CHAPTER 2

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

2.1 Poly(vinyl chloride)

Poly(vinyl chloride), $-(-CH_2-CHCl-)-$, commonly known as PVC, is a synthetic thermoplastic polymer.[1] Today the amount of PVC produced is second only to the production of all polyolefins (low and high density polyethylene and polypropylene together).

The reasons for its enermous versatility and range of applications derive from a suitable basic structure which gives rise to a relatively tough and rigid material which can modify its physical characteristics to produce a range of flexible products, an low price with ease of processing and very good technical and chemical properties.

The history of the preparation of PVC actually begins with that of the discovery of the vinyl chloride monomer which were observed by Regnault in 1835.[2] In 1872, Baumann described the preparation of poly(vinyl chloride) from the monomers. In 1972, Fritz Klatte patented a process for the production of vinyl chloride by the reaction between hydrogen chloride and acetylene. However, commercial production of poly(vinyl chloride) did not really begin until 1931, in Germany.

The pattern of consumption of PVC can be divided into two distinct classes by its application; Rigid applications and flexible applications. The rigid and flexible PVC are different because of its basic structure since the structure of the polymer, with a chlorine atom situated on each alternate carbon of the polymer chain, lead to a very rigid and relatively tough plastic, in the unplasticised state.

While as the flexible PVC or plasticised PVC contains plasticisers in high enough quantity to impart these properties to the materials. Since, the dipole bonding between PVC chain is much reduced, leading to increased freedom of chain movement and turn to be an flexible material.

Commercial applications of flexible PVC may include alternative cable insulation, since the cable industry is still a major comsumer of PVC world-wide. Other applications are flexible film and sheet, fabric coating, flexible profile and tubing, and flooring, etc.

While the biggest single application of rigid PVC is pipe and conduit extrusion, primarily for domestic drainage and sewage pipes, land drainage pipes, waste pipes,portable water pipes, rainwater pipes and conduits of electric cable. The second largest application area is rigid profile such as window frames and sills, patio doors, external cladding and ranch fencing. Other applications include bottles, rigid foil and sheet, recording disks, etc.

2.1.1 Physical and Chemical Properties.

The physical and chemical properties of poly(vinyl chloride) are shown in Table 2.1 and Table 2.2 , respectively.

2.1.2 PVC Production

PVC is prepared by polymerization of vinyl chloride monomer using peroxide as the initiator. Commercial production of vinyl chloride monomers starts with either of two raw materials: acetylene or ethylene.[3] With acetylene feed, the synthesis is completed by the simple addition of hydrochloric acid (Eq.2.1)

$$HC{\equiv}CH + HCl \longrightarrow H_2C\text{-}CHCl \qquad (2.1)$$

TABLE 2.1 PROPERTIES OF POLY(VINYL CHLORIDE)[4]

Glass transition temperature (T_g)	81°C (354°K) T_g varies considerably with variations in the method and temperature of polymerization
Solvents[a]	
Theta solvent	Benzyl alcohol at 155.4°C
Solvents for high molecular weight resins	Tetrahydrofuran, acetone–carbon disulfide mixtures, methyl ethyl ketone
Solvents for low molecular weight resins	Toluene, xylene, methylene chloride, ethylene chloride, perchloroethylene–acetone mixtures, 1,2-dichlorobenzene, tetrahydrofurfuryl alcohol, dioxane, acetone–carbon disulfide mixtures, cyclopentanone, diisopropyl ketone, mesityl oxide, isophorone, dimethylformamide, nitrobenzene, hexamethylphosphoramide, tricresyl phosphate
Nonsolvents	Aliphatic and aromatic hydrocarbons, vinyl chloride monomer, alcohols, glycols, aniline, acetone, carboxylic acids, acetic anhydride, esters, nitroparaffins, carbon disulfide, nonoxidizing mineral acids, concentrated alkalies

Mark–Houwink–Sakurada parameters (for viscosity–molecular weight correlation)	Solvent	Temp. (°C)	$K \times 10^5$ (dl/gm)	a
	Benzyl alcohol (theta solvent)	155.4	156	0.50
	Chlorobenzene	30	71.2	0.59
	Cyclohexanone	20	11.6, 13.7, 112.5	0.85, 1, 0.63
		25	24, 12.3, 204, 208, 174	0.77, 0.83, 0.56, 0.56, 0.55
		30	16.3	0.77
	Tetrahydrofuran	20	1.63	0.92
		25	49.8, 16.3	0.69, 0.766
		30	219, 83.3	0.54, 0.83

Price–Alfrey copolymerization parameters (See also Table IV)	$e = 0.20$ $Q = 0.044$

[a] Solvents are somewhat dependent on the molecular weight distribution of a polymer sample.

Table 2.2 Polyvinyl Properties.[5]

Property	(PVC) Rigid Vinyl Chloride	PVC Acetate (Copolymer)	Vinylidene Chloride Compound
Molding qualities	Good	Good	Excellent
Specific gravity (density)	1.30-1.45	1.16-1.18	1.65-1.72
Tensile strength (psi)	5000-9000	2500-4000	3000-5000
Compressive strength (psi)	8000-13,000		2000-2700
Izod, impact (ft-lb/in)	0.4-20.0		0.3-1.0
Hardness, Rockwell	M110-M120	R35-R40	M50-M65
Thermal expansion (10^{-5}/°C)	5.0-18.5		19.0
Resistance to heat (°F)	150-175	130-140	160-200
Dielectric strength (volts/mil)	400-500	300-400	400-600
Dielectric constant (60 Hz)	3.2-3.6	3.5-4.5	4.5-6.0
Dissipation factor (60 Hz)	0.007-0.020		0.030-0.045
Arc resistance, (seconds)	60-80		
Water absorption (24 hrs, %)	0.07-0.4	3.0+	0.1
Burning rate (in/min)	Self-exting.	Self-exting.	Self-exting.
Effect of sunlight	Needs stabilizer	Needs stabilizer	Slight
Effect of acids	None to slight	None to slight	Resistant
Effect of alkalies	None	None	Resistant
Effect of solvents	Soluble in ketones and esters	Soluble in ketones and esters	None to slight
Machining qualities	Excellent		Good
Optical	Transparent	Transparent	Transparent

An oxychlorination reaction (Eq.2.2) is used with an ethylene base feed to produce ethylene dichloride.

$$2HCl + 1/2O_2 + Cl_2 + 2H_2C{=}CH_2 \longrightarrow 2ClH_2C\text{-}CH_2Cl + H_2O \qquad (2.2)$$

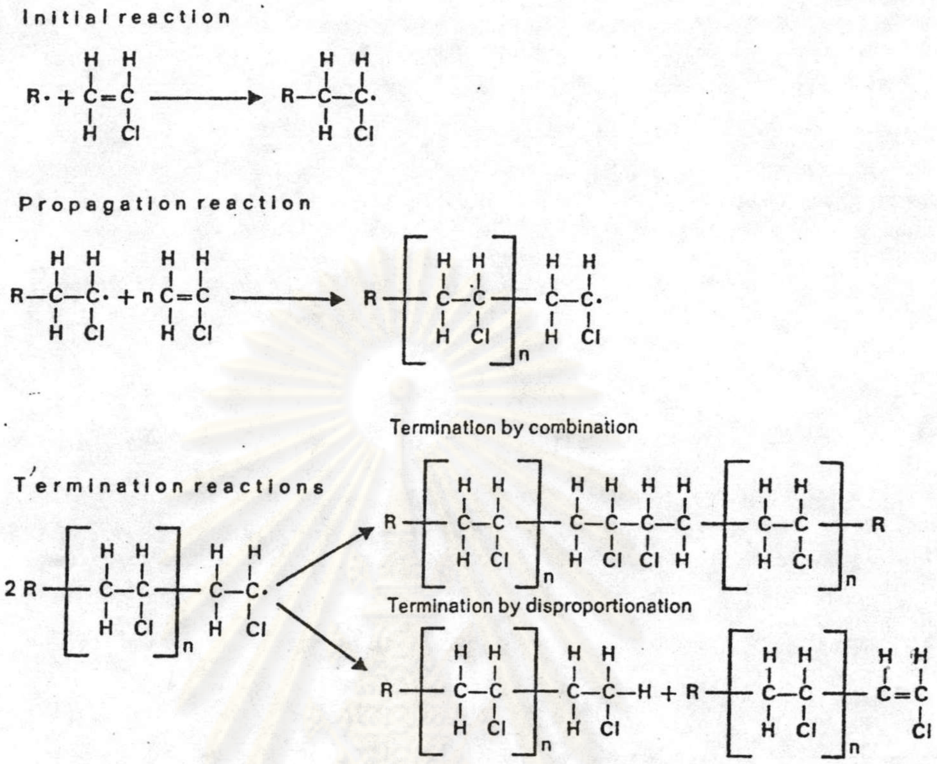
Then the ethylene dichloride is dehydrochlorinated to form vinyl chloride (Eq.2.3)

$$ClH_2C\text{-}CH_2Cl \longrightarrow H_2C{=}CHCl + HCl \qquad (2.3)$$

Although vinyl chloride monomer can be produced by either of the above reaction, current economics favor the ethylene approach because ethylene is considerably lower in cost compared to acetylene. Thus, most new vinyl chloride plants are utilizing the oxychlorination route.

Polymerization of vinyl chloride monomer is a radical chain reaction which may be triggered off by energy from a natural source (light) or an artificial source (electron beam) or by a radical forming catalyst.[6,7] When the initial radical has been formed, a series of monomers attach themselves to such radicals and the double bond in the vinyl chloride is broken (SCHEME 2-1). The radical function is maintained as the chain grows until finally a termination reaction occurs. This can be the result of a combination of two macroradicals or of a disproportionation reaction.

There are four basic manufacturing processes for PVC production namely suspension, mass, emulsion and solution. In each process, polymerization is initiated by free radicals produced by thermal decomposition of peroxide-type initiators and proceeds exothermally at a temperature between 40 to 70 °C.[6] Vinyl chloride is a gas at room temperature (b.p. -13.9 °C).[8] Thus, the reaction is carried out in pressure vessels equipped with agitators and heat-removal systems



SCHEME 2.1 Polymerization of vinyl chloride[7]

capable of precise temperature control.

