

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber^[3,4]

There are many higher plants that produce rubber. However, only natural rubber from *Heavea brasiliensis* is the important commercial source. The Heavea tree produces rubber as milky colloidal suspension, containing about 30% polyisoprene. Latex that can be harvested easily by trapping consists of particles of rubber hydrocarbon and non- rubber constituents suspended in an aqueous serum phase. The average rubber hydrocarbon content of latex may range between 30% and 45% of the whole latex. The composition of fresh latex is shown in Table 2.1.

Table 2.1 The composition of fresh latex

Composition	Percent
Rubber hydrocarbon	30.0 – 45.0
Proteinous substance	2.0 – 2.5
Water	38.5
Neutral lipids	1.4
Phospholipids	0.6
Ash	0.5
Inositols and carbohydrates	1.6
Other nitrogenous compound	0.3

The latex is normally called “field” latex, and it contains only 30% dry rubber content (DRC). Dry rubber content of commercial natural rubber latex concentrate is 60% or more. The latex concentrates must be preserved to inhibit bacterial growth that could destabilize the latex and result in spontaneous coagulation. Centrifuged latex concentrates are usually preserved with 0.7%w/v of ammonia, known as high ammonia (HA) latex concentrate.

Chemical formula and properties of natural rubber

Natural rubber is a polymer of isoprene. Isoprene was found to have the formula of C_5H_8 , which has the following structure:

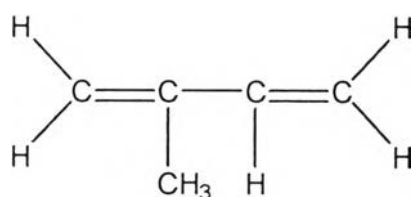


Figure 2.1 Chemical structure of isoprene

The isoprene units are linked together at carbon atoms 1 and 4 in a head – to – tail arrangement.

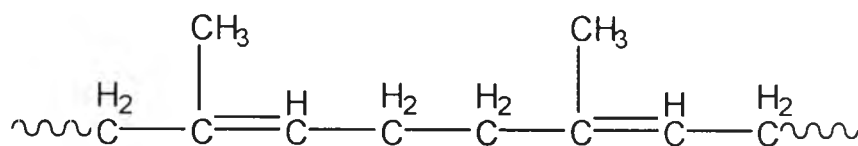


Figure 2.2 Head – to – tail arrangement of polyisoprene

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.

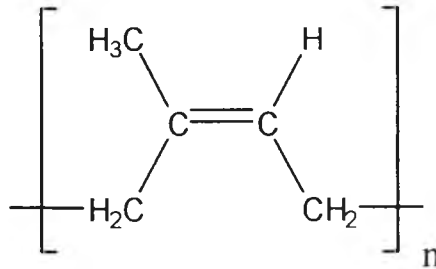


Figure 2.3 cis – polyisoprene

Molecular weight of natural rubber^[5] is about $1.0 - 1.3 \times 10^6$ with broad molecular weight distribution (MWD). The broad MWD of natural rubber is presumed to be derived 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 Molecular Weight of Polymer^[6]

Molecular weight of polymer is 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 polydisperse or heterogeneous in molecular weight. When one discusses the molecular weight of a polymer, one is actually involved with its average molecular weight.

2.2.1 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 was 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 shown in Figure 2.4.

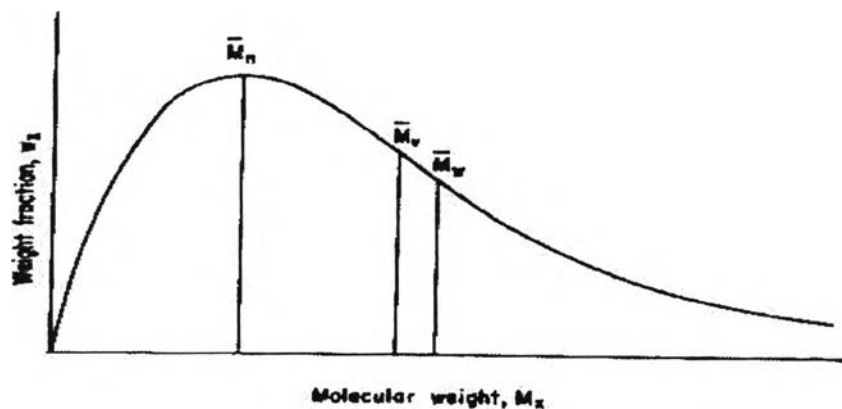


Figure 2.4 Distribution of molecular weights in a typical polymer sample ^[6]

