

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber [2,3]

On tapping the *Heavea brasiliensis* tree, natural rubber latex exudes, which has a rubber content between 25 and 40 percent by weight. The variation is due to factors such as the type of tree, the tapping method, the soil conditions, and the season. The latex is normally called 'field' latex, and its average rubber content is 30 percent by weight. This material is not utilized in its original form due to its high water content and susceptibility to bacterial attack. It is necessary to preserve and concentrate it, so that the end product is stable and contains 60 percent or more of rubber. All the important processes of fabrication of latex articles begin with latex that has a 60 percent minimum rubber content. Extensive blending of the concentrated latex ensures a consistent high quality material meeting national and international specifications.

Latex concentrate is differentiated by the method of concentration and the type of preservative used. In addition to the general-purpose type of latex, there are special forms such as double centrifuged latex, creamed/centrifuged latex and modified types such as prevulcanized latex. Three methods of concentration are employed, centrifugation, evaporation and creaming; centrifugation is the preferred method and accounts for 95 percent of total production. Details of the preservation systems used in centrifuged concentrate are given in Table 2.1. The predominant lattices are the HA and LA-TZ types. Latex concentrate prepared by evaporation is usually stabilized by potassium hydroxide, whilst creamed latex is normally preserved with 0.7 percent ammonia.

Most commercial natural rubber contains 93-94%wt of cis-1,4-polyisoprene. In this configuration, carbon atoms 1 and 4 are both on the same side of double bond.

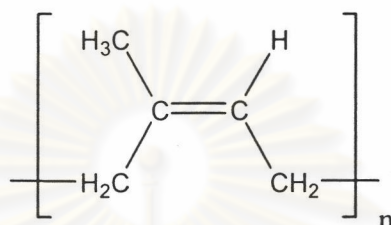


Figure 2.3 Cis – polyisoprene

Molecular weight of natural rubber is about $1.0 - 1.3 \times 10^6$ with broad molecular weight distribution (MWD). The broad MWD of natural rubber is presumed to derive from the branching and crosslinking by certain special functional groups in rubber molecule. There are two components called sol and gel in natural rubber. The sol phase is a rubber part that dissolves easily in good solvent such as toluene, cyclohexane. The gel phase swells without dissolving. Commercial natural rubber contains 5 – 50% gel phase.

2.2 Natural Rubber Composition

2.2.1 Dispersed Phase

The rubber in natural latex is cis-1,4-polyisoprene with a molecular weight in the region of one million. The molecular weight cannot be known precisely because there is always a proportion of the rubber which is insoluble. This proportion, the gel content, steadily increases as the latex is stored, presumably due to a process similar to the 'storage hardening' which occurs in dry rubber. After about two to three months storage the hardening ceases and the gel content may be as high as 50 percent in toluene. The measurement of gel content is complicated by the fact that

the amount of gel is solvent-dependent, which suggests that much of the apparent cross-linking does not involve covalent bond. As a result of storage hardening the rubber in mature latex concentrate has a Mooney Viscosity greater than 100. Increases in rubber hardness, however, do not produce any discernible change in the film-forming properties of latex.

The molecular weight of the 'sol fraction' of the rubber in mature concentrated latex can be determined, for example, by gel permeation chromatography. Results of such measurements are shown in Figure 2.4. For a LA-TZ latex, the rubber from which was dissolved in tetrahydrofuran. The gel content in the solvent was about 40 percent and the average molecular weight (\bar{M}_w) of the sol fraction was 880,000.

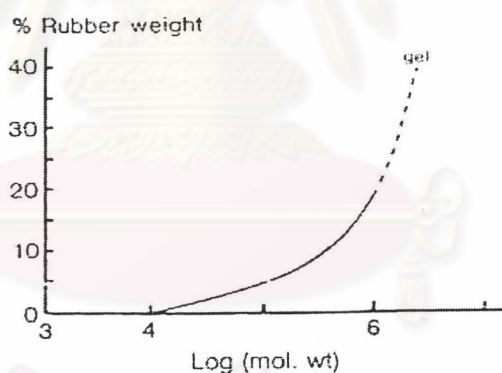


Figure 2.4 The molecular weight distribution of NR latex rubber (LA-TZ)

2.2.2 Non-rubber Materials in the Serum

The non-rubber materials in the serum from latex concentrates comprise a wide variety of chemical species. The major constituents are known to be proteins and their decomposition products, fatty acid soaps, and a range of organic and inorganic salts.

The overall compositions of both HA and LA-TZ lattices are summarized in Table 2.2 for both the latex and the total solid film. These figures can only be regarded as an approximate guide to the composition of natural lattices and much more research needs to be done before a precise composition can be established.

Table 2.2 Overall compositions in percentage by weight of lattices and total solids films

	HA		LA-TZ	
	Latex	TSC	Latex	TSC
Rubber	59.67	97.61	59.61	97.62
Protein,etc	1.06	1.73	1.03	1.69
Soaps	0.23	0.38	0.23	0.38
Salts	0.40	0.28	0.38	0.32
Ammonia	0.68	-	0.21	-
Water	37.96	-	38.54	-

2.2.3 Adsorbed Non-rubber Materials

When in the tree, the particles in natural latex are presumed to possess an adsorbed layer of a protein-lipid complex, similar to the membranes of many biological cells. As a consequence of the addition of ammonia to preserve the latex concentrate, the lipid materials are believed to hydrolyze slowly, releasing fatty acid soaps which can later adsorb onto the particle surface. The adsorption of these soaps accounts for the spontaneous rise in mechanical stability when ammoniated concentrate is stored.

Nevertheless, little direct knowledge of the materials adsorbed on the latex particles exists. The surface proteins have never been isolated as such and they are often presumed to be similar to those identified in the serum but they may be different.

2.3 Prevulcanization of Natural Rubber (NR) Latex [4]

2.3.1 Definition and Importance

Prevulcanization of NR latex is defined as a process in which chemical crosslinking of rubber chains takes place inside each particle disperse in aqueous latex serum. Drying of prevulcanized latex produces a crosslinked film without the need for further heating. One of the principle advantages of prevulcanized latex is that effective control of the physical properties can be exercised before manufacturing those articles. For this reason, the prevulcanized NR latex is the most industrially important type of chemically-modified latex. It is especially useful for being directly employed in the dipping operation in small to medium sized factory. It is also applied in other fields such as adhesives, latex foam, carpet backing and textile combining.

2.3.2 Sulfur Prevulcanization

Mineral sulfur is widely used as an ingredient to provide crosslink between rubber chains in the vulcanization process. In sulfur prevulcanization, vulcanized latex is prepared by heating NR latex, mixed with the dispersions of sulfur and an accelerator at 50-80°C. Accelerator employed in latex mixture is usually ultra-fast dithiocarbamate, such as zinc diethykdithiocarbamate (ZDEC), due to the fact that reaction in latex proceeds much more rapidly than that in dry rubber at the same temperature with the same vulcanizing ingredient. The speed of the prevulcanization reaction seems to be associated primarily with the presence of non-rubber constituents which also act as accelerator in latex. Chemical network structure of sulfur vulcanized rubber can be presented in Figure 2.5.

