followed by mechanical properties and melt index. It was found that photodegradability increases with the increase of carbon monoxide concentration in both cases.

Kapko [16] studied 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

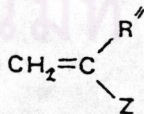
determined. The tensile strength decrease (in %) was almost proportional to the deterioration of PE, caused by irradiation.

Guillet and Troth [17] claimed in the patent related to photodegradable polymer masterbatches. Polymer compositions photodegradable upon exposure to UV radiation comprise a blend of a synthetic polymer and a ketone copolymer, containing about 0.01 to about 5 weight per cent carbonyl groups.

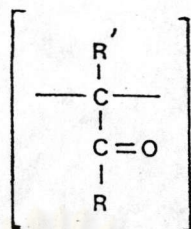
The UV photodegradable addition ketone copolymers used for blending with synthetic polymers in composition of the invention. In general they comprise copolymers of at least one unsaturated ketone of general formula



where R' represents a hydrogen atom or lower alkyl group, an R represents an alkyl, alkaryl, alkenyl or aryl group, having from 1 to 9 carbon atoms, and at least one vinylidene monomer of general formula



where R'' represents hydrogen, halogen or an alkyl group, and z is a functional group such as aryl, substituted aryl, carboxylic acid, lower alkyl carboxylate, lower alkyl, lower alkenyl, hydrogen, halogen, nitrile, lower acryloxy, lower alkoxy or amido. The copolymer thus contain the structural unit



which is responsible for the photodegradability on exposure to UV radiation.

Bailey and Taylor [18] claimed in the patent related to photoreactive plastic composition and articles degradable ultraviolet radiation and a process for their manufacture. A photoreactive plastic composition degradable by UV radiation, said composition consisting essentially of a photodegradable polymer having uniformly dispersed therein about 0.01-10% by weight of at least one photosensitizer. There is also provided a process for the preparation of the photoreactive plastic composition. The photoreactive plastic compositions are useful for making plastic articles, particularly plastic packaging materials.

Typical of the photosensitizers are aliphatic and aromatic ketones, for example, acetophenone, acetoin, benzophenone, benzoin, and anthrone. Also useful as photosensitizer are quinones, peroxides and hydroperoxides.