Table 2.3 Compares the bulk,suspension,and emulsion processes and some of the properties of resulting resins. This excludes solution polymerization, since it is used for making PVC in speciality applications in limited production quantities.[9]

Figure 2.1 shows the suspension process, which is the most preferred one.[10] Vinyl chloride droplets are suspended in water by means of protective colloids such as polyvinyl alcohol, gelatin or methyl cellulose and rapidly agitated. Reactions, which may take up to 10 hours, are carried to a predetermined end point since they do not go to completion. Unreacted monomer is removed from the vessel by vacuum and is stripped from the slurry. The slurry is largely

TABLE 2.3 COMPARISON OF BULK, SUSPENSION, AND EMULSION POLYMERIZATION PROCESSES[9]

Bulk polymerization	Suspension polymerization	Emulsion polymerization
Monomer is polymerized as such without any other medium.	Monomer is suspended in another liquid phase (usually water), aided by suspending agents and strong agitation.	Monomer is emulsified in water by addition of surfactants and moderate agitation.
Monomer-soluble initiators are used.	Monomer-soluble initiators are usually used.	Water-soluble initiators are usually used.
Heat removal is difficult and involves risks. Sometimes controlled by evaporation of monomer.	Heat is easily controlled by dissipation to the suspending medium. Safety hazards are less than in bulk processes.	Heat is easily controlled by the aqueous system which acts as heat transfer agent. Safety hazards are low.
Product does not need to be dried.	Product is readily separated from slurry and can be dried easily.	PVC–latex is formed. To isolate resin, a coagulation step or spray drying is required. Drying costs are high.
The improved two-step process permits control of particle size within a narrow angle.	Particle size, shape, and porosity can be controlled easily.	Particle size can be controlled easily.
Molecular weight distribution is less readily controlled than by other methods.	Good control of molecular weight distribution.	Good control of molecular weight distribution.
Polymer is free of extraneous materials. Heat stability, dynamic stability, and clarity are better than in polymers produced by other methods.	Polymer has lower heat stability and clarity than bulk polymer.	Poor heat stability because of excessive emulsifying agents.
Good processability, suitable for rigid polymer applications because of good heat and dynamic stability and good transparency. Used in packaging articles.	Good processability. Used for general purpose applications, e.g., in extrusion, calendering, molding, and in electrical grade PVC compounds. This process can also be used for specialty-type resins.	The extremely fine resin particles give specific properties such as excellent fusion power to form rigid solids and its ability to form plastisols. This latter property is an important factor in favor of this process.

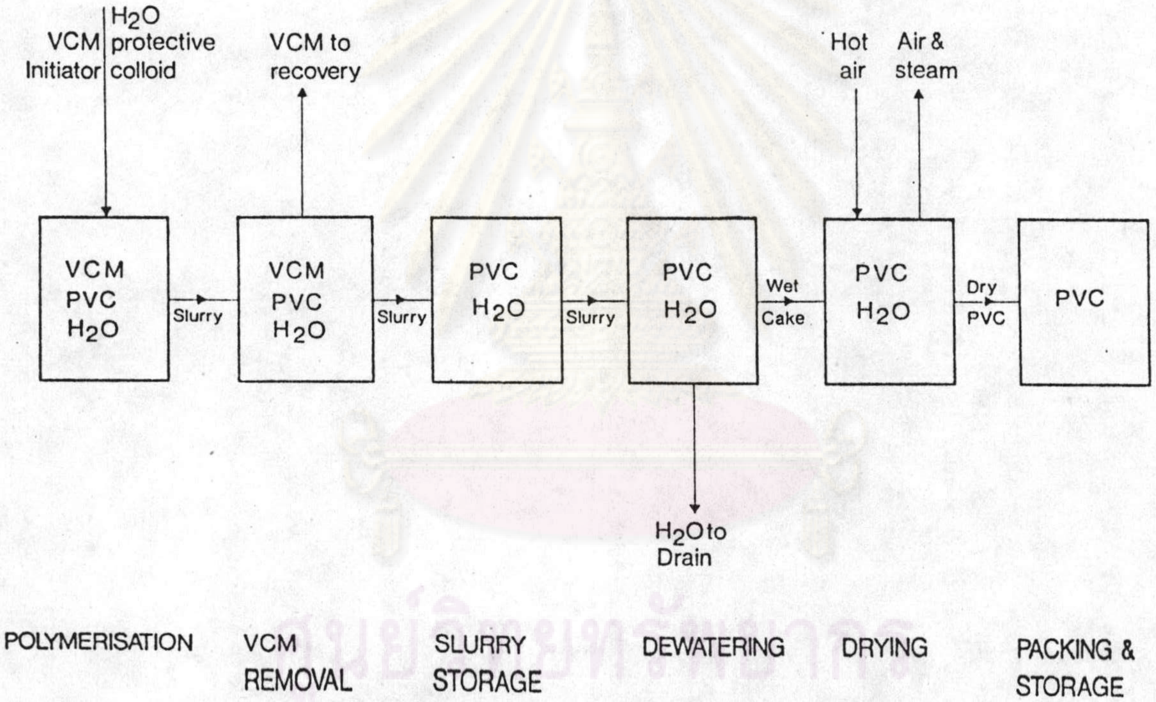


FIG. 2.1 Diagram of suspension polymerisation process.[11]

dewatered in a centrifuge and then dried. The number average molecular weight of PVC is usually of the order of 60,000 .[3]

2.1.3 Rigid PVC

2.1.3.1 Applications

Rigid applications developed more slowly because of the greater difficulty in processing unplasticised compositions, which were found to degrade readily at the melt temperature. The success in overcoming problems in processing and stabilization is amply demonstrated by the very considerable tonnages consumed throughout the world. Consumption in the U.S.A. has averaged between two and three million tonnes per annum in recent years, whilst the consumption in Western Europe, in 1981, was estimated to be 3.3 million tonnes.[2] The consumption of PVC in Western Europe in 1980 (include the UK.) splits into broadly defined application areas as shown in table 2.4 .

It is evident from Table 2.4 that rigid applications account for over 60% of the total usage, having grown considerably in the last two decades, whilst some of the flexible applications which were the earliest to be exploited have shown only modest growth rates. The biggest single application area is clearly that of pipe and conduit extrusion, primarily made up of domestic drainage and sewage pipe, land drainage, waste pipe, potable water pipe, rainwater goods and conduit for electric cables. The second largest application area is "rigid profiles",which covers a wide variety of products, but is dominated by building applications, and in Germany, by the large volume of PVC window frame manufactured as well as patio doors, skirting boards, ranch fencing,etc.

Other applications of rigid PVC include bottles, since PVC is employed so extensively for bottling fruit squashes, edible oil and vinegar, as well as a wide range of toiletries and domestic products.

Table 2.4 West European consumption of PVC (1980)[2]

Application	Tonnes x 10^3
Bottles	258
Rigid foil and sheet	369
Rigid injection moulding	84
Pipe and conduit	908
Rigid profile	560
Records	75
Miscellaneous	69
Total rigids	2323
Coated fabrics and paper	189
Flexible film and sheet	358
Flooring	199
Flexibles profiles and tubing	145
Cables	352
Miscellaneous	43
Total flexibles	1286
Other unspecified	141
Total consumption	3750

2.1.3.2 The Processing of rigid PVC

The particular problems of processing rigid PVC arise from those fundamental properties of the polymer which are also the source of its particular advantages. Since, Poly (vinyl chloride), as commercialy manufactured, is a predominantly amorphous polymer although there is a low but significant degree of crystallinity with regions of syndiotactic structures.

In contrast with highly crystalline polymers it does not exhibit a sharp melting point, but gradually softens above T_g ultimately forming a viscous melt which becomes more fluid with increasing temperature. In the absence of heat stabilisers, degradation through dehydrochlorination would generally occur before temperatures for satisfactory processing could be reached, even with the addition of stabilisers. The temperature at which the degradation and subsequent coloration occurs quite rapidly is not far above that reached in some melt processing operations. Thus, there is a requirement for careful temperature control, steamlined flow paths, and absence of stagnation in the processing of rigid PVC compositions.

With continuing improvements in machine design , in formulation technology and in the range of polymer grades available, rigid PVC is processed today by all the major techniques available to the plastics industry. A general outline of the main available types of commercial PVC compounds and their processing is given in Table 2.5

Table 2.5 **Commercial PVC Compounds: General Outline of Types**[12]

General type	*Nature of composition*	*Common applicational types*[a]
Extrusion compounds	Rigid	Pipe (various kinds) Rainwater goods (down pipe; guttering) Electrical conduit Profiles (including window frames) Sheeting General purpose
	Flexible	Electrical wire and cable coverings (various kinds) Covering for: chain-link fencing wire clothes lines Hose Profiles Seals and gaskets General purpose
Injection-moulding compounds	Rigid	Pipe fittings Electrical junction boxes Industrial mouldings General purpose
	Flexible	Footwear Grommets, gaskets, bushes Toys General purpose
Blow-moulding compounds	Rigid	Bottles, jars, other containers
	Flexible	Sachets (for toiletries, etc.)
Masterbatches	Rigid and flexible	Colour Filler
Powder coating compounds[b]	Mainly flexible	Wire coating (fencing) Dishwasher baskets Weather and wear resistant (railings, outdoor furniture) General purpose
Pastes	—	Fabric and paper coating Dip-coating and moulding Rotational casting and slush moulding Casting Spraying

[a] Various grades available within each type. See also Tables 3.3–3.7, and relevant information on the processing and applications of PVC compositions in other chapters.

[b] Primers required for application of the coating compounds to metal surfaces are normally available from the compound suppliers.