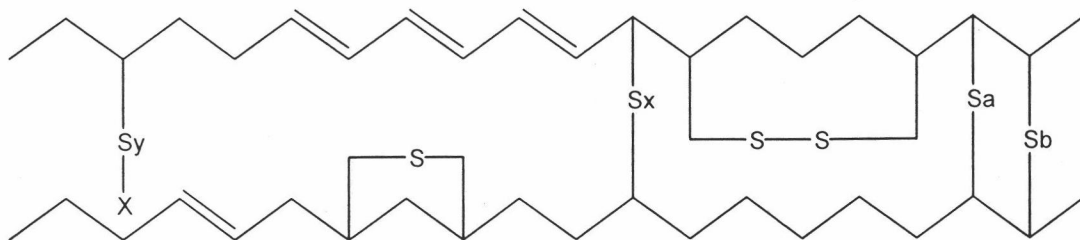


Figure 2.5 A diagrammatic representation of network structure of sulfur vulcanized rubber (x, y, a and $b = 1-9$, $x =$ accelerator fragment)

2.4 Vulcanization [5]

Useful rubber articles, such as tires and mechanical goods, cannot be made without vulcanization. Unvulcanized rubber is generally not very strong, does not maintain its shape after a large deformation and can be very sticky. In short, unvulcanized rubber can have about the same consistency as chewing gum.

2.4.1 Definition of Vulcanization

The term *vulcanization* is generally applied to rubbery or elastomeric materials. These materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Vulcanization can be defined as a process which increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus, vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network. (Figure 2.6)

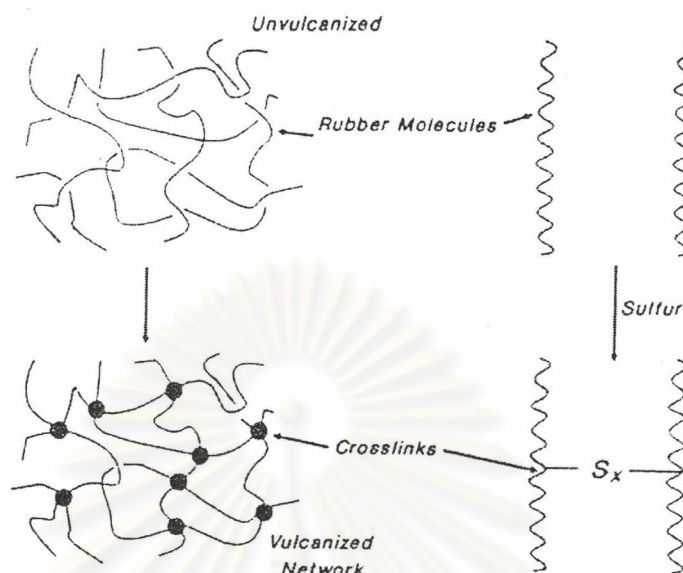


Figure 2.6 Network formation after vulcanization

2.4.2 Effects of Vulcanization on Vulcanizate Properties

At the molecular level, vulcanization causes profound chemical changes. The long rubber molecules (molecular weight usually between 100,000 and 500,000) become linked together with junctures (crosslinks) spaced along the polymeric chains, with the average distance between junctures corresponding to a molecular weight between crosslinks of about 4,000 to 10,000. As a result of this network formation, the rubber becomes essentially insoluble in any solvent and it cannot be processed by any means which require it to flow, e.g., in a mixer, in an extruder, on a mill, on a calendar, or during shaping, forming, or molding. Thus it is essential that vulcanization occurs only after the rubber article is in its final form.

Major effects of vulcanization on use-related properties are illustrated by the idealization of Figure 2.7. It should be noted that static modulus increases with vulcanization to a greater extent than does the dynamic modulus. The dynamic modulus is a composite of viscous and elastic behavior, whereas static modulus is largely a measure of only the elastic component of rheological behavior.

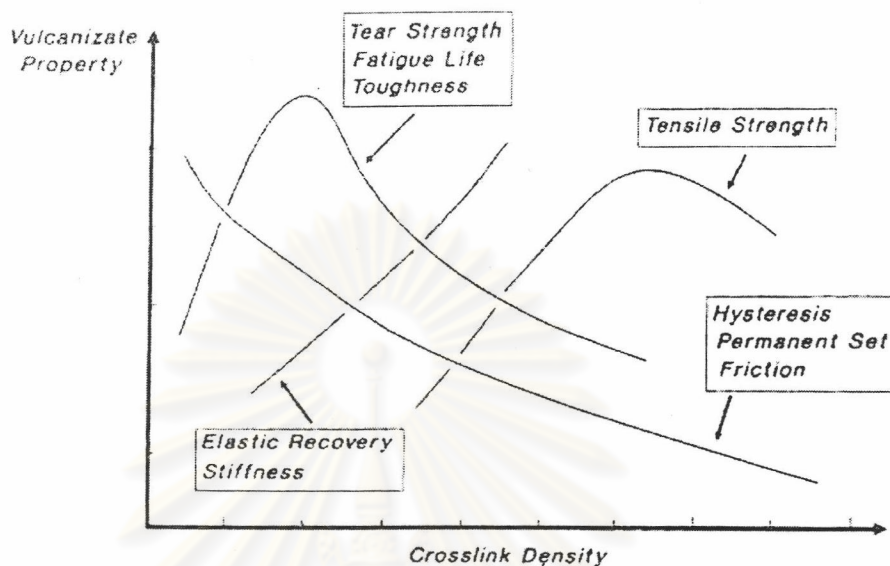


Figure 2.7 Mechanical properties as a function of the extent of vulcanization

Hysteresis is reduced with increasing crosslink formation. Hysteresis is the ratio of the rate-dependent or viscous component to the elastic component of deformation resistance. It is also a measure of deformation energy which is not stored (or borne by the elastic network) but which is converted to heat. Vulcanization then causes a trade-off of elasticity for viscous or plastic behavior. Tear strength, fatigue life, and toughness are related to the breaking energy. Values of these properties increase with small amounts of crosslinking but they are reduced by further crosslink formation. Properties related to the energy-to-break increase with increases in both the number of network chains and hysteresis. Since hysteresis decreases as more network chains are developed, the energy-to-break related properties are maximized at some intermediate crosslink density.

It should be noted that the properties given in Figure 2.7 are not only functions of crosslink density. They are also affected by the type of crosslink, the type of polymer and the type and amount of filler.

