



Chapter 2

Theoretical Consideration and Literature Review

2.1 Polyethylene

Polyethylene, $n(\text{CH}_2-\text{CH}_2)_n$ is the most extensively used thermoplastic. The ever-increasing demand for polyethylene is partly due to the availability of the monomer, ethylene, from abundant raw materials : associated gas , and naphtha. The ease of processing of the polymer, its relative low cost , its resistance to chemicals, and its flexibility are also strong influences. All these and other factors lead to generally strong market demand for polyethylene.

High pressure polymerization of ethylene was introduced in the 1930's. The discovery of new titanium catalysts by Karl Ziegler in 1953 opened a new era for the polymerization of ethylene at lower pressures.

The two most widely used grades of polyethylene are low density polyethylene, LDPE, which has branched chains , and high density polyethylene, 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 back-bone of the polymer. HDPE is more closely packed because of the absence of branches and thus the molecules are closer to one another and less permeable to gases.

Several processes can produce polymers with a wide range of densities that cover both the low and high density ranges as well as medium density polymers.

2.1.1 Physical and chemical properties

Probably the most important property of polyethylene is its molecular weight and its distribution within a sample. Methods used to determine molecular weights are numerous. A widely used one is viscosity determination. The melt viscosity and the melt flow index, MFI, measure the extent of polymerization. A polymer with a high melt flow index has a low melt tensile strength.

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 alkalis. 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 polyethylene is relatively low, but impact resistance is high. The use of polyethylene in insulation is due to its excellent electrical resistance properties.

Table 2.1 [3] gives some of the properties of low and high density polyethylenes.

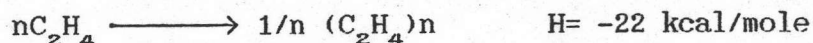
Table 2.1 Typical Properties of Polyethylenes

Polymer	Melting point range °C	Density g/cm ³	Degree of crystallinity %	Stiffness modules psix10 ³
Branched, Low density	107-121	0.92	60-65	25-30
Medium density	0.935	75	60-65
Linear, High density				
Ziegler type	125-132	0.95	85	90-110
Phillips type	0.96	91	130-150

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



Decomposition



2.1.3 High density polyethylene

All high density polyethylenes 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 a metal oxide, usually either chromium oxide or molybdenum oxide. Catalyst preparation and activation are very important. They 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 circulation gas.

The heat of reaction is removed by circulating the gas through heat exchangers, then compressing it for recycling to the reactor. In the Hoechst process, ethylene recycle and monomer recovery systems are not required because of the almost complete conversion of the ethylene. Yield is more than 99 percent. Because of the small amount of catalyst used, its removal from the polymer is not necessary. The polymer is usually in the form of a powder or granules, depending on reaction temperature. Either solution or suspension reaction conditions may be used. Above 130°C, the hydrocarbon is a solvent for the polymer; below this temperature, the polymer forms a suspension. Typical reaction conditions for three of the major process are given in Table 2.2 [3].

Table 2.2 Typical Reaction Conditions for Some Processes for the Production of HDPE

	Union Carbide	Hoechst AG	Naptha Chimie
Temperature	85-105°C	80-90°C	60-100°C
Pressure	below 300 psig	below 147 psi	220-440 psi
Catalyst	supported chromium

The polymerization may be in the gas phase as in the Union Carbide process or in the liquid phase where a hydrocarbon diluent is added. This requires a hydrocarbon recovery system. Branching in HDPE, and accordingly its density, cannot be adjusted in the same way as with LDPE. Other molecules are put into basic polyethylene to modify its properties to specific applications. They are doing this in both the liquid phase and the vapor phase and at high and low pressure. Branching in HDPE is incorporated in the backbone of the polymer by adding varying amounts of comonomer. Hexene is frequently used as the comonomer.

"To anyone but an expert, the line that differentiates low density from high density polyethylene resins is becoming more blurred."

2.1.4 Application

Products made from polyethylene are numerous and range from building 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 are 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 and/or abrasive materials, 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 use include notebook and reference book covers, wall covering tags labels, etc. The point-bonded, spun-banded polyethylene are used, for example, as laboratory coats, aprons, garments and sleeping bag liners.

2.1.5 Processing

Although plastic materials may in principle be processed in a variety of physical states (in solution, in emulsion, as a paste or as a melt), melt processing is used almost exclusively with polyethylene.

Polyethylene is processed by a wide variety of techniques. There is insufficient space here to deal adequately with the principles and practice of these processes or even with the particular characteristics of polyethylene being fabricated by these processes.

Compression moulding is used only occasionally with polyethylene. In this process the polymer is heated in a mould at about 150°C , compressed to shape and cooled. The process

is slow since heating and cooling of the mould must be carried out in each cycle and it is employed only for the manufacture of large blocks and sheets, for relatively strain-free objects such as test-pieces, and where alternative processes cannot be used because of lack of equipment.

A very large number of products are produced by injection moulding. In this process the polymer is melted and injected into a mould which is at a temperature below the freezing point of the polymer so that the latter can harden. For mouldings with a minimum frozen-in strain operating conditions should be so selected that the mould cavity pressure drops to zero as the material sets. Because of the tendency of the material to crystallise, high shrinkage values are observed ranging from 0.015-0.050 cm/cm with low density materials to 0.025-0.060 cm/cm with high density polymers. High mould temperatures, desirable to reduce strains through freezing of oriented molecules, lead to increased shrinkage since there is more time available for crystallisation. High cavity pressures reduce shrinkage since during much of the cooling part of cycle there is only pressure reduction in the polymer and not physical contraction. High cavity pressures also reduce packing near the point of entry into the mould which can occur as the material in the cavity shrinks. Since it is partially solidified material which is packed into the mould, and which often freezes while the molecules are oriented, a weakness of the part around the gate can occur and so "packing" should be reduced as far as possible. Melt temperatures are of the order of 160-190°C for low density polymers and up to 50°C higher with high density materials. In order to achieve these melt temperatures cylinder temperatures may be anything from 30 to 100 deg C higher.

Many articles, bottles and containers in particular, are

made by blow moulding techniques of which there are many variations. In one typical process a hollow tube is extruded vertically downwards on to a spigot. Two mould halves close on to the extrudate (known in this context as the "parison") and air is blown through the spigot to inflate the parison so that it takes up the shape of the mould. As in injection moulding, polymers of low, intermediate and high density each find use according to the flexibility required of the finished product.

Another moulding process based on the extruder is "extrusion moulding". Molten polymer is extruded into a mould where it sets. Since satisfactory mouldings can be produced using low moulding pressures, cheap cost moulds can be used. The process has been used to produce very large objects from polyethylene. The techniques of screw-preplasticising with injection moulding can be considered as a development of this process.

Approximately three-quarters of the polyethylene produced is formed into products by means of extrusion processes. These processes will differ according to the product being made, i.e. according to whether the end-product is a film, a coated paper sheet, a tube, a rod or a wire covering. In principle the extrusion process consists of metering polymer (usually in granular form) into a heated barrel in which a screw rotates. The rotation of the screw causes the granules to move up the barrel where they are compacted and plasticised. The resultant melt is then forced under pressure through an orifice to give a product of constant cross section. Although the polymer may be processed on a variety of different machines screws usually have a length-diameter ratio in excess of 16:1 and a compression ratio of between 2.5:1 and 4:1. (The compression ratio can be considered as the volume of one turn of the screw channel at the feed end to the volume of one turn at

Table 2.3 Processing Behavior and Applications of PE Injection-Molding Compounds

Density:	0.92	0.93	0.94*	0.95	0.96
<i>MFI</i> 190/2.16: > 25-15	Most easy flow; mass articles without particular stressing	Easy flow, moldings with large surfaces, little warping, good gloss	Easy flow, shock-proof moldings without particular stiffness	Easy flow, low warping, difficult to inject, household goods	Easy flow, hard, stiff, basins, sieves, dishes, transport cases, protective headwear
15-5	Articles with greater strength, less surface gloss	Little-stressed moldings with good surface gloss	Good shock resistance, little stress corrosion, highly stressed technical moldings	Easily processed, resistant to shock, screw caps, closures, technical moldings	Resistant to shock and creep, mechanically strongly stressed moldings, e.g., rubbish bins*, seating shells
~ 1.5	Very good mechanical strength and resistance to stress corrosion		Good resistance to creep, little tendency to stress corrosion, particularly stressed closures	Resistant to stress cracking, good surfaces, highly stressed technical moldings	
< 1				High molecular weight, most highly stabilized, pressure armatures, pipe bends, fittings	

* Mostly blends of PE-LD/HD, now also low-density PE-LLD.

the delivery end of the barrel.) Since well over half the polyethylene extruded is converted into film, film extrusion processes will be considered in somewhat greater details.

There has been extensive investigation into the effect of processing conditions on clarity, haze and gloss of polyethylene film. It can easily be demonstrated that the presence of haze and lack of clarity of low and intermediate density polymers is due to crystallisation (which though not developing structures large enough to impede the passage of light tends to cause surface distortions).

although a large proportion of polyethylene film is made by the tubular process some film is produced by extruding flat film from a slit die either into a water bath or on to a chilled casting roll. Although extrusion directly into water results in the most rapid quenching and tends to give products of highest clarity the presence of antistatic and slip additives tends to cause water to carry-over from the cooling bath and become trapped in the rolled film. For this reason the chill-roll process is usually preferred. Because of the higher cooling rates there are possible with chill-roll processes higher linear output rates can be achieved than with tubular processed. In addition since high melt temperatures can be used (which reduce melt roughness) and quenching is carried out within an inch or two of the die lips (which reduces surface effects due to crystallinity) products of high clarity may be obtained. In comparison the principal advantages of the tubular process are the ease with which bags and sacks may be made from the extruded tube and the ability to make wide sheet from fairly simple dies.

Calendering processes, of great importance in the production of sheet materials from PVC compounds, are little used with polyethylene because of the difficulty in obtaining a

smooth sheet. Commercial products have however been made by calendering low density polymer containing a small amount of a peroxide such as benzoyl peroxide to give a stiff but crinkly sheet (Crinothene) which is suitable for lampshades and other decorative applications.

2.2 Introduction of photodegradation

Sunlight has been recognized as an important factor in the deteriorative ageing and weathering processes which occur in commercial polymers. 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 400-700nm) 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 KJmol^{-1} respectively whereas the strengths of C-C and C-H bonds are approximately 420 and 340 KJmol^{-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 component of sunlight is sufficient to break chemical bonds and that the shortest wavelengths will be the most effective.

Of course it is not enough that sufficiently energetic quanta be 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 the photophysical aspect of photo-degradation. 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 reaction.

The first chemical step in photo-degradation is usually a 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. The varying sensitivities result from differences in the chemical structure. As shown in table 2.4 [2], the maximum sensitivity 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 range of solar ultraviolet radiation is about 6 % of the total radiation of the sun which reaches the earth's surface (Figure 2.1) [2]. 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.

