

CHAPTER 2

LITERATURE SURVEY

Photodegradation of polyolefin films have been studied in many places in the world such as Europe, America and subtropical climate in Hong Kong. Lee (1991) studied the outdoor weathering of photoactivated and non photoactivated polyethylene six-pack ring and several types of plastic bag films in a subtropical climate (Hong Kong). The result showed that photoactivated low density polyethylene, high density polyethylene and six-pack ring sample were found to degrade significantly when exposed outdoors in a subtropical climate condition. The films had lost 80% of its original elongation after outdoor exposure for 90 days. All the films became entirely brittle after exposure for 120 days. The oxidation reaction and morphology change were detected by infrared (IR) spectra and differential scanning calorimetry (DSC) measurement.

Binns et. al. (1992) reported the study of reactive species generated during the initial stages of polymer photodegradation by using low temperature ESR technique. The generation of free radicals can be monitored and quantified during exposure, and the obtained radical yields can then be correlated with the

chemical structure of the polymer to provide a rapid predictive evaluation of the exterior durability of the polymer.

Karen (1992) examined the effects of pigments and other additives that influence the degradation rate of polyethylene films in accelerated weathering. Six films of similar chemical composition, with varying pigments, were exposed to UV in QUV for maximum of 72 hours. During the exposure, tensile strength, elongation and toughness were measured. Results from this study showed that with appropriate selection of coloring agent used in the plastic processing, increased degradation rates can be achieved.

The study of thermal and photodegradation of two commercial polymer, stabilized and unstabilized low-density polyethylene(LDPE) carried out by Sebaa et. al. (1992) . The resistance to UV light irradiation as probed by deformation at break was superior in stabilized LDPE. Simple correlations were not observed between the lost of mechanical properties, the rate of oxidation and the morphology.

Study of the natural and accelerated UV photoaging of linear low density polyethylene (LLDPE), namely ethylene-butene (EB) and ethylene-hexene (EH), by the changes of the elongation at break and the degree of oxidation by monitoring carbonyl group was done by Tidjami(1993) . He found that the weathering resistance of polymer based on the only mechanical changes or chemical structural alterations may lead to drastic errors, as confirmed by the

divergence recorded in the calculation of the acceleration factor using two difference criteria : the loss of elongation at break and the degree of oxidation measured by the absorbance at 1715 cm^{-1} .

Malik, Tuan and Spirk(1994) studied about models are used for estimation of HALS stabilization efficiency in polyolefins : the empirical relationship suggested by Moisan and theoretical model for additive loss proposed by Billingham and Calvert. It is shown that Moisan's empirical relationship is valid also for HALS-stabilized polyolefins. According to this relationship, an efficient light stabilizer should be highly soluble in the polymer, while its diffusion rate has to be minimal. In the Billingham and Calvert model, the failure criterion was more precisely defined by the introduction of the critical stabilizer concentration.

The relationship between degradation and mechanical behaviour of polymers was examined by Raab (1994) . This study supplemented by several original photographs and diagrams presents a structural model of the degradation of thermoplastic polymer materials in solid state. Degradation in solid state is distinctly delocalised and heterogeneous invature. So, the progress of degradation can be recorded more sensitively by measuring the mechanical strength properties.

Saleh and Elizabeth (1994) studied the environmental degradation of high-density polyethylene (HDPE) blended with carbonmonoxide and

nonblended HDPE. The analysis showed that an environmental degradation causes reductions of molecular weight, increasing of polymer chain mobility leading to a higher degree of crystallinity, accounts for the loss of ductility, indicated by a sharp elongation. The presence of carbon monoxide in the blended samples accelerates the process of environmental degradation, but the degradation mechanisms appear to be similar to nonblended HDPE.

2.1 Polyolefin films

Polyolefins are produced by the polymerization of small molecules called α -olefins. α -olefins are unsaturated, aliphatic hydrocarbons possessing a single double bond between the first and second carbon atoms and having the general chemical formula $C_n H_{2n}$. Examples of commonly used α -olefins include ethylene ($CH_2=CH_2$), propylene ($CH_3-CH=CH_2$), and butene ($CH_3-CH_2-CH=CH_2$). The polyolefins that are most widely produced commercially are low density polyethylene (LDPE), high density polyethylene (HDPE) and polypropylene (PP).