Reversion is a term generally applied to the loss of network structures by non-oxidative thermal aging. It is usually associated with isoprene rubbers vulcanized by sulfur. It can be the result of too long of a vulcanization time (overcure) or of hot aging of thick section. It is most severe at temperatures above about 155 °C. It occurs in vulcanizates containing a large number of polysulfidic crosslinks. Though its mechanism is complex, a good deal about the chemical changes which occurs during the reversion of natural rubber has been deduced.

Sometimes the term *reversion* is applied to other types of non-oxidative degradation, especially with respect to rubbers not based on isoprene. For example, thermal aging of SBR, which can cause increased crosslink density and hardening, has been called reversion because it can be the result of overcure.

2.4.3 Sulfur Vulcanization [4]

Sulfur is the main curing agent for most crude rubbers that contain enough double bond in their macromolecules. The sulfur-only vulcanization proceeds via a polar or ionic mechanism, where species of the type RS_x^+ (R = rubber chain) added onto the double bond. Sulfur is combined in the vulcanization network of rubber similar to the network structure of sulfur-prevulcanized latex as illustrated in Figure 2.5.

Since the vulcanization of rubber by heating with sulfur alone is a relatively slow process and exhibits a poor efficiency, it is necessary to add accelerators to increase the rate of vulcanization. These accelerators are usually complex sulfur-containing organic compounds such as tetraalkylthiuram disulfide, zinc dialkyldithiocarbamate, and related compounds, as well as a few non-sulfur compounds such as aryl guanidines. Many accelerators function best in the presence of activators, like zinc oxide (ZnO) and stearic acid. Due to the importance of solubility of the accelerator and activator, a rubber-soluble soap, e.g., the zinc salt of a long chain fatty acid, is usually interacted with molecular sulfur (S_8) to form a sulfurating reagent or zinc perthio-salt (XS_xZnS_xX). This salt reacts with the rubber

hydrocarbon (RH) to give a rubber-bound intermediate (RS_xX) which subsequently reacts with a molecule of rubber hydrocarbon (RH), or itself, to give polysulfide crosslink, and more accelerator is regenerated. The polysulfide ($RS_{x-1}R$) in turn can lose sulfur to give monosulfidic and disulfidic crosslinks, or can give cyclic sulfide with loss of crosslink. With a large accelerator: sulfur ratio, most of the polysulfidic is transformed into monosulfide crosslink, and the undesirable cyclic sulfide formation is suppressed. The general mechanism of the accelerated sulfur vulcanization is shown in Figure 2.8.

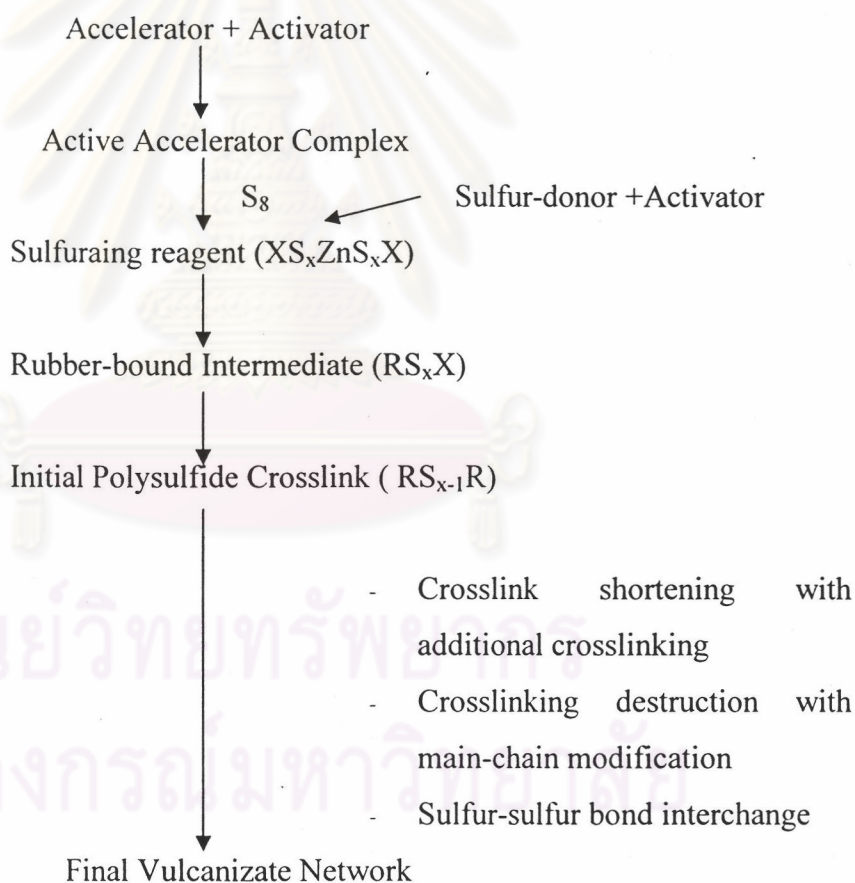


Figure 2.8 General mechanism of accelerated sulfur vulcanization (R = rubber chain, H = allylic proton and X = accelerator)

2.5 Molecular Weight of Polymer [6]

Molecular weight of polymer is generally very high, ranging from about 25,000 g/mol to 1,000,000 g/mol or higher. Polymers differ from small-sized compounds in that they are polydispersed or heterogeneous in molecular weight. When one discusses the molecular weight of a polymer, one is actually involved with its average molecular weight.

2.5.1 Molecular Weight Average

There are three molecular weight averages in common use.

1. Number – average molecular weight, \bar{M}_n

Number-average molecular weight involves a count of the number of molecules of each species divided by the total number of molecules. \bar{M}_n was defined as:

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Where N_i is the number of moles whose weight is M_i .

The methods for measuring \bar{M}_n are those that measure colligative properties of solution–vapor pressure lowering (vapor pressure osmometry), freezing point depression (cryoscopy), boiling point elevation (ebulliometry) and osmotic pressure (membrane osmometry). The most common methods are membrane osmometry and vapor pressure osmometry. Vapor pressure osmometry, which measures vapor pressure indirectly by measuring the change in temperature of a polymer solution on dilution by solvent vapor. It is generally useful for polymers with \bar{M}_n below 10,000

- 15,000. Membrane osmometry is limited to polymers with \bar{M}_n above about 20,000
- 30,000 and below 50,000.

2. Weight – average molecular weight, \bar{M}_w

The principal method of determining the weight – average molecular weight is light – scattering that is greater for larger – sized molecules than for smaller – sized molecules \bar{M}_w is defined as:

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

The lower limit of \bar{M}_w by the light scattering method is close to 5,000 – 10,000. Below this molecular weight, the amount of scattered light is too small to measure accurately.