2.3 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):

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

Table 2.4 Wavelength of UV Radiation (Energy of a Photon) at which various polymers have maximum sensitivity

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 acetale copolymer	327,364	87,79
Polypropylene	370	77

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

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

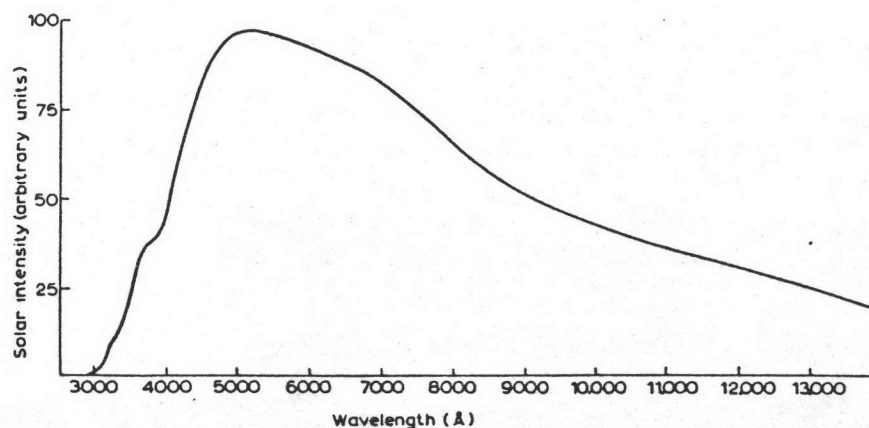


Figure 2.1 UV and visible spectrum of sunlight at noon in midsummer in Washington, D.C.

where h is Planck'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: $h = 6.62 \cdot 10^{-27}$ erg sec, ν sec⁻¹, $c^* = 3 \cdot 10^{10}$ 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

singlet 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_0). An excitation of a molecule from the ground state to the first excited singlet state ($S_0 \longrightarrow S_1$) is shown in Figure 2.2 [2]. 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_0 state are also possible.

A direct excitation from S_0 to an excited triplet state is not allowed. This transition is however, possible by intersystem crossing an example of which is shown in Figure 2.3 [2]. 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 $T_1 \longrightarrow S_0$ 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 $T_1 \longrightarrow S_0$ transition is called phosphorescence.

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 ($50-100 \text{ \AA}$; So-called resonance excitation transfer) or over shorter distances without a real collision but by overlapping of the electron clouds of the participating species ($10-15 \text{ \AA}$; referred to as exchange energy transfer).

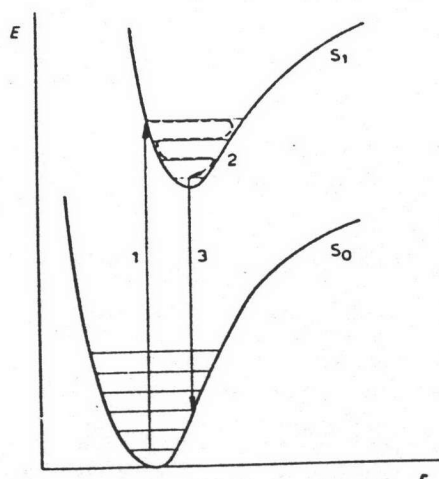


Figure 2.2 Potential energy curves of a molecule (S_0 = ground state, S_1 = first excited singlet state): (1) absorption (2) vibrational relaxation; (3) fluorescence

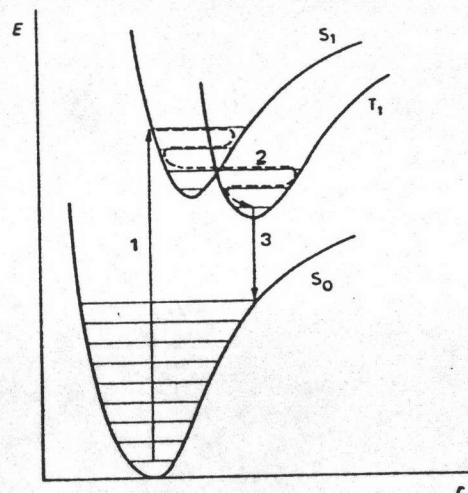


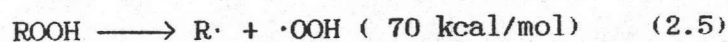
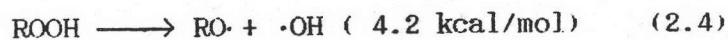
Figure 2.3 Potential energy curves of a molecule (T_1 = first excited triplet state) (1) absorption (2) intersystem crossing by vibrational relaxation (3) phosphorescence

2.4 Photochemical processes

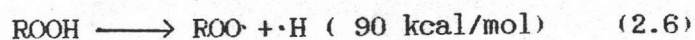
The chemical processes of photodegradation include isomerization, dissociation, and decomposition of a molecule as a direct consequence of its photophysical excitation, as well as those nonunimolecular chemical reactions which are facilitated by the absorbed energy. Obviously, a photochemical reaction 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 2.4 [2] a or when a dissociative excited state is formed (Figure 2.4 b) [2] in which repelling of the atoms occurs at any separation distance. Dissociation can also occur after intersystem crossing to an excited triplet state above the dissociation limit (Figure 2.5 a) [2] or to a dissociative potential curve (Figure 2.5 b) [2].

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:



Dissociation of the O-H bond is less easy:



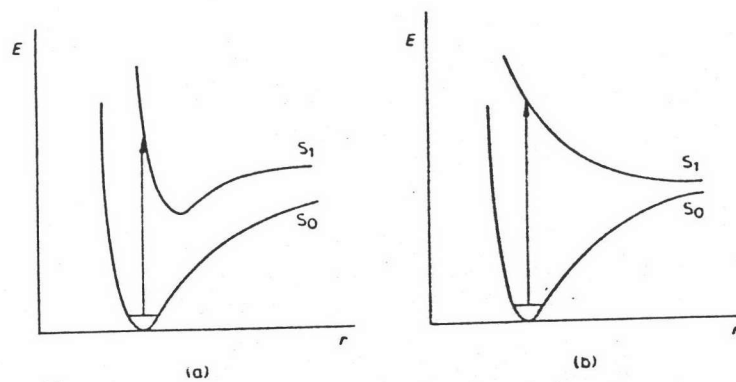


Figure 2.4 Photodissociation of a molecule: (a) excitation above the dissociation limit of the S_1 potential curve; (b) formation of a dissociative excited state

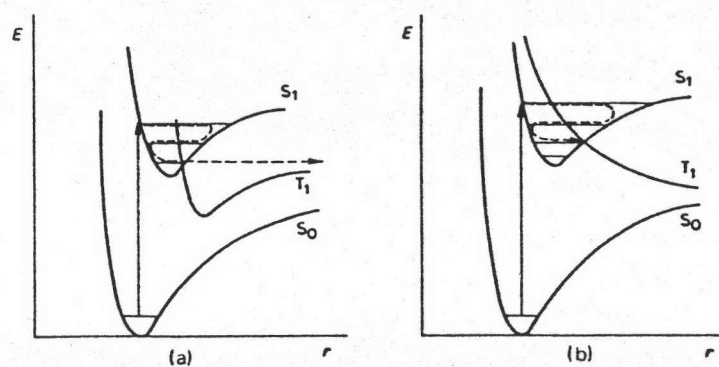
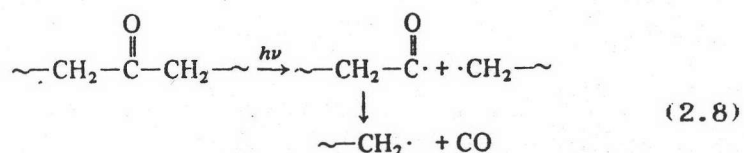


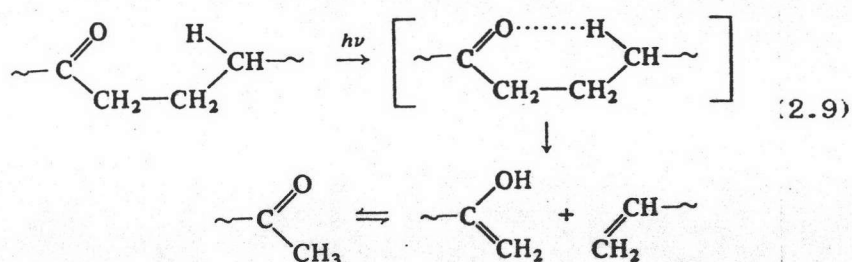
Figure 2.5 Photodissociation of a molecule after intersystem crossing: (a) do above the dissociation limit of the T_1 potential curve; (b) to the dissociative excited triplet state.

Because of low bond dissociation energy, decomposition according to reaction (2.4) [2] is predominant in polymer photooxidation.

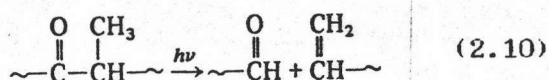
The role of carbonyl groups in polymer photooxidation is of great importance because once they have been formed they absorb UV light readily, hence, excitation to singlet and triplet states is easy. The excited carbonyl groups decompose via Norrish reactions of types I, II and III. The Norrish-I reaction 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 α -carbon atom results in decomposition by α -scission to an olefin and an alcohol or ketone. For example in the case of polyethylene, a terminal double 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 temperatures.

2.5 Photooxidation

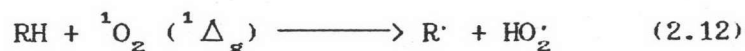
The formation of polymer radicals



by scission of a C-H bond is a possible consequence of UV irradiation. The probability of reaction (2.11) 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 depend on 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 . Beside 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.

Another significant difference between thermal and photooxidation is that many of the oxidation products incorporated in the polymer absorb UV light better than the original polymer. Thus the autoaccelerative character of the process is even more pronounced in photooxidation, and relatively high oxidation rates can be measured at much lower temperatures in the presence than in the absence of light. Completely "pure" polymers do not exist. During synthesis, processing, and storage, various amounts of carbonyl and hydroperoxy groups accumulate in the material. These chromophores absorb UV light to a much greater extent than the polymer. Initiation of degradation consists mainly of the decomposition of these chromophores. Thus, because of the high initiation rate and because of the short kinetic chains resulting from the lower temperatures, the autocatalytic character of photooxidation is usually hidden. Figure 2.6 [2] compares the oxygen absorption of linear polyethylene samples at 100°C in the dark and at 30°C when exposed to UV radiation.

In photooxidation the sample thickness is an important factor. As shown in Figure 2.7 [2], the extent of oxidation decreases exponentially with increasing distance from the surface: oxidation mainly occurs in a very thin surface layer of the material.

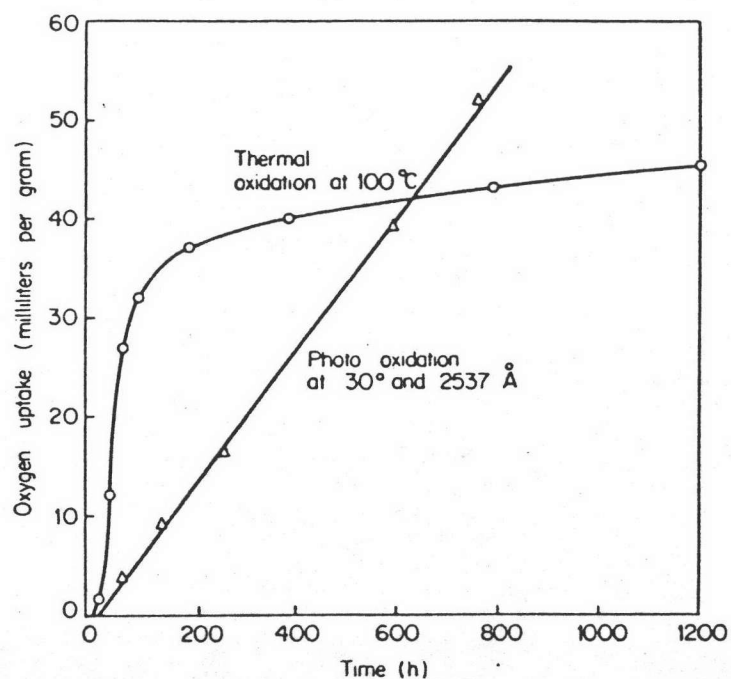


Figure 2.6 Oxygen absorption of linear polyethylene samples at 100°C without, and at 30°C with, UV irradiation

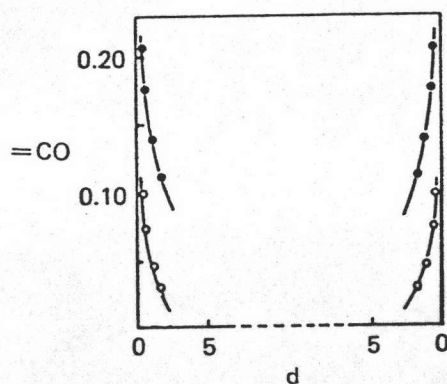


Figure 2.7 Relative amount of carbonyl (=CO) groups formed as a function of the distance (c) from the surface of a 22 μm polypropylene film irradiation time; o=40 hours; • =80 hours.