The polyolefins form an important class of thermoplastics from any stand point but they are particularly important as film formers since they include low and high density polyethylene and polypropylene. Low density

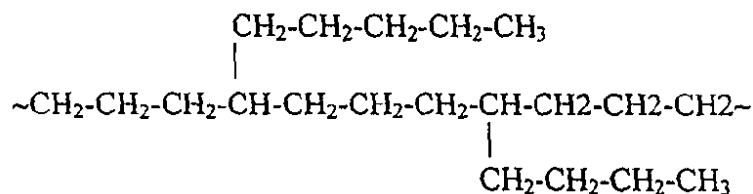
polyethylene film constitutes the major portion of the total film market but high density polyethylene and polypropylene are by no means minor components.

2.1.1 Low Density Polyethylene

The polymerization of ethylene can occur over a wide range of temperatures and pressures but most commercial high pressure process utilize pressures between 1000 and 3000 atmospheres (1.45×10^4 - 4.35×10^4 lb/in²) and temperatures between 100 and 300 °C. Temperatures higher than 300 °C tend to cause degradation of the polyethylene. The simplest structure for the polyethylene molecule is a completely unbranched chain of -CH₂- units as show



At the high pressure, the straight forward process chain growth and a great deal of chain branching occurs which has an important bearing on properties of low density polyethylene. Both short and long branch chains are produced, examples of which are shown below



It will be noticed that each branch chain contains a terminal methyl (-CH₃) group. The occurrence of these branch chains prevents a close packing of the main polymer chains and this accounts for the fact that the process just described produces low density polyethylene.

Properties

The structure of the low density polyethylene molecule also affects properties other than density (The density can vary between about 0.916 g/cm³ and 0.935 g/cm³). One important property is crystallinity. The great length of polymer chains means that a certain amount of entanglement normally occurs and this prevents complete crystallization on cooling; there are thus disordered areas between the crystallinities. Areas where the chains are parallel and closely packed are largely crystalline while the disordered areas are amorphous. The chain branching will tend to reduce the possibility of an ordered arrangement and so reduce the crystallinity. The crystallinity of low density polyethylene usually varies between 55 and 70% (compared with 75-90% of high density polyethylene). The other property of importance which is affected by the chain branching is softening. The fact that the chains cannot approach so closely to each other means that the attractive forces between them are reduced and less energy in the form of heat, is necessary to cause them to move relative to each other and thus flow. The softening point of low density polyethylene is slightly

below the boiling point of water and so the material cannot be used where boiling water or steam sterilization are involved.

Low density polyethylene is a tough, slightly translucent material and is waxy to the touch. It can be blow extruded into tubular film or extruded through a slit die and chill-roll casting process gives a clearer film but even blown film can be produced with good clarity with improvements in cooling of the bubble. Low density polyethylene film has a good balance of properties such as tensile strength, burst strength, impact resistance and tear strength. In addition, it retains its strength down to quite low temperatures (around -60°C to -70°C). It is a good barrier to water and water vapour but is not so good resistance, particularly to acids, alkalis and inorganic solutions and, sensitive to hydrocarbons and halogenated hydrocarbons and to oils and greases. So that low density polyethylene is used in the fields of packaging, building, horticulture and agriculture.

2.1.2 High Density Polyethylene

Following ICI's discovery of low density polyethylene, the next most important step came in the early 1950s when Professor Ziegler, in the course of work on organometallic compounds, discovered catalysts which enabled the polymerization of ethylene to be carried out at near atmosphere pressures and temperatures. At about the same time, two other low pressure methods were

developed in the U.S.A. by Phillips Petroleum Company and Standard Oil of Indiana.

