

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Crosslinkable Polymer

Generally, chemically crosslinked polymers can be grouped into two types. The first is that it obtained from the reactions of bifunctional monomers having functionality greater than two such as polyesters from the reaction of phthalic anhydride with glycerol, or polyurethane from the reaction of isocyanate with glycerol. The other is by an addition of chemical agent or by explosion to electromagnetic wave such as crosslinking of ethylene-propylene-diene elastomer (EPDM) by incorporation with sulfur, or crosslinking of polyethylene by organic peroxide or gamma radiation. The crosslinked polymers cannot melt or flow or dissolve in any solvent due to the formation of three dimension network, which lead to an improvement of their physical properties.

2.1.1 Degree of Crosslinking [1]

Degree of crosslinking is usually expressed as a number of crosslink per gram or per unit volume of polymer. If C is the moles of crosslink per unit volume, n is the number of network chains per unit volume, d is the density of crosslinked polymer, and M_c is the number average molecular weight of polymer segment between crosslinks, thus

$$C = n/2 = d/2M_c \quad (2.1)$$

i.e., the number of gram-mole of crosslink per gram of the network polymer is equal to $M_c/2$ [1].

Two approaches, swelling and mechanical measurements, are widely used to determine the degree of crosslink. When polymer is placed in a suitable solvent, the

polymer imbibes the solvent and undergoes swelling. At equilibrium, the swelling by a good solvent is given by

$$v = 1/M_c = \frac{V_p + \chi V_p^2 + \ln(1-V_p)}{d_r V_o (V_p/3 - V_p/2)} \quad (2.2)$$

where v is the effective number of moles of the crosslinked chain per gram of polymer, M_c is the molecular weight between crosslinks, V_p is the volume fraction of polymer in the swollen mass, V_o is the molar volume of solvent, χ is the polymer-solvent interaction parameter, and d_r is the density of the polymer.

The volume fraction of polymer in a swollen mass can be calculated from Equation (2.3), where d_s is the density of solvent.

$$V_p = \frac{1}{1+Q} \quad (2.3)$$

$$Q = \frac{\text{(weight of solvent in gel)} \times (d_r/d_s)}{\text{weight of gel}} \quad (2.4)$$

The stress strain curve of a polymer well above its glass transition or in the swollen stage can be also determined the crosslink density [1]. For a rubber, the force F required to stretch a specimen to an extension ratio α is given by

$$F = \frac{A_o d_r RT (\alpha - 1/\alpha^2)}{M_c} \quad (2.5)$$

where A_o is the cross-sectional area of the sample, and α is the ratio of the length of the stretched sample (L) to its original (L_o). Equation (2.5) is valid only for very small deformations. At the moderate extension, a modified expression, Equation (2.6) is applicable.

$$F = A_o (\alpha - 1/\alpha^2) (C_1 + C_2/2) \quad (2.6)$$

where C_1 and C_2 are constant.

The value of C_2 approaches to zero at high degree of swelling, therefore

$$F = \frac{A_0 d_r RT (\alpha - 1/\alpha^2) V_p^{1/3}}{M_c} \quad (2.7)$$

$$\tau = nRT(\alpha - 1/\alpha^2) V_p^{1/3} \quad (2.8)$$

where stress τ is equal to F/A_0 , n the crosslink density as number of crosslinks per unit volume, and V_p the volume fraction of polymer in the swollen sample.

Young's modulus E of a sample relates to Equation (2.8) as shown in Equation (2.9).

$$E = 3nRTV_p^{1/3} = nRT(L_0/L_s) \quad (2.9)$$

where L_0 is the length of the dry sample, and L_s is the length of sample at equilibrium swelling.

2.1.2 Effect of Crosslinking on Physical Properties [1]

Crosslinking changes and generally enhances physical properties usually above the glass-transition temperature. An uncrosslinked polymer at the elevated temperature may be viscous liquid incapable of sustaining a constant load, but a crosslinked polymer behaves as an elastic material, which can sustain a load. Creep, compression set, and stress relaxation are also improved on the crosslinking. Among the other properties, thermal expansion and heat capacity are lowered, and heat distortion temperature, tensile strength, and refractive index are raised. Glass-transition temperature also increases with increasing the crosslink density.

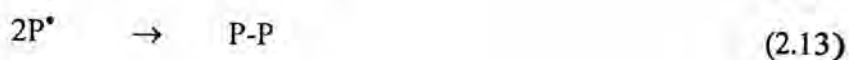
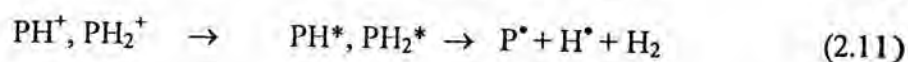
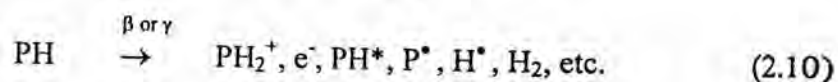
2.2 Crosslinking Processes of Polyolefins [2-5]

The three ways of crosslinking polyolefins are of great commercial interest. The first was the radiation process invented in the middle of the fifties. The second was the peroxide crosslinking process discovered a few year later. The third was silane crosslinking, being introduced in the late 1960s.

2.2.1 Radiation Crosslinking

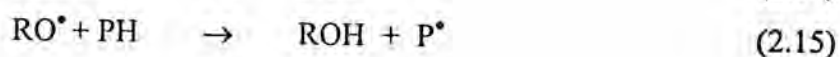
The radiation of crosslinking is achieved by means of explosion polymers to high energy ionizing radiation (β or γ radiation), which can be induced the free radical formation on polymer backbone. Coupling of the two polymer radicals establishes the crosslinking. The advantages of this method are among the followings, (a) decomposed products are not part of process; (b) the method is not chemically or physically complex; (c) finally it can be performed "on-line" subsequent to the polymer processing step by relatively quick procedure. However, there are several disadvantages for examples prevention of radiation damage cannot be avoid, and it cannot produce the thick section. The application of solid-state high-energy accelerators has reduced the price of high-energy accelerators , but investment cost is still considerable.