3. Viscosity – average molecular weight, \bar{M}_v

Solution viscosity measures the viscosity – average molecular weight. Viscosity, like light scattering, is greater for the larger – sized polymer molecules. \bar{M}_v was defined as:

$$\bar{M}_v = \left(\frac{\sum N_i M_i^{a+1}}{\sum N_i M_i} \right)^{1/a}$$

Where a is a constant. \bar{M}_v depends on a as well as on the distribution of molecular weight species. For many polymers \bar{M}_v is 10 – 20% below \bar{M}_w .

For a polydisperse polymer with the differences between the various average molecular weights increasing as the molecular – weight distribution becomes

broader. Distribution of molecular weights in a typical polymer sample is shown in Figure 2.9

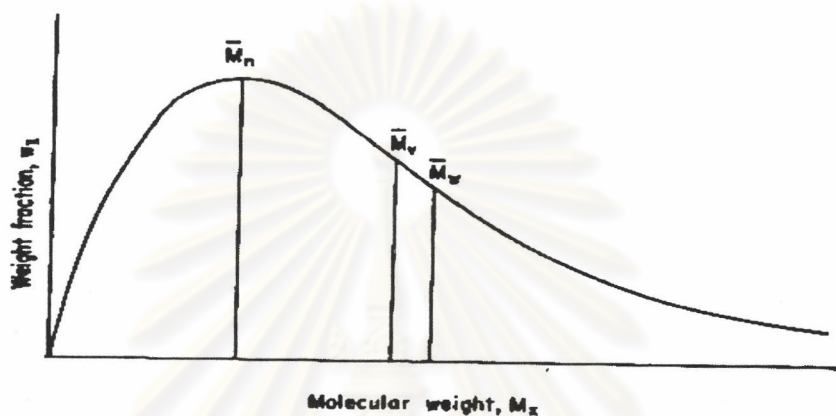


Figure 2.9 Distribution of molecular weights in a typical polymer sample

2.5.2 Molecular Weight Measurement [7]

Size exclusion chromatography (SEC), also referred to gel permeation chromatography (GPC) is the method most widely used today for determining the molecular size and molecular weight distribution.

Gel permeation chromatography (GPC) makes use of the size exclusion principle. The size of the molecule, defined by its hydrodynamic radius, can or cannot enter small pores in a bed of cross-linked polymer particles, the most common form of the stationary phase. The smaller molecules diffuse into the pores via Brownian motion (See Figure 2.10) and are delayed. The larger molecules pass by and continue in the mobile phase.

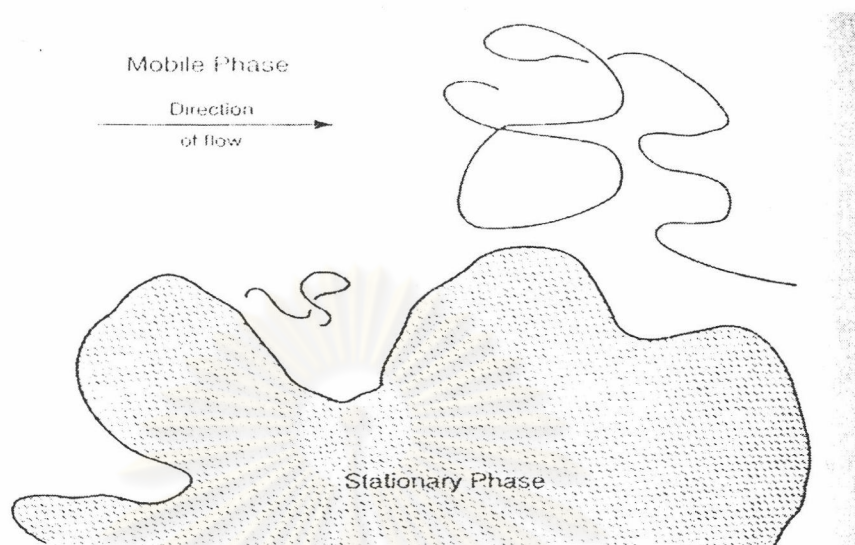


Figure 2.10 The size exclusion effect

The instrumentation most commonly used in GPC work is illustrated in Figure 2.11. The stationary phase consists of small, porous particles. While the mobile phase flows at a specified rate controlled by the solvent delivery system, the sample is injected into the mobile phase and enters the columns. The length of time that a particular fraction remains in the columns is called the *retention time*. As the mobile phase passes the porous particles, the separation between the smaller and the larger molecules becomes greater (see Figure 2.12). While separation of polymer chains according to size remains the most important experiment, there are many other aspects, as described below.