The Ziegler catalyst which are organo-aluminium compounds. The combination of aluminium triethyl and a titanium derivative such as the tetrachloride is the active catalyst. The catalyst system is suspended in a liquid hydrocarbon through which the ethylene through, is passed. The pressure is near atmospheric and the temperature is around 50-75°C. Polyethylene settles out as a granular powder and the resultant slurry is stirred until the viscosity becomes so high as to interfere with efficient dispersion. The removal of catalyst residues is important as the electrical properties of the polymer which due to severely affected. One method used is to add dry hydrochloric acid gas which forms alcohol soluble complexes with titanium (this being the more difficult metal to remove). After preliminary washing with alcohol, the polymer is well washed with water. The resultant slurry is filtered or centrifuged and then dried.

The Phillips process, the utilised catalyst is partly reduced chromic oxide supported on steam activated silica-alumina, operates at higher pressures (between 2750-3450 kN/m² or 400-500 lb/in²) and higher temperatures (between 100-175 °C). The liquid medium is usually cyclohexane and at these temperatures the polyethylene dissolves and is removed as an approximately 10% solution. The catalyst is removed quite simply by centrifuging. Recently

(during the late 1960s) Union Carbide Corporation introduced a gas phase process for the manufacture of high density polyethylene, based on a catalyst system. Ethylene, a small quantity of hydrogen, catalyst and co-monomer are fed continuously to a gas phase reactor where polymerization takes a pressure about 1960 kN/m^2 (286 lb/in^2) and temperatures within the range $85\text{-}100^\circ\text{C}$. This process is no need for separation of solvent from the polymer because, gas phase polymerization requires no solvent. The removal of catalyst residues is not necessary and no need to wash and dry.

Properties

The high density polyethylene produced by low pressure process. Its structure is linear and closely packed. Some short branched chains are formed but are not too many. The ranging of density are around $0.941\text{-}0.965 \text{ g/cm}^3$. It is stiffer, harder and has less waxy feel than low density polyethylene. It can be made by blow extrusion or slit die extrusion (with chill roll casting or water quenching). The blown film extrusion is a rather milky but, translucent. The softening point of high density polyethylene is higher (about 121°C) and so it can be steam sterilized.

Tensile strength is higher than that of low density polyethylene as is the bursting strength but impact strength and tear strength are both lower. Because of their linear nature the high density polyethylene molecules tend to align themselves in the direction of flow and the tear strength of the film is much

lower in the machine direction. High density polyethylene has a better resistance to chemicals, oils and grease than low density polyethylene. In addition it is subject to environmental stress cracking in the same way as low density polyethylene but the effect can be reduced again by using high molecular weight grades which is likely to be a problem.

2.1.3 Polypropylene

This polymer, which has the basic structure unit is
$$\begin{array}{c} \text{CH}_3 \text{ H} \\ | \quad | \\ [-\text{C}-\text{C}-] \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$$
, was

directed towards the use of Ziegler-type catalysts. Natta (in Italy) showed in 1954 that it was possible to prepare analogous polymers of propylene and polypropylene was first marketed in 1957. He found that in the Ziegler catalyst system, aluminium triethyl plus titanium tetrachloride, the titanium tetrachloride was replaced by titanium trichloride, a stereospecific catalyst was formed which yielded crystalline high molecular weight polymer of propylene. A stereospecific catalyst is one which controls the position of each monomer unit as it is added to the growing polymer chain, thus allowing the formation of a polymer of regular structure from an asymmetric monomer unit such as propylene.

Basically Natta's polymerization of propylene is similar to the Ziegler process for the preparation of high density polyethylene. The gas, under a

pressure of about 100 atmospheres ($1.015 \times 10^3 \text{ N/m}^2$ or $1.4 \times 10^7 \text{ lb/in}^2$), is led into a reaction vessel in which is a well-stirred dispersion of catalyst in a liquid hydrocarbon. The temperature is kept low enough to ensure precipitation of the polypropylene as it is formed. Stirring is continued until the polymer content is between 35 and 40%, when the slurry is pumped to a flash drum where the unreacted propylene is removed and recycled. The slurry is then centrifuged to remove the liquid hydrocarbon. Catalyst removal from the polymer is carried out by extracting with a weak solution of hydrochloric acid gas in methyl alcohol. After removal of the extraction, the polymer is washed with water to remove the acid, steam distilled to remove solid traces, dried, extruded and pelletised.