Its chemistry can be summarized as follows [3]



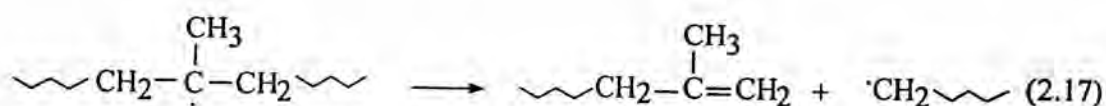
2.2.2 Peroxide Crosslinking

The polyethylene may be crosslinked using a various organic peroxide compounds (ROOR) as disclosed in many patents [7-11]. Upon certain temperature, it dissociates into radicals (RO[•]) which subsequently abstract hydrogen atoms from polymer chains to yield polymer radicals (P[•]). Combination of P[•] leads to the crosslinked polymer.

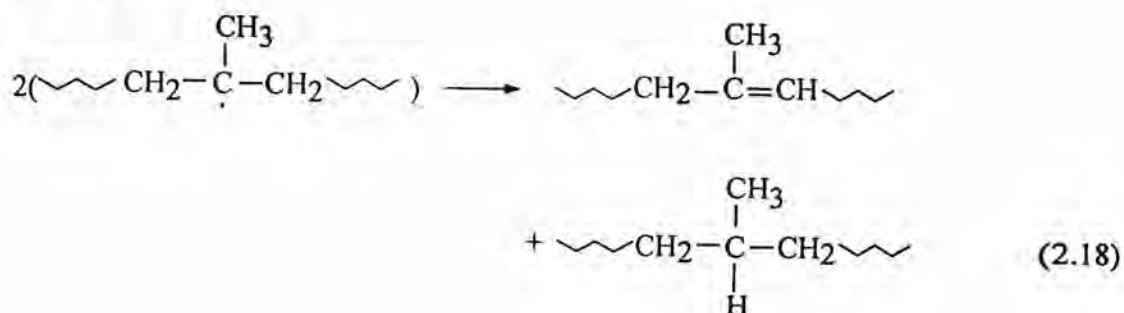


Moreover, the other side reactions of free radicals can take place resulting in the decrement of efficiency of crosslinking. These are chain cleavage (Eq. (2.17)), disproportionation (Eq. (2.18)), intermolecular recombination (Eq. (2.19)), and recombination with primary radicals (Eq. (2.20) and (2.21)). In addition, the primary radicals can continuously decomposed (see also Scheme 1.).

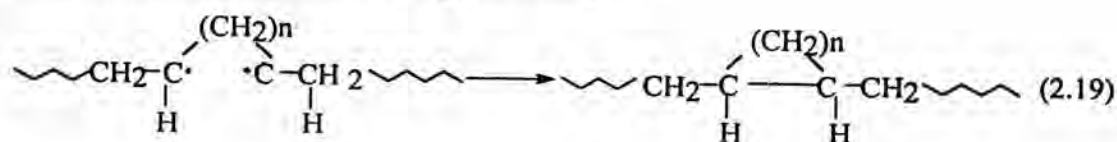
Chain cleavage :



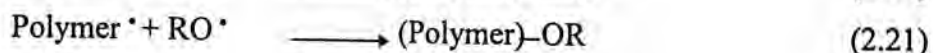
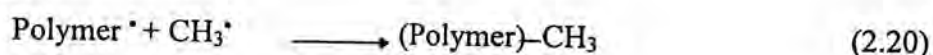
Disproportionation :



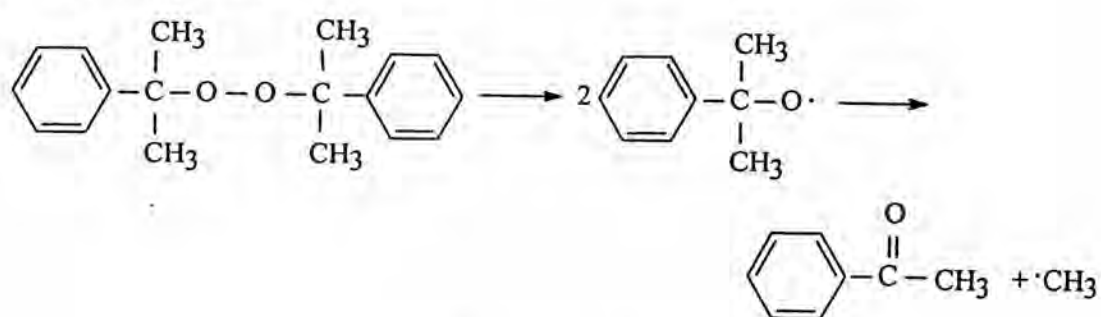
Intermolecular recombination (ring formation) :



Recombination :

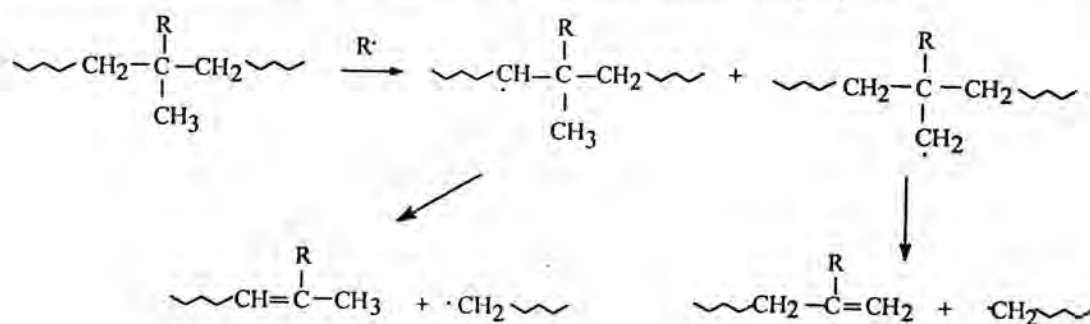


Peroxy decomposition :