2.1.3.2.1 Extrusion[7]

Extrusion is much favoured as a method of processing PVC because of the variety of articles which can be produced that way. The extruded head can be adapted to produce pipes, tubes, monofilaments, sheeting, panels, floor coverings or building profiles. Cables with PVC sheating can also be extruded. A blow-head can be fitted to the extruder to produce hollow articles and blown film. Extruder heads can be quickly and easily changed for the different types of articles, and the initial cost of installing the equipment is fairly low. The main parts of the machine and the extented unit for rigid PVC profiles are shown in Fig. 2.2 and Fig. 2.3

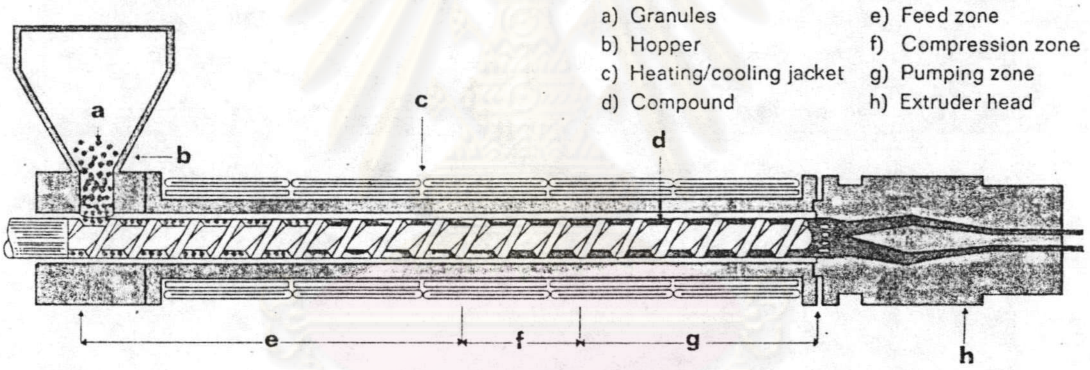


Fig 2.2 Sectional view of single screw extruder[7]

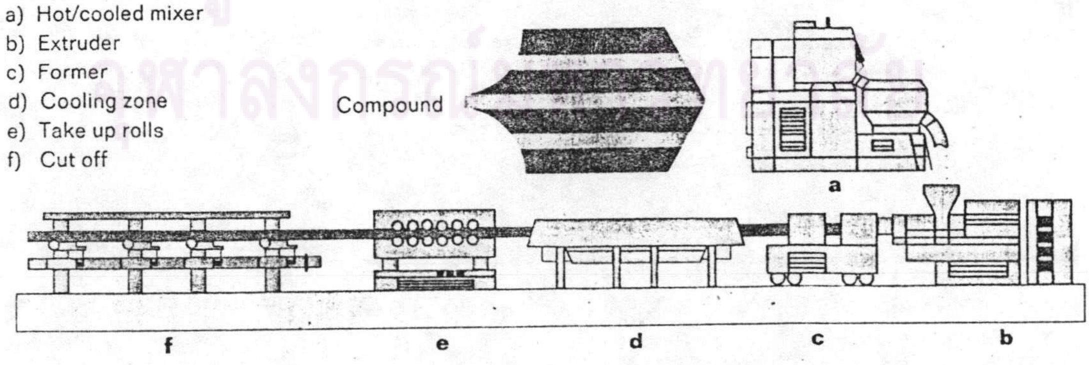


Fig 2.3 Extruder unit for rigid PVC profiles[7]

The most important type is the single screw extruder. Twin-screw extruders are also used chiefly for producing high quality rigid PVC tubes, profiles or panels with very good dimensional stability. The diameter of the screw varies between 30 and 250 mm on a single screw machine, and the length to diameter (L:D) ratio is 20-30 :1. The twin-screw machine has a screw of 50-120 mm diameter and the L:D is 12-16 :1.

Next to the length and diameter of the screw, its geometry is the most important factor. Screws vary a great deal in construction, and the choice of the right one for the purpose depends on the composition, density and form (powder mixture or granules) of the compound.

The PVC compound is fed from the hopper into the feed zone of the screw, where it is compressed, plasticised and homogenised, and is then forced under high pressure through the extrusion head. The hot profile after passing, if necessary, through a former, is air or water cooled.

PVC compounds for extrusion must have good flow properties and require careful preparation; they are made by the hot mixing process in a high speed mixer.

Extremely high rates of shear are set up in an extruder, particularly when processing rigid PVC, and the melt reaches very high temperatures. The flow properties of the compound are thus very important as well as its heat stability. Good flow is ensured by the use of suitable stabilisers and lubricants; indeed the additives generally, and the amounts used (such as plasticisers, fillers and pigments as well as stabilisers and lubricants) affect the processing properties of the compound as much as its other properties and those of the finished article.

:- Extrusion blow moulding[7]

Both in the commercial and the technical sense, bottles are by far the most important among the blow moulded PVC articles. Extrusion blow moulding is the predominant method. Injection blow moulding of PVC is less widespread, principally because the greater thermal severity of this process has delayed and complicated its application.

The general, basic configuration of a typical extrusion blow-moulding typical die is similar to that in pipe extrusion, with a spider supported core to form the parison tube. As in pipe extrusion, the spider legs should be suitably profiled and the melt temperature high enough to ensure full merging of the melt after its passage through the spider zone; otherwise flow lines can result in the parison and the blown article. The die head temperature is usually kept slightly below that of the melt. All internal part of the die should be steamlined and smooth with the number of joints kept to a minimum. A channel in the core, opening into the interior of the parison, serves as a passage for air which is blown in to provide shape support during extrusion.

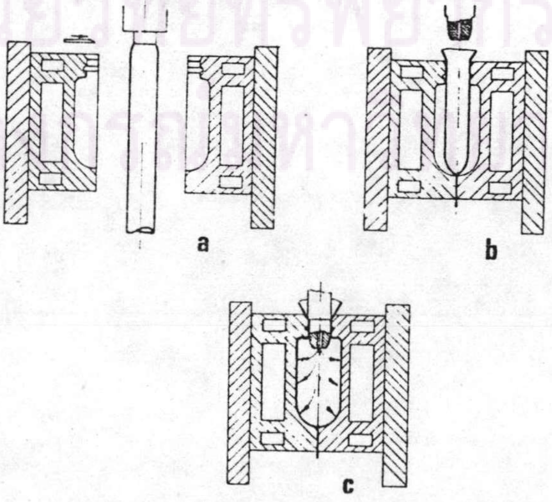


Fig 2.4 Bekum blow moulding process[7]

2.1.3.2.2 Injection moulding[7]

With the introduction of the preplasticising injection moulding machine about 15 years ago, the injection moulding of PVC has gained in importance. The machine first made the processing of unplasticised PVC possible; new fields of application of PVC were opened up and increasing quantities of boots and shoes. Shoe soles, containers, sleeves, valves, fittings and many other electrical and engineering parts are now manufactured by this process.

The main advantage of the preplasticising injection machine over the old plunger type machine is that it puts less stress on the PVC and gives a more uniform melt. The movement of the material improves the transfer of heat from the outside, and also some of the heat necessary for plasticisation is generated by friction inside the melt. On a single screw injection moulding machine PVC is processed in three main steps, which are illustrated in Fig 2.5a- 2.5e

If the mould is filled too quickly or the injection time is too short the moulded articles will be porous or contain bubbles. If the injection time is too long, particles of the compound may solidify, resulting in inadequate compression and giving porous or otherwise unsatisfactory mouldings.

Thin-walled articles with long flow paths are particularly difficult and for satisfactory results the viscostity of the melt must be as low as possible during filling of the mould. With thick-walled articles, the poor thermal conductivity of PVC can lead to heat degradation during the relatively long cooling time in the mould. The manufacture of such articles from rigid PVC is therefore best carried out by compression moulding, where less heat is applied to the material. This method combines the features of an extrusion and a screw injection moulding in what is known as a flow injection machine. Whereas in injection moulding, the plasticised melt builds up in front of the screw, in flow injection it is forced continuously into the mould.

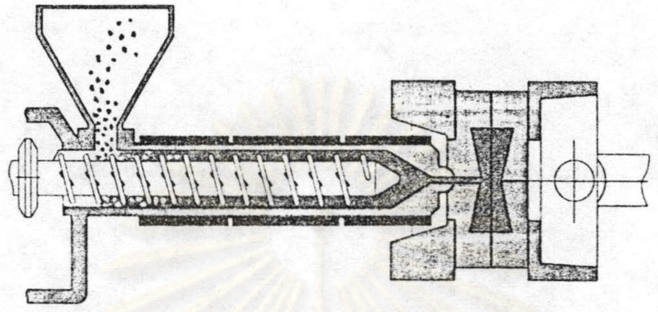
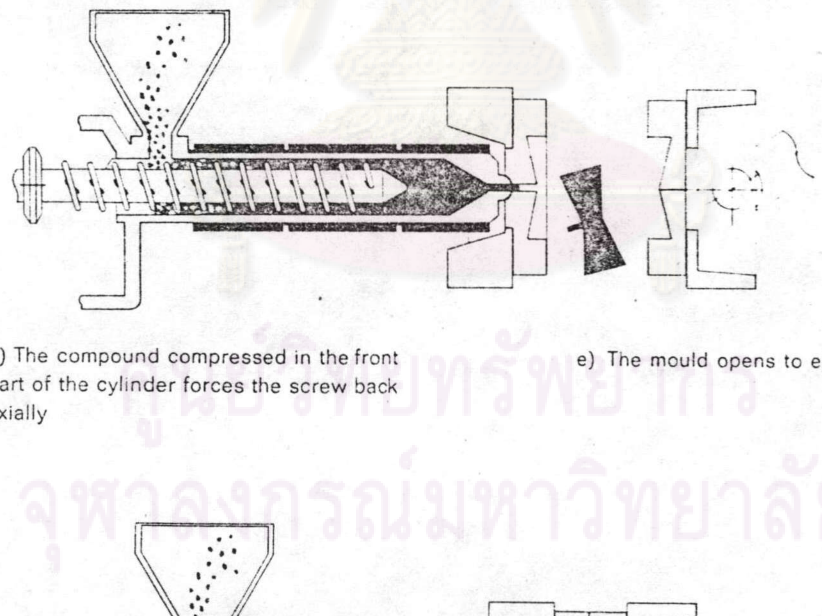


Fig 2.5 Sectional view of screw injection moulding machine[7]

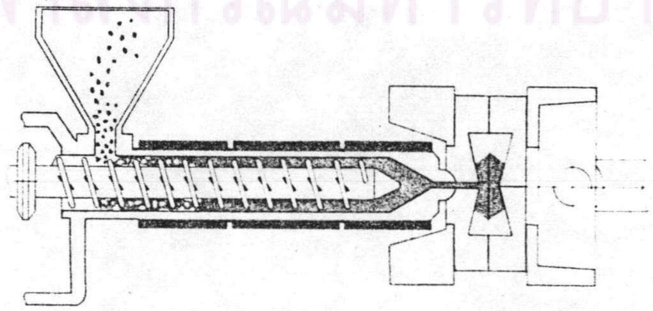
a) **Injection:** the compound is plasticised and moved forward

d) **Mould:** controlled pressure is applied to the nozzle and sprue channels until the moulded piece has cooled



b) The compound compressed in the front part of the cylinder forces the screw back axially

e) The mould opens to eject the piece



c) The compound is forced by the screw through the nozzle and into the mould. This is the actual injection step.

