

## **CHAPTER II**

### **LITERATURE REVIEW**

#### **2.1 Antioxidants**

Virtually all polymeric materials, both of synthetic or natural origin, undergo reactions with oxygen. Technically it is important to distinguish whether such oxidation reactions are taking place as purely thermal processes at usually elevated temperatures, or with the assistance of light (mainly ultraviolet). Oxidation can manifest itself in every stage of the life cycle of a polymer, i.e. during manufacturing and storage of the material, or during processing and use.

Plastics are very different from each other as far as their inherent resistance to oxidation is concerned. As examples, polystyrene and polymethyl methacrylate are quite stable, also at normal processing temperatures. Highly unsaturated polymers are much more sensitive to oxidation. Differences in stability against oxidation may arise not only from the broad variety of chemical structures of polymers, but within a given polymer type, also from differences in the manufacturing process (nature and amount of catalyst residues) and in morphology (crystallinity, orientation).

The typical manifestations of oxidation are summarized by the term aging phenomena and are very dependent on the polymer type and its use. On the one hand, the manifestations of oxidation concern polymer, e.g. discoloration (yellowing), loss of gloss or transparency, chalking and surface cracks. On the other hand, there occurs more or less simultaneously a loss of mechanical properties such as impact strength, elongation, and tensile strength. With ongoing aging, the characteristics of a plastics article are modified in such a way that it loses its usefulness.

Fundamentally, there are various means available to retard thermal oxidation (methods of stabilization):

- Structural modification of the polymer, e.g. by copolymerization with vinyl groups containing antioxidants. For this concept, Gugumus (1997) was studied the effect of type of HDPE, Ziegler-type (Ti catalyst) and Phillips-type (Cr catalyst). The results derived that Ziegler-type has more thermal oxidation resistivity than Phillips-type.

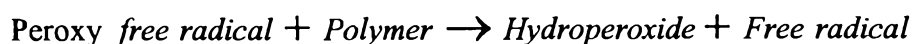
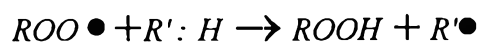
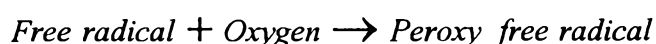
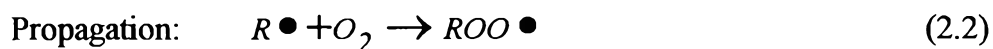
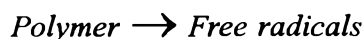
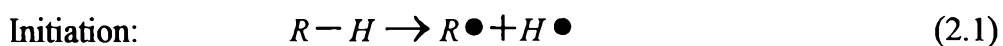
- capping of the endgroups; this procedure is common mainly for polyacetals,

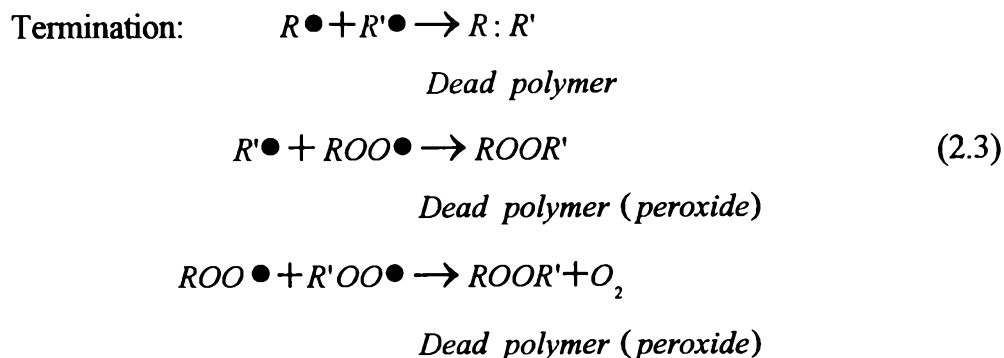
- physical stabilization by orientation of the polymer (stretching), addition of stabilizing additives : antioxidants, stabilizer.

However, this research was concentrated on physical stabilization (addition of antioxidants). The mechanisms of degradation are now clearly known.