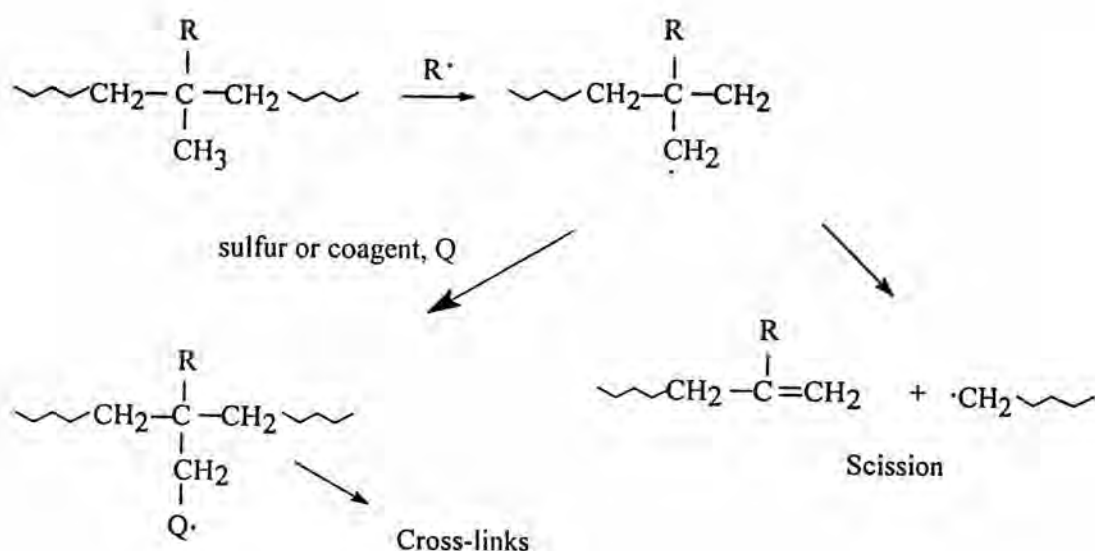
Scheme 1

Not only the side reactions mentioned above but also the branching of saturated hydrocarbon polymers reduce the efficiency of crosslinking. Let's the efficiency of crosslinking reaction of the linear polyethylene is assumed to be 1.0, saturated ethylene propylene rubber (EPR) has an efficiency of about 0.4, but butyl rubber cannot be cured at all [12]. Upon depletion of the peroxide compounds, branched polymers, however, undergo chain scission (Scheme 2), resulting in the reduction of the average molecular weight of the crosslinked polymer.



Scheme 2

The so-called coagent such as m-phenylenebismaleimide, sulfur, high-1,2 (high vinyl) polybutadiene, diallyl phthalate, ethylene duacrylate and triallyl cyanurate can be used to suppress the scission (Scheme 3). In addition to those coagents, especially, triallyl cyanurate and vinyl compounds have been used in making XLPE, as disclosed in patents [13,14].



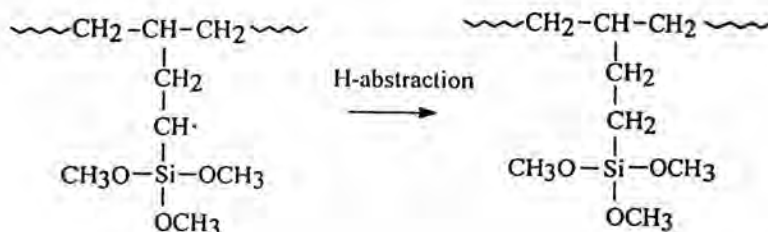
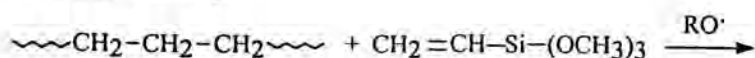
Scheme 3

2.2.3 Silane Crosslinking

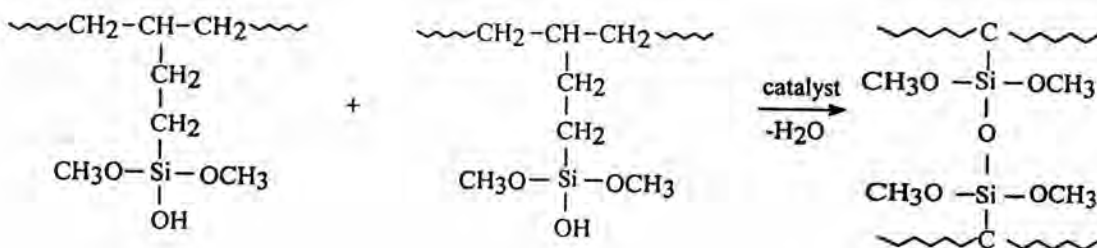
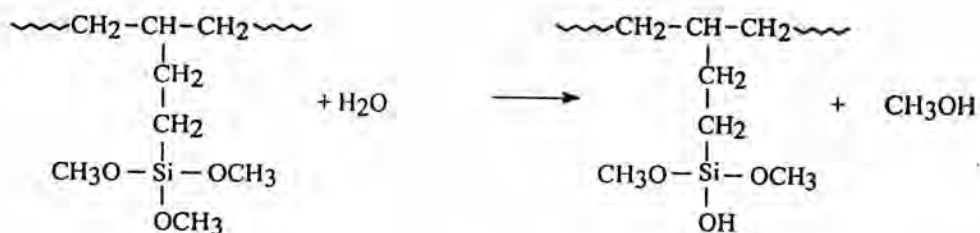
Uses of polymer grafted alkoxy-silanes, such as vinyltrimethoxy-silane via a peroxide induced grafting, are another useful compounded materials for preparation of the crosslinked polyethylene. The compound is exposed to a source of moisture, typically hot water or steam, resulting in the crosslinked polymer via Si-O-Si bond formation which is different from C-C linkages. An organotin compound, such as dibutyl- or dioctyl-tin dilaurate is added to promote the hydrolysis of polymer bound alkoxy-silane usually introduced in the form of polymer masterbatch. This process consists of two steps including the grafting and the crosslinking (see Scheme 4). The trade name of such the process is well known as the Sioplas[®] process. The hydrolysis

by-product is an alcohol, typically methanol, which must migrate out of the crosslinked polymer matrix in order to drive the reaction to complete. This indicates clearly that the rate of crosslinking depends on the rate of moisture penetrates into the polymer matrix. Thus, the thickness of final product is limited due to the hydrophobic nature of polymer.