2.1.3.2.3 Calendering[7]

calenders are used to produce rigid and flexible films and floor coverings. They differ in the number of bowls and the way these are arranged on the machine. For PVC there are usually four bowls arranged in various ways (see the I,F,L,Z and S types in fig 2.6 Fig 2.7 shows the arrangement of a calendering unit for flexible PVC sheeting.

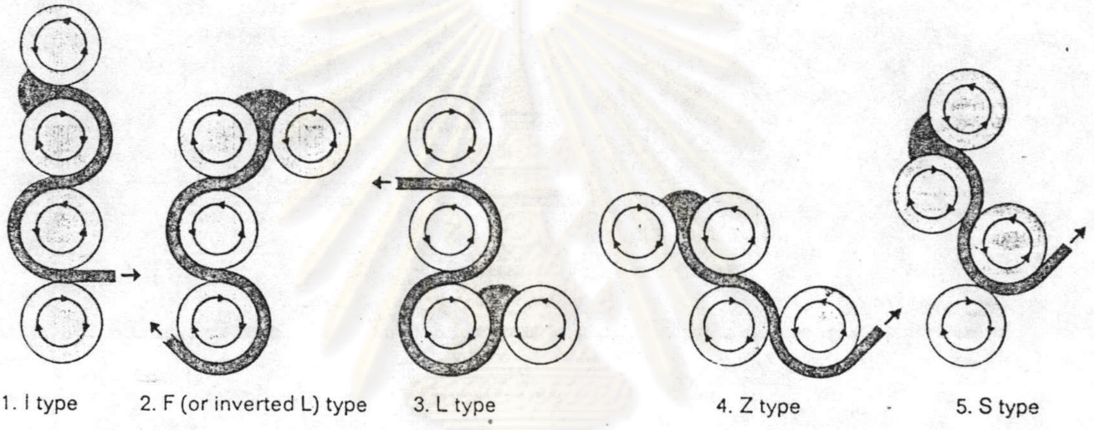


Fig 2.6 Common types of calendering bowl arrangement[7]

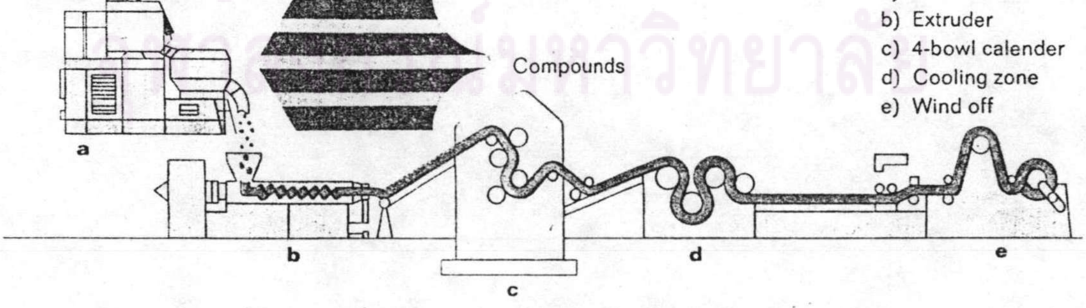


Fig 2.7 Calendering unit arranged for flexible PVC sheeting[7]

The materials (PVC, plasticisers, stabilisers, lubricants, fillers, pigments) are mixed, fused on a roll mill and then rolled out into a sheet. The sheet prepared in this way, which has been plasticised and homogenised, is carried into the calender nip on a transporter belt. There are also other methods using an internal mixer or multiscrew extruder.

An embosser is often placed between the calender and cooling zone so that the sheet can be embossed while it is still hot from the calender. Rollers then carry the sheet into the cooling zone, which consists of three or more water cooled bowls. It is then trimmed by a cutter and wound off on a batch roll.

The surface and general appearance of the sheeting will of course depend on the surface quality of the bowls, and will be affected by the slightest crack or pinhole. Uniform heating of the bowls is also very important.

There are basically no differences in the methods used in processing plasticised and unplasticied sheeting; but in plasticised sheeting good flow properties will depend chiefly on the type and amount of plasticiser used, whereas with unplasticised sheeting the stabeliser and internal lubricant are more important in this respect. The surface area of film in contact with the bowls is considerable, and calls for the use of fairly large amounts of external lubricant.

2.2 Introduction of photodegradation

Most commercial polymers undergo chemical and physical modifications when they are exposed for a long time to the combined action of sunlight, atmospheric oxygen, moisture and pollutants.[1] The extent of this degradation depends primarily on the presence within the polymer of light absorbing structures. Polymers containing aromatic or carbonyl groups in their monomer unit are likely to absorb the terrestrial sunlight (wavelength > 290 nm) and usually become photosensitive materials. On the other hand, some polymers that do not possess in their structural unit any chromophore absorbing above 250 nm, like polyolefins, still appear to be degraded by sunlight during outdoor exposure.[2] Since a basic law in photochemistry states that a photochemical reaction can only occur if light has been absorbed, it implies that those polymers must contain chromophore groups absorbing the solar radiations, either as external impurities or as functional groups incorporated into the polymer backbone.

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 2.6, the maximum sensitivity of several polymers (as determined by the bond dissociation energies) is in the range of 290 and 400 nm.

Table 2.6 Wavelength of UV Radiation (Energy of a Photon) at which Various Polymers have Maximum Sensitivity.[12]

POLYMER	NM	KCAL/MOL
Styrene-acrylonitrile copolymer	290, 325	99, 88
Polycarbonate	295, 345	97, 83
Polyethylene	300	96
Polystyrene	318	90
Poly(vinyl chloride)	320	89
Polyester	325	88
Vinyl chloride-vinyl acetate copolymer	327, 364	87, 79
Polypropylene	370	77

When the polymer system absorbs UV energy, some of its electrons are raised to higher orbitals and energy levels, which are less stable and thus activated[13]. For example, and electron in ground state energy level S_0 can be activated by UV light, raising it to higher energy orbitals S_1 or even S_2, and possibly also involving smaller vibrational energy levels as well. Since these are activated and unstable, they may undergo rapid transitions from singlet to triplet stage, and tend to discharge their excitation energy by a variety of mechanisms. These may be classified as (1) photophysical processes, involving no permanent chemical change; and (2) photochemical processes, leading to degradation reactions.

2.3 Photophysical Process

When light interacts with molecule, the electrons are set into motion by the oscillating electric field of the light.[2] As the incident photon exchanges its energy with the molecule, a valence electron is promoted from the highest occupied molecular orbital to one of the unoccupied molecular orbitals, with formation of an excited singlet state molecule. Each photon activates only one molecule with the requirement that the law of energy is fulfilled, i. e. $E = hv$, where E is the difference in energy between two electronic states of a molecule, h is Planck's constant and ν is the frequency of the light. Owing to the quantised nature of electronic states, E can only take discrete values, The energy of a photon is directly related to its wavelength by the equation

$$E\ (\mathrm{kJ\ mol^{-1}}) = \frac{1.95 \times 10^{5}}{(\mathrm{nm})}$$

Thus, photons associated with 250 nm and 300 nm radiations carry energies of 478 kJ $\mathrm{mol^{-1}}$ and 398.3 kJ $\mathrm{mol^{-1}}$ respectively. If the energy of the absorbed photon, $h\nu$, is greater than the ionisation potential, i.e. the energy required to completely remove a valence electron from a molecule, then an electron is ejected and a positive molecular ion is left behind.