The molecular weight of the polyolefins rapidly decreases during photooxidation. The average number of chain scission (s) in a polypropylene sample as a function of irradiation time is shown in Figure 2.8 [2]. After longer UV irradiation, microcracks appear and the sample becomes opaque and brittle. In stabilized samples, brittleness sometimes occurs before oxygen containing groups appear in the polymer.

Photodegradation at low temperatures is favorable to random scission processes. Polymethyl methacrylate and polymethylstyrene, known to depolymerize quite readily, have only a low monomer when irradiated at room temperature, due to the low kinetic chain length. For example, the maximum zip length in PMMA is about five monomer units per absorbed quantum; however, at 160°C this value is as high as 220. The mechanism of polyacrylonitrile photodegradation is also different from that of the thermal process. At low temperatures, UV irradiation leading to random scission dominates and side chain polymerization, characteristic of thermal PAN degradation, is negligible.

As previously mentioned, 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. Metal compounds can, however, be useful in some cases, e.g., by decomposing hydroperoxides without formation of radicals or by functioning as UV absorbers.

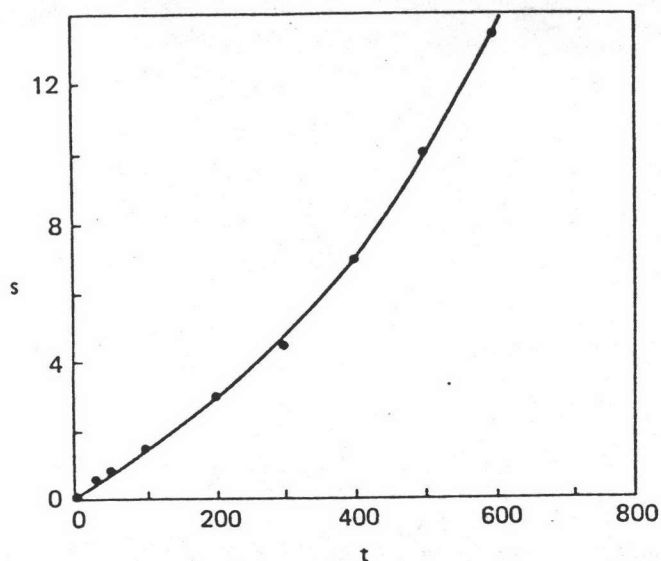


Figure 2.8 Average number of chain scissions ($S = P_{n,0}/P_{n-1}$) in one original macromolecule as a function of time (t_1 in hours) during UV irradiation of a polypropylene sample.

2.6 Sensitized photodegradation

The ever-increasing amount of plastics used for disposable packaging material and their potential for causing permanent pollution of the environment have prompted workers to seek methods of producing polymers with controlled service life. After having finished its useful function, e.g., as a container for milk or as a sandwich bag, the plastic becomes a waste material; it is desirable that this waste decompose with the aid of sunlight, humidity, and bacteria as rapidly as possible. Another type of application in which controlled lifetime is a significant feature of the material is the use of plastic mulch films for protection of important plants by covering the soil (increasing temperature, retaining soil humidity, suppressing weeds, etc.). When the plant has grown and

strengthened, the film should disappear, again partly with the aid of sunlight. In agricultural and horticultural applications, however, the material must spend its useful life outdoors. Mulch films must be sensitized for photodegradation but also stabilized to an extent which insures their preplanned service life. After the consumption of stabilizer, the remainder of photosensitizer causes rapid degradation of polymer to low molecular weight compounds which are small enough to be decomposed by microorganism. Thus, the complete deterioration of plastic waste and the control of service life of plastics are rather complex procedures.

In preparing photosensitive polymeric compositions for use in fabricating environmentally degradable plastic products, the usual approach is to incorporate a single photosensitizing additive. Within limits, the degradability of the composition can be regulated by varying the concentration of the sensitizing additive. This approach is satisfactory in a number of applications, e.g., where the product is a thin film of a polymer which undergoes relatively easy photodegradation.

In attempting to prepare photodegradable plastic articles of reasonable thickness, such as plastic bottles having a wall thickness of 0.01 - 0.05 inch, the aforementioned "prior art" method is not always effective; this is particularly true when the polymer is relatively resistant to photo-oxidative degradation. The relatively slow degradation rates observed in the case of thickwalled samples may be attributed to the following factors.

Firstly, though sunlight is a broad-spectrum source of ultraviolet and visible radiation, only those wavelengths of light corresponding to the ultraviolet absorption band of the photosensitizing additive are actually effective in promoting photodegradation; light of other wavelengths is not effective in promoting photodegradation, since it is not absorbed, and hence

energy from light of these wavelengths is "wasted".

Secondly, there is a limit to the extent to which the rate of photodegradation can be increased by increasing the concentration of a single photosensitizing additive. If the concentration is too high, essentially all of the light of photochemically active wavelengths is absorbed near the exposed surface of the sample, and the remainder of the material is actually protected from photodegradation.

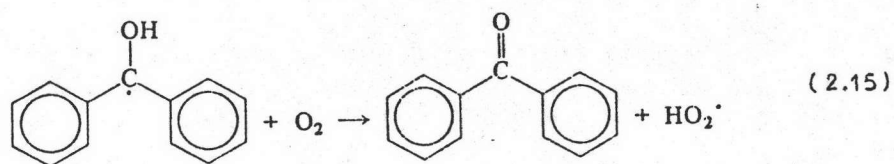
Such difficulties can be overcome, at least in part, by the use of degradable compositions containing two or more photosensitizing additives, particularly if the sensitizers absorb radiation in different regions of the ultraviolet spectrum. This approach makes it possible to maximize the energy absorbed from sunlight and hence, if the additives are photochemically active, to maximize the rate of photodegradation.

The use of multiple-sensitizer additive systems also offers an approach to the problem of excessive absorption of UV radiation near the surface of a thick-walled article, since lower concentrations of the individual sensitizers can be used, and since degradation will then involve light of two or more photochemically active wavelength ranges, each with its own characteristic relation between intensity and distance from the surface of the article. By the proper choice of sensitizing additives and adjustment of their concentrations, compositions of substantially improved degradability can be obtained. In some cases it may be desirable to employ a high concentration of one additive, which absorbs strongly in a given wavelength range, in order to promote rapid photodegradation near the surface, while simultaneously employing a lower concentration of a second additive which absorbs in a different wavelength range, in order to promote more gradual degradation of the remainder of the material. The first sensitizer will then promote surface

embrittlement and cracking, while the second will promote subsequent disintegration of the bulk of the material, e.g., by facilitating the propagation of cracks initiated at the surface.

A photosensitizer usually has a high absorption coefficient for 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.

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 radical and regenerate a benzophenone molecule:

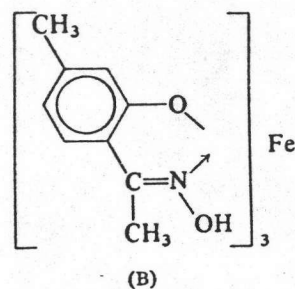
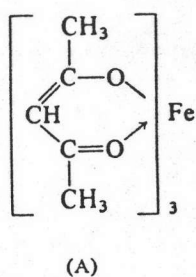


Quinones behave similarly: their excited state has a biradical character, the biradical abstracts hydrogen from the polymer and hydroquinone forms. For example, the addition of various quinones sensitizes the photodegradation of polyisoprene solutions. The sensitizing effect is drastic, especially with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

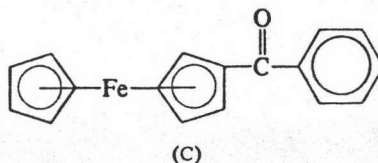
Various nitrogen containing chromophores, e.g., azo, nitroso, and aromatic amino compounds, decompose to radicals when excited by UV light. For example, 2-chloro-2-nitroso-propane was found to sensitize photodegradation of polyisoprene even more

effectively than anthraquinone. Some N-halide 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 that certain iron complexes, e.g., Fe(II) and Fe(III) complexes of dithiocarbamates and 2-hydroxyacetophenone oximes, exhibit a delayed action as UV sensitizer. Fe(III) acetyl acetonate (A) has an immediate effect, however, the effect of the Fe(III) can be observed only an induction period of significant length. Ferrocene derivatives such as benzoylferrocene (C) and act as photosensitizers.



(2.16)



Inorganic metal oxides and salts, e.g., ZnO, TiO₂, and FeCl₃ accelerate photodegradation. It is assumed that free radicals are formed from these compounds during irradiation.

Another type of photosensitized polymer contains the sensitizer 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 and relatively high 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.

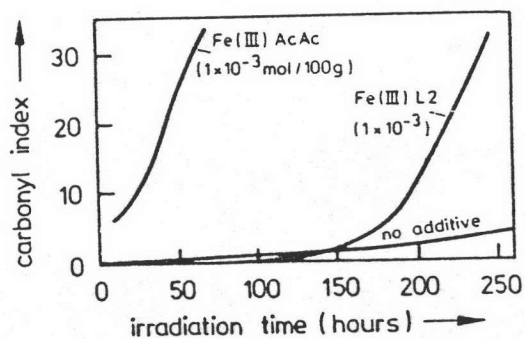
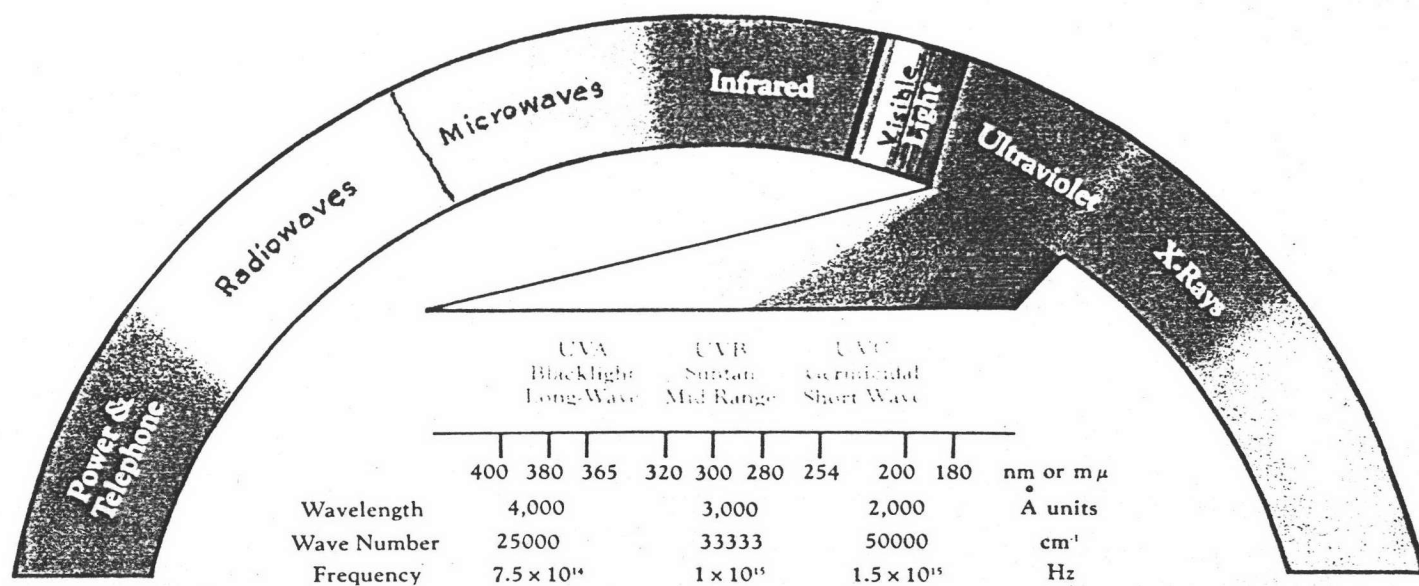