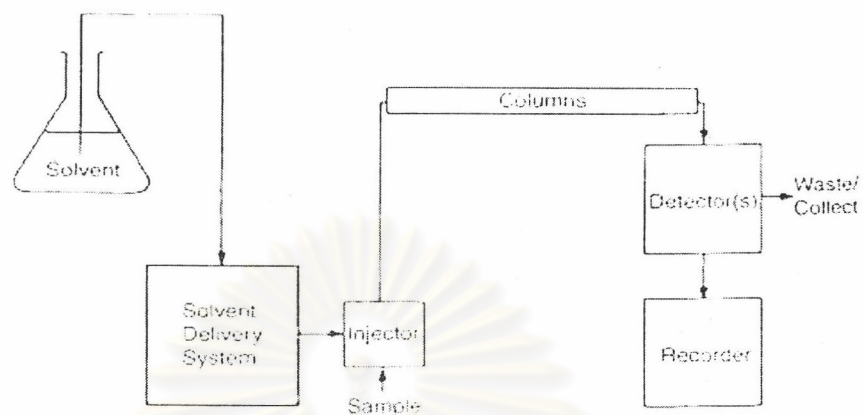


Figure 2.11 An illustration of the modules that make up GPC instrumentation

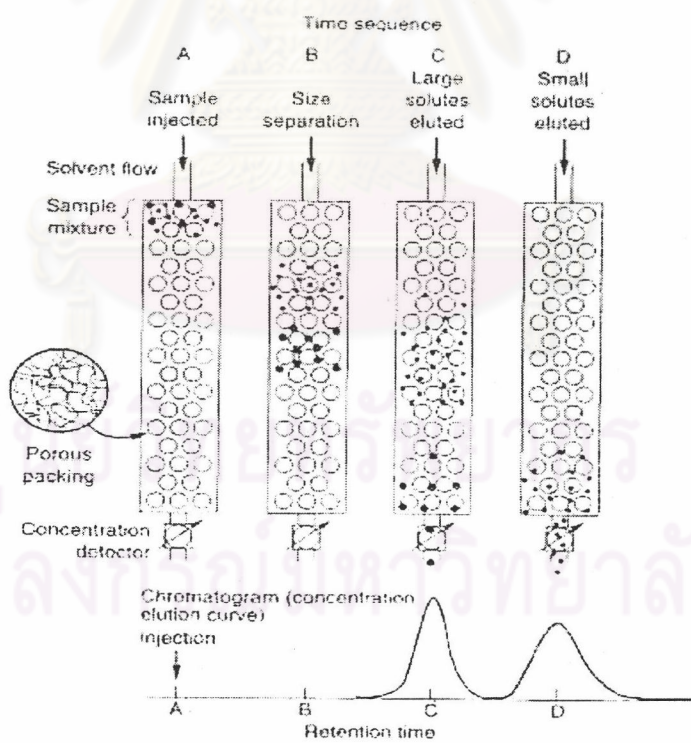


Figure 2.12 Illustration of the GPC experiment

With the exception of proteins and a very few other macromolecules, most polymers exhibit some form(s) of heterogeneity. The most important is the molecular weight distribution (MWD), sometimes called a molar mass distribution, or polydispersity index (PDI), equal to $\overline{M}_w/\overline{M}_n$. Another type of heterogeneity involves a distribution of chemical composition, including statistical, alternating, block, and graft copolymers. Still another type of heterogeneity relates to functionality, particularly end groups. Macromolecules with terminal functional groups are usually called telechelics or macromonomers. Molecular architecture provides yet another type of heterogeneity, dictated by the shape of the chain. While most synthetic polymers form random coils, an increasing number of polymers are rod shaped, or form rings. Many polymers are branched. Each of these types of heterogeneity must be taken into account when measuring molecular weight by relative methods.

There are two very popular relative methods of characterizing polymers with one or more of the above heterogeneities. Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC) or gel filtration chromatography, is one of several chromatographic methods available for molecular weight (molar mass) and molecular weight distribution. While GPC has its greatest value for measuring the molecular weight and polydispersity of synthetic polymers, a closely related method, high performance liquid chromatography (HPLC) is more useful for separating and characterizing polymers containing functional groups, such as proteins and pharmaceutical polymers containing special active group. Both of these methods depend on distribution coefficients.

2.6 Degradation of Polymer [8]

Degradation may happen during every phase of a polymer's life such as during its synthesis, processing and use. Macromolecules are composed of monomeric units that are joined by chemical bonds to each other. The monomeric units contain chemical bonds, which either are in the main chain of macromolecule

or connect various atoms or side groups to it. The dissociation energy of carbon – carbon bonds in the middle is 75 – 85 kcal/mol. The most important types of energy that causes degradation are that of the ultraviolet (UV) of sunlight. The wavelength is 300 nm and energy is about 95 kcal/mol, which is higher than most bond dissociation energy in polymers. UVB radiation that is in the range of 290 – 315 nm, is important in the degradation of polymers.

Chain scission and crosslinking lead to a change of molecular weight distribution. Oxidation and other chemical reactions in the side chains also, cause changes in chemical composition, which may result in discoloration. The dissociation energies of the various bonds in the polymer may determine the course of degradation. Table 2.3 shows bond dissociation energies of various single bonds.

Table 2.3 Bond dissociation energies of various single bonds

Bond	Bond dissociation energies (kcal/mol)	Bond	Bond dissociation energies (kcal/mol)
$C_2H_5 - H$	99	$C_6H_5 - CH_3$	94
$n-C_3H_7 - H$	98	$C_6H_5CH_2 - Cl$	72
$t-C_4H_9 - H$	91	$CH_3 - Cl$	84
$CH_2 = CHCH_2 - H$	82	$C_2H_5 - Cl$	81
$C_6H_5 - H$	103	$CH_2 = CHCH_2 - Cl$	65
$C_2H_5CH_2 - H$	83	$CH_3 - F$	108
$C_2H_5 - CH_3$	83	$CH_2H_5 - F$	106
$n-C_3H_7 - CH_3$	83	$HO - OH$	51
$t-C_4H_9 - CH_3$	81	$t-C_4H_9O - OH$	36

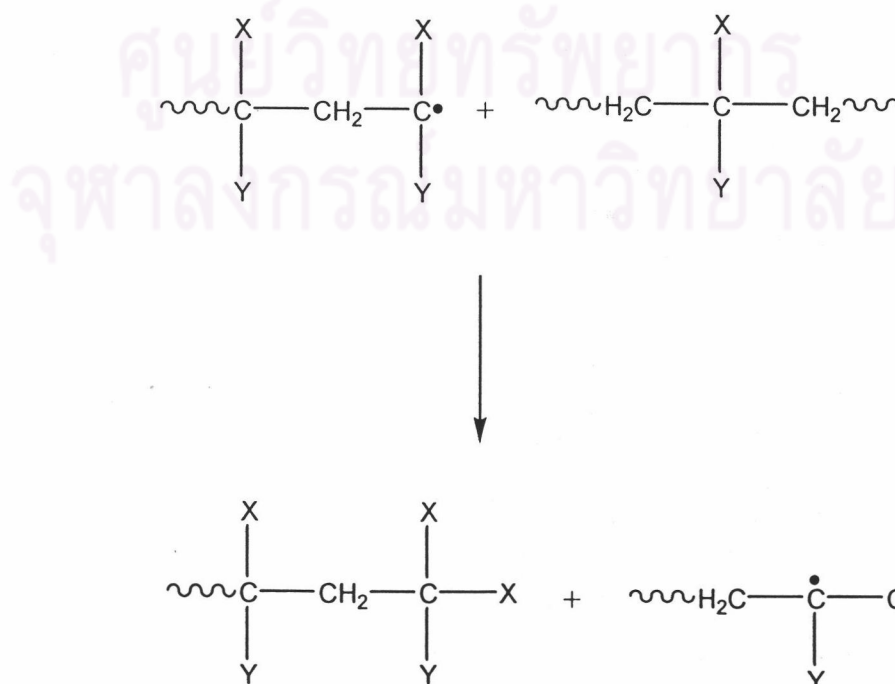
2.6.1 Random Chain Scission and Crosslinking

Typical examples for degradation processes with random chain scission character are hydrolysis, thermal degradation and degradation by radiation. Degradation by UV radiation usually occurs by a mechanism involves free radical formation, as follows:

a) Initiation by main chain scission is a necessary condition of depolymerization because this process produces the terminal active site capable of depropagation. In initiation by random chain scission, two macroradicals are formed with different terminal groups.

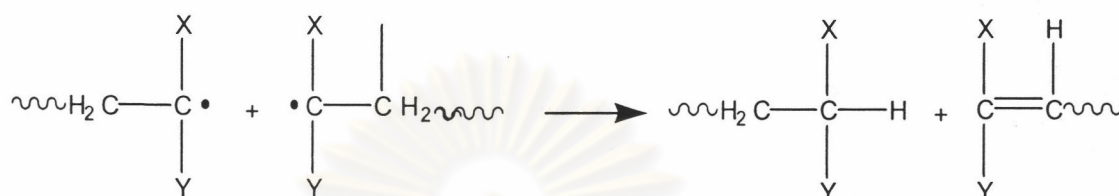


b) The terminal radicals formed in the initiation step or in the depropagation steps must be stable enough not to participate in various side reactions such as chain transfer. A very common way of chain transfer is H - abstraction from another macromolecule.