Step 1 : Grafting



Step 2 : Crosslinking

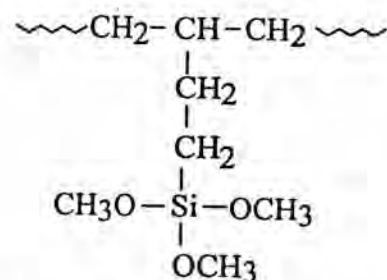
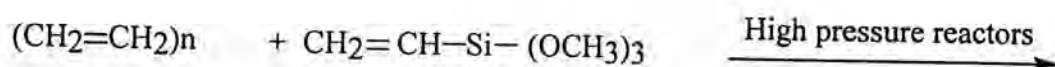


Scheme 4

The Monosil process discovered in 1974 is a one step version of the Sioplas process. Polyethylene, silane, peroxide and crosslinking catalyst are introduced

simultaneously directly in a specially made long extruder. The process is popular to fabricate cables or pipes.

In 1986, a new process of silane crosslinkable polymers was introduced [3]. Ethylene-vinylsilane copolymer was produced using high pressure reactor of LDPE production (Scheme 5). Crosslinkable terpolymers, by addition of, for the example, butylacrylate together with silane are also possible to produce.



Ethylene-Vinylsilane copolymer

Scheme 5

2.3 Major Compositions of the Peroxide Crosslinked Polyolefins

Typical main components in the peroxide crosslinked polyolefins are polyolefins, crosslinking agents, and additives such as inhibitors or antioxidants and crosslinking co-agents.

2.3.1 Polyolefins

Low density polyethylene (LDPE) has been widely used in a many applications, especially, in wire and cable. It is more amorphous, less crystalline structure, leading to less stiffness and better low temperature properties than high density polyethylene (HDPE) which is mostly used in hot-water pipe application.

Most LDPE contains up to 5% of ethylene vinyl acetate (EVA) for improved flexibility, low temperature properties and for allowing of higher filler loading with good mechanical properties. Linear low density polyethylene (LLDPE) has a similar structure to HDPE with more side branches and tougher, providing improved physical properties compared to the conventional LDPE, and more flexible and better impact resistance than HDPE. The requirement to reduce the quality of poly(vinyl chloride) (PVC) used in wire and cable results in a dramatic increase of the use of XLPE.

Crosslinked elastomers such as ethylene-propylene-diene copolymer (EPDM) and chlorinated polyethylene (CPE) are useful materials for making hose and for application in wire and cable. Fluoroelastomers are useful in steam/water and amine resistance applications. Polybutadiene uses in golf ball manufactured. They are all crosslinked or vulcanized or cured with peroxide [15].

2.3.2 Crosslinking Agents

Many organic peroxides are recommended to use for making XLPEs depending on types of used polymers. In order to avoid the decomposition of peroxide and precuring, the temperature during compounding must be lower than the peroxide decomposition temperature. For compounding of DCP with LDPE using the extrusion process, an acceptable compounding temperature should be between 120 and 130 °C. The other major peroxide, 2,5-dimethyl-2, 5- bis(t-butylperoxy)hexyne-3(DMTBH) can be compounded upto 150°C [16].

Since acetophenone is the major decomposition by-product from the decomposition of DCP. It is unpleasant odor and sometimes is totally unacceptable. α , α' -bis(t-butylperoxy)diisopropyl benzene is recommended to use instead [15].

2.3.3 Inhibitors or Antioxidants

The most crosslinked polyolefins should contain an antioxidant(s) to prevent the precuring during compounding. In addition, it improves not only the physical properties, especially the aging properties, but also the degradation by environment or

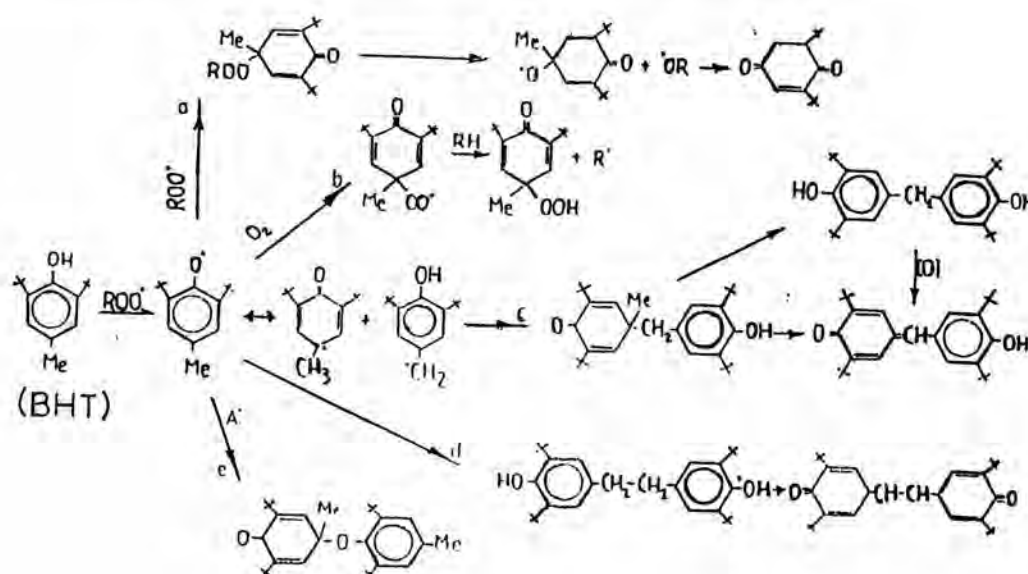
metal catalysis [17]. The modern theories of mechanisms of antioxidant action are divided into two classes [18].