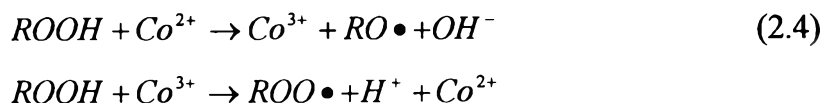
## 2.2 Degradation Mechanism

Polymers such as PE are not usable outdoors without appropriate stabilizer because of the presence of readily removable hydrogen atoms on the tertiary carbon atoms. PE and many other polymers (RH) are attacked during processing or outdoor use in the absence of stabilizers because of a chain degradation reaction, as shown in the following equations:



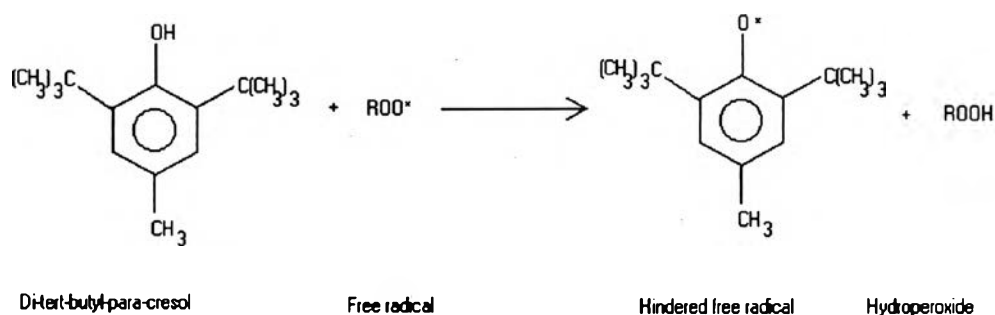


The rate of the free-radical chain reactions shown above is accelerated by the presence of heavy metals such as cobalt(II) ions or the others transition metal, depend on selected catalyst of polymerization, as shown in (2.4)



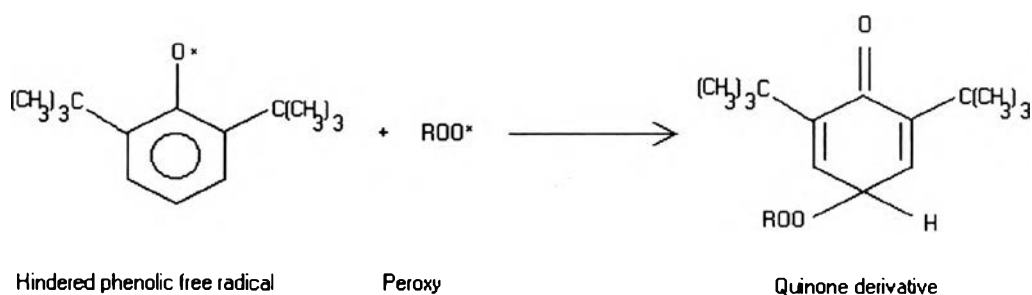
As the equation above, catalytic degradation, Park *et al.* (1999) was investigated the catalytic degradation of polyethylene in a fixed-bed reactor composed of a melter and a catalytic cracking bed. Compared with those obtained by thermal degradation, the catalytic degradation products are distributed in a narrow range of carbon numbers. In contrast, the rate of chain-reaction degradation is inhibited by the presence of small amounts of antioxidants. The first synthetic antioxidants were synthesized independently by Caldwell and by Winkelman and Gray by the condensation of aromatic amines with aliphatic aldehydes. While unpurified commercial products such as phenyl- $\beta$ -naphthylamine are toxic, they are still used as antioxidants for rubber tires.

Many naturally occurring antioxidants are derivatives of phenol and hindered phenols, such as di-tert-butyl-para-cresol. As shown by Figure 2.1, the antioxidant acts as a chain-transfer agent to produce a dead polymer and a stable free radical that does not initiate further chain-radical degradation.



**Figure 2.1** Stabilized free radical by Di-tert-butyl-para-cresol.

However, the phenoxy free radical may react with other free radicals to produce a quinone derivative. Derivative of quinone can generate color in polymer as show in Figure 2.2.



**Figure 2.2** Quinone derivative generated by free radical inhibiting reaction.

Chemical reaction of antioxidant, rheological properties and discolouration are also important for testing of antioxidants as presented in Epacher *et al.* (1999a) research work. They showed that the reactions of hindered phenolic antioxidant which possibly took place in the melt HDPE, including discolouration, stabilizer consumption, change of rheological and mechanical properties seem to be proportional to each other. Stabilizer consumption leads to colour development and made the changes in the vinyl content of the HDPE which seems to be responsible for the decrease of melt flow index values.