Figure 2.9 Carbonyl Index (IR absorbance due to =CO groups related to a reference absorbance) as a function of time during UV irradiation of low density polyethylene samples: Fe(III)AcAc = Fe(III) acetylacetonate Fe(III)L₂ = Fe(III) 2-hydroxy-4-methylacetophenone.

2.7 Ultraviolet light

An important thing to know is that ultraviolet is not a single entity, but is a wide band of wavelengths. 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 cause 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 far UV (200-280 nm), the adjectives near and far indicating the relative distance from visible light. Medical literature subdivides UV light, even further into three UV ranges: UV-A being radiation 315 nm and above, UV-B, 280-315 nm and UV-C, radiation equaling 280 nm and below.

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 glow 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 fluorescence lingers and disappears slowly 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.

2.8 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:

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 incorporated 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.

In view of the second and third requirements two otherwise promising classes of additives—peroxidic compounds and organic dyes—were excluded from consideration. For the same reasons, metallo-organic additives were not examined in great details. In view of present concerns over toxicity and environmental contamination, most halogenated compounds were also excluded from consideration.

2.8.1 Ultra-violet Absorbers and Related Materials

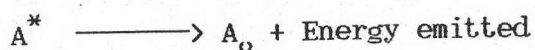
On exposure to ultra-violet light, particularly in an oxygen - containing atmosphere, physical and chemical processes may occur leading to such effects as discolouration, surface cracking, hardening and changes in electrical properties. Because polymers vary in their chemical nature the effects differ from one polymer to another. For most purposes the effects are undesirable but occasionally may be utilized in a positive manner - for example, to effect cross linking or deliberately to initiate degradation.

The greatest damage is caused by shorter wavelengths, i.e. less than 400 nm, but as the Earth's atmosphere absorbs most light rays shorter than about 300 nm the main damage is done, in terrestrial applications, by rays of wavelength in the range 300-400 nm (figure 2.10) [4].

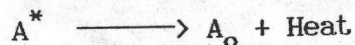
When a molecule(A) absorbs a quantum of light, it is activated to an electronically excited state A^* , after which a number of processes may occur. These may be summarized as follows:

(1) Photophysical processes

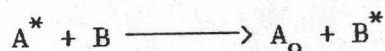
(a) Emission of energy (e.g. phosphorescence or fluorescence)



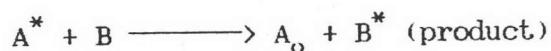
(b) Generation of heat (radiationless conversion)



(c) Energy transfer



- (2) Photochemical processes
 (d) Consequence of energy transfer



(e) Reaction of excited molecule equivalent to effect occurring with thermally excited molecules.

Reactions (d) and (e) occur much less frequently than reactions (a)-(c) but occur at a sufficient rate to cause changes in most polymers. There are three methods available for combating such effects; light screens, ultra-violet absorbers and quenching agent.

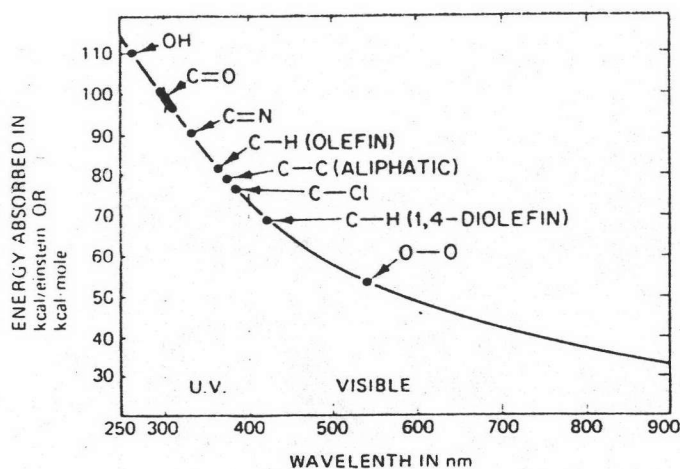


Figure 2.10 Relationship of energy absorbed by molecule to wavelength of incident light. Dissociation energies of various bonds are indicated to show wavelength below which breakdown may occur. (After Scott!)

2.8.2 Ultraviolet absorbers

Ultraviolet absorbers are a form of light screen which absorb primarily the ultra-violet range. It is a requirement for most ultra-violet absorbers that absorption in the visible range be negligible; if this were not so the resultant instant colour formation could be worse than that

experienced after prolonged exposure of the polymer.

The ultra-violet absorber could dispose of absorbed energy by radiation, by conversion into heat or by chemical changes leading to stable products. The most important commercial absorbers, such as the o-hydroxybenzophenones, o-hydroxyphenylbenzotriazoles and salicylates, appear to function by conversion of electronic energy into heat. The properties of the main types of ultra-violet absorbers are summarised in table 2.5 [4].

Table 2.5. Some commercial ultra-violet absorbers

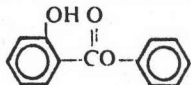
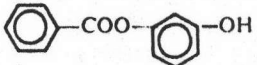
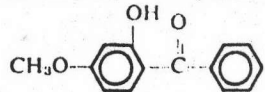
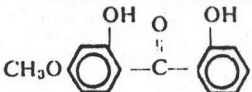
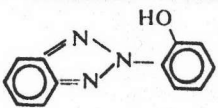
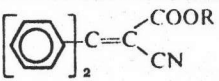
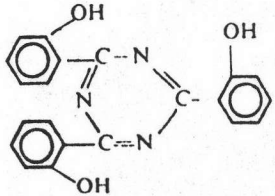
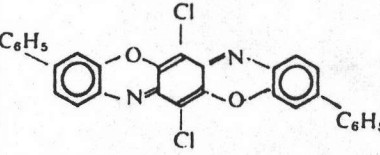
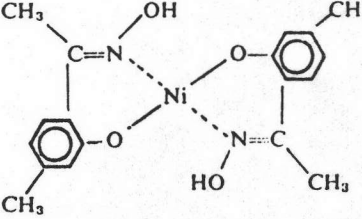
<i>Ultra-violet absorber</i>	<i>Formula</i>	<i>Type</i>	<i>Comments</i>
Phenyl salicylate		Salicylate	Rather weak.
Resorcinol monobenzoate		Benzoate	Converted in sunlight to a dihydroxybenzophenone. Used in cellulose.
2-Hydroxy-4-methoxybenzophenone		Substituted monohydroxybenzophenone	Negligible absorption in visible range.
2,2'-Dihydroxy-4-methoxybenzophenone		Substituted dihydroxybenzophenone	Stronger than the monohydroxy compound but some absorption in the visible range.
2-(2-Hydroxyphenyl)benzotriazole		Benzotriazole	Powerful.
		Substituted acrylonitrile	Some use in PVC and polyolefins.

Table 2.5 Some commercial ultraviolet absorbers (continued)

<p>1,3,5-Tris-(2-hydroxyphenyl)- triazine</p>		<p>Triazine</p>	<p>Powerful but some absorption in visible range.</p>
<p>6,13-Dichloro-3,10-diphenyl- triphenodioxazine</p>		<p>Oxazine</p>	<p>Excitation dissipated by radiation (fluorescence). Very effective in cellulose acetate-butyrates but reddish brown in colour.</p>
<p>—</p>		<p>Nickel(II) chelate</p>	<p>Appears to function as a quenching agent in polypropylene</p>

2.9 Literature Review

There are many reports investigating the photodegradation of polymers in different ways. As regards to the mechanical properties, there some papers have investigated the changes in artificial weathering and natural weathering with and/or without introducing photosensitizers into the polymer.

Seven species of thermo-plastic films (PETP, PA, LDPE, HDPE, PVC, PA and POM) were exposed to outdoor conditions for studying the influence of the exposure site, starting season, exposure period and thickness of films. The differences depending on the exposure site were recognized. As regards to the starting season of exposure, degradation rates for a short period were largest in the case of the starting season being in the summer, moderate in the spring and smallest in autumn; however, during exposure for twelve months, no differences were recognized. It is considered that the main reasons causing such differences were in the differences of U.V. dosage.

As regards to the thickness of the film, the thinner the thickness, the faster the degradation (table 2.6) [11].

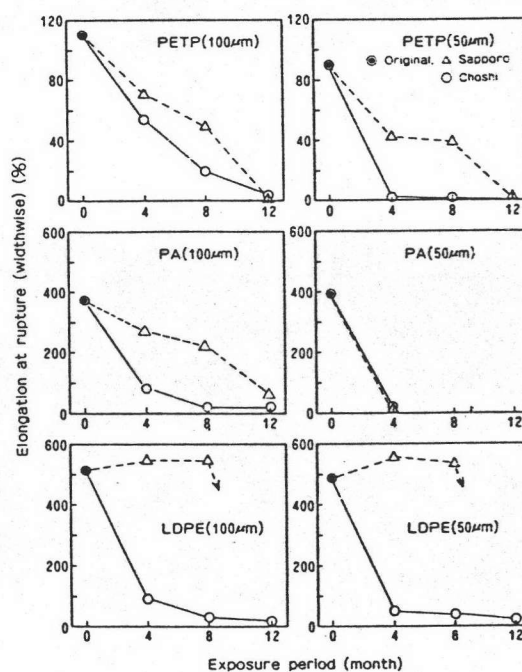


Fig. 2.11 Differences of exposure site in changes of elongation at rupture by outdoor exposure (started in July).