2.2.2 Viscosity – average molecular weight determination^[7]

Solution viscosity is basically a measure of the size or extension in space of polymer molecules. It is empirically related to molecular weight for linear polymers. Dilute – solution viscosity is usually measured in capillary viscometers of the Ostwald – Frenske or Ubbelohde type that is shown in Figure 2.5. The viscosity measurement is made in a constant temperature bath having a temperature variation within the range of $\pm 0.2^\circ\text{C}$.

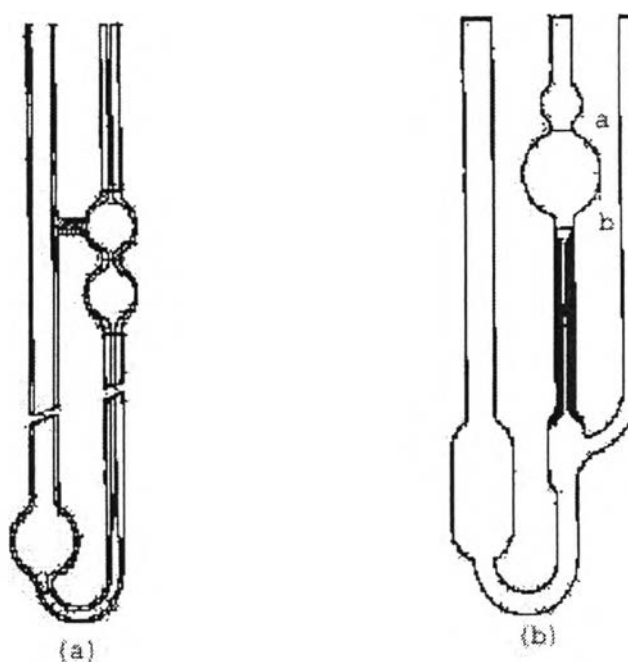


Figure 2.5 Capillary viscometers commonly used for measurement of polymer solution viscosities: (a) Ostwald – Frenske and (b) Ubbelohde

Intrinsic viscosity measurements are carried out in dilute solution and result in \bar{M}_v . Mark and Houwink arrived at an empirical relationship between the molecular weight and the intrinsic viscosity: $[\eta]$.

$$[\eta] = K\bar{M}_v^a$$

Where K and a are constants for a particular polymer–solvent pair at a particular temperature.

The intrinsic viscosity is independent of concentration by virtue of extrapolation to $c = 0$ but is a function of the solvent used.

The intrinsic viscosity was defined as:

$$\begin{aligned} [\eta] &= \left(\frac{\eta_{sp}}{C} \right)_{c=0} \\ &= \left(\frac{\ln(\eta_{rel})}{C} \right)_{c=0} \end{aligned}$$

Where η_{rel} is relative viscosity. The relative viscosity is ratio of viscosity of polymer solution, η and solvent viscosity, η_o .

$$\eta_{rel} = \eta / \eta_o$$

Where η_{sp} is specific viscosity. The specific viscosity is the relative viscosity minus one. Usually η_{sp} is a quantity between 0.2 and 0.6 for the best results.

$$\eta_{sp} = \eta_{rel} - 1$$

2.3 Degradation of polymer^[8,9]

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 cross linking 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 2.2 showed bond dissociation energies of various single bonds.