The main electronic absorptions consist of transitions from ground singlet states (S_o) to excited singlet states (S_i^*) since singlet-triplet transitions are forbidden by the spin-selection rule

Absorption: $S_o + h\nu \longrightarrow S_i^* \longrightarrow S_1^* + \text{heat}$

For most photochemical reactions, only the lowest excited singlet state (S_1^*) and the lowest excited triplet state (T_1^*) have to be considered for the initiation step. Excited singlet states are short-lived species, with lifetimes in the range 10^{-9}-10^{-6}s. They disappear by various competitive photophysical processes shown schematically in Fig.2.7

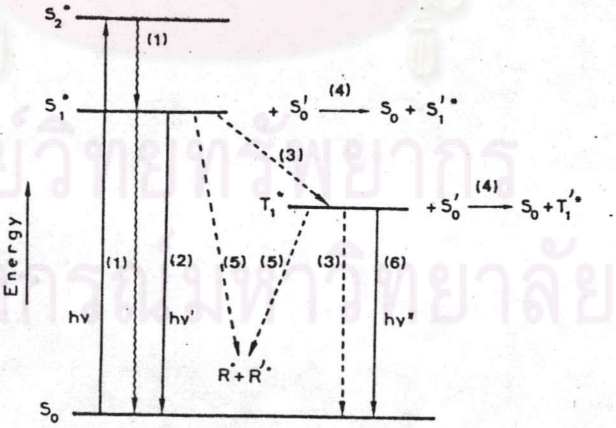


Fig. 2.7 Various deactivation pathways of electronically excited states of a molecule : (1) internal conversion, (2) fluoresence, (3) intersystem crossing, (4) energy transfer, (5 photoclevage, (6) phosphorescence.[2]

1. Internal conversion which regenerates the ground state molecule, with thermal dissipation of the absorbed energy

$$S_1^* \longrightarrow S_o + \text{heat}$$

2. Radiation emission (fluorescence)

$$S_1^* \longrightarrow S_o + h\nu'$$

3. Intersystem crossing to generate the first excited triple state

$$S_1^* \longrightarrow T_1^* + \text{heat}$$

4. Energy transfer to a ground state molecule

$$S_1^* + S_o' \longrightarrow S_o + S_1'^*$$

5. Dissociation into free radicals by intramolecular bond cleavage

$$S_1^* \longrightarrow \dot{R} + \dot{R}'$$

6. Radiation emissiom from the triplet state (phosphorescence

$$T_1 \longrightarrow S_o + h\nu''$$

The relative importance of these various reactions will depend on the nature of the excited chromophore, process (2) being favoured in aromatic compounds while process (3) occurs preferentially in molecules containing carbonyl groups. Reaction (5) is primarily responsible for the photodegradation of polymers since it leads to a fragmentation of the polymer chain with formation of radicals which can further propagate the degradation. This cleavage reaction most often proceeds from excited triplet states which have longer lifetimes than S_1^* states since the return to the singlet ground state is spin-forbidden .

The bond breaking reaction can only occur if the excitation energy of the molecule exceeds the bond dissociation energy of if the excited state is a repulsive one. In the case of PVC, three types of bonds are involved, with corresponding dissociation energies, namely C-H (410 kJ mol^{-1}); C-C (340 kJ mol^{-1}) and C-Cl (325 kJ mol^{-1}). From energy considerations, the most likely bond to be broken in PVC is the C-Cl bond. In this process, a chloride radical is evolved together with a polymeric radical, but the polymer backbone remains intact.

2.4 Photochemical Processes[14]

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 protential curve or when a dissociative excited state is formed 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 of to a dissociative potential curve.

An especially important case of photodecomposition is the radiation-induced decomposition of hydroperoxides formed during polymer oxidation. The energy of UV light is sufficient to cause both of the following decompositions:

$$ROOH \longrightarrow RO\cdot + \cdot OH \quad (\sim 42 \text{ kcal/mol}) \qquad (2.4)$$

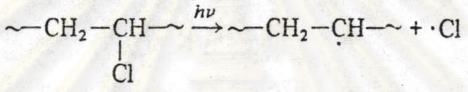
$$ROOH \longrightarrow R\cdot + \cdot OOH \quad (\sim 70 \text{ kcal/mol}) \qquad (2.5)$$

Dissociation of the O-H bond is less facile:

$$\text{ROOH} \longrightarrow \text{ROO}\cdot + \cdot\text{H} \quad (\sim 90 \text{ kcal/mol}) \qquad (2.6)$$

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

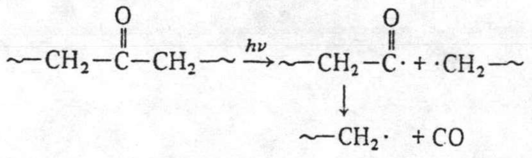
Another important decomposition reaction is the photolytic scission of the C-Cl bond in PVC:



$$\sim\!\text{CH}_2-\underset{\text{Cl}}{\underset{|}{\text{CH}}}-\sim \xrightarrow{h\nu} \sim\!\text{CH}_2-\dot{\text{C}}\text{H}-\sim + \cdot\text{Cl} \qquad (2.7)$$

which can initiate the photodegration of the polymer. An obvious difference from thermal degradation of PVC is that in photodegradation of PVC (similar to thermo-oxidative degradation) the participation of radicals in the process is more pronounced.

The role of carbonyl groups in polymer photooxidation is of great importance because once they have been formed the 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:

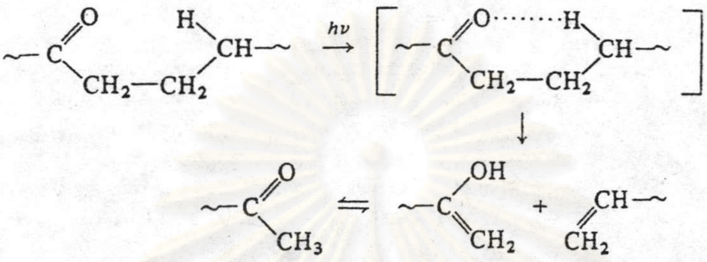


$$\sim\!\text{CH}_2-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{CH}_2-\sim \xrightarrow{h\nu} \sim\!\text{CH}_2-\overset{\overset{\text{O}}{\|}}{\text{C}}\cdot + \cdot\text{CH}_2-\sim \qquad (2.8)$$

$$\downarrow$$

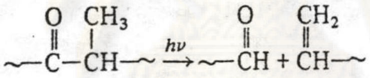
$$\sim\!\text{CH}_2\cdot + \text{CO}$$

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



(2.9)

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:



$$\sim\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\sim \xrightarrow{h\nu} \sim\overset{\overset{\displaystyle O}{\|}}{CH} + \overset{\overset{\displaystyle CH_2}{\|}}{CH}-\sim$$

(2.10)

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[14]

Polymer photooxidation is very similar to thermal oxidation of polymers; its mechanism includes the same reactions shown in Figures 6.1,6.4 and 6.5.Significant differences exist with respect to the photochemical decomposition of the hydroperoxide and carbonyl groups, as well as with regard to the initiation reaction. The formation of polymer radicals

$$RH \longrightarrow R. + H. \qquad (2.11)$$

by scission of a C-H bond is a possible consequence of UV irradiation. The probability of reaction (7.11) 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. Ther are two types of excited singlet oxygen ($^1O_2$) having different excitation energies above their ground state. The lower (more stable) excited singlet state ($^1\Delta_g^+$) has an energy excess of 22.5 kcal/mol; the higher ($^1\Sigma_g^+$), 37.5 kcal/mol. Singlet oxygen can be formed by direct irradiation of O_2 ; although this excitation is unfavorable, it is possible in the upper layers of the atmosphere. Ozone photolysis, which is very rapid in the upper atmosphere, leads to the formation of singlet oxygen. Singlet oxygen also forms easily in polluted (urban) atmospheres. This may cause the rapid deterioration of polymers in urban areas. Molecular oxygen can act as a deactivator of various excited species present in the polymer. Quenching usually results in formation of singlet oxygen. The lifetime of singlet oxygen in solution strongly depends on the solvent; for example, the lifetime of $^1O_2$ ($^1\Delta_g$) in methanol is 2 µsec, in benzene 24 µsec, and in carbon tetrachloride 700 µsec. Besides initiation of oxidation by hydrogen abstraction from a saturated hydrocarbon

$$RH + {}^1O_2\,({}^1\Delta_g) \longrightarrow R\cdot + HO_2\cdot \qquad (2.12)$$

intiation 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 that 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.

As previously shown, sample thickness is an important factor in thermal oxidation owing to its governing of transport processes (O_2 diffusion into the polymer, effusion of volatile products). In photooxidation the sample thickness is even more important than in thermal degradation. As shown in Fig 2.8, the extent of oxidation decreases exponentially with increasing distance from the surface: oxidation mainly occurs in a very thin surface layer of the material.

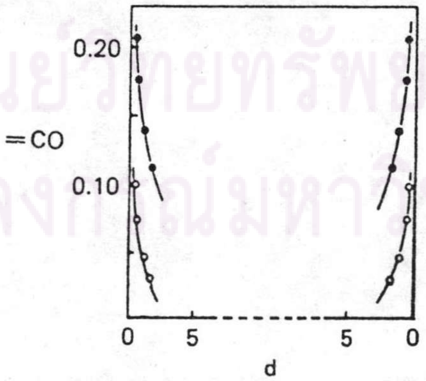


Fig. 2.8 Relative amount of carbonyl (=CO) groups formed as a function of the distance (d) from the surface of a 22 *um* polypropylene film irradiation time : o = 40 hours ; • = 80 hours[14]

The molecular weight of the polyolefins rapidly decreases during photooxidation. The average number of chain scissions (s) in a polypropylene sample as a function of irradiation time is shown in Figure 2.9 . 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.

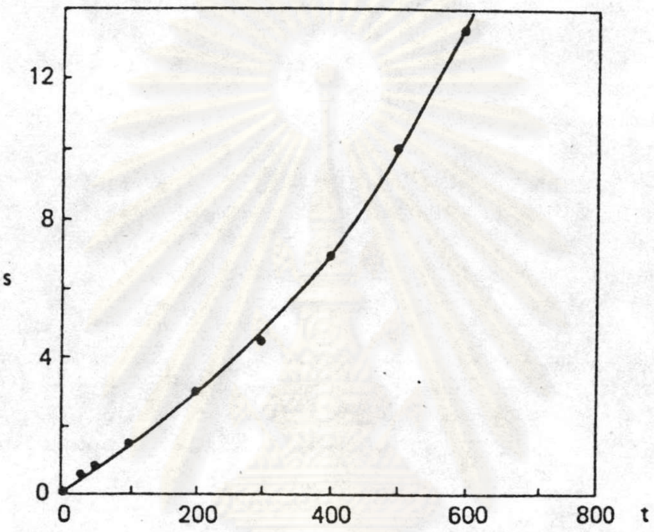


Fig. 2.9 Average number of chain scissions (S - $P_{n,o}/P_{n-1}$) in one original macromolecule as a function of time (t_1 in hours) during UV irradiation of polypropylene sample.[14]

As previously mentioned.(this will be discussed in connection with sensitized photodegradation), 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 of by functioning as UV absorbers. these possibilities will be discussed in connection with photostabilization of polymers.