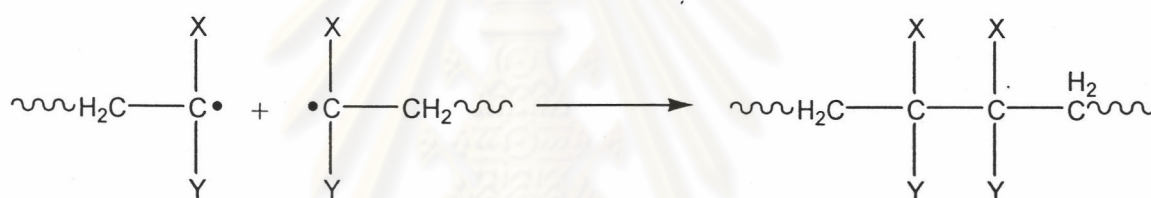


c) Termination can be a uni- or bimolecular reaction for example:

Disproportionation:



or *recombination:*



The termination products are of high molecular weight, they can participate in further reactions.

2.6.2 Degradation without Chain Scission

A very important type of polymer degradation consists of those processes, which take place without scission of the main polymer chain; characteristic of this kind of degradation is the participation of side groups in the reaction. For example, vinyl polymers of structure $(-\text{CH}_2 - \text{CHX}-)_n$ where X is an electronegative group. HX elimination is the most common form of degradation.



The elimination of side groups from polymer likes the elimination of HX from low molecular weight compounds, usually proceeds via a nonradical mechanism. Reactions of the polymer side groups are important not only with respect to degradation but also for intentional alteration of some polymers such as preparation of poly(vinyl alcohol) from poly(vinyl acetate) that is carried out by alcoholysis of the acetate groups by methanol.

2.6.3 Oxidative Degradation [9]

Although all polymers degrade at high temperatures in the absence of air, degradation is almost always faster in the presence of oxygen. Oxidation of hydrocarbons is normally auto-accelerating, i.e. the rate is slow or even negligible at first but gradually accelerates, often to a constant value. The addition of an initiator normally removes the slow auto-accelerating induction time and antioxidants and stabilizers extend it.

Ground state oxygen is unusual in that it exists in the triplet state, i.e. it is a diradical (I). Although excited singlet oxygen (II) can be important as an autooxidation initiator under certain circumstances, oxygen normally reacts with organic compounds in a radical chain reaction involving the ground state.

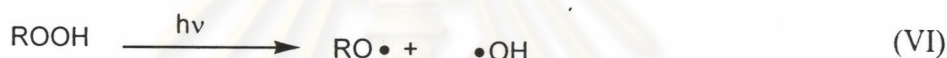


Each cyclical sequence of reactions (III) and (IV) absorbs one molecule of oxygen and leads to the formation of hydroperoxide.

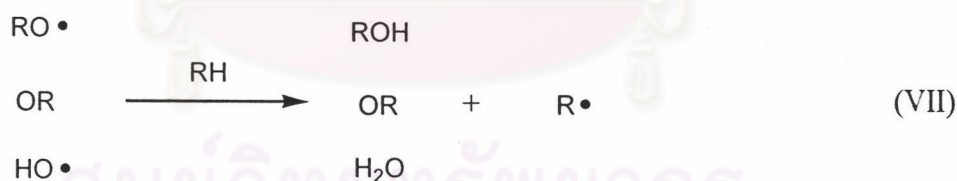


Since reaction (III) is a radical pairing process it has a low activation energy and occurs with high frequency. The second step (IV) on the other hand involves the breaking of a carbon-hydrogen bond and has a higher activation energy. In most polymers at normal oxygen pressures, the rate of this step in the chain reaction determines the overall rate of oxidation.

The radical chain reaction can be initiated by any radical generators. Initiation normally occurs by thermolysis or photolysis of the hydroperoxide formed in the chain reaction.



Since both the alkoxy and hydroxyl radical are efficient hydrogen abstracting agents, they effectively inject new radicals into the radical chain (III), (IV) by reaction (VII).



2.6.4 Photodegradation

Polymers have different photodegradative sensitivities to ultraviolet light at different wavelengths, as shown in Table 2.4. The maximum sensitivity of several polymers is in the range of 290 and 400 nm.

Tables 2.4 Wavelength of ultraviolet radiation at which various polymers have maximum sensitivity

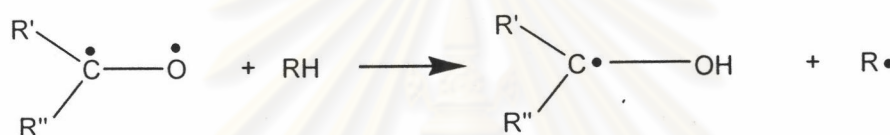
Polymer	Wavelength (nm)	kcal/mol
Styrene – acrylonitrile copolymer	290, 325	99, 88
Polycarbonate	295, 345	97, 83
Polyethylene	300	96
Polystyrene	318	90
Poly(vinyl chloride)	320	89
Polyester	325	88
Vinyl chloride – vinyl acetate copolymer	327, 364	87, 79
Polypropylene	370	77

2.6.4.1 Photo-oxidation

The term ‘weathering’ is used as a comprehensive description of all possible changes which may occur in polymers upon outdoor exposure. It thus embraces not only changes in mechanical behavior (tensile strength, impact strength, etc.) but also aesthetically undesirable changes such as discoloration, loss of gloss. Although moisture and humidity can have secondary effects in weathering, the primary process occurring is photo-oxidation or perhaps more accurately, photo-initiated oxidation, since, as has already been seen, the effect of light is primarily on the generation of free radicals. Light has relatively little effect on the propagating steps of the radical chain reaction.

The nature of the initiating reaction in the photo-oxidation of polymers has aroused considerable scientific controversy in recent years since ‘pure’ polymers do not normally contain functional groups capable of acting as sensitizing species. For example, pure hydrocarbons show no UV absorption in the spectral region found in sunlight (i.e. > 285 nm) and yet all the commercial polymers photo-oxidize readily.

It was noted that a variety of oxygen-containing groups are formed during the processing of polymers even under nominally oxygen-free conditions, due to oxygen dissolved in the polymer. By far the functional groups that are easily detected are the group of carbonyl compounds absorbing in the IR in the region $1710\text{-}1735\text{ cm}^{-1}$. Some of these compounds have strong absorbance in the sun's special region and show characteristics luminescence associated with the excitation to the triplet state. The triplet states of carbonyl compounds are highly chemically reactive species and can undergo transformation in polymers as shown below



The alkyl radicals produced can react with oxygen as in reaction (III). Polymers have to be processed very severely before applicable quantities of carbonyl compounds appear since they are formed by thermolysis or photolysis of hydroperoxides. Polymers which have been subjected to very severe processing in order to produce carbonyl compounds in the polymer chain photo-oxidise much more rapidly than mildly processed polymers .