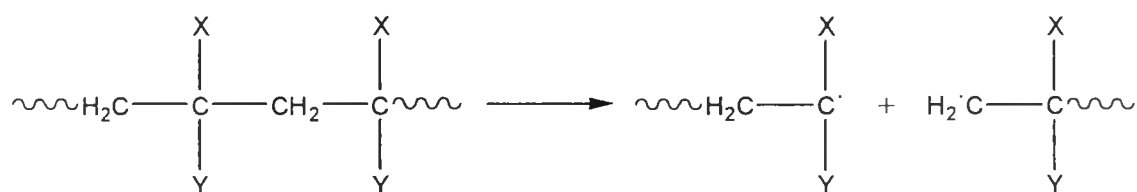
Table 2.2 Bond dissociation energies of various single bonds

Bond broken	Bond dissociation energies (Kcal/mol)	Bond broken	Bond dissociation energies (Kcal/mol)
$C_2H_5 - H$	99	$C_6H_5 - CH_3$	94
$n-C_3H_7 - H$	98	$C_6H_5CH_2 - Cl_3$	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

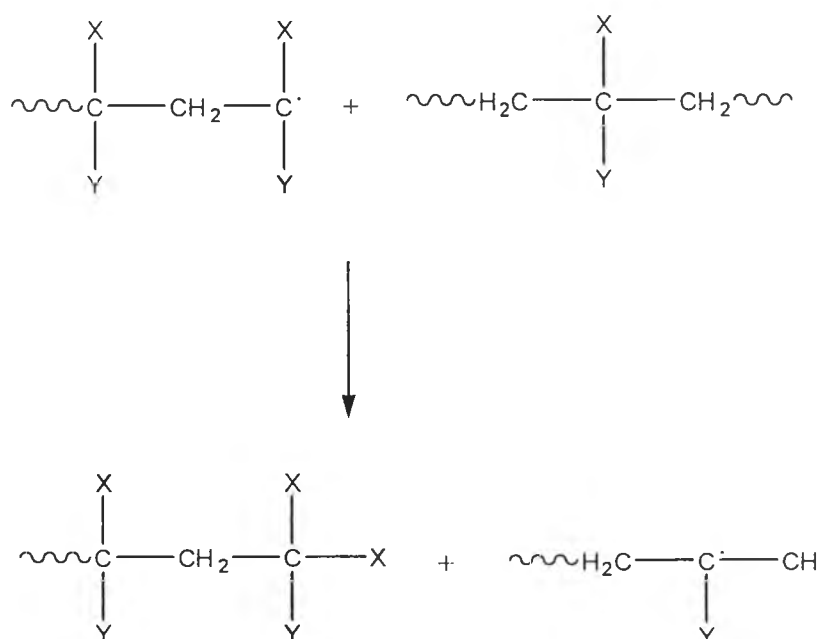
2.3.1 Random chain scission and cross linking

Typical examples for degradation processes with random chain scission character are hydrolysis, high temperature, 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.

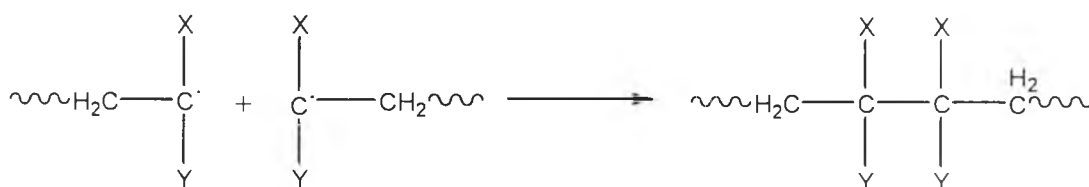


c) Termination can be a uni- or bimolecular reaction for example:

Disproportionation:



or recombination:



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

2.3.2 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.