2.5.1 photooxidation of PVC[2]

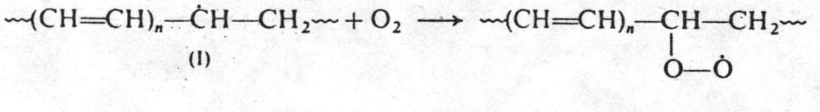
As mentioned before, molecular oxygen may readily react with the unstable transients arising by UV irradiation, either by deactivating the excited states (quenching reaction) or by combining with free radicals to form peroxy PO_2) radicals (scavenging reaction):

Quenching : $A^* + O_2 \text{ ----> } A + O_2^*$
Scavenging : $\dot{P} + O_2 \text{ ----> } PO_2.$

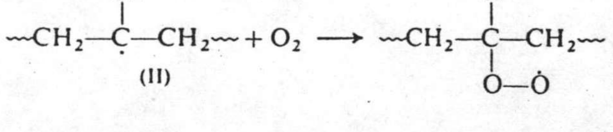
During the photodegradation of PVC in the presence of oxygen, the scavenging reaction is expected to start an autooxidation process and thus to be responsible for the production of such photosensitive structures as hydroperoxide or carbonyl groups. Besides ruptures of the polymer chain, peroxide crosslinks occur in the photooxidation of PVC as a result of the various reactions of the $PO_2\cdot$ radicals. All these chemical changes lead ultimately to a deterioration in the mechanical properties and embrittlement of the UV-oxidised material.

(1) Initiating radicals

Due to their short lifetime, excited singlet polyenes are not likely to be quenched by O_2, so that the main effect of atmospheric oxygen will be its rapid reaction with alkyl radicals to create peroxy radicals ($PO_2\cdot$) on the polymer chain.

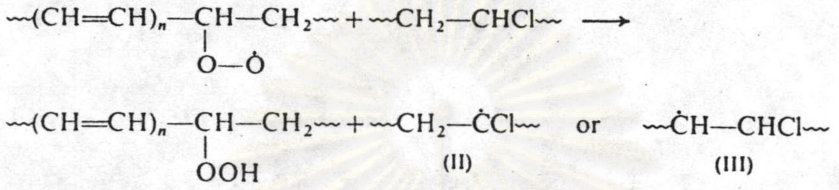


$$\sim(CH{=}CH)_n{-}\underset{(I)}{\dot{C}H}{-}CH_2\sim + O_2 \longrightarrow \sim(CH{=}CH)_n{-}\underset{O-\dot{O}}{\underset{|}{CH}}{-}CH_2\sim \qquad (2.13)$$



$$\sim CH_2{-}\underset{(II)}{\overset{\overset{Cl}{|}}{\dot{C}}}{-}CH_2\sim + O_2 \longrightarrow \sim CH_2{-}\overset{\overset{Cl}{|}}{\underset{\underset{O-\dot{O}}{|}}{C}}{-}CH_2\sim \qquad (2.14)$$

These radicals are considered to be the main initiating species of the PVC oxidation and the direct precursors of the oxygenated structures detected the aged polymer. By abstract hydrogen atoms easily from the CHCl or CH_2 groups of the polymer to give hydroperoxide groups and regenerate a propagation radical (II) or (III) (with n = o), respectively :

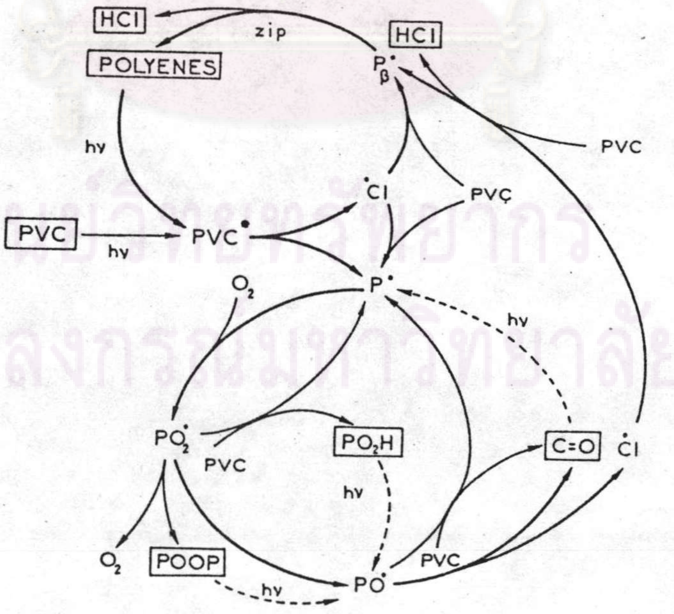


$$\sim(CH{=}CH)_n{-}\underset{\displaystyle O{-}\dot{O}}{\underset{|}{CH}}{-}CH_2\sim + \sim CH_2{-}CHCl\sim \longrightarrow$$

$$\sim(CH{=}CH)_n{-}\underset{\displaystyle OOH}{\underset{|}{CH}}{-}CH_2\sim + \underset{(II)}{\sim CH_2{-}\dot{C}Cl\sim} \quad \text{or} \quad \underset{(III)}{\sim\dot{C}H{-}CHCl\sim} \qquad (2.15)$$

(2) Reaction scheme

During the photooxidation of PVC, the dehydrochlorination still occurs. Therefore, the overall mechanism of the photooxidation of PVC can finally be represented by the following reaction scheme (SCHMEME 2-2)



SCHEME 2-2 Schematic representation of the various processes occurring during the UV photolysis of PVC in the presence of O_2. Final products are in boxes.[2]

since P: $(\sim(CH{=}CH)_n{-}\dot{C}H{-}CH_2\sim)$ and $(\sim CH_2{-}\dot{C}Cl{-}CH_2\sim)$

$\dot{P}_{\beta}$.: $(\sim(CH{=}CH)_n{-}\dot{C}H{-}CHCl\sim)$

The upper cycle corresponds to the zip-dehydrochlorination which is apparently not very much affected by the presence of O_2 and involves as chain carrier species the chlorine radical and the short lived β-chloroalkyl (or polyenyl) radical(III), designated here by $\dot{P}_{\beta}$. The net result of this chain reaction is the production of HCl and conjugated polyene sequences which are responsible for the discoloration of the irradiated PVC.

The oxidation process is represented by the lower cycle which includes several chain reactions. The major species are the O_2-scavengeable radicals (I)

$$(\sim(CH{=}CH)_n{-}\dot{C}H{-}CH_2\sim)$$

and (II)

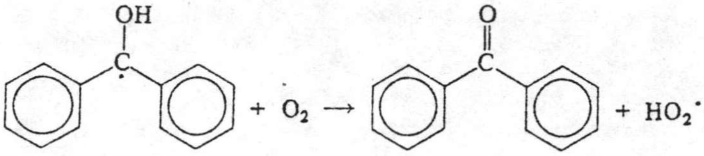
$$(\sim CH_2{-}\dot{C}Cl{-}CH_2\sim)$$

designated here by $\dot{P}$; through the intermediate peroxy ($PO_2\cdot$) and alkoxy ($PO\cdot$) radicals, they generate oxygenated structures on the polymer backbone (mostly carbonyl and hydroperoxide groups), and lead also to the fragmentation of the PVC chain and to the formation of peroxide crosslinks. The subsequent photoreactions of these oxidation products are represented by dashed arrows.

2.6 Sensitized Photodegradation[12]

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 bacterial 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 sunlinght. 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 the polymer to low molecular weight compounds which are small enough to be decomposed by microorganisms. Thus, the complete deterioration of plastic wastes and the control of service life of plastics are rather complex procedures. A photosensitizer usually has a high absorption coefficient for UV light; the cxcited 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:

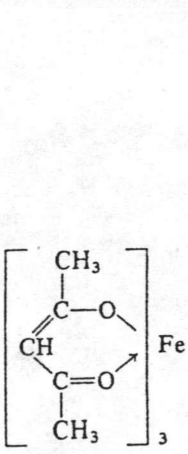


(2.16)

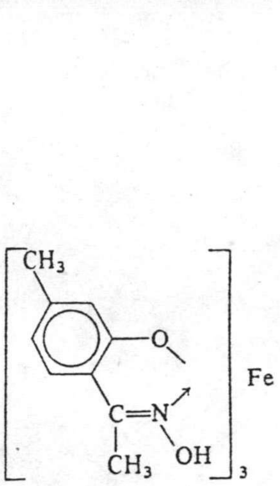
Quinones behave similarly: their excited state has biradical character, the biradical abstracts hydrogen from the polymer and hydroquinone forms. For example, the addition of various quinones sensitizes the photodegradation of polyisoprene solutions. The sensitizing effect is drastic, especially with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

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

Both organic and inorganic metal compounds can sensitize photodegradation. Especially interesting is the fact that certain iron complexes, e.g., Fe(II) and Fe(III) complexes of dithiocarbamates and 2-hydroxyacetophenone oximes, exhibit a delayed action as UV sensitizers. Fe(III) acetylacetonate (A) has an immediate effect; however, the effect of the Fe(III) complex of 2-hydroxy-4-methylacetophenone (B), as shown in Figure 2.10 , can be observed only after an induction period of significant length. Ferocene derivatives such as benzoylferrocene (C) can act as photosensitizers.