Properties

Polypropylene has lower density than low density polyethylene (about 0.90 g/cm^3), is harder and higher softening point. Polypropylene film can be manufactured either by blow extrusion or by slit-die extrusion with subsequent cooling by chill-roll or water bath quench. The position is complicated by the fact that both methods have been used to produce a range of films which vary in the amount of orientation built into the film. Commercially, the films with unbalanced orientation, polypropylene films are used in the field of packaging.

2.2 Photo-oxidation of polymer

The properties of polymeric materials are affected by radiation as a result of the chemical changes in the polymer molecules. These changes include molecular weight and structure. Secondary effects are on crystallinity and on molecular architecture in the amorphous phase. Degradation of polymers is frequently taken to mean reduction in molecular weight, or deterioration in some desirable property, but these are unnecessarily narrow definition; as an increase in modulus due to crosslinking may be beneficial in one application, but the accompanying decrease in fracture strain may be a disadvantage in another application. Therefore, it is appropriate to consider degradation as may change in the molecular, morphological or material properties of a polymer resulting from irradiation. Many synthetic polymeric materials are oxidized in contact with the atmosphere. At room temperature in the absence of light the reaction may be very slow. But at elevated temperature or during exposure to ultraviolet light the rate of oxidation is often quite rapid.

Appreciable decomposition of polyethylene occurs when the material is exposed to sunlight for less than two years, and the preliminary effects of photooxidation are evident after only a few months. Polypropylene is even more susceptible to photooxidative breakdown. However, polyisobutylene is

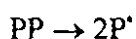
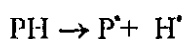
more stable under these conditions than polyethylene and polystyrene. Polystyrene is especially susceptible to photooxidation. The phenyl groups absorb ultraviolet radiation from sunlight and transfer the energy to nearby units on the polymer to generate a cascade of reactions. Oxygen radicals, hydroperoxide units, carbonyl group formation, chain cleavage, and even phenyl group ring cleavage reactions occur. The overall effect is for the polymer to become yellow and brittle.

Polymers such as polyisoprene or polybutadiene, which contain unsaturated linkages, can be attacked by atmospheric ozone as well as by oxygen. Again, free radical cleavage and crosslinkage processes are responsible for the loss of advantageous polymer properties following oxidation. Poly(vinyl chloride) is especially sensitive to oxidation and dehydrohalogenation reactions. On the other hand, fluorine containing organic polymers are surprisingly stable.

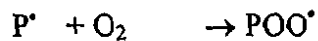
Photooxidation scheme

The photooxidation of organic polymer generally proceeds through free-radical reactions. Free radicals are formed by the thermal or photolytic cleavage of bonds. The radicals then react with oxygen to yield peroxides and hydroperoxides by processes that illustrate follow:

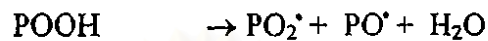
Chain Initiation



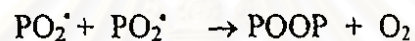
Chain Propagation



Chain Branching



Chain Termination



(P' represents a polymer radical)

Figure 2.1 Oxidation and Photooxidation scheme (R. Gachter and Muller, 1985)

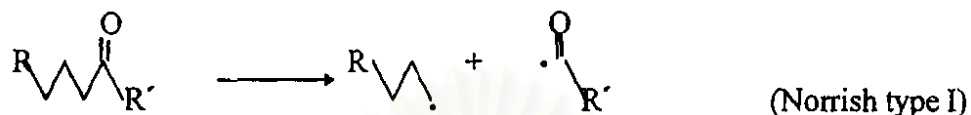
2.2.1 Photooxidation of Polyolefins

Photodegradation of polyolefins is caused mainly by the presence of catalyst residues, hydroperoxide groups, carbonyl groups, and double bonds introduced during polymer manufacturing, processing or storage.