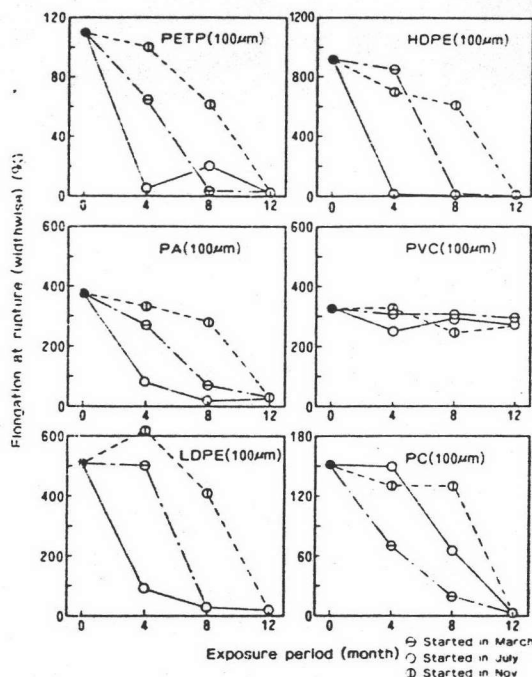


Fig.2.12 Influences of starting season in changes of elongation at rupture. (Choshi)

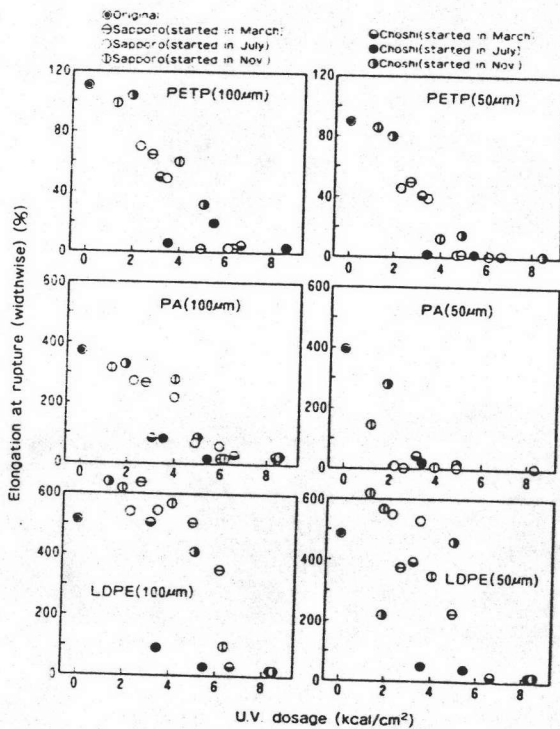


Fig. 2.13 Correlations of U.V.dosage to elongation at rupture.

Table 2.6 Degradation rates of outdoor exposed films
(Sapporo, Started in July, widthwise)

	Nominal thickness m	* ¹ $d_t \rightarrow 1/2$ month	* ² $U_o \rightarrow 1/2$ month	* ³ $d_t \cdot U_o \rightarrow 0$ month
PETP	100	5.5	4.5	12
	50	5.5-6		12
	38	1.5-2		
	16	1.2-1.5		
PA	100	8	8	12
	50	2		4
	30	0.5		
LDPE	100	12	9-12	
	50	4-5		
	20	0.7		
HDPE	100	4.5	4.5	6
	50	1.5		(2.5)
	20	0.5		
PVC	100	(12)		
	50	(4)		
	20	(0.3)		
PC	100	8	(7)	10
POM	100	0.5	0.5	4

*¹ Period when elongation at rupture reduce by half.

*² Period when rupture energy reduces by half.

*³ Period when elongation and energy become zero.

An important report of LDPE film containing quinoid sensitizers, anthraquinone, α -butylanthraquinone and 2-octanoyloxyanthraquinone were carried out in Czechoslovakia [16]. LDPE films were exposed to 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 studied is summarized in figure 2.14 and infrared-spectra of undoped and doped LDPE samples with irradiation time are shown in figure 2.15 by following the 1718 cm^{-1} band which corresponds 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.

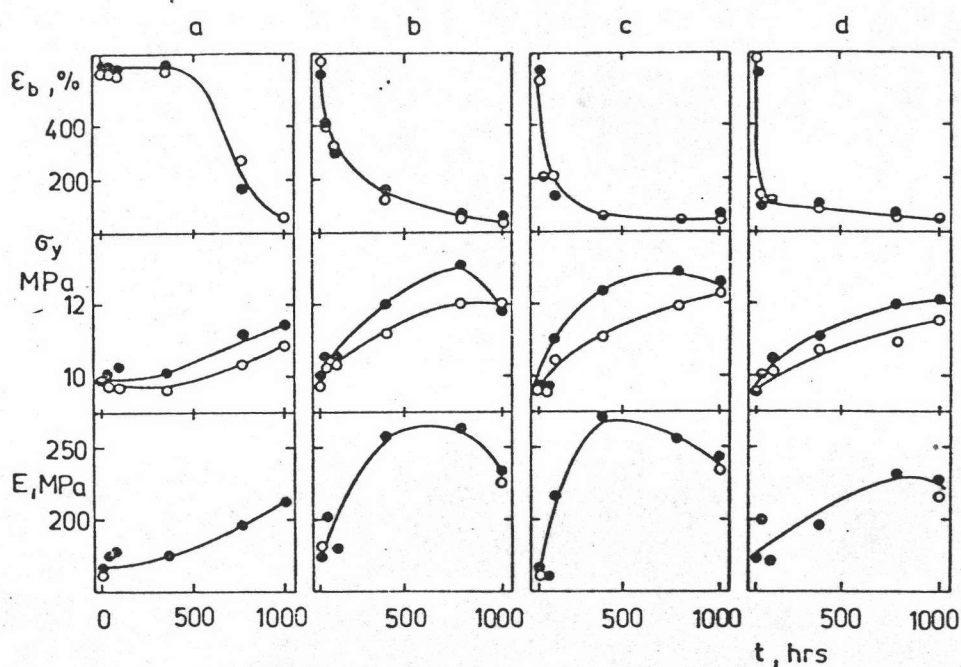


Fig. 2.14 Strain at break (ϵ_b), yield stress (σ_y) and Young's modulus (E) as a function of irradiation time for four LDPE samples: a, undoped sample; b, sample doped with anthraquinone (I); c, 2-butylanthraquinone (II); d, octanoyloxyanthraquinone (III); samples tested after (○) 4100 h and (●) 22 200 h of dark storage.

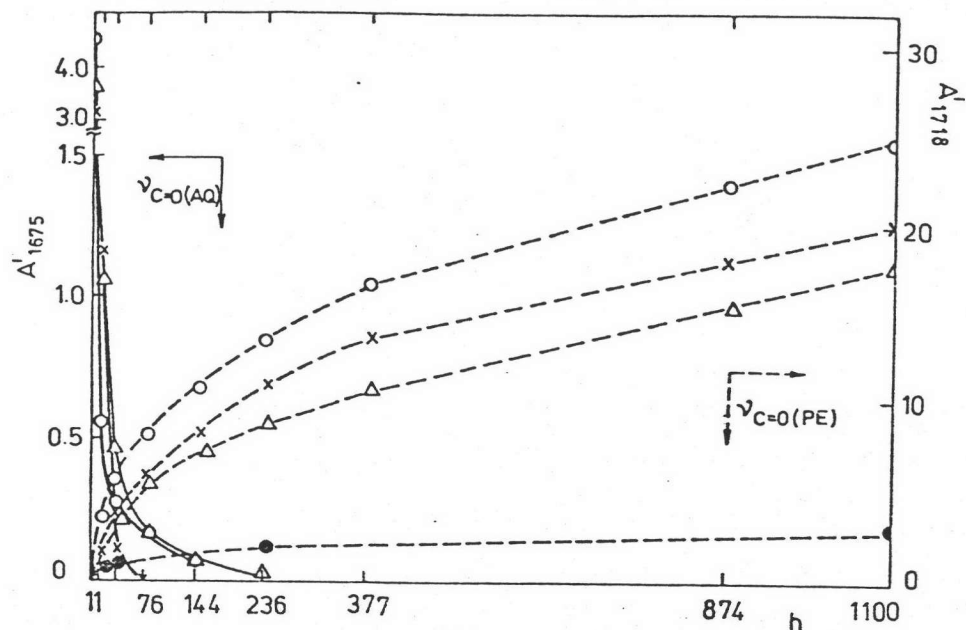


Fig. 2.15 Changes of the relative infra-red absorbance of carbonyl groups in polyethylene chains (A'_{1718}) and of carbonyl groups in anthraquinone and its derivatives (A'_{1675}) in (●) neat LDPE and LDPE doped with (x) I, (O) II and (Δ) III, during irradiation.

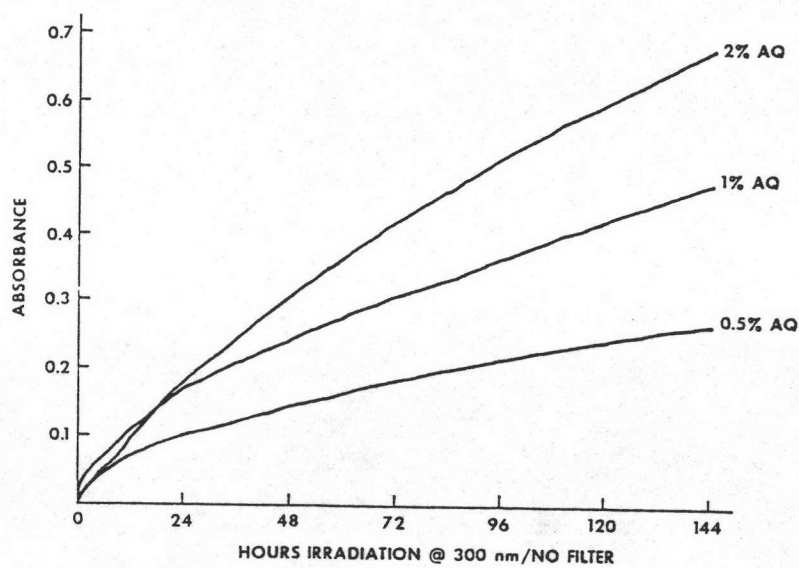


Fig. 2.16 Carbonyl infrared absorbance changes in irradiated anthraquinone-sensitized polyethylene films.

A number of additives previously observed to promote photo-oxidative degradation of PE films have 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. Effects of time and additive concentration were determined by infrared measurements of carbonyl absorbance in UV exposed films as shown in figure 2.16-2.19 [22].

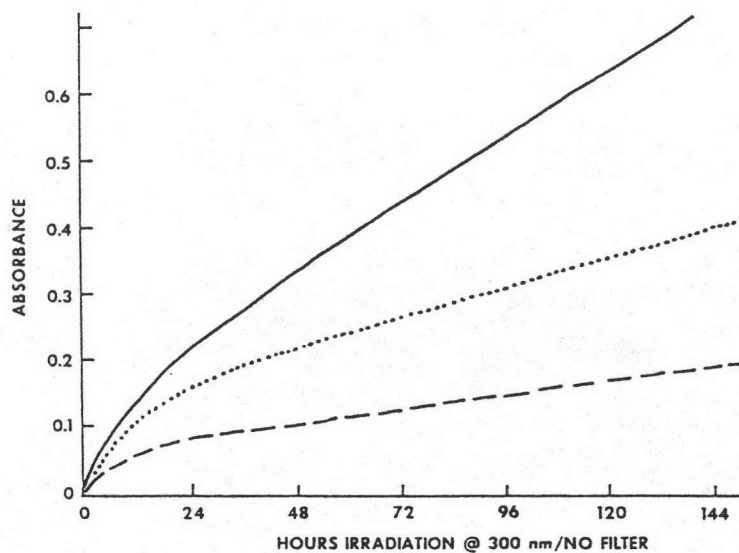


Fig. 2.17 Carbonyl infrared absorbance changes in irradiated polyethylene films sensitized with 4,4'-oxydibenzophenone. (—) 2% ODP, (· · · ·) 1% ODP, (---) 0.5% ODP.