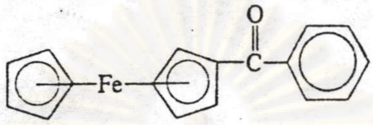


(A)



(B)

(2.17)



(C)

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

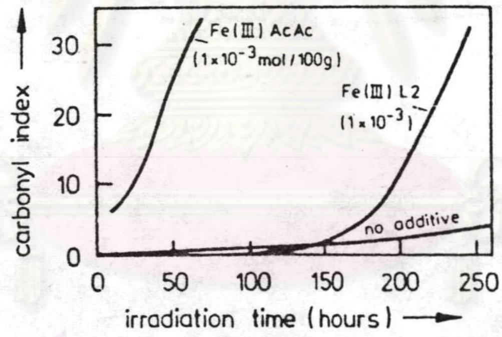


Fig. 2.10 Carbonyl index (IR absorbance due to =CO groups related to a reference absorbance) as a function of time during UV irradiation of low density polyethylene samples: Fe(III) AcAc = Fe(III) acetylacetonate : Fe(III)L2 = Fe(III) 2-hydroxy -4-methylacetophenone.[12]

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, the yield of photolytic scission is small when CO is in the backbone and relatively high when CO is in a pendant group. Vinyl polymers and polyamides have been prepared with pyridine or pyrazine rings in the backbone. Polymers with unsaturated bonds in the main chain are sensitive to photodegradation.

2.7 Light Source

The course of a photochemical reaction usually depends on the intensity and wavelength of the incident light. Therefore, the only strictly reliable information on the effect of sunlight on polymers will be that obtained from outdoor exposure.[2] The ultraviolet part of the terrestrial sunlight (290-400nm) represents only about 5% of the total radiation, but it causes the most damage to polymeric materials for two main reasons:(1) UV radiation is more energetic ($300<E<410$ kJ mol^{-1}) than visible light and (2) UV radiation is more likely to be absorbed by polymers which are usually transparent to radiations >400nm. Fig 2.11 shown UV and spectrum of sunlight at noon in midsummer in Washington,D.C. and Fig 2.12 show the comparative energy scales.

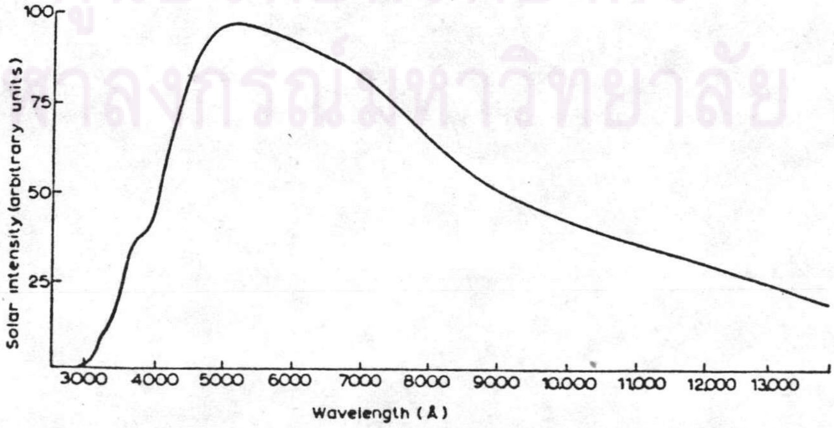


Fig. 2.11 UV and visible spectrum of sunlight at noon in midsummer in Washington, D.C.[2]

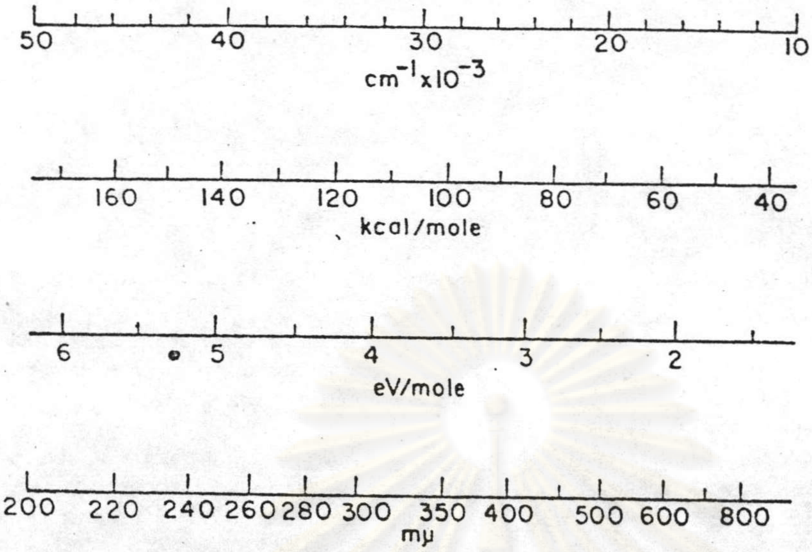


Fig.2.12 Comparative energy scale[13]

In order to reduce the duration of the experimentation, which may last for months or years. The most common irradiation device is the Xenotest or Weatherometer which reproduces as faithfully as possible the conditions of natural weathering, but with an accelerating factor of 10 to 20.[2] Xenon lamps are commonly used since their emission spectrum follows pretty well that of terrestrial sunlight. Fluorescent lamps or Pyrex-filtered medium-pressure mercury lamps which have their emission maxima at 366 nm can also be employed for irradiations in the rage 300-450 nm. Since PVC has a very low absorption in this wavelength region, prolonged exposure time is still needed before some degradation can be detected. For this reason, mechanistic investigations have often been carried out by using the polychromatic light of medium-pressure mercury lamps which stretches from 248 to 578 nm. The high rate of degradation which is then observed is mainly due to the drastic increase of the intensity of the light absorbed by the irradiated polymer.

2.8 Identification and Selection of Photosensitzers.

In order to obtain the suitable sentisizer that can work efficiency in practical for our blow moulding PVC samples, there are many characteristics to consider.

1. Effective sensitization for photooxidation degradation of rigid PVC by the wavelength of maximum photosensitivity should be in the range 300-400 nm. within the range of ultraviolet light so that the degradation would occur rapidly in the sunlight but almost not happen under normal indoor illumination.
2. Minimal effect on color and transparency of the polymer.
3. Non-toxic and should not cause contamination to the environment.
4. The additive should be in solid form in order to be intimately mixed with other ingredients in the mixer.
5. The additive should have high boiling point since it could be in corporated with processed PVC at high temperature and should remain well disposed in the polymer.

Additives peroxidic compounds and organic dyes were not interesting because its against with the second and the fifth requirement.

Metallo-organic additives was out of consideration since its cause serious toxicity and environmental contamination.[16,17]

From investigation, Quinones served all the requirements then benzophenone and anthraquinone were used as the prefered photosensitizers.

2.9 Literature Review

After 60 years of production of PVC , today PVC is one of the most widely used polymer. During this period, there were many research works relating to the photodegradation of PVC. Some of these works are the studies of the physical and chemical modifications of polymers when exposed to natural weathering and artificial weathering. Some of them are as follow :

S.Suzuki, O.Nishimura and H.Kubota studied the weatherability of plastic films by observing in the mechanical properties of outdoor exposured films.[18] Seven species of the general purpose thermoplastic films (PVC, PETP, PA, LDPE, HDPE, PC and POM) were exposed to outdoor condition. Their mechanical properties were measured and the influence of the exposure site, the starting seasons, exposure period and the thickness of film were examined.

As regarded, the starting season of exposure, for the short period, the degradation rate was largest in the case of starting in the summer, however, in exposure for twelve months, no differences were recognized. It was considered that main reasons causing such differences were in the differences of UV dosage. For effect of the film´s thickness , it was found that the thin film degraded faster than the thick film as in Fig. 2.13. The exposure period for elongation at rupture or the rupture strain energy which decreased to half value were used for comparing the degradation rate.

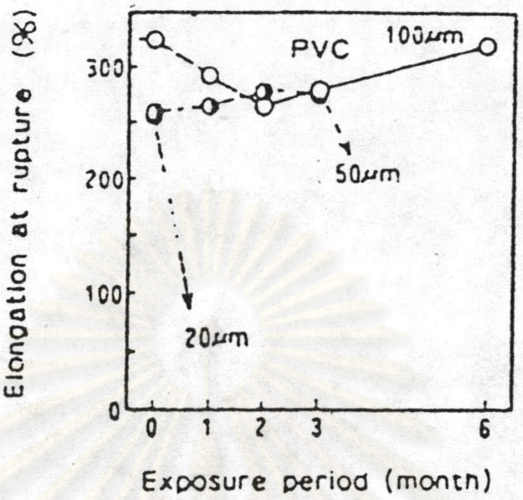


Fig. 2.13 Dependences of thickness in changes of elongation at rupture by outdoor exposure[18]
(Supporo : started in July)

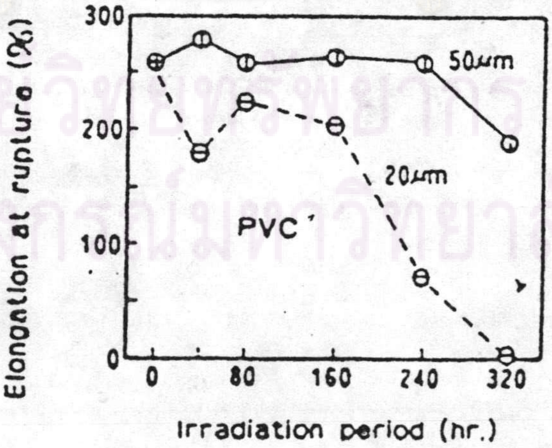


Fig. 2.14 Dependences of thickness in changes of elongation at rupture by Sunshine Weathermeter[19]

S. Suzuki, O. Nishimura and H. Kubota studied the weatherability of plastics films by observing the mechanical properties of accelerated weathered films.[19] As part of the previously report , accelerating weathering tests were carried out concerning with the seven species of films, by using the Sunshine type Weatherometer and Fademeter. The elongation at rupture were measured and the degradation tendencies were compared.

The Influence in thickness of PVC films in elongation at rupture was studied. And the rapid degradation tendencies was recognized in thinner films. Nearly the same degradation tendencies were recognized both in Weatherometer and in Fademeter but the degradation rate was higher in the Fademeter than in the Weatherometer as shown in Fig. 2.14.

H. Kubota, S. Suzuki and O. Nishimura studied the comparison of degradation tendencies of weathered thermoplastics.[20] Five kinds of thermoplastic sheets (PVC, PMMA, ABS, POM, PE) were exposed outdoor for five years at four different sites and the degradation tendencies in mechanical, surface and molecular properties were compared.