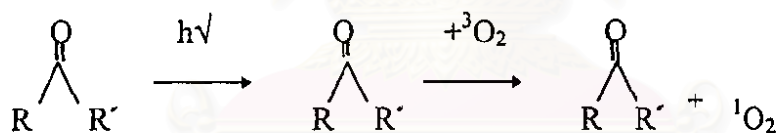
The exposure of polyolefins at high energy radiation causes the formation of various free radicals. Some of these radicals combine with oxygen dissolved in the polymers to initiate chain reaction and form thermally unstable products. The oxidative process will involve peroxy radicals derived directly from the radiation reactions and also these initial peroxy radicals attack on the polymer (photooxidation scheme). Hydroperoxide (ROOH) are believed to

slowly breakdown and produce carbonyl compounds. The carbonyl compounds are predomina those expected from the Norrish type I and II process.

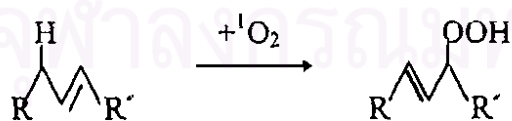
(R. Gachter and Muller, 1985)



Some previous work shows carbonyl compounds to be involved in the formation of singlet oxygen ($^1\text{O}_2$) through energy transfer from their excited triplet state to oxygen in the ground state ($^3\text{O}_2$) (W. Schnabel, 1981)



The lifetime of singlet oxygen in polymers is long enough to allow its reaction with double bonds leading to the formation of allylic hydroperoxides

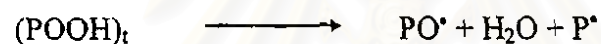


Singlet Oxygen reactions, showed that polymers with unsaturation in pendant groups or in the backbone exhibited reactivity. Polymers not containing olefinic unsaturations were unreactive. On the other hand, the alkoxy radicals resulting

from the decomposition of allylic hydroperoxides may also lead to disproportionation and cross-linking.

Photochemical reaction of polyolefin (F. Gugumus, 1995)

Photoinitiation



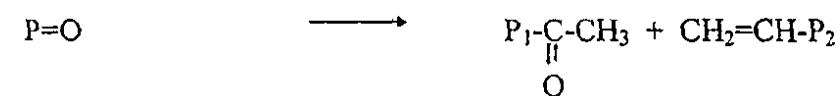
Propagation



Photoreactions of peroxy radicals



Photolysis reactions



Termination

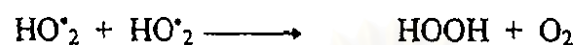
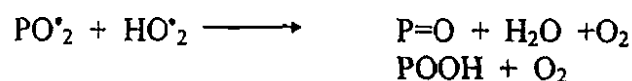
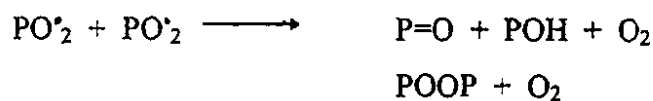