2.6.4.2 Sensitization by Pigments

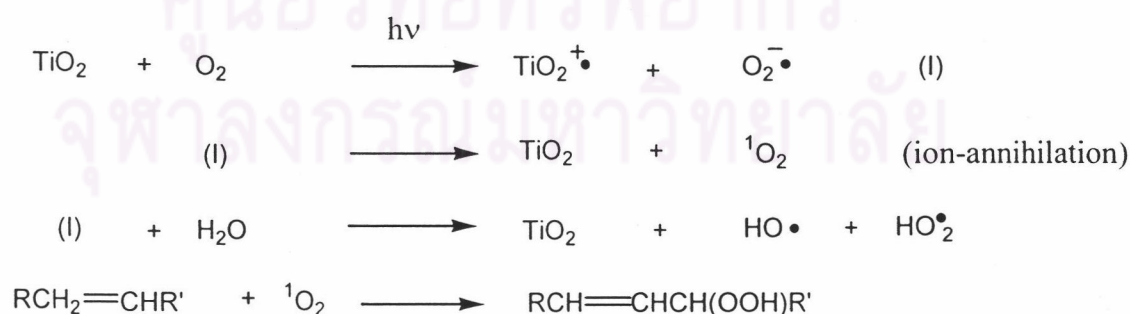
A photosensitizer usually has a high absorption coefficient for ultraviolet light. The excited compound both decomposes into free radicals and initiates degradation or oxidation of polymer or transfers the excitation energy to polymer or oxygen. A good sensitizer should be easily admixed with polymer and must not decompose thermally or in the dark. Examples of photosensitizer are polycyclic aromatic compounds, quinones, nitrogen containing chromophores, inorganic metal oxides and salts such as zinc oxide (ZnO) and titanium dioxide (TiO₂).

2.7 Titanium (IV) oxide, titanium dioxide (TiO₂) [10, 11]

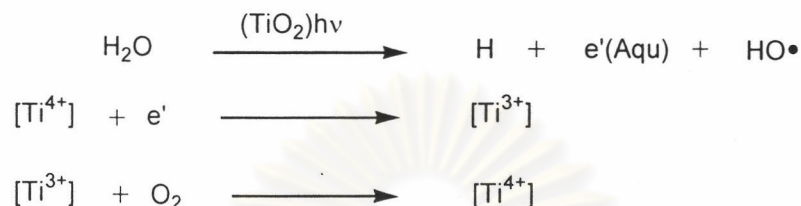
Pigments are widely used in polymer materials to provide characteristics to suit a particular commercial application. Inorganic and organic pigments are used primarily to impart color to the polymer while others such as silica is used to impart haze or act as an antiblocking agent. In many cases pigments can have a marked influence on the thermal and photochemical stability of the polymer material. For example, by absorbing and/or screening light energy, they can exhibit a protective effect or alternatively they may be photoactive and sensitize the photochemical breakdown of the polymer. One of the most widely used pigments in this regard is titanium dioxide, often referred to as simply "Titania".

The ability of TiO₂ to catalyze the photo-oxidation of polymer systems has received much attention in terms of their mechanistic behavior. In this regard much of the information originates from work carried out on TiO₂ in polymers, coatings and model systems. To date there are three current mechanisms of the photosensitized oxidation of polymers by TiO₂.

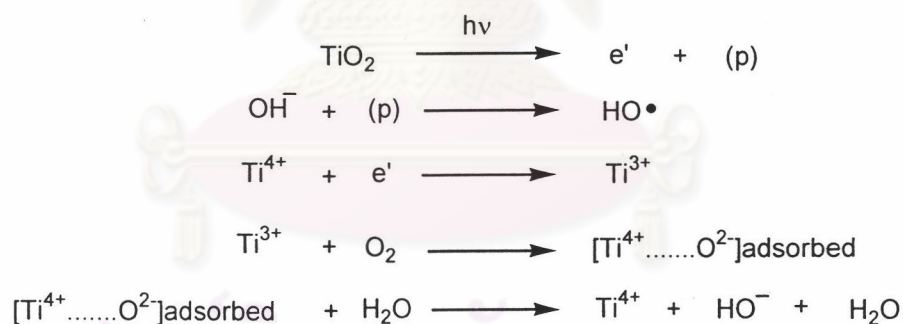
1. The formation of an oxygen radical anion by electron transfer from photoexcited TiO₂ to molecular oxygen. A recent modification of this scheme involves a process of ion-annihilation to form singlet oxygen which then attacks any unsaturation in the polymer.



2. Formation of reactive hydroxyl radicals by electron transfer from water catalyzed by photoexcited TiO_2 . The Ti^{3+} ions are reoxidised back to Ti^{4+} ions to start the cycle over again.



3. Irradiation of TiO_2 creates an exciton (p) which reacts with the surface hydroxyl groups to form a hydroxyl radical. Oxygen anions, which are also produced which are adsorbed on the surface of the pigment particle. They generate active perhydroxyl radicals.



TiO_2 exists in three morphological crystalline forms, modifications; anatase, brookite and rutile. Brookite is rare and orthorhombic. The other two are tetragonal but are not isomorphous. They are also of different crystal habit; rutile forms slender, prismatic crystals that are frequently twinned, but anatase usually occurs in near regular octahedral. Structure of rutile and anatase are shown in Fig. 2.13. A summary of the crystallographic properties of the three varieties is shown in Table 2.5.

Brookite is the least stable and has never been used commercially as a pigment. Anatase and rutile exhibit different photo-activities when incorporated into

a number of commercial polymers and coatings. Differences in the photo-activities of the two modifications of titania depends markedly upon the manufacturing history of the TiO_2 . Anatase is generally more photo-active than rutile type. During the weathering of commercial polymers and coatings containing white pigments such as TiO_2 , oxidation occurs at the surface layers of the material which eventually erodes away, leaving the pigment particles “chalking”. TiO_2 pigments absorb strongly in the near UV region with anatase having a cut-off point at 340 nm and rutile at 370 nm.