The data obtained from the outdoor exposure indicated that the changes in properties increased with the irradiation time. The tensile properties, color, gloss, the thickness of degradation layer were different depending on exposure site localities and environmental conditions. Fig. 2.15 showed that the exposure site locality, the lower latitude , and environmental condition , such as air pollutant, increased the degradation rate.

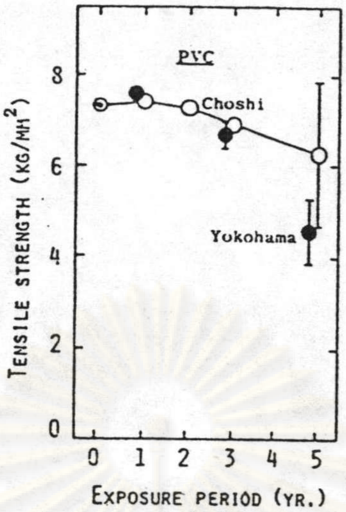


Fig. 2.15 Effect of exposure site and environmental conditions on tensile strength.[20]

Christian Decker and Michel Balendier studies the photooxidation of poly(vinyl chloride).[21] Unstabilized commercial PVC films, 30 µmthick, was irradiated at room temperature in a quartz reactor under a pressure of 900 torr of pure oxygen with a Philips (HPK 125 W.) High Pressure Mercury lamp. Dehydrochlorination was shown to proceed effectively in irradiated PVC with a concomitant discoloration of the polymer due to polyene formation which was easily identified by UV spectroscopy.

Large amount of hydrogen chloride was evolved during the photooxidation of PVC at a rate which increased with irradiation time. The infrared spectrum of oxidised PVC films revealed the presence of carbonyl groups with a maximum of absorption at 1730 cm^{-1} and of hydroxyl groups, mostly hydroperoxide with a broad absorption centered on 3550 cm^{-1} as in Fig. 2.16.

They observed embrittlement of the oxidised PVC film and the drop in the viscosity during the exposure to UV light, in the presence of oxygen, also, gel permeation chromotography analysis shows a broadening of the molecular weights distribution of the oxidised PVC towarded both the lower and the higher molecular weights as in Fig. 2.17. It indicated that crosslinking occured competely with the chain scission process.

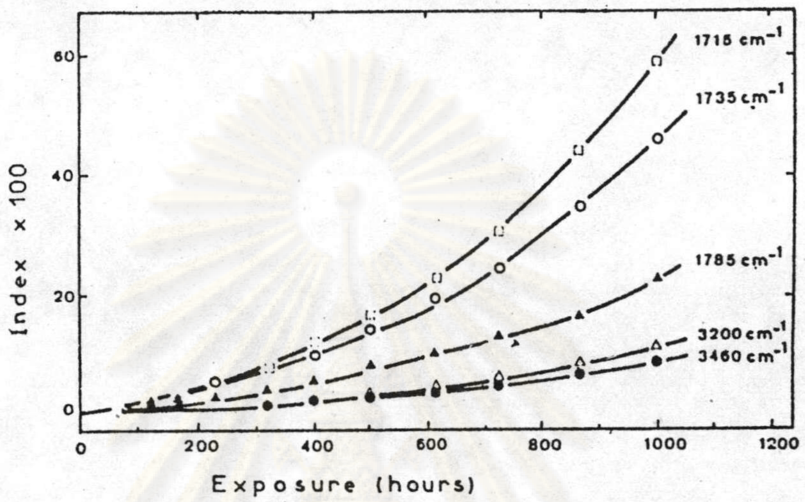


Fig.2.16 Dependence of functional group indices on exposure for PVC films : carbonyl band at 1715 cm^{-1} (□), 1735 cm^{-1} (○) and 1785 cm^{-1}(▲), hydroxyl band at 3200 cm^{-1} (△) and 3460 cm^{-1} (●)[21]

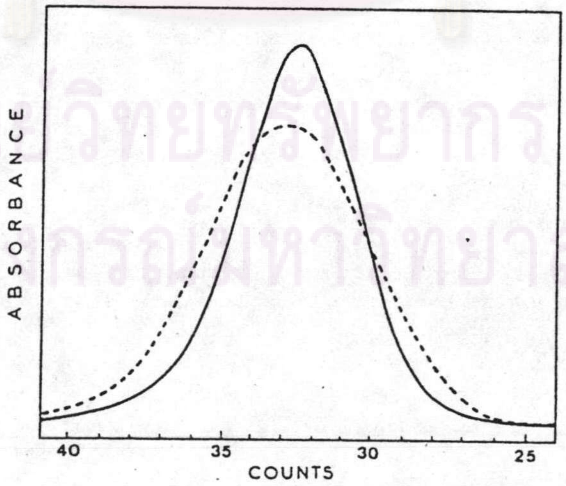


Fig.2.17 GPC molecular weight distribution of PVC samples. ---,Before degradation; ---, after 1 hr. of iiradiation in the presence of O_2[21]

L. Lapcik, J. Stefanec, J. Valasek, M. Ceppan, A. Blazkova, et. al. studied the photodestruction of poly(vinyl chloride) by observing the influence of monochromatic ultraviolet radiation on physical properties of polymer.[22] The photooxidation degradation of poly(vinyl chloride) by the action of monochromatic radiation of the wavelength of 405 + 10 nm in air was studied at 25° C. The average thickness of the films was varied in the range 12 - 13 um. The influence of exposure on the following physical properties of polymer film was examined : optical properties (absorption in the UV, visible and infrared region), content of gel fraction and molecular weight of the soluble fraction of the exposed sampled.

It was found that the absorption in the UV and IR region and the gel fraction increased with exposure time. Figure 2.18 shows the molecular weight of soluble fraction decreased with expusure time.

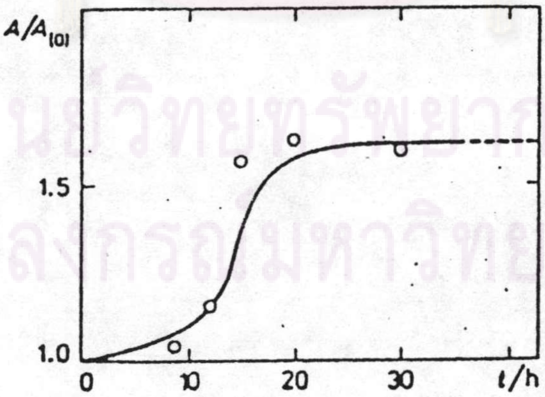


Fig.2.18 Variation of relative molecular weight of the soluble fraction with photooxidation time[22]

A. Torikai, H. Tsuruta and K. Fueki studied the elementary processes in the photodegradation of poly(vinyl chloride). Unplasticized poly(vinyl chloride) films[23], average thickness was 0.06 mm., was irradiated with a Toshiba (H- 4000 P) medium pressure mercury lamp whose wavelength distribution was similar to sunlight. The optical absorption spectra of photoirradiated PVC films increased in intensity with irradiation time.

The final products formed were detected by Infrared absorption measurements. The 250 and 280 nm bands were attributed to those of the allyl type radical, $-CH_2-CH=CH-CH-CH_2-CHCl-$ and the dienyl to tetraenyl type radical, $-CH_2-(-CH=CH-)_n-CH-$ (n = 2-4), respectively as in Fig. 2.19

On increasing the light intensity and the irradiation temperature, new absorption bands appeared in the optical spectra of the PVC films as shown in Fig. 2.20. The broad bands at ~410 nm and 620 nm were assigned to the polyenyl radiacals, $-CH_2-(-CH=CH-)_n-CH-$, which are formed by succession of dehydrochlorination.

The Infrared spectrum analysis was a useful tool for identifying the final products which were formed by a sequence of elementary reactions. The peak centred at 1730 cm^{-1} and 1610 cm^{-1} were assigned to C=O streching (ν C=O) and C=C streching (ν C=C) vibrations, respectively. These absorption band increased in intensity with an increased in the irradiation time. These experimental results showed that a wide distribution of the conjugation number existed in the oxidation products of photoirradiated PVC.

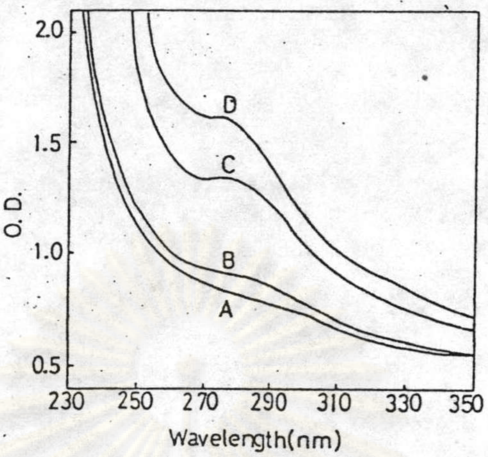


Fig.2.19 UV absorption spectra of photoirradiated PVC films at 40° C and 10 cm from the light source : (A) unirradiated ; (B) irradiation time 10 min ; (C) 30 min ; (D) 50 min.[23]

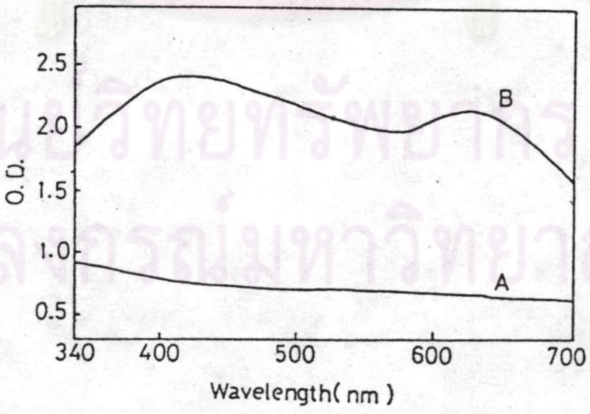


Fig.2.20 Optical absorption spectra of photoirradiated PVC films at 100° C and 5 cm. from the light source : (A) unirradiated ; (B) after irradiation for 30 min.[23]