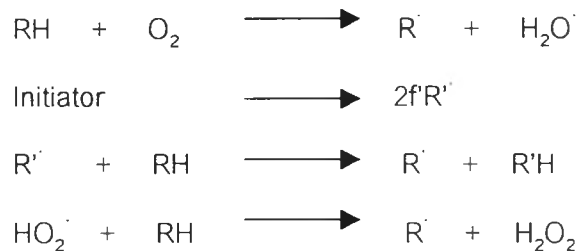


The elimination of side groups from polymer likes the elimination of HX from low molecular weight compounds, usually proceeds via a nonradical mechanism. Reactions of the polymer side groups are important not only with respect to degradation but also for intentional alteration of some polymers such as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

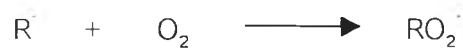
2.3.3 Oxidative degradation

Oxidative degradation of polymers is a free radical chain reaction. A scheme including the most important steps in polymer oxidation is shown in Figure 2.6.

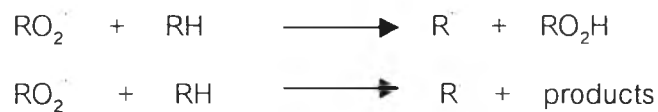
I. Initiation:



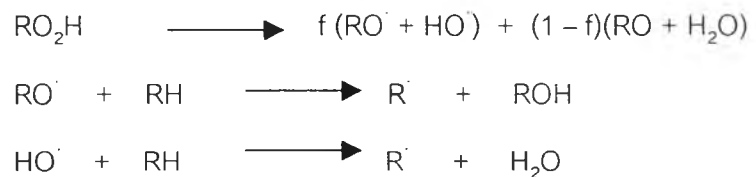
II. Radical conversion (stabilization):



III. Chain propagation:



IV. Degenerate chain branching:



V. Termination:



: f denotes the efficiency of initiation (radical yield)

Figure 2.6 Simplified general scheme of polymer oxidation

In the case of polymers containing alkyl substituted double bond such as polyisoprene, the oxidation of polymer bond proceeds by epoxidization to oxirane (Figure 2.7). Epoxidation process occurs very fast. Oxirane is subsequently converted to oxygen-containing products that are illustrated in Figure 2.8.



Figure 2.7 Epoxidation process

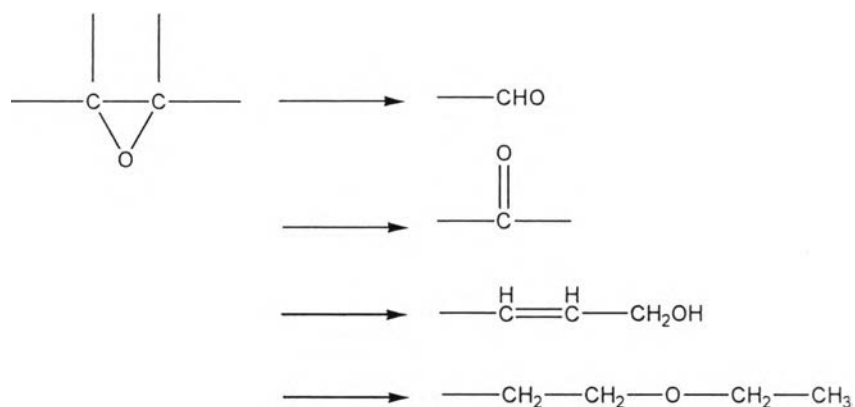


Figure 2.8 Products from oxirane

2.3.4 Photodegradation

Polymers have different photodegradative sensitivities to ultraviolet light of different wavelengths, as shown in Table 2.3. The maximum sensitivity of several polymers is in the range of 290 and 400 nm.

Tables 2.3 Wavelength of ultraviolet radiation at which various polymers have maximum sensitivity

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

Photooxidative degradation

Photooxidation of polymer is very similar to thermal oxidation of polymers. Significant differences exist with respect to the photochemical decomposition of the hydroperoxide and carbonyl groups, as well as with regard to the initiation reaction. The formation of polymer radicals by scission of a C–H bond is a possible consequence of ultraviolet irradiation.



Another significant difference is that many of oxidation products incorporated in the polymer absorb ultraviolet light better than the original polymer.

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 and inorganic metal oxides and salts such as zinc oxide (ZnO) and titanium dioxide (TiO₂).