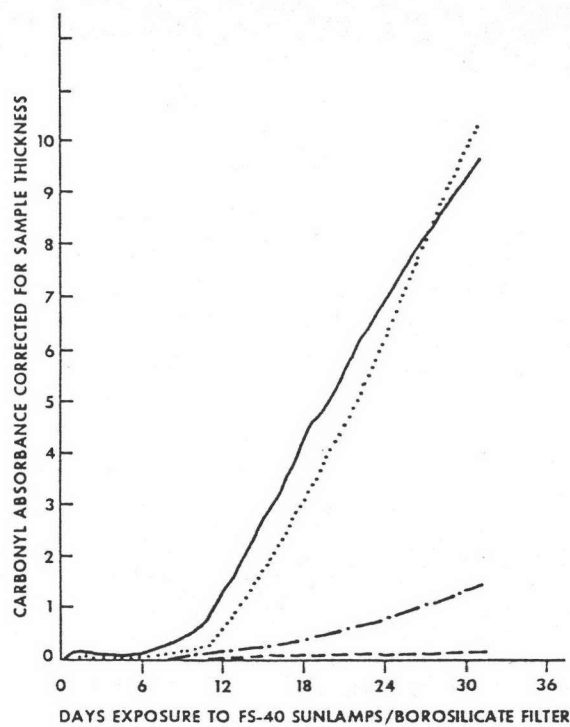


Fig. 2.18 Photo-oxidation of polyethylene films sensitized with Ferric dibutyldithiocarbamate. (.....) 0.10% FeDBDTC, (—) 0.05% FeDBDTC, (---) 0.01% FeDBDTC, (-·-·-), 0.50% FeDBDTC.

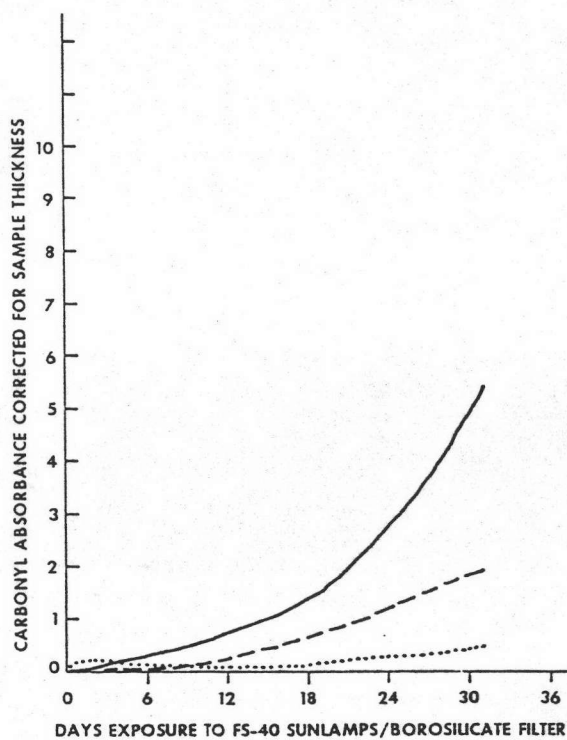


Fig. 2.19 Photo-oxidation of polyethylene films sensitized with ferrous stearate. (—) 0.05% Fe stearate, (---) 0.01% Fe stearate, (.....) no additive.

The activity of Schiff's bases of cinnamic aldehyde and aromatic amines in the controlled photodegradation of PE was studied. *N*-cinnamylidene anilines containing different substituents in the amine ring (methyl group, halogen, or amine group) and *N*-cinnamylidene α -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 substituents 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 h exposure to artificial UV light which was the equivalent of 1.5–2.0 years exposure to natural sunlight in the medium geographic latitudes.

[18]

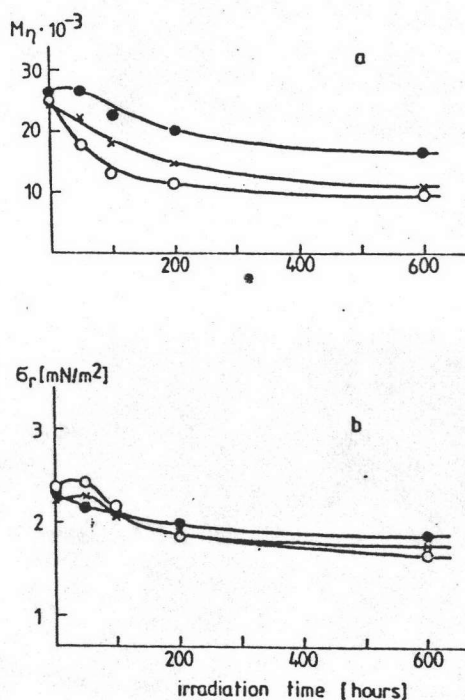


Fig. 2.20 Changes in the molecular weight M_n (a) and the tensile strength σ_r (b) of the PE films irradiated with the filtered UV light, containing: (○) 0.5% of *N*-cinnamylidene *o*-bromoaniline (NCBA); (×) 0.1% of *N*-cinnamylidene α -naphthylamine (NCNA); (●) 0.5% of *N*-cinnamylidene aniline (NCA).

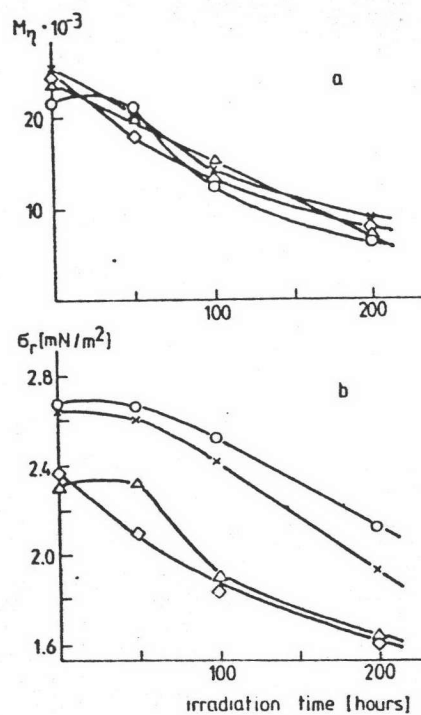


Fig. 2.21 Changes in the molecular weight M_n (a) and the tensile strength σ_r (b) of the PE films irradiated with the filtered UV light, containing: (○) 0.5% of NCBA and 1.0% of stannous laurate; (×) 0.5% of NCBA and 2.0% of stannous laurate; (△) 0.1% of NCNA and 1.0% of stannous laurate; (◇) 0.1% of NCNA and 2.0% of stannous laurate.

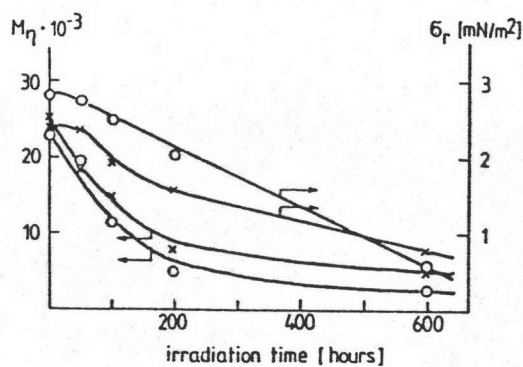


Fig. 2.22 Changes in the molecular weight M_n and the tensile strength σ_r of the PE films irradiated with the filtered UV light, containing: (○) 0.5% of NCBA and 2.0% of stannous laurate; (×) 0.1% of NCNA and 2.0% of stannous laurate.

TABLE 2.7
Results of testing the Sensitizing Activity of Schiff's Bases*

Additive	Concentration (wt %)	Irradiation time (h)	I_{∞}	Molecular weight	
				Before irradn.	After irradn.
<i>N</i> -cinnamylidene <i>p</i> -toluidine	0.1	80	0.63	25,000	16,000
	0.5	80	0.63	25,200	15,900
	1.0	80	0.71	24,900	15,100
<i>N</i> -cinnamylidene <i>o</i> -bromoaniline	0.02	40	0.51	28,000	15,400
	0.05	40	0.69	28,200	15,000
	0.1	40	0.97	27,300	12,100
	0.5	40	1.47	27,700	11,800
	1.0	40	1.23	26,800	11,500
<i>N</i> -cinnamylidene <i>p</i> -bromoaniline	0.1	40	0.76	28,800	15,200
	0.5	40	0.70	26,100	14,700
	1.0	40	0.85	25,700	14,000
<i>N</i> -cinnamylidene <i>p</i> -chloroaniline	0.1	40	0.57	25,900	16,200
	0.5	40	0.82	26,400	14,800
	1.0	40	0.69	25,700	15,000
<i>N</i> -cinnamylidene <i>p</i> -nitroaniline	0.1	40	0.16	26,300	23,000
	0.5	40	0.52	26,000	21,300
	1.0	40	0.14	27,100	25,200
<i>N</i> -cinnamylidene <i>o</i> -bromo- <i>p</i> -nitro aniline	0.05	40	0.69	26,400	16,900
	0.1	40	0.76	25,800	15,300
	0.5	40	0.70	27,000	16,000
<i>N,N'</i> -bis-cinnamylidene	0.5	80	0.10	30,000	29,400
<i>p</i> -phenylene diamine	1.0	80	0.05	27,200	28,000
	2.0	80	0.10	28,300	27,600
<i>N</i> -cinnamylidene α -naphthylamine	0.02	40	0.51	29,500	22,300
	0.05	40	0.69	29,300	16,600
	0.1	40	0.75	30,600	13,300
	0.5	40	0.76	29,800	15,400
	1.0	40	0.34	29,800	23,400
<i>N</i> -cinnamylidene aniline	0.1	80	0.63	24,200	15,700
	0.5	80	0.69	25,500	14,900
	1.0	80	0.71	25,200	15,100
<i>N</i> -benzylidene aniline	0.1	80	0.39	28,900	20,500
	0.5	80	0.33	29,300	20,500
	1.0	80	0.33	29,000	21,000
<i>N</i> -benzylidene α -naphthylamine	0.1	80	0.21	30,100	28,900
	0.5	80	0.25	30,000	29,300
	1.0	80	0.22	29,800	29,000
Polyethylene without additive	—	80	0.55	28,800	21,000

*Films irradiated with nonfiltered UV light.

TABLE 2.8
Changes in the Physical Properties (Molecular weight M_n and Tensile Strength σ) of the Sensitizers Containing Polyethylene Films after 200 h Irradiation with the Filtered UV Light

Sensitizer	Film properties before irradiation		Film properties after irradiation in					
	M_n	σ_0	Vacuum		Air		Oxygen	
			M_n	σ_x	M_n	σ_x	M_n	σ_x
1	25,300	2.35	24,100	2.35	12,100	1.95	12,500	1.88
2	23,000	2.81	22,800	2.70	5200	2.03	3900	1.85
3	24,600	2.25	23,000	2.19	14,600	1.92	13,800	1.80
4	23,200	2.31	21,800	2.36	9200	1.58	7600	1.48
PE without additive	28,800	2.61	27,100	2.60	20,800	2.56	20,200	2.20

*Sensitizing systems were: (1) 0.5% of *N*-cinnamylidene *o*-bromoaniline (NCBA); (2) 0.5% of NCBA and 2% of stannuous laurate; (3) 0.1% of *N*-cinnamylidene α -naphthylamine (NCNA) (4) 0.1% of NCNA and 2% of stannuous laurate.