Figure 2.2 Photochemical reaction of Polyolefin

Photochemical reaction of Polyethylene

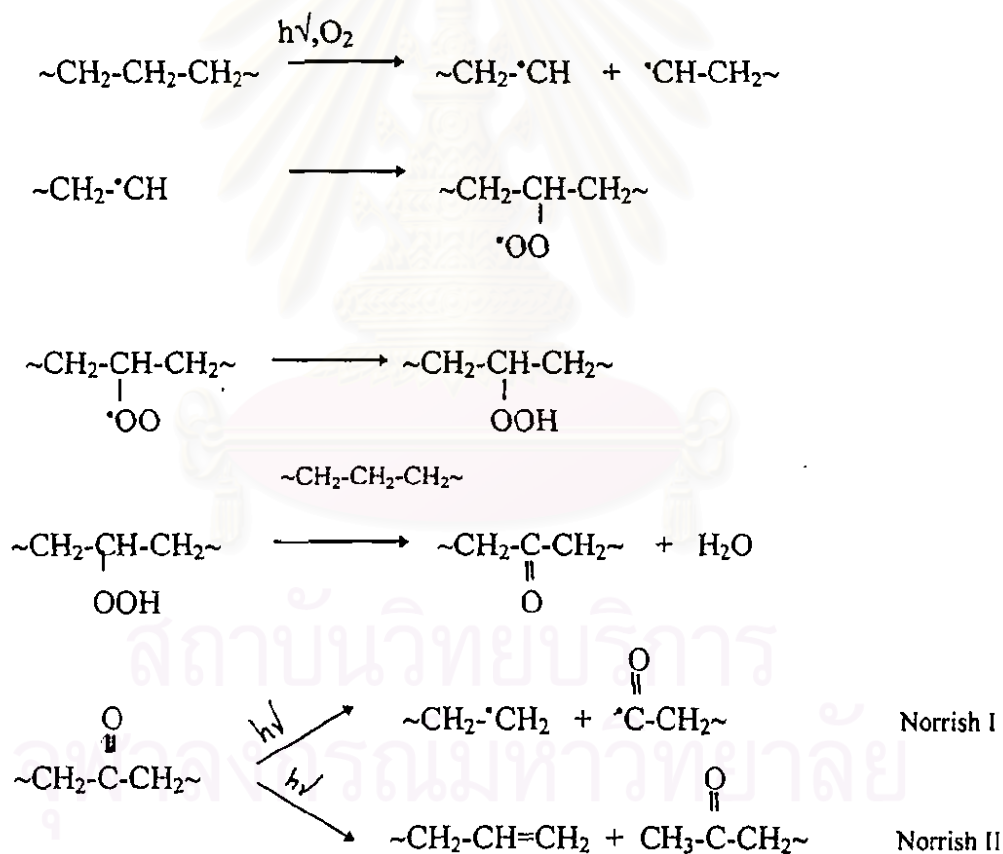


Figure 2.3 Photochemical reaction of polyethylene

Photochemical reaction of polypropylene

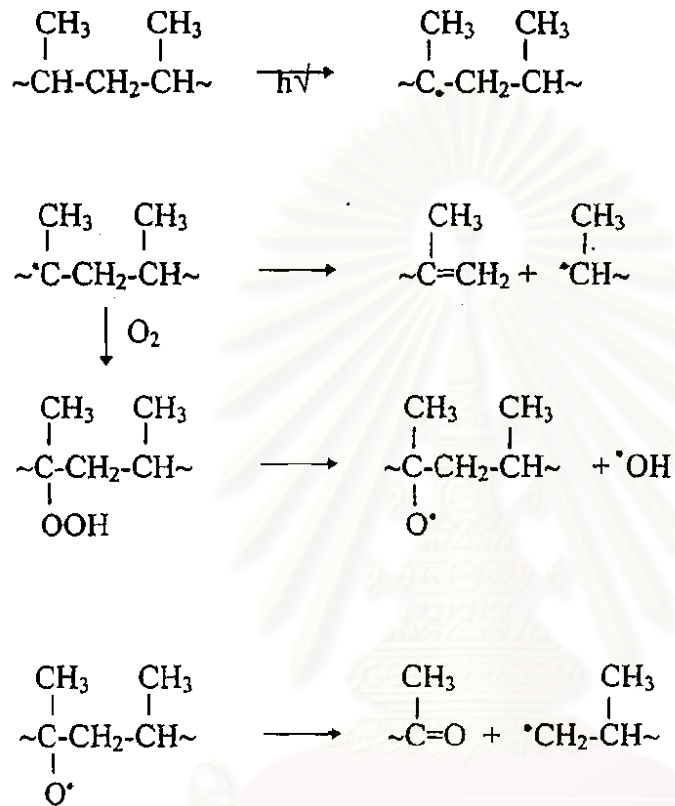


Figure 2.4 Photochemical reaction of polypropylene

2.3 Factors comprising weather

The principle factors which influence the natural exposure during natural weathering are