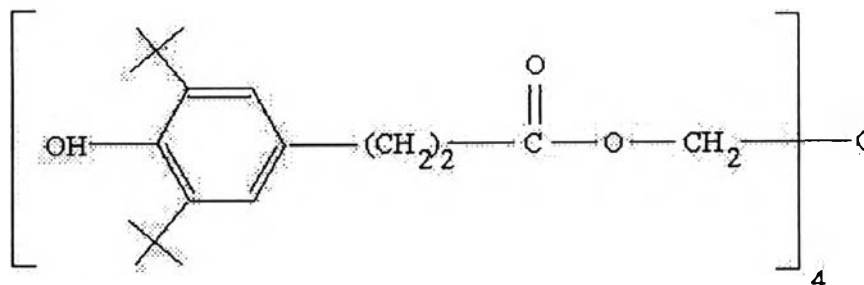
## 2.3 Types of Antioxidant

Generally, antioxidants are divided into two types.

### 2.3.1 Primary Antioxidants

Primary antioxidants react rapidly with peroxy radicals and are termed 'radical scavengers'. Chain breakers are mainly sterically hindered phenols (the most important) and secondary aromatic amines. The main hindered phenolic antioxidant is butylated hydroxy toluene (BHT), commonly used in polyolefins, styrenes and vinyl polymers.

As primary antioxidant, hindered phenolic antioxidants are high molecular weight materials, suitable for polymer systems sensitive to thermal and oxidative degradation that produce free radicals and peroxides. They give protection against degradation at high processing temperatures and are highly efficient, of low volatility, non-staining and have wide toxicological clearance. The efficiency can be enhanced by using with other antioxidants such as phosphites and thioesters, producing synergistic effects for effective and economical formulations. They are normally available as free-flowing powders, but 50% aqueous dispersions are also available. Although many degradation reaction is occurred in polymer, antioxidant is effective at very low dosages (0.01-0.1%) in low and high-density polyethylene (especially carbon black-filled grades for pipe and copper cable insulation). For this work phenolic primary antioxidant were employed for processing and long term thermal stabilization. It is highly effective, non discoloring stabilizer for plastics, protects substrates against thermo-oxidative degradation. Chemical structure of phenolic antioxidant is presented in Figure 2.3.

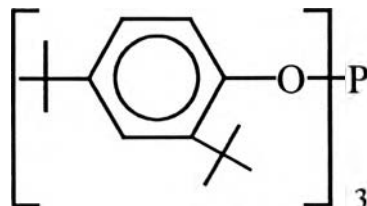


**Figure 2.3** Chemical structure of primary phenolic antioxidant.

### 2.3.2 Secondary Antioxidants

Secondary antioxidants react with hydroperoxides (ROOH) to produce non-radical products and are often termed 'hydroperoxide decomposers'. Peroxide-decomposing antioxidants are normally used as secondary additives, differing from primary phenols and amines in that they are decomposed by reaction with hydroperoxide, rather than containing it. They are particularly useful in synergistic combinations with primary antioxidants.

Phosphite/phosponites are the most effective stabilisers during processing, protecting both polymer and primary antioxidants. Hydrolytically stable phosphites are the most frequently-used processing stabiliser in high-performance additive systems. Figure 2.4 gives the chemical structure of secondary antioxidant used in this study



**Figure 2.4** Chemical structure of secondary antioxidant.

However, antioxidant technology still develops to get the better stability properties (Johnson, 1999). A new series of antioxidant from Ciba

Specialty Chemical Corp. was introduced as processing stabilisers. It is the Irgastab FS stabilizer, which reportedly provides good thermal and process stability. Furthermore, to earn excellent color stability. In this system, a hindered amine light stabilizer is used instead of a hindered phenolic thermal stabilizer such as Irganox 1010 and Reonox 10, and is combined with a secondary antioxidant dialkylhydroxylamine, which acts as a peroxide de-composer, radical scavenger, and reducing agent. For this work secondary antioxidants were Irgfos 168 and Reonox 68.

Instead using of only primary or secondary antioxidant, It was used to compound together at proper ratio of primary antioxidant to secondary antioxidant to get synergistic effects.

## 2.4 Synergism and Antagonism

Most stabilisers for polymers contain a combination of antioxidants acting by different mechanisms and normally complementary. The antioxidant, which destroys hydroperoxides (e.g. Irgafos 168 or Reonox 68), thereby reducing the concentration of radicals in equation (2), will in consequence slow down the destruction of a chain-breaking antioxidant. By the same token, an effective chain-breaking antioxidant reduces the amount of hydroperoxide formed in an autoxidising system and hence protects a peroxide decomposer. This co-operative interaction, which is commonly called synergism, leads to an overall antioxidant effect which is greater than the sum of the individual effects and very often to an effectiveness much greater than can be achieved by either antioxidants alone even at much higher concentrations Figure 2.5. The phenomenon is therefore of considerable practical and theoretical significance.