Table 2.9 Differences depending on exposure site of mechanical properties.

	PS	PVC	PMMA	ABS	POM	PE
Difference of latitudinal order depending on exposure site	o	o	x	o	o	o
Difference depending on atmospheric conditions	x	o	x	x	x	o

o: Yes, x: No.

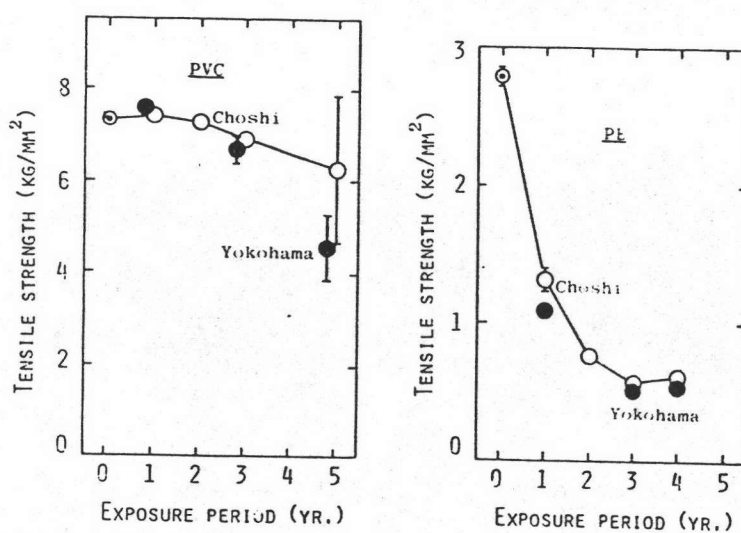


Fig. 2.23 Effect of environmental conditions on tensile strength.

The five kinds of thermoplastic sheets (PVC, PMMA, ABS, POM and PE) of about 3 mm thickness (ABS 3.5 mm thickness) were placed under outdoor exposure for five years (partially for four years) at four different sites in Japan [13] and artificially exposed using four types of weathermeters and three types of fademeters, and the degradation tendencies in mechanical surface and molecular properties were compared. From the data obtained from the degradation with the passage of time, differences depending on exposure site localities, environmental conditions and accelerating testers were quantitatively evaluated by kind of plastic and by property.

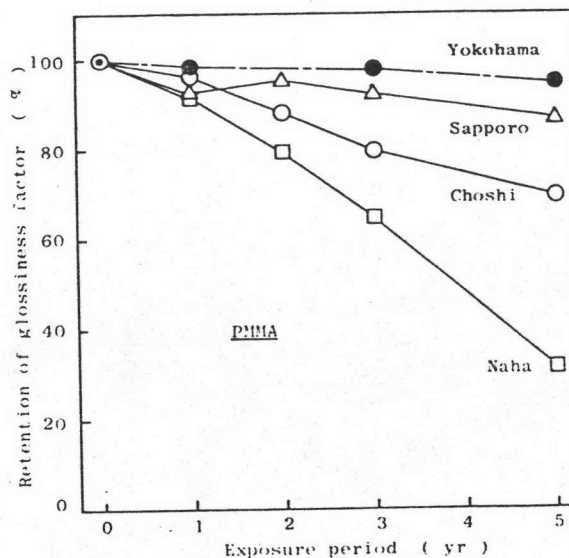


Fig. 2.24 Changes of glossiness factor by outdoor exposure of PMMA.

Table 2.10 Differences depending on exposure site of color, gloss and thickness of degradation layer.

	Character	PS	PVC	PMMA	ABS	POM	PE
Difference of latitudinal order depending on exposure site	ΔE	Δ	o	o	Δ	o	o
	Gs	x	o	o	x	x	x
	t_d	o	o	o	o	o	Δ
Difference depending on atmospheric conditions	ΔE	x	o	o	o	o	Δ
	Gs						
	t_d	x	o	x	x	x	o

o: Yes, x: No, Δ : Partially yes.

ΔE : Color, Gs: Gloss, t_d : Thickness of degradation layer.

Table 2.11 Order of acceleration of tensile strength

		PS	PVC	PMMA	ABS	POM	PE
Weathermeter	Xenon Lamp		2	1	3	3	3
	U.V. Carbon			2	1	2	2
	Sunshine Carbon	1			2	1	1
	Dew-cycle						
Fademeter	Xenon Lamp	2	1				
	U.V. Carbon	2	3				
	Sunshine Carbon						

Table 2.12 Order of acceleration of elongation at rupture.

		PS	PVC	PMMA	ABS	POM	PE
Weathermeter	Xenon Lamp			1	3	3	3
	U.V. Carbon			2	1	1	2
	Sunshine Carbon	1	2		2	2	1
	Dew-cycle						
Fademeter	Xenon Lamp	2	1	2			
	U.V. Carbon						
	Sunshine Carbon	2	3				

Table 2.13 Order of acceleration of surface change.

		PS	PVC	PMMA	ABS	POM	PE
		Gs	ΔE	t_d	ΔE	t_d	Gs
Weathermeter	Xenon Lamp			1	1		3
	U.V. Carbon	2				2	
	Sunshine Carbon	3	1			1	2
	Dew-cycle						
Fademeter	Xenon Lamp		3	2			
	U.V. Carbon	1		2			
	Sunshine Carbon		2			3	1

Gs: Gross, ΔE : Color difference, t_d : Thickness of degradation layer.

Table 2.14 Accelerating factor of outdoor exposure site and accelerated weathering tester.

Exposure	PS	PVC	PMMA	ABS	POM	PE
	d_t	d_t	M_n	d_f	t_d	t_d
Sapporo	0.91	0.81	0.86	1.1	0.87	1.04
Choshi	1.00	1.00	1.00	1.0	1.00	1.00
Yokohama	0.94	1.56	0.95		0.71	1.15
Naha	1.53	1.43	1.55		1.00	1.85
X-W		8.6				4.4
UV-W		7.2	8.8	3.1	8.3	
S-W	11			3.6	12	7.3
D-W						
X-F		12	16			
UV-F			10			
S-F	9.0			3.1	8.0	8.1

The values from Choshi were selected as the standard.

d_t : Elongation at rupture, t_d : Thickness of degradation layer
 M_n : Number-average molecular weight, d_f : Max. deflection.

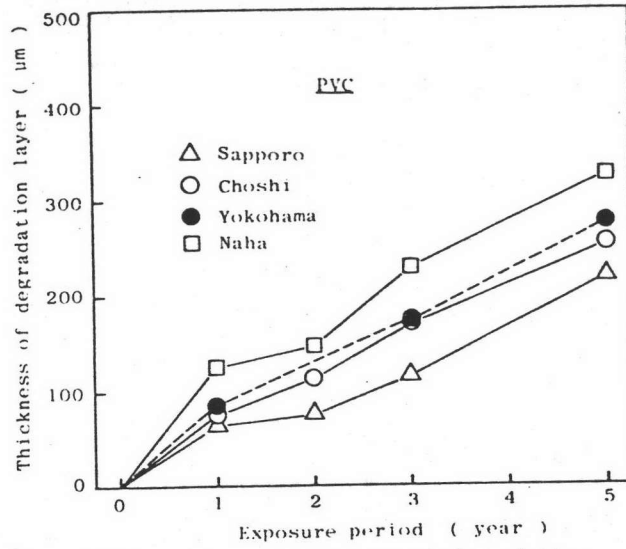


Fig.2.25 Changes of thickness of degradation layer by outdoor exposure.

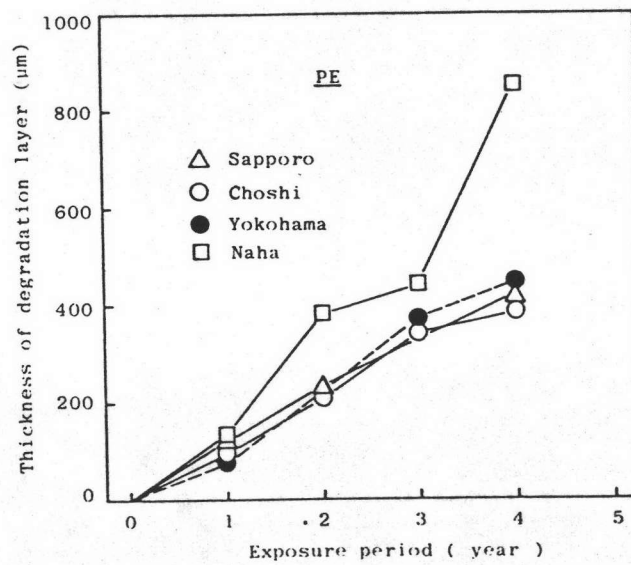


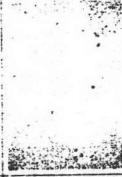




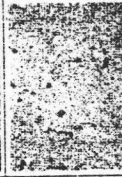
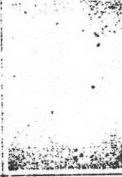

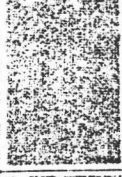









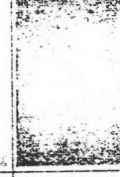





Fig.2.26 Changes of thickness of degradation layer by outdoor exposure.

Exp. Site	P S *	PVC	PMMA	ABS	POM	P E *
SAPPORO						
CHOSHI						
YOKOHAMA						
NAIHA						

0.2mm

Photo. 1. Differences in surface change depending on the exposure sites.
 (Outdoor exposure, Five years lapse ; Four years lapse for * mark)

SAMPLE	WEATHERMETER						FADENMETER		
	S-W	X-W	UV-W	D-W	S-F	X-F	UV-F		
P S									
PVC									
PMMA									
ABS									
POM									
P E									

Photo.2. Differences in surface change by the apparatus.
 (1920 hours lapse for D-W, 2000 hours lapse for other apparatuses)

0.2 mm

The environmental degradation of a stabilized LDPE film was studied in Italy [14]. The polymer degradation started in the first 2400 h of exposure. Irregular changes in tensile strength and elongation at break up to exposure time of 7080 h were observed. The relative optical density of the carbonyl and vinyl groups increases regularly during the whole exposure time, while a small change in the relative optical density of the vinylidene groups was observed. The thermal oxidation strength decreased after 7080 h of exposure. The crystallinity remained steady. Reflection of FT-IR measurements indicated that the oxidation reaction proceeded at the same rate on both sides of the film.

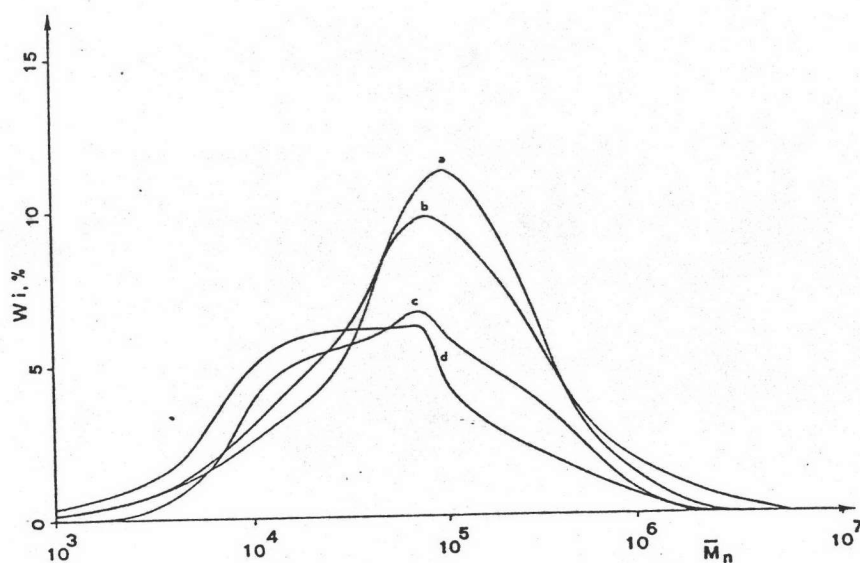


Fig. 2.27 Gel-permeation chromatograms of polyethylene in *o*-dichlorobenzene at 135°C: a, initial film; b, film aged for 2400 h; c, film aged for 6000 h; d, film aged for 7080 h.