2.4 Titanium (IV) oxide, titanium dioxide (TiO₂)^[10]

Titanium dioxide (TiO₂) is industrially important compounds as a white pigment for paints. TiO₂ is also an accelerated photodegradation agent. It is assumed that free radicals are formed from compound during irradiation. TiO₂ exists in three crystalline 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 Figure 2.8. A summary of the crystallographic properties of the three varieties is shown in Table 2.4.

TiO₂ as a white pigment depends on its lack of absorption of visible light. Pure anatase is transparent to the whole of the visible spectrum and pure rutile is nearly. Pure anatase is an active photocatalyst for destruction of a paint film. Pure rutile, on the other hand, is a much less active photocatalyst.

Table 2.4 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	$D_{4a}^{19} 4TiO_2$	$D_{4h}^{15} 8TiO_2$	$D_{4h}^{14} 2TiO_2$
dimensions, Å			
a	3.758	9.166	4.584
b	-	5.436	-
c	9.514	5.135	2.953

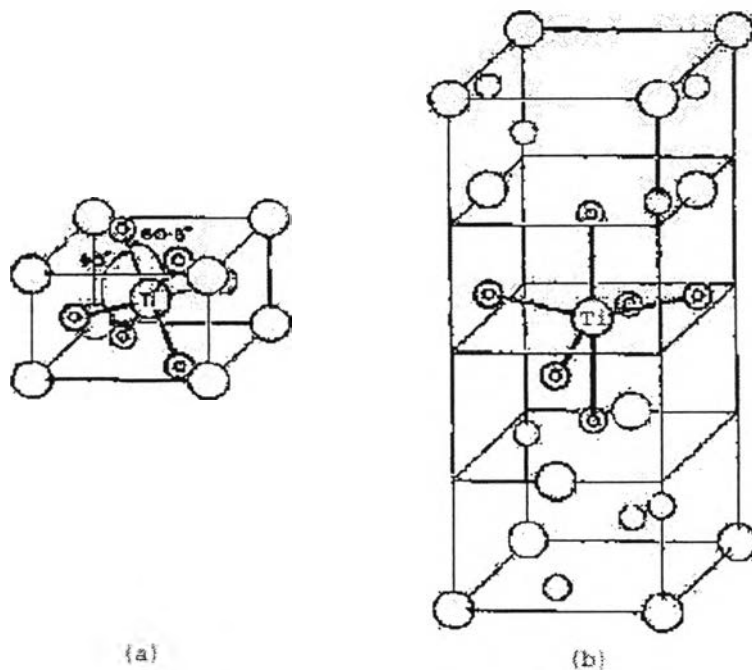


Figure 2.9 Structures of titanium dioxide (a) rutile (b) anatase^[11]

2.5 Microcapsule^[12]

Microcapsule is a vessel, package or container of microscopic size having a polymer wall. It can enclose and protect fine particles of a substance in the core. In general, microcapsules have a size ranged from 5 to 200 μm . Microcapsules may assume various shapes such as globular, spheroidal, kidney-like, rice grain-like, flocculent and massive. Walls may have a single – layer structure or a multilayer structure.

Examples of applications of microcapsules

1. Pressure – sensitive copying paper
2. Medicines
3. Perfumes and fragrances
4. Oil capsules
5. Rust inhibitor capsules
6. Adhesives

2.5.1 Microencapsulation utilizing phase separation from an aqueous solution system

In this process, the starting material for formation of a capsule wall is a water-soluble polymer. A condensed phase of the polymer is separated from an aqueous solution to form the capsule wall.

There are four types of encapsulation utilizing the system of phase separation from an aqueous solution.

1. Complex coacervation or phase separation resulting from two oppositely charged colloids neutralizing one another.
2. Simple coacervation where a nonelectrolyte such as alcohol, causes formation of a separate polymer – rich phase.
3. Salt coacervation where a polymer separates as a result of a salting – out process.
4. Precipitating and insolubilizing a polymer by changing pH of the aqueous solution system.

Complex coacervation process

When an aqueous solution of a positively charged colloid and a negatively charged colloid are mixed, a phase separation results due to an electrical interaction. The different phases consist of a condensed colloid phase and a dilute colloid phase. The condensed colloid phase may be used as a wall film of a capsule. This process has an advantage in that a water-insoluble liquid material can be encapsulated with high efficiency in large quantity.