2.3.3.1 Chain breaking antioxidant

The chain breaking antioxidant composes of three mechanisms.

A) Chain-breaking donor Mechanism (CB-D)

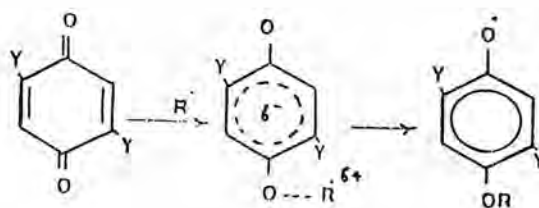
The most important commercial examples of these antioxidants are the hindered phenols, such as of 2,6-di-tert-butyl-4-methyl phenol (BHT), and aromatic amines, such as diphenyl amine. The reaction mechanism to show how BHT reacts with radical species and/or oxygen molecule is given in Scheme 6.



Scheme 6 Chemistry of oxidation of 2,6-di-tert-butyl-4-methyl phenol (BHT) [18].

B) Chain-breaking acceptor mechanism (CB-A)

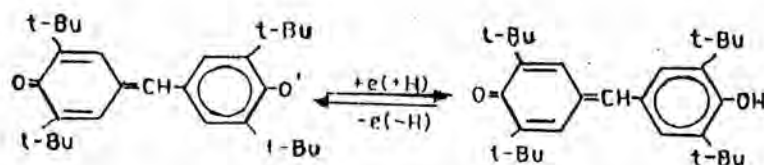
When polymers are exposed to UV light or sheared, the alkyl radicals (R^{\bullet}) can be formed. They can induced further degradation of polymer. The mechanism of this type of antioxidant inhibited the degradation is given in Scheme 7. The examples of these compounds are quinone compounds.



Scheme 7

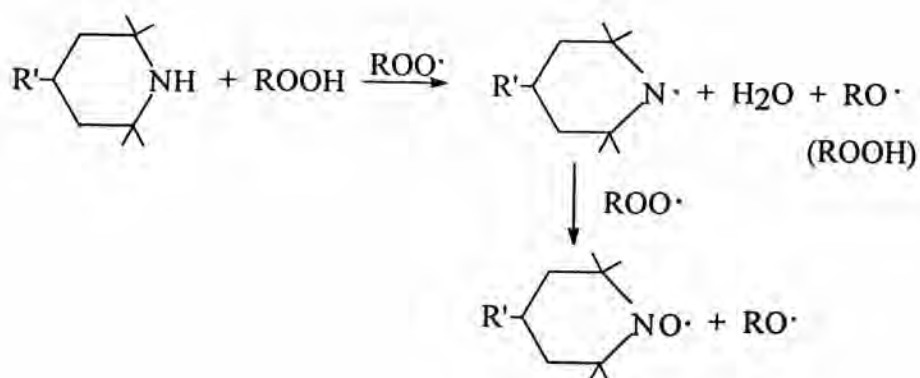
C) Catalytic (Redox) chain-breaking antioxidant

The mechanism of catalytic chain-breaking antioxidant for polyolefins is illustrated here using two recent examples. The first is the antioxidant that involves a cyclical regenerate reaction mechanism which also involves alternating CB-A and CB-D antioxidant steps (Scheme 8).



Scheme 8

The last example is the stable nitroxyl radicals derived from hindered piperidine light stabilizers of which the best known commercial compound is Tinuvin 770 (I). The mechanism of hindered piperidines shows in Scheme 9.



Scheme 9 Mechanism of hindered piperidines

2.3.3.2 Preventive Antioxidant

Peroxides are both thermally and photolytically unstable, giving rise to $\text{RO}\cdot$ or $\text{HO}\cdot$ radicals which react rapidly with hydrocarbon to give alkyl radicals. They can feed back into the main autooxidation cycle. Preventive antioxidants are the substances that react with peroxides not giving rise to free radical fragments of peroxide. In some way they stabilize the peroxide compounds for example by absorbing UV irradiation, or by deactivating transition metal ions preventing the reinitiation of the chain reaction. Two main types of preventive antioxidants are the phosphite ester, such as trialkyl phosphates, and sulfur containing compounds, such as thiodipropionate ester.

2.3.4 Additives

The most crosslinking polyolefins are compounded with additives such as slipping agent, antiblock, flame retardant, pigment, antistatic, scorch resistant and carbon black to improve properties of product both before and after crosslinking. Typical amount of the additives used in polyolefins will not affect on the final properties of XLPEs[2].

2.4 Kinetics of Crosslinking Reaction of Polyethylene in the Absence of an Inhibitor

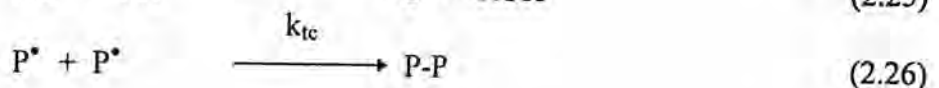
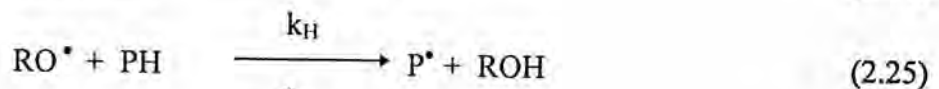
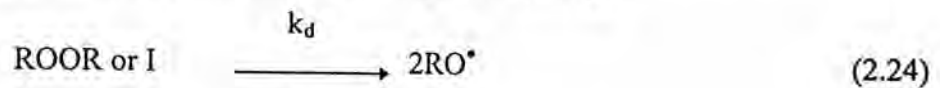
2.4.1 The Kinetics Mechanism

The mechanism of crosslinking reaction is similar to the radical polymerization composed of initiation, propagation and termination steps. The initiation involves the production of free radical species usually via homolytic cleavages of the initiator to produce a pair of primary radicals R^* (Equation (2.22)), and an addition of the radicals to the first monomer molecule to produce the chain initiating species, M^* (Equation (2.23)) [6].