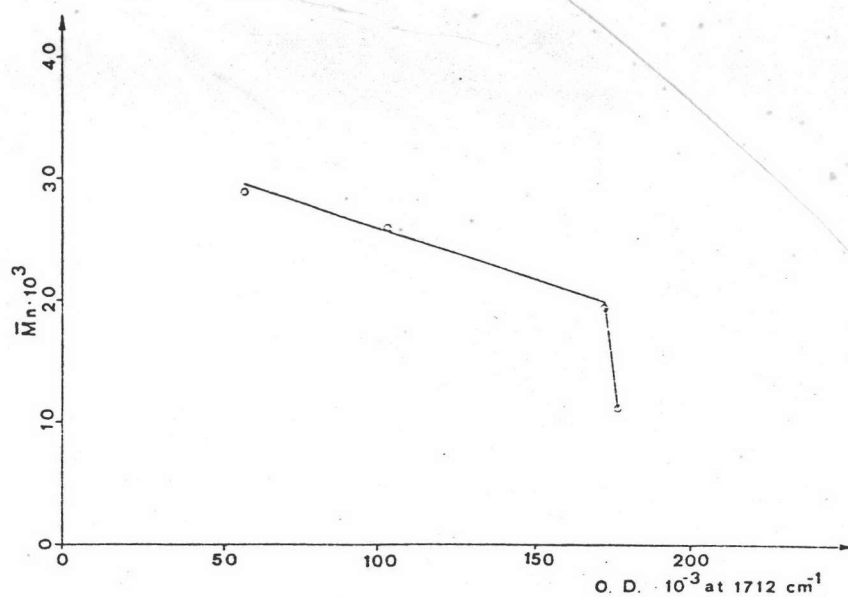


Fig. 2.28 \bar{M}_n values versus relative optical density of the carbonyl groups (1712cm^{-1}).

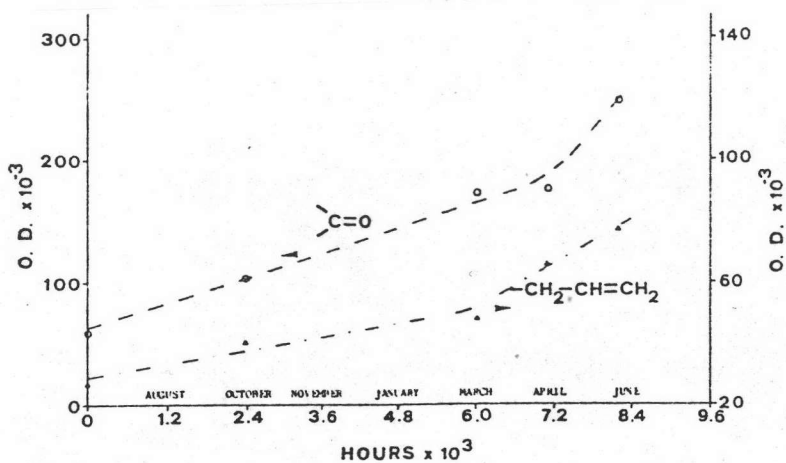


Fig. 2.29 Time dependence of the relative optical density: \circ , carbonyl groups (1712cm^{-1}); \blacktriangle , vinyl groups (908cm^{-1}).

TABLE 2.15
Main Characteristics of the Samples Aged for 7080 and 8160 h Compared with Those for the Starting Material

Exposure hours	Crystallinity (%)	σ_r (kg cm^{-2})	ϵ_r (%)	OD 1712cm^{-1}	OD 908cm^{-1}	\bar{M}_n
0	29.7	170.3	500.0	0.057	0.026	29 100
7 080	31.0	208.8	547.5	0.176	0.065	11 250 ^a
8 160	30.6	162.4	450.0	0.248	0.077	nd ^b

^a Small quantities of gel are present.

^b Gel-permeation chromatographic measurements were not carried out on the samples exposed more than 7080 h because of the presence of gels observed under measurement conditions.

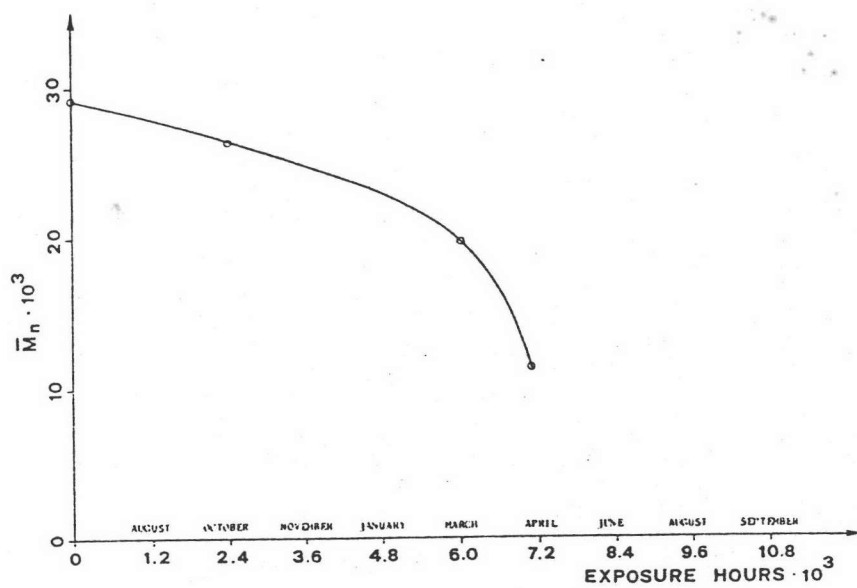


Fig. 2.30 Time dependence of \bar{M}_n .

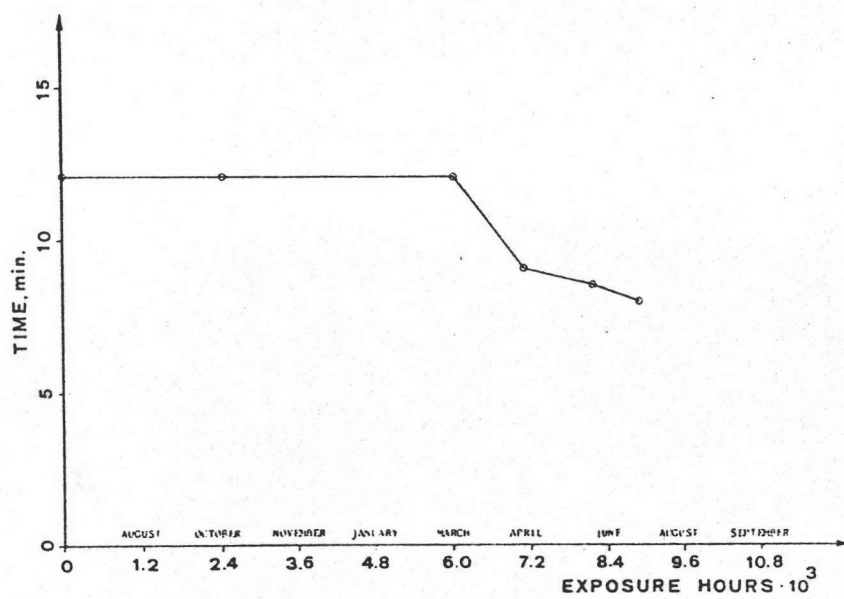


Fig. 2.31 Time dependence of the oxidation strength at 200°C in air.

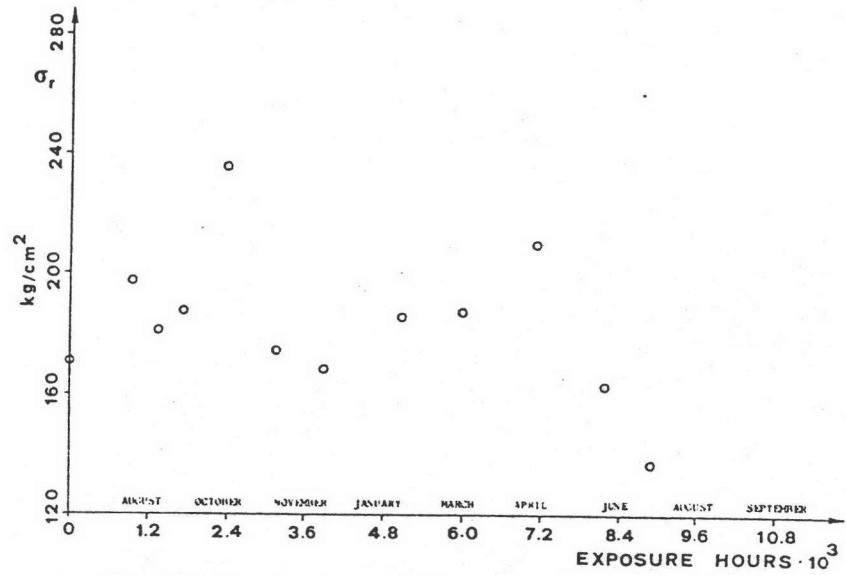


Fig. 2.32 Time dependence of the tensile strength at break.

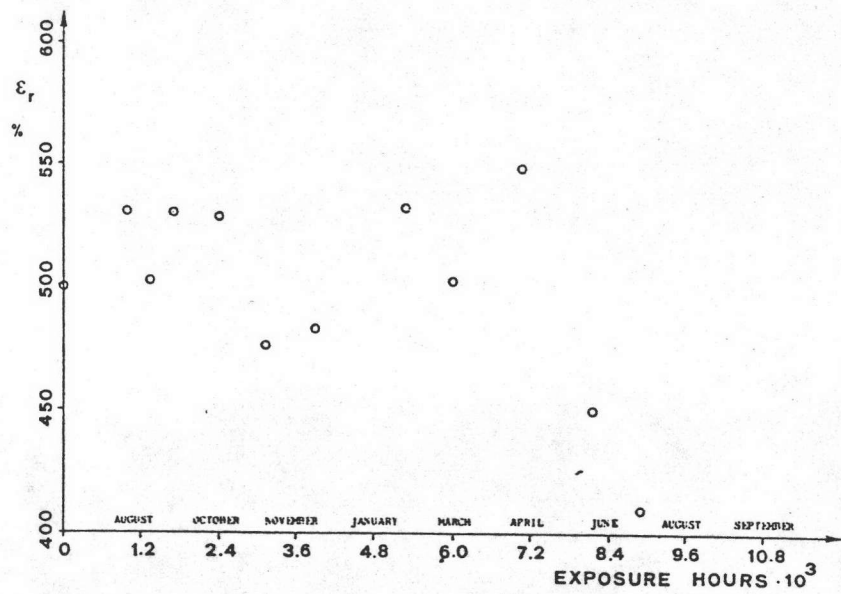


Fig. 2.33 Time dependence of elongation at break.