Occasionally the reverse phenomenon is observed, that is, two antioxidants interact to decrease the sum of their individual effects. This is described as antagonism, (Figure 2.5).

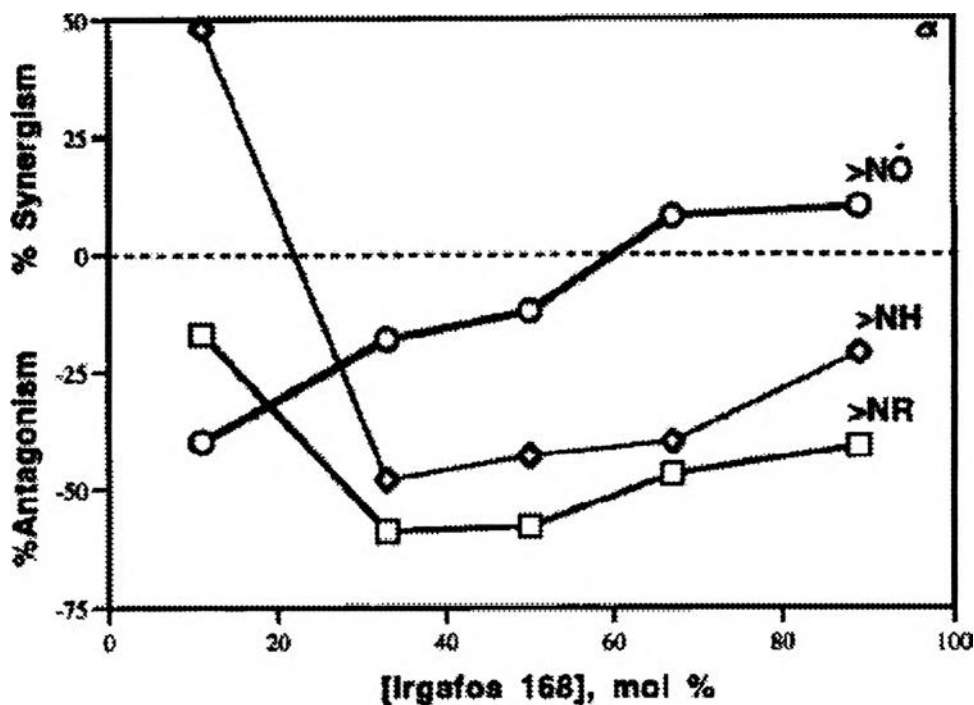


Figure 2.5 Synergistic and antagonistic effect of interaction between primary and secondary antioxidants.

Many research work were carried out to study the synergistic effect. Liauw *et al.* (1999) studied the effect of interactions between stabilisers and silica used. They observed that under thermooxidation of polyolefin film, combination of Irganox 1010 with a polymeric hindered amine light stabilisers (HALS)(Chimassorb 944) gave stronger synergism effect when silica was presented. Not only study synergism or antagonism effect of thermo-oxidative antioxidant was carried out but photo-oxidative antioxidants are also studied as Bauer *et al.* (1997) work. They found that, when increasing the amount of secondary antioxidants Irgafos 168 in polypropylene mixture, the extent of antagonism was decreased.



## 2.5 Testing of Antioxidants

The most relevant tests for antioxidant performance consist of measurements of key properties under storage, processing or using conditions. In this respect, simulation of processing by single or multiple extrusion, injection molding. However, tests for polymer behavior during storage and use is often tedious and very time consuming. It could take several years to determine the long-term stability of a plastic at ambient temperatures. For these reasons, various accelerated test methods was developed with the main goal to reduce testing time. This is achieved by increasing the test temperature, reducing sample thickness or by testing in pure oxygen at atmospheric conditions. These tests may be performed with actual plastics (preferred) as well as with model compounds or model systems.

### 2.5.1 Testing With Model Systems

Fundamental experimentation with model compounds has been used widely. Rather often the method used consists of following the oxidation kinetics of low molecular weight analogs of polymers and to determine the influence of added antioxidants. Model compounds that have been used are;

- ethylene dibenzoate, diethylene glycol dibenzoate and 2-hydroxyethyl benzoate for saturated polyesters,
- low molecular weight amides for polyamides,
- branched, low molecular weight hydrocarbons for polyolefins,
- cumene, tetralin or decalin because their oxidation to the corresponding hydroperoxides and products of further reaction can be easily followed.