2.5.2 Gelatin^[13]

Gelatin is a valuable raw material for microencapsulation utilizing coacervation process. Gelatin is a water-soluble protein which is nontoxic and has a good film – forming property. Gelatin molecules like those of other proteins that are large and

complex. Values for the average molecular weight range from 15,000 – 250,000. Gelatin is composed of about 18 different amino acid which are linked together in an ordered fashion. Amino acids obtained by gelatin is shown in Table 2.5. Gelatin is composed of 50.5% carbon, 6.8% hydrogen, 17% nitrogen and 25.2% oxygen.

Table 2.5 Amino acids obtained by complete hydrolysis of gelatin

Amino acids	%by wt	Amino acids	%by wt
Alanine	11.0	Methionine	0.9
Arginine	8.8	Phenylalanine	2.2
Aspartic acid	6.7	Proline	16.4
Glutamic acid	11.4	Serine	4.2
Glycine	27.5	Threonine	2.2
Histidine	0.78	Tyrosine	0.3
Hydroxyproline	14.1	Raline	2.6
Leucine and isoleucine	5.1	Crystine	Trace
Lysine	4.5	-	-

2.5.3 Gum arabic^[14]

Gum arabic or gum acacia is the oldest and best known natural gums. Gum arabic is a dried exudates obtained from the various species of trees in the genus *Acacia* of the *Leguminosae* family. Gum arabic exists in nature as a neutral or slightly acidic salt of a complex polysaccharide containing calcium, magnesium and potassium salts with a molecular weight of about 240,000 – 300,000.

The uses of gum arabic are wide and varied such as in food industry, bakery products and beverages. Furthermore, gum arabic has found specialized use in glues, transparent cements and mounting pastes.

2.6 Literature review

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

Allen and Katam^[16] studied the degradation of linear low density polyethylene with titanium dioxide 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 which made polymer stable.

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 shown 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.

Konar, Samanta and Avasthi^[19] studied oxidative degradation of ethylene propylene diene (EPDM) rubber using phase-transferred permanganate as an oxidant. IR spectrum of the oxidized showed a new peak near 1735 cm^{-1} due to the carbonyl stretching vibration, which may arise from carbonyl, ester or ketone groups.

Angulo-Sanchez, Ortega-Ortiz and Sanchez-Valdes^[20] 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 \bar{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.

Kaminska, Kaczmarek and Kowalonek^[21] studied photooxidative degradation of poly(ethylene oxide) with cobalt (II) chloride by a short wavelength ultraviolet radiation. Rate of degradation was highest in the initial stage (1 h) of exposure. After 2 h the rate of degradation decreased slowly. An IR spectrum of degraded poly(ethylene oxide) showed peaks at 3100 – 3600 and 1700 – 1760 cm⁻¹ regions indicated the existence of carbonyl and hydroxy/hydroperoxy groups.

Erdem and coworkers^[22] studied the encapsulation of TiO₂ particles via styrene miniemulsion polymerization. Interfacial tensions between oil and aqueous phases were used to prepare the miniemulsions containing TiO₂ particles within the droplets. The presence of TiO₂ particles within the droplets limited the ability to reduce the droplet size although miniemulsion droplets were in the size range of 150 – 200 nm.

Palmieri, Lauri and Martelli^[23] studied methoxybutropate microencapsulation by gelatin-acacia complex coacervation. Methoxybutropate is a water-insoluble molecule. Suspension was homogenized at 10,000 rpm. Microparticles were recovered by dehydration with isopropanol, spray-drying and freeze-drying. Particles obtained by treatment with isopropanol were in the form of agglomerates of single microcapsules and the particle size was greater than ones obtained by spray-drying. Spray-drying broke down the particle cluster so that single microcapsules can be recovered. Single microcapsules could not be recovered using freeze drying because the uncoacervated excess of colloidal polymers form bridges between particles after water sublimation.