2.3.1 Radiation

The composition of the nature radiation is ultraviolet, visible and infrared light. The ultraviolet is probably the most potent single factor of degradation although infrared is the most potent (approximately 5% ultraviolet energy, 45% visible and 50% infrared radiation). The wavelengths of sunlight is reaching at the earth's surface that cause most degradation of polymers are in the ultraviolet range of 300-400 nm and only about 5% of the total sunlight fall into this category. The energy of light depends on its wavelength such as at 300 nm the energy sufficient to break carbon bonds in polymer is 95 kcal/mole (398 kJ/mole). The energy to break the bonds between atoms based on a study of small molecules is known to be in range 50-100 kcals/mole, When a molecule absorbs ultraviolet light it becomes highly activated or electronically excited. In some instances the excited molecule initiate a photochemical reaction involving itself and sometimes neighbouring molecules. The intensity of the radiation rather than the ultraviolet light and re-emit this energy to non-destructive wavelength.

In order for radiant energy to initiate reactions it must be absorbed. The frequency of ultraviolet energy absorbed depend in part on the chemical structure of the group irradiated (that are given in table 2.1)

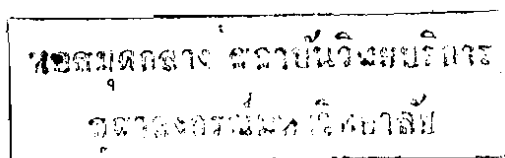


Table 2.1 Energy of radiation of different wavelengths and bond energy of typical bonds found in polymers (R. Guchter and Muller, 1985)

Wavelength (nm)	Energy		Bond Type	Bond Energy (kJ.mole ⁻¹)
	(kcal.mole ⁻¹)	(kJ.mole ⁻¹)		
290	100	419	C-H	380-420
300	95	398	C-C	340-350
320	90	375	C-O	320-380
350	81	339	C-Cl	300-340
400	71	297	C-N	320-330

The combinations of ultraviolet light with water or heat result in greater decomposition than with ultraviolet alone. This is because of modifications to the polymer by heat or moisture or oxygen result in shifts in the ultraviolet absorption to wavelengths at which photochemical degradation can occur.

2.3.2 Temperature

It is not quite correct to divorce infrared radiation from temperature but here is meant the thermal state both very hot and very cold, that an exposed article can achieve. The effect of alternating hot days and cold nights can be

drastic, often causing crazing of the surface due to excessive expansion and contractions. This is particularly true if internal tensions exist in the materials due to earlier thermal shock in exposed samples. For example, in many areas the temperature of samples exposed at 45° south often reaches 65.5°C during the day and in desert areas may drop about 37.8°C after sunset. The effect of fatigue coupled with the frequency and intensity of thermal changes are significant which increase on the rate of degradation of exposed polymers follows the same law that applies to chemical reactions.

2.3.3 Oxygen

The oxygen in the air, although hardly a part of any climate, is still of importance in the exposure of polymeric materials because so many of them absorb oxygen through their surface. This affects the rate of degradation although, as a rule, it is a very slow process.

2.3.4 Water

The action of water (rainfall, dew) is complex and will depend on the nature of the polymer and moulding process. It may wash away soluble degradation products which might decompose catalyst. On the other hand it may wash away soluble compounding ingredients such as plasticizers, stabilizers, self extinguishing additives etc. It can be particularly undesirable

in the case of thin films containing slightly soluble light stabilizers and antioxidants. Polymer containing hydrolysable groups are formed as a result of oxidation are naturally susceptible to degradation by water. Hygrothermal shocks due to temperature variations accompanied by changes in humidity are particularly potent.