Another test method used consists of examining the reaction of antioxidants with well-defined hydroperoxides or peroxy radicals  $RO_2^*$ . Cumene hydroperoxide is very often used for this purpose. By homolysis of compounds

yielding carbon-centered radicals in the presence of oxygen it is possible to generate peroxy radicals in the system. Günter *et al.* (1996) used model hydroperoxide to investigate the effect of sulphurous acid esters as secondary antioxidants, the reactions of sulphites with cumene hydroperoxide (CHP), tert-butyl hydroperoxide (TBHP) and  $\alpha$ -tetralyl hydroperoxide ( $\alpha$ -THP). They found that all sulphites investigated decompose hydroperoxides in a nonradical way. For quantitative determination of the effectiveness of antioxidants, measurement of oxygen uptake remains an important method. It is performed with liquid model compounds or model compounds in solution or with the polymer as such. For this research work is not concern about model systems test.

### 2.5.2 Practical Testing

This work is mainly concentrated on ageing test, thermal stability test, and thermooxidative stability test. There are numerous methods of assessing thermooxidative stability of plastics. Among the preferred ones are different thermo analytical techniques such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). These methods have a big advantage of yielding data in a very short time.

Effect of type of polymer, effect of molecular weight and effect of catalyst residue are significantly important. Allen *et al.* (2000) studied the thermal and photooxidative behavior of three non-additive polyethylenes, HDPE, LLDPE and a metallocene grade material. The polyethylene samples were examine by thermal methods (DSC, TGA), FTIR analysis, derivative UV and luminescence spectroscopic techniques. They found that the vinyl types and concentrations reflect the thermal stability of the polymer materials but differences in catalyst residues did not show any significantly effect. The differences in the light stability of the polymers with the metallocene exhibiting the greatest intensity and least stability followed by HDPE and LLDPE. For thermal decomposition, the lowest was LLDPE exhibits, the higher HDPE, while the metallocene the highest.

One purpose of adding additive and stabilizers into polymer is to extend product lifetime. So post-use polyethylene must have a good thermal degradation resistance and oxidative degradation resistance. Kyriakou *et al.* (1999), studied the oxidative induction time method based on thermogravimetric analysis for monitoring the restabilization of post-use LDPE. Recyclostab 421 antioxidant (phenolic and organophosphite mixture) from Ciba Geigy Ltd. was used in the work. Oxidative induction time values of restabilized samples were higher than non-restabilized samples at every remelting cycle.

To test the performance of antioxidants in polymer, as mentioned above, accelerated aging in ovens at relatively high temperature, but generally below the polymer melting point, in circulating medium, is one of the most widely used test methods (e.g. DIN 53383 part 1, ISO 4577-1983). In this technique, the test criteria include spectroscopic data such as carbonyl (e.g. DIN 53383 part 2) or hydroxy group concentrations obtained by IR spectroscopy, discoloration measured by colorimetry and mechanical characteristics such as impact strength, elongation and tensile strength. The oven aging technique resembles conditions encountered in service much more closely than the preceding ones. It is the method of choice where time allows assessing the performance of antioxidants under conditions of actual use or during storage.

As mentioned above the effects of the environmental mediums are taken effect on polymer degradation. Dörner and Lang (1998a and 1998b) were studied the effect of various stabilizer systems on the ageing behavior of medium density polyethylene (MDHD or PE-MD) in hot water compare to air, 95°C of compression molded plaques. The results shown that, oxidative induction time values (OIT) of MDPE samples which under went ageing in air is higher than oxidative induction time values of MDPE samples which under went ageing in water.

The performance of antioxidants in polymer processing some times was tested in the polymer melt. It is best assessed by multiple extrusions, film

blowing or injection molding. According to Epacher *et al.* (1999b) as presented above (1999a), they studied processing history by multiple extrusion that affected on rheology of HDPE sample, the results showed that the increasing of processing history, decreasing of MFI. Although some thermal analytical methods such as DTA/DSC may give useful indications concerning performance, the most important polymer characteristics to be observed under these conditions are changes in melt flow index or melt flow (DIN 53735, ISOP 1133-1981, ASTM D 1238-88) and possible discoloration (e.g. yellowness index according to ASTM D 1925-70).

## **2.6 Objectives**

1. To study the effect of antioxidants on extrusion grades HDPE.
2. To study the effect of the ratio of primary and secondary antioxidants on the stability of HDPE.
3. To study the effect of temperature and shear during processing on the thermo-mechanical stability of HDPE
4. To determine the most economically and cost-effectively antioxidants From different producers.

## **2.7 Statement of Problems**

1. How does the processing history affect the virgin HDPE and stabilized HDPE sample
2. How do the antioxidants at various ratios affect on the mechanical properties, rheology property and change in functional group before and after ageing in circulating hot air oven.
3. Which is the ratio of antioxidants, that having a good anti-thermal degradation and having good process stability.