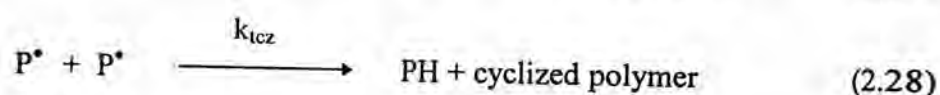
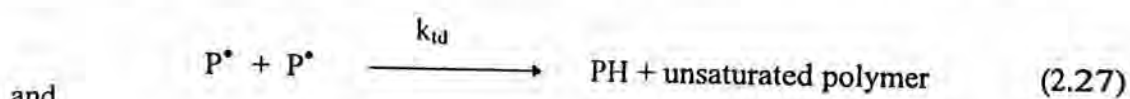


The polymer radicals grow by the addition of a large number of monomer molecules to the growing radicals, which is called the propagation step. They stop growing and terminate by an annihilation of radical centers occurring by the bimolecular combination of the radicals or by disproportionation, which hydrogen atom of one radical is transferred to other radicals to obtain saturated and unsaturated chain ends of the resulting polymers.

In case of the peroxide crosslinking reaction, the primary radicals RO^* are derived from the thermal cleavages of the peroxide initiator $ROOR$ (Equation (2.24)). Then they abstract hydrogen atoms from the polymer chains PH to produce polymer radicals (Equation (2.25)). Crosslinked polymers $P-P$ obtained by the coupling or combination of the two polymer radicals P^* (Equation (2.26)).



Side reactions other than the combination reaction may occur, for examples



2.4.2 The Kinetics Expression

Derivation of the kinetic expressions including the crosslinking rate and rate constants of the crosslinking reaction of polyethylene has not yet been found in details in any literatures. Attempts have been made here.

From Equation (2.24), the rate of appearance of primary radicals (R_d) by the thermal cleavages of ROOR is expressed as

$$R_d = \frac{d[RO^{\bullet}]}{dt} = -\frac{d[I]}{dt} = 2k_d[I] \quad (2.29)$$

where k_d is the initiator dissociation rate constant.

Integration of the above equation yields

$$[I] = [I]_0 e^{-k_d t} \quad (2.30)$$

where $[I]_0$ and $[I]$ is the concentration of initiator at the initial and at any time.

From Equation (2.25), the rate of primary radical consumption can be expressed as

$$R_H = k_{II} [RO^{\bullet}] [PH] \quad (2.31)$$

where k_H is the rate constant for Equation (2.25).

The rate (R_t) of polymer radicals consumption (Equations (2.26), (2.27) and (2.28)) can be expressed as

$$\begin{aligned} R_t &= R_{tc} + R_{td} + R_{tcz} \\ &= (k_{tc} + k_{td} + k_{tcz})[P^*]^2 \end{aligned} \quad (2.32)$$

where k_{tc} is the rate constant for termination by combination, k_{td} is the rate constant for termination by disproportionation, and k_{tcz} is the rate constant for termination by cyclization.

The steady state assumption is applied in that the rate of appearance of primary radicals is equal to the rate of generation of polymer radicals (or the rate of consumption of primary radicals), i.e., Equation (2.29) is equal to Equation (2.31).

$$2k_d[I] = k_H[RO^*][PH] \quad (2.33)$$

$$\text{or } [RO^*] = \frac{2k_d[I]}{k_H[PH]} \quad (2.34)$$

It is the fact that every mole of initiator dissociation does not produce two polymer radicals. Thus, Equation (2.34) can be rewritten as

$$[RO^*] = \frac{fk_d[I]}{k_H[PH]} \quad (2.35)$$

where f is the initiator efficiency defined as the mole fraction of the primary radicals that abstract hydrogen atom from polymer chains. The value of f is less than unity due to (a) the side reactions of those radicals with other species rather than the polymer chain and (b) self decomposition, especially for DCP, acetophenone is the compound produced from such the reaction.

Also according to the steady state assumption, the concentration of radicals increases initially, but almost instantaneously reaches a constant. The rate of radicals

concentration changes quickly, then become and remain zero thoroughly during the reaction taking place. This means that R_H and R_t are equivalent, i.e.,

$$R_H = R_t \quad (2.36)$$

Substitutions of $[RO^*]$ and R_t (Equations (2.35) and (2.32)) into Equation (2.36), one obtains

$$[P^*]^2 = \frac{2fk_d[I]}{k_{tc}+k_{td}+k_{tcz}} \quad (2.37)$$

The crosslinking polymers achieve only by the combination, therefore, rate of combination reaction (R_{tc}) is the rate of crosslinking reaction (R_x) which can be written as

$$R_x = k_{tc}[P^*]^2 \quad (2.38)$$

Substitution of Equation (2.37) yields

$$R_x = \frac{k_{tc} 2fk_d[I]}{k_{tc}+k_{td}+k_{tcz}} \quad (2.39)$$

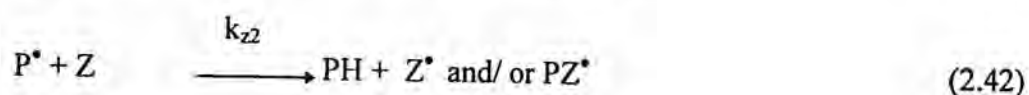
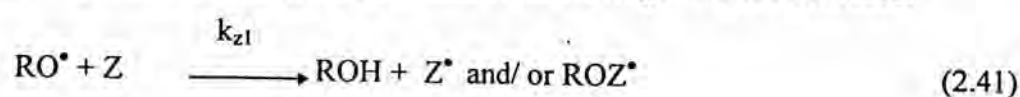
Let's k_x is the overall rate constant for the crosslinking reaction in the absence of inhibitor and is equal to $2fk_{tc}k_d / (k_{tc}+k_{td}+k_{tcz})$. Then Equation (2.42) is simplified to be

$$R_x = k_x [I] \quad (2.40)$$

The rate of crosslinking is proportional to initiator power of 1 and independent upon the polymer concentration.

2.5 Kinetics of Crosslinking Reaction of Polyethylene in the Presence of an Inhibition

The kinetic mechanism of crosslinking reaction in the presence of an inhibitor Z is as same as that aforementioned except the additional reactions of radical species with the inhibitor in the mechanism. The major radical species including RO^* and P^* is accounted in the inhibition reactions (Equations (2.41) and (2.42)) but the others such as the decomposition of RO^* giving radicals of the its fragments are excluded.



where k_{z1} and k_{z2} are respectively the rate constants for the inhibition reaction of RO^* and P^* .

The inhibitor may add to the radicals to form PZ^* and ROZ^* . The other possible reaction is that the hydrogen atom of the inhibitor may be transferred to the radicals to yield PH or ROH. PZ^* and ROZ^* , which are inactive radical species. According to the steady state assumption, the changes of concentration of all of the radicals are always equal to zero, i.e.,

$$\frac{d[RO^*]}{dt} = R_d - R_H - R_t - R_{z1} - R_{z2} = 0 \quad (2.43)$$

where R_{z1} and R_{z2} are respectively the rates of inhibition reactions of Equations (2.41) and (2.42), which are equal to

$$R_{z1} = k_{z1} [RO^*][Z] \quad (2.44)$$

$$R_{z2} = k_{z2} [P^*][Z] \quad (2.45)$$

Substitution of Equations (2.31), (2.44) and (2.45) into (2.43), one obtains

$$R_d - k_H[RO^\bullet][PH] - R_t - k_{z1}[RO^\bullet][Z] - k_{z2}[P^\bullet][Z] = 0 \quad (2.46)$$

In the case of using a high efficiency inhibitor, the hydrogen abstraction and bimolecular termination reactions can be negligible, so that Equation (2.46) can be rewritten as

$$R_d = k_z[RO^\bullet][Z] \quad (2.47)$$

Substitution of the left-hand-side of Equation (2.47) by $2fk_d[I]$ with minor rearrangement, one obtains

$$[RO^\bullet] = \frac{2fk_d[I]}{k_z[Z]} \quad (2.48)$$

Application of the steady state assumption and substitution of Equations (2.31), (2.32) and (2.48) into Equation (2.36), one obtains

$$[P^\bullet]^2 = \frac{2fk_d k_H [I][PH]}{(k_{tc} + k_{td} + k_{tcz}) (k_z[Z])} \quad (2.49)$$

Substitution of Equation (2.49) into the rate of crosslinking reaction in the presence of inhibitor R_x' , which is similar to Equation (2.38)), one obtains

$$R_x' = \frac{2fk_d k_H [I][PH]}{(k_{tc} + k_{td} + k_{tcz}) (k_z[Z])} \quad (2.50)$$

or

$$R_x' = k_{xz} [I] [PH] [Z] \quad (2.51)$$

where k_{xz} = Overall rate constant in the presence of the inhibitor which is equal to Equation (2.52)

$$k_{xz} = \frac{2fk_d k_H}{(k_{tc} + k_{td} + k_{tcz}) k_z} \quad (2.52)$$

2.6 Literature Reviews

There have been many studies on the kinetics of crosslinking reaction of polyethylene using mostly the rheometric technique. While the technique of calorimetry have not been found to be used. Literature relevant to this study have been reviewed.

Vandump, J., and Oosterwijk, H. H. J. [19] studied the kinetics and mechanism of the thermal reaction between tert-butyl perbenzoate and n-alkanes using Monsanto rheometer under the conditions as closed as possible to those during actual crosslinking of polyethylene. Product analysis allowed a description of the fate of 90 to 95% of peroxide fragments. Approximately 50 to 60% substrate radicals formed upon hydrogen abstraction which were found to combine and give the crosslinks, whereas about 30% showed disproportionation, thus leading to substrate unsaturation. The two competitive reactions account for 85-90% of the generated substrate radicals. The model system provides a simple and convenient method for comparing the crosslink efficiencies of peroxides. There were some data reported for some commercial peroxides. In order to facilitate an extrapolation of the results in liquid alkanes towards solid polyethylene PE, the influence of substrate viscosity and temperature on the peroxide decomposition rate, product distribution, and crosslink efficiency were studied. In n-alkanes peroxide decomposition follows the first order kinetics well, with an Arrhenius activation energy of 32.9 ± 0.5 kcal/mol. In addition, the kinetics in the model system were compared with those calculated from Rheometer measurements on the curing of unfilled PE and ethylene propylene dicyclopentadiene terpolymer (EPDM). Only minor differences in the peroxide decomposition rate and the overall activation energy were found.

Sen, A. K., Bhattacharyya, A. S., De, P. P., and Bhowmick, A. K. [20] studied the effect of blend ratio and peroxide concentration on the crosslinking characteristics of EPDM-PE blends using Differential Scanning Calorimetry, Brabender Plasticorder

and Rheometer. Crosslinking of EPDM-PE blends followed the first order reaction kinetics. The curing exotherm increased but the activation energy decreased with the increase in EPDM content in the blends. The same increased, however, with the increase in concentration of dicumyl peroxide upto a certain level; the activation energy was almost independent upon the peroxide concentration. The cure rate increased whereas the optimum cure time and the energy consumption for curing decreased with the increase in the ratio of EPDM-PE. A method for determination of the crosslinking efficiency in the case of the blend system was developed from high temperature modulus to predict the properties and the curing behavior of the blends.

Phillips, P. Y., Kao, Y. H. and Gohil, R. M. [21-24] studied the crystallinity in chemically crosslinked low density polyethylene which concerned to its structure, crystallization kinetics, and morphology. The presence of crosslinks distorted the crystal structure of PE. Dicumyl peroxide served as a nucleating agent for polyethylene. The crystallinity and melting temperature of polyethylene decreased with the increase of peroxide amounts. Electron microscopy studies of the crosslinked polyethylene showed that with the increase of the crosslinking conventional superstructure, their nucleation density and the nature of lamellae were greatly modified. With the increase of the crosslinking, the growth of spherulites was suppressed producing sheaves and ultimately bundles of lamellae. Lamellae organization prevailed at all levels of crosslinking studied. Crosslinks exert a profound effect on the nature of the nucleation process as well as on the nucleation density; it was mainly heterogeneous in nature. The growth features indicated the presence of orientation effects, similar to those induced by externally applied stress, at high crosslink levels and temperature. The values of the Avrami exponent obtained from kinetics studies were correlated with the observed morphologies. An increasing resistant to attack by etchant on the crosslinked polyethylene samples was attributed to the growth of compact bundled of lamellae as well as to the crosslink themselves. The major causes of multiple melting peaks observed at low and high temperatures were due to (a) considerable changes in the interfacial structure of

lamellae crystals and the interlamellar materials, and (b) reorganization of lamellae crystal as well as the presence of compact bundles of lamellae.

Dainichi-Nippon Cables Ltd. [25] reported that the chemically crosslinked polyethylene had unique characteristics among the crosslinked polymers used industrially. First, the number average molecular weight before the crosslinking was very small; second, an appreciable amount of soluble was contained in its crosslinked state. In order to obtain precise values of the crosslink density in such the material, a new proposed equation developed was based on the Flory-Rehner equation, but the number average molecular weight of polymer prior to crosslinking was modified in the terms of soluble fraction. The new equation was proved to give reliable values over a wide ranges of crosslink density. The rate of crosslinking of polyethylene with DCP is first order reaction controlled by the rate of thermal decomposition of peroxide.

Takanori, Y., and Tadao, S. [26] studied the chemically crosslinking reaction mechanism of polyethylene using electron spin resonance (ESR) with DCP at high temperature between 145 and 180°C. The crosslinking reactions were induced by the alkyl radicals formed by the thermal decomposition of DCP above 120°C.

Shuji, S., Hideyo, W., Yasumasa, W., and Tomoyuki, N. [27-28] studied the crosslinking reactions of LDPE, HDPE, and ethylene propylene rubber with DCP in the presence of 2, 4-diphenyl-4-methyl-1-pentene (alpha-methylstyrene; MSD). The scorch time was found increase at 145°C as well as the crosslinking efficiency at 180°C. The scorch inhibition mechanism was explained by the addition-fragmentation reaction between MSD and the polymer radical. In addition, the model reaction for crosslinking of polyethylene in the same condition said earlier was carried out using n-undecane instead of PE using di-t-butyl peroxides as initiator at 140°C. Undecyl radicals produced by the hydrogen abstraction by peroxide radical from n-undecane effectively added to the double bond of MSD to form adduct radicals, which then underwent fragmentation to give olefins and cumyl radicals. The concentration of olefins initially increased, but decreased through a maximum. It was found that the

olefins are intermediate products which further reacted with undecyl radicals, resulting in the formation of compounds with two or three undecyl groups.

Kim, K. J., Ok, Y. S., and Kim, B. K. [29] investigated the crosslinking of HDPE done in situ using twin screw extruder at 230°C with 1, 3-bis (t-butyl-peroxy-isopropyl)benzene and coagent pentaerythritol triacrylate (PETA), triallyl isocyanurate (TAIC), alone or together. Crosslinking was obtained with PETA alone as well as peroxide, but not with TAIC alone. When TAIC or PETA was used in combination with peroxide, a synergistic reduction in the melt index and an increase in modulus and impact strength were obtained. The most significant improvement from peroxide of PETA treatment was the impact strength, which was increased over fivefold with 0.1 phr peroxide, and over sevenfold with 0.2 phr PETA.

Crouzet, C., Jang, B. Y., and Marchal, J. [30] studied the crosslinking of HDPE induced by the thermolysis of cyclic perketal by evolved gas analysis (EGA). The kinetics of 18 products had been established. The formation of these products led to a material balance which accounted for 97% of the thermolyzed peroxide. The yield of alkyl macroradicals useful for crosslinking reaction had been deduced from a material balance. The efficiency of crosslinking was half a crosslink induced by the perketal molecule. The lack of perturbation in first order kinetics provided for the rapid determination of crosslinking yield by measuring the concentration of a gas evolved during the reaction.

Hulse, G., Kersting, J. R., and Warfel, D. R. [31], studied the chemistry of dicumyl peroxide- induced crosslinking of linear polyethylene and low molecular weight alkane. The efficiency of intermolecular coupling was 40% for an alkane and 25-30% for the polymer system. Competing reactions, which reduce coupling efficiency, were mainly disproportionation of the initially formed radicals and to a minor extent further reactions involving the products from the peroxide decomposition. The low efficiencies found were similar to the studies of the initial radicals which were produced by radiolysis in polymer and alkane systems.

Chodak, I., and Rado, R. [32] investigated the possibility of the utilization of the bimolecular cumyl hydroperoxide redox decomposition catalyzed by Co (II) naphthenate for the polymer crosslinking. The study of the mechanism and the kinetics of this reaction was performed both in a model medium heptane and polymer or polymer solution. In the case of the redox initiation, the value of the crosslinking efficiency was found to be about 0.4. It could be attributed mainly to the formation of ions and, partly, to recombination of peroxy radical producing dialkyl peroxide.