2.4 Tensile Properties

Tensile properties are most widely used for defining both the quality of production of polymeric materials, their design and engineering behavior. Tensile properties may also be used indirectly to measure other properties of a material for which a correlation exists. For example, a plastic film having high tensile strength, and measurement of tensile properties will correlate well with measurement of impact strength on such an item. This properties may be used to monitor or follow the progress of chemical or physical changes in polymer. For example, polymer exposed to high heat or ultraviolet light may undergo depolymerization and oxidation reactions which will be reflected in changes in tensile properties. In a similar manner, when polymer are exposed to an aggressive chemical environment, they may become either more brittle or less brittle, and the changes can be conveniently followed through measurement of tensile properties.

Definitions

The tensile properties, as they are normally obtained, may be defined as follows:

- 1) Tensile stress is the tensile load per unit area of minimum original cross section within the gauge boundaries carried by the test specimen at any given moment. It is expressed in force per unit area.
 - 2) Tensile strength is the maximum tensile stress supported by the specimen during a tension test.
 - 3) Tensile strength at break is the tensile stress at the moment of rupture of the test specimen.
 - 4) Elongation is the increase in length produced in the gauge length of the test specimen by a tensile load. It is expressed in units of length, commonly as a percentage.
 - 5) Elongation at break is the elongation at the moment of rupture of the test specimen.
 - 6) Strain is the ratio of the elongation to the gauge length of the test specimen, that is the change in length per unit of original length. It is expressed as a dimensionless ratio.
 - 7) Yield point is the first point on the stress-strain curve at which an increase in strain occurs without an increase in stress.
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8) Proportional limit is the greatest stress or strain which a material is capable of sustaining without any deviation from proportionality of stress to strain.

9) Modulus of elasticity is the ratio of stress to corresponding strain below the proportional limit of a material. It is expressed as force per unit area.

10) Work to cause rupture is the area under the stress-strain curve. It is a measure of the amount of energy or work which must be done to rupture secondary (yield point) and primary (rupture) bonds.

The important problem of comparing tensile properties becomes less misleading if three considerations are taken

1. First of all, it has already been stated that no known relationship exists between the tensile properties as they are commonly run under standard conditions and the end use performance of a part made from that polymers. In some rather rare instances, the time, temperature, and environment of the application are similar enough to the conditions of testing to allow the data to be used for engineering purposes. These case are rare indeed.

2. Secondly, the standard tensile properties with the exception, perhaps, of the modulus of elasticity, are most useful only for identification, specification and quality control purposes. This is particularly true of the quality of the polymer.

3. Finally, the modulus of elasticity is a reliable means of measuring the stiffness of a material. It is not as sensitive to changes in testing speed in many instances, particularly in the range of speeds used in standard tensile testing.

2.5 Chemical properties

In most cases of deterioration during exposure to natural weathering changes in the chemical nature of the polymer, particularly at the surface, take place and these can be followed by standard or special analytical procedures. Sensitive chemical test may detect changes associated with degradation before noticeable changes in mechanical properties occur but most of the chemical tests applied measure the product of oxidative degradation. Examples of such tests are

1) Colour reactions

Wright and Gray described the use of N,N dimethyl-p-phenylenediamine to react with oxidation products on the surface of the sample, to produce a coloured product and the intensity of this colour formation is proportional to the amount of oxidative degradation which has occurred. The process has been used successfully on PVC, polyester resins, polymethyl methacrylate and cellulose acetate butyrate.

2) Carbonyl content of polyolefins

Bolland discusses the oxidative degradation of polyolefins and shows that the carbonyl content increase during exposure and is readily measured by ultraviolet spectrograph or infrared spectrograph which is widely used.

3) Volatile products

Volatile products evolved during degradation have also been measured to assess the progress of degradation.

2.6 Fourier transform infrared spectroscopy (FT-IR)

Infrared spectroscopy in which the incident beam is split into two waves the spectral information of the sample is contained in the phase difference between the two waves, after they have been recombined. This is performed by the use of a michelson interferometer. An interferogram is obtained from the detector which is digitised and transformed from the time domain by a mathematical Fourier transform operation and the resultant signals are converted to a conventional infrared spectrum. These operations are carried out by a computer. The advantages of FT-IR over conventional IR are its abilities to detect weak signals and to obtain a complete spectrum in a few seconds.