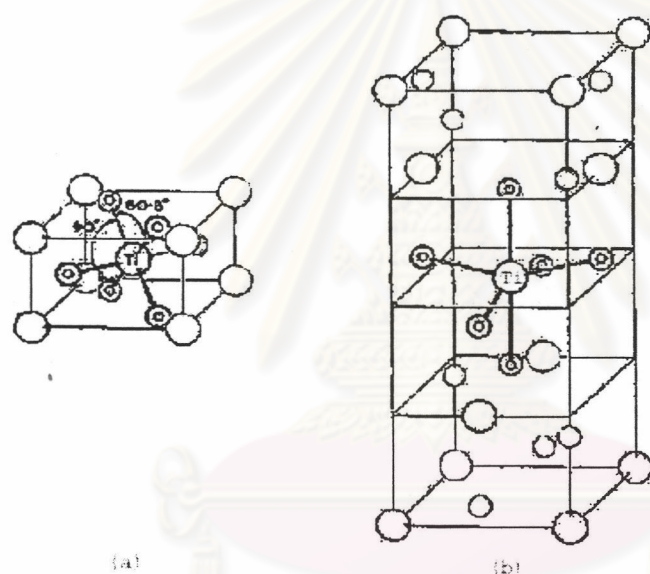


Figure 2.13 Structures of titanium dioxide (a) rutile, (b) anatase [12]

Table 2.5 Crystallographic properties of anatase, brookite and rutile

Mineral	Anatase	Brookite	Rutile
Crystalline	tetragonal	Orthorhombic	tetragonal
Optically	uniaxial, negative	Biaxial, positive	uniaxial, positive
Density, g/ml	3.9	4.0	4.23
Hardness, Moh's scale	5½ - 6	5½ - 6	6 - 6½
Unit cell	$D_{4a}^{19}4\text{TiO}_2$	$D_{4h}^{15}8\text{TiO}_2$	$D_{4h}^{14}2\text{TiO}_2$
Dimensions, Å			
A	3.758	9.166	4.584
B	-	5.436	-
C	9.514	5.135	2.953

2.8 Literature Review

Cho and Choi [13] investigated the solid-phase photocatalytic degradation of poly(vinyl chloride) (PVC)-TiO₂ composite film under the ambient air. TiO₂-embedded PVC showed highly enhanced photo-degradation. Irradiating the composite film for 300 hours under air reduced its average molecular weight by two-thirds and weight by 27%. The SEM images of the irradiated composite films showed the development of cavities around the embedded TiO₂ particles and implied that active oxygen species which were photo-generated on TiO₂ surface desorb and diffuse across a few micrometers to react with the polymer matrix.

Chen and coworkers [14] investigated titanium dioxide mediated photocatalytic degradation of polyvinyl alcohol (PVA) under UV lamps. The results indicated that the optimum dosage of TiO₂ in the photo-degradation of PVA was 2.0 g/l. For extremely few of TiO₂, the degradation rates were lower because that the limiting factor for the low rate was the lack of required amount of the catalyst. In superfluous TiO₂, the UV was diffused by TiO₂ particles. The results also indicated that it was more effective for PVA to be degraded under acidic or alkaline condition.

Under different pH conditions, the main pathways of producing hydroxyl radical are probably different, therefore, producing rate of hydroxyl radical are different. As well as TiO₂ concentration, there was an optimum peroxide concentration on the rate of PVA destruction.

Allen and coworkers [10] studied thermal and photochemical activities of nano and micron particle grade anatase and rutile TiO₂ in monomodal metallocene polyethylene and alkyd paint film. Photo-oxidation studies on PE containing nano-particle and pigmentary grade. TiO₂ showed that in general the former are more photo-active with anatase and rutile forms exhibiting high activity. Photo-oxidation studies showed a clear demarcation between nano-particle and pigmentary grade. TiO₂ with the anatase form was more active. SEM analysis showed the formation of pits and holes formed as a consequence of oxidation of the polymer at the particle surface and subsequently spreading out from the particle.

Gesenhues [15] studied the effect of photodegradation catalyst and ultraviolet protection of TiO₂ on photodegradation of poly(vinyl chloride) with and without moisture. Moisture or water was an accelerator to oxidation reaction because the surface of TiO₂ can release hydroxyl radicals, which are more active oxidizing species than oxygen anions.

Allen and Katami [11] studied the degradation of linear low density polyethylene with TiO₂ pigments under ultraviolet light and heat. At 90°C and under ultraviolet light, all pigments (rutile, anatase) were oxidative degradation catalysts. Oxidative catalytic property of pigment was enhanced at wavelength of 365 nm. Rutile can scatter ultraviolet light at 254 nm. It does behave as UV screener and stabilize the polymer.

Angulo-Sanchez, Ortega-Ortiz and Sanchez-Valdes [16] reported the photodegradation of low-density polyethylene (LDPE) films formulated with titanium (IV) oxide acetylacetonate (TAc) and titanium dioxide pigment (TiO₂). Number-average molecular weight (\bar{M}_n) of LDPE with TAc decreased rapidly at short ultraviolet exposure with a tendency to level off later. LDPE with TiO₂

behaved in a similar way but showed higher values of \overline{M}_n for the same exposure time. Molecular weight results suggested that there was some chain recombination at short exposure time. Elongation at break decreased when the time of ultraviolet exposure increased.

Kurian and coworkers [17] studied the degradation of natural rubber latex thread under ultraviolet radiation. The thread samples were exposed to ultraviolet radiation in the region of 290 – 350 nm for 24, 48 and 96 hours. Tensile strength of thread samples decreased when UV exposure time increased. The tensile strength of the thread having zinc diethyl dithiocarbamate (ZDEC) and zinc mercaptobenzothiazole (ZMBT) combination is lower than the thread having zinc dibutyl dithiocarbamate (ZDBC)/ZMBT, and ZDBC/ZDEC. Ultraviolet light caused considerable deterioration of the tensile strength of the thread.

Menon, Pillai and Nando [18] studied thermal degradation of natural rubber vulcanizates modified with phosphorylated cashew nut shell liquid. Thermal degradation of natural rubber occurred at 200–475°C. Degradation of natural rubber in air showed the two-stage decomposition. The first stage of degradation occurred in the temperature range of 300–420 °C. The second stage occurred in temperature range of 460–560°C. Under nitrogen atmosphere, the degradation occurred only in the temperature range of 300–420°C.

Phetphasit and Phinyocheep [19] studied degradation of purified natural rubber. There were better degradation results for natural rubber which was purified by the elimination of proteins, than the unpurified natural rubber. This may be due to the presence of non-rubber constituents which act as antioxidant, or the presence of microgels, which retard the oxidative degradation in the system. It was found that the radical initiator $K_2S_2O_8$, propanol and the temperature played important roles in the degradation .

Riyajan and coworkers [20] studied controlled photodegradation of natural rubber glove by encapsulated benzophenone (BP) and 2,6-di-*t*-butyl-*p*-cresol toluene (BHT). The efficiency of controlling photodegradation was improved by

encapsulated BP or BHT/BP. It was clearly observed that the photodegradation of NR in the presence of BP was faster than that of BHT/BP. It was found that the optimum ratio of BP:BHT for both raw and cured NRs was 1:2. It can be explained that BP accelerated photodegradation of NR films, while BHT retarded the degradation. In the case of cured NR, the encapsulated BHT/BP can effectively control the photodegradation better than the unencapsulated BHT/BP, especially, at the initial stage.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย