Concentration Effects in Polymer-bound Antioxidants

by
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SUMMARY

CONCENTRATION EFFECTS IN POLYMER-BOUND ANTIOXIDANTS

The reaction of acrylic-containing antioxidants with polypropylene has been studied. 2,2,6,6-tertmethyl-4-piperidylacrylate (AOTP), 2-hydroxy-4-(2'-acryloyloxy)ethyloxylbenzophone (HEAB) and 3,5-di-tertbutyl-4- hydroxylbenzlacrylate (DBBA) were bound successfully in polypropylene (PP) in the presence of a peroxide (Triganox101) and a polyfunctional agent (Tris) during melt processing.

Concentrates of polymer-bound AOTP, HEAB and DBBA were used as masterbatch additives in unstabilised PP for studies of concentration effects in polymer-bound antioxidant systems on thermal and photostabilisation of PP. Bound AOTP was found to be an effective photo- stabiliser and its efficiency increased almost linearly with an increase in concentration up to 3.0% (w/w in PP). However, further increase in concentration of bound AOTP did not affect photostabilisation of PP in spite of the fact that no physical loss occured during UV aging. In a thermal air circulating oven aging at 140°C, the parent bound AOTP itself was not an effective thermal stabiliser. However, bound AOTP oxidised by m-chloroperbenzoic acid was found to be effective for inhibiting thermal oxidation of PP film and its efficiency was proportional to its concentration. This confirms that the oxidised piperidine is not only a photostabiliser but also a thermal antioxidant.

In this work attempts have also been made to investigate the effects of these bound antioxidants in two or three component synergistic systems and to study mechanism of antioxidant action of nitroxyl radical containing a hindered phenol in model systems. The implication of these results for the theories of antioxidant behaviour in PP is discussed.

Key Words:
Polymer-bound antioxidant
Masterbatch
Photostabilisation
Thermal stabilisation
Antioxidant mechanism

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I am truly thankful to my wife for her encouragment.

Declaration

The work described herein was carried out at the University of Aston in Birmingham between August 1988 and July 1990.

It has been done independently and submitted for no other degree.

Hu Gang

Hu Gang

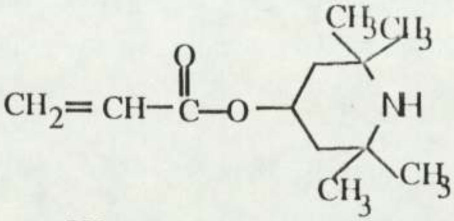
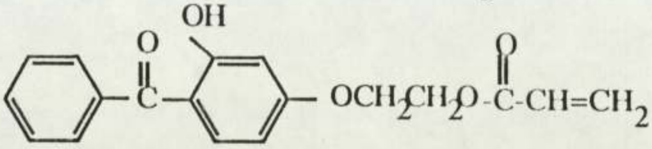
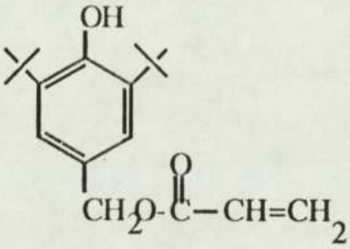
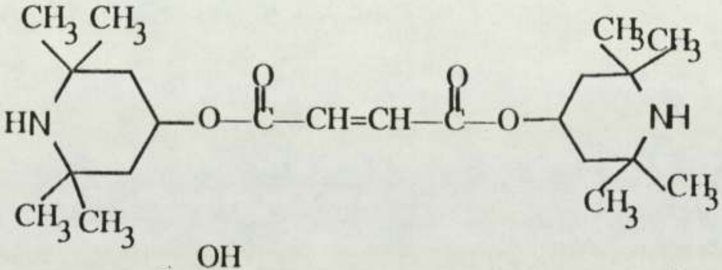
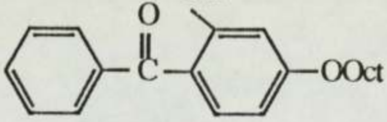
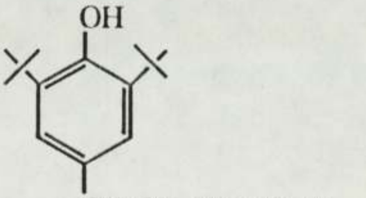
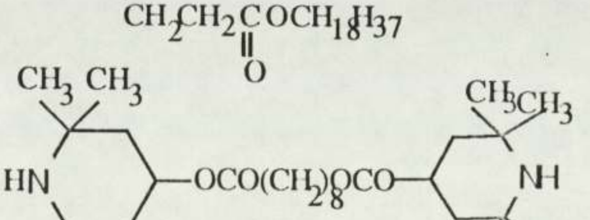
August 1990

To My Wife And Our Daughter

Content

List of Figures and Table

List of Abbraviations for Additives

Compound	Structure	Code
2,2,6,6-tetramethyl-4-pipridylacrylate		AOTP
2-hydroxyl-4-(2'-acryloxyl)-ethyloxybenzophenone		HEAB
3,5-di-tertbutyl-4-hydroxylbenzlacrylate		DBBA
Bis-(2,2,6,6tetramethylpiperidin-4-yl)maleate		BPHE
2-hydroxy-4-octyloxy-benzophenone		UV531
n-octadecyl-3-(3',5-di-tertbutyl-4-hydroxyphenyl)proprionate		Irganox 1076
Bis(2,2,6,6-tetramethylpiperidinyl) sebacate		Tinuvin 770

Chapter One

Introduction

1 Introduction

1.1 Polymer Autooxidation

With the development of science and technology many kinds of man-made macromolecular materials are created to meet the demands of industry and daily life to replace metal, paper, leather, wood etc.. They have unique advantages over these traditional materials in versatility, ease of processing and cheapness. However, it has been observed that the applications of many synthetic materials are limited to some extent by the problem of their sensitivity to oxidative degradation primarily under the condition of heat and light. It is therefore practically important to inhibit the oxidation of polymers if a reasonable service life is to be expected of them.

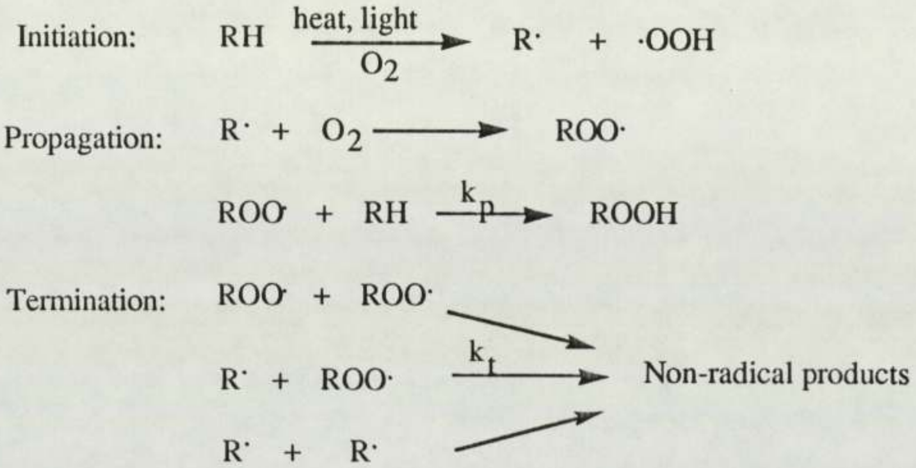
Although the autooxidation of simple low molecular weight organic compounds has been studied quite extensively and is well understood[1] there still remain many problems to be clarified for the oxidation of polymers[2]. Generally speaking, the rates of oxidation of most polymers are very low without radiation at ambient temperature. This is because the rate of production of initiating radicals is much less than that in low molecular weight organic compound systems. The free radical chain reaction of autooxidation degradation results from heat, photo and mechano-chemistry, or from radiation of high energy source. These may occur during processing operation (melt degradation), on exposure to air at elevated temperature (thermal oxidation) and, on exposure to sunlight and other high energy sources (photo oxidation).

Small amount of peroxides, oxygenated compounds, and impurities incorporated into polymers in the course of processing may have significant effects on the rate of initiation and overall rate of oxidation. So various oxygen-containing groups are introduced along the polymer chain or at its ends by oxidation and some low molecular weight products are also formed. As a result of the degradation reaction it causes deterioration in physical properties and as the oxidation proceeds decrease in molecular weight and discolouration of the polymer are observed. In the absence or deficiency of oxygen crosslinking also takes place, which invariably increases stiffness, creep resistance and brittleness. Furthermore the oxidised polymers have lower mechanical strength and fatigue easily under an external stress.

Thus the oxidative degradation of polymers is considered generally to be a deleterious process and many scientists have devoted extensive effects to inhibit or suppress it in order to extend the service life of polymer.

1.1.1 Free Radical Chain Mechanism in Autooxidation

Like small molecular organic compounds, the oxidation of polymers is a radical reaction. During the oxidation there are three main processes which include initiation, propagation and termination shown in scheme 1.1[3].



Scheme 1.1 General free radical reaction in autooxidation

In the above scheme, R· is the alkylradical, ROO· is the alkylperoxyl radical derived from the organic substrate (RH), kp and kt are the rate constants of propagation and termination respectively. Hydroperoxide initiation plays an important role in the oxidation chain reaction as a result of direct oxidation of substrate by molecular oxygen through the action of environmental factors e.g. heat and light, this mechanism was originally observed in studies of unsaturated polymers[4,5]. Many scientists have shown strong evidence to support this autooxidation mechanism of polymers[6-14]. The oxidation degradation of polyolefins are also typically based on the hydroperoxide initiation mechanism[15]. The details of this are reviewed below.

1.2 Thermal and Photo Oxidation of Polyolefins

1.2.1 Thermal Oxidation of Polyolefins

Like low molecular weight compounds, the polyolefins consist simply of carbon-carbon and hydrogen-carbon bonds in which hydrogen may be easily attacked by free radicals generated in high temperature or other severe environments. Alkylradicals are formed and react with oxygen to give alkylperoxyl radicals and hydroperoxides which cause seriously chemical property change of the polyolefins, namely[16]:

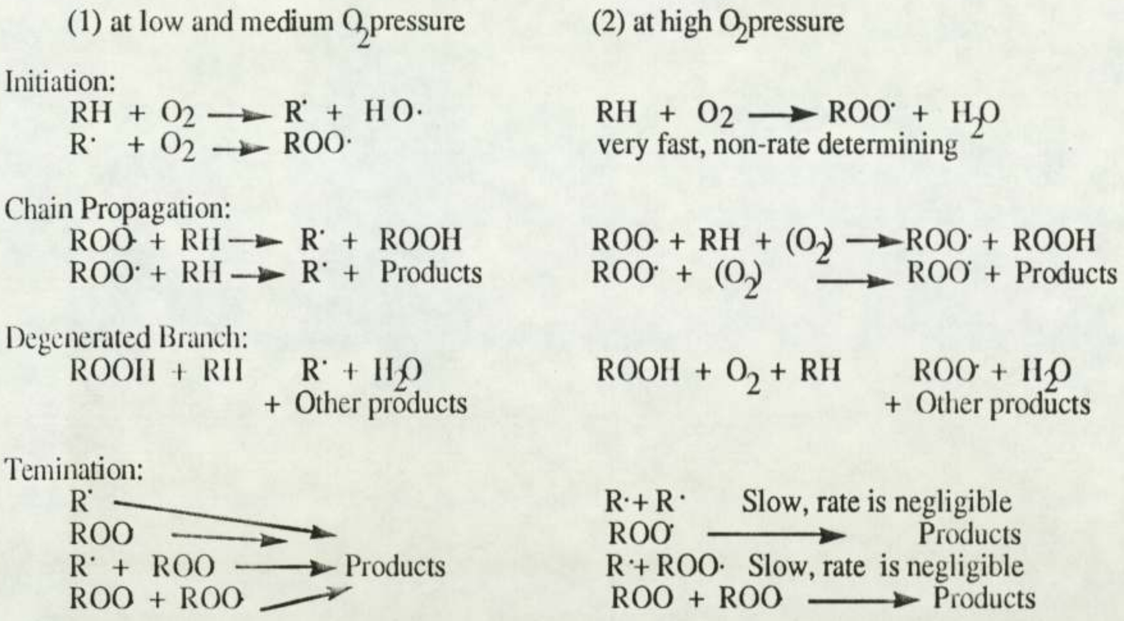
(1) formation of oxidised structures in the chain,

(2) fragmentation of the chain, and

(3) formation of low molecular weight products.

Polyolefin oxidation mechanism has been proposed by different authors generally from the basic mechanism of Bolland and Gee[17, 18]. The oxidation of polyolefins can occur under two kinds of conditions[16]. One is under low and medium oxygen pressure, and another is under a high oxygen pressure. The rate of the former process is determined by the reaction of alkylradicals(R·) and peroxyl radicals(ROO·). in the latter situation, the oxidation of the radicals is very fast compared to the other propagation steps. In this case, only the reaction of ROO· radicals is rate determining. The oxidation mechanism is shown in scheme 1.2.

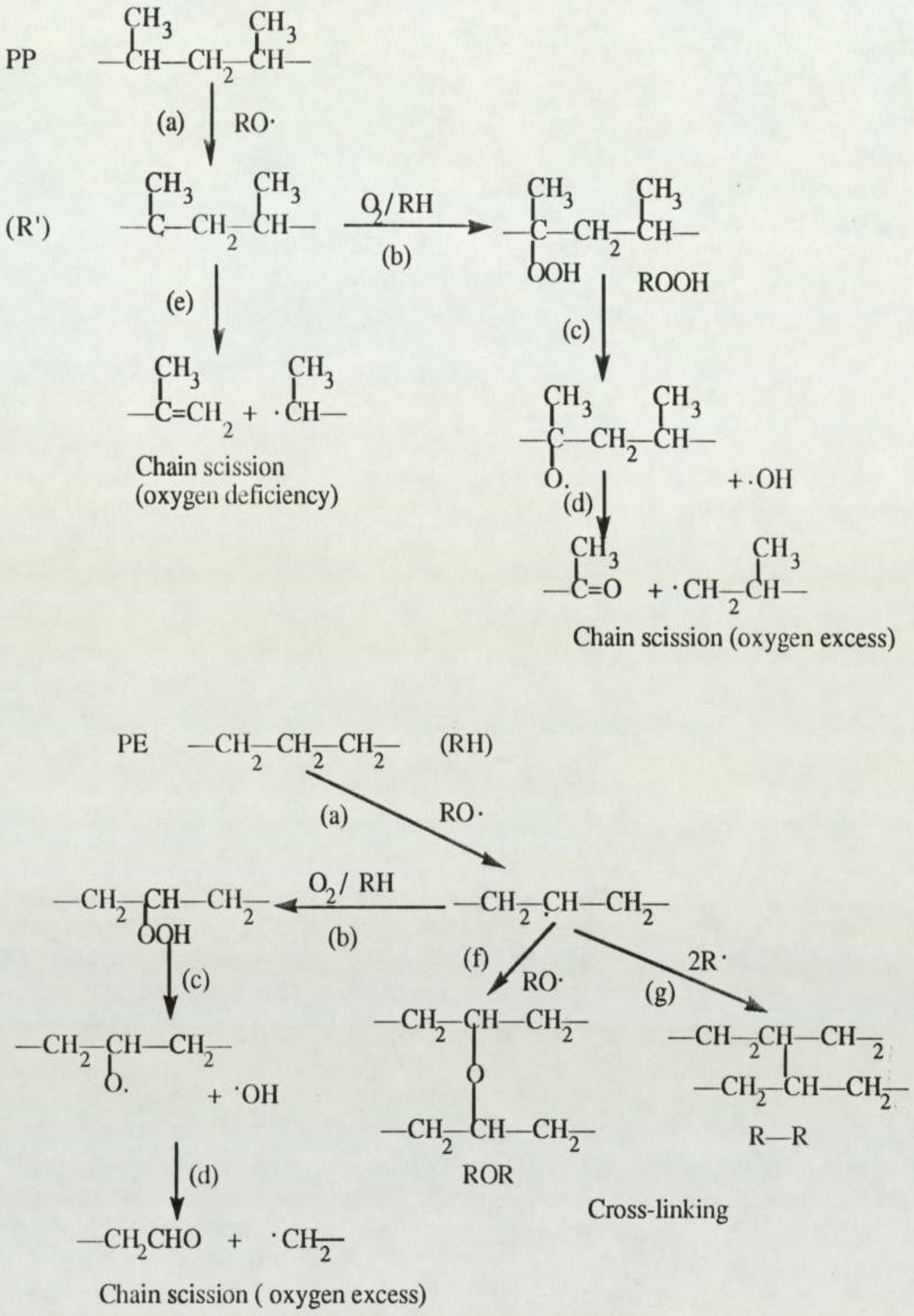
Scheme 1.2 Oxidation mechanism scheme of polyolefins (1) and (2)



Comparing polyethylene with polypropylene there are different behaviours between them during processing operation due to their structure difference shown in scheme 1.2.1. During high temperature processing in a shear mixer, without oxygen or in the case of oxygen deficiency polypropylene undergoes an increase in melt flow index (MFI), which is the weight of polymer extruded through a standard orifice in a given time and is inversely related to molecular weight, or decrease in molecular weight. However, the MFI of polyethylene decreases due to crosslinking. In the case of oxygen excess the oxidation of hydroperoxide initiation plays a key role to lead to chain oxidation scission in both polymers.

1.2.2 Photo-Oxidation of Polyolefins

Long chain alkanes should not absorb light beyond about 200 nm, well below the UV cut off of terrestrial sunlight (about 285 nm). They might be considered as firmly stable polymers. However, many unexpected defects remain in polyolefins throughout their synthesis and processing. Hence these kinds of defects are sensitising species to make polyolefins absorb UV light in the spectral region found in sunlight (ie>285 nm) and all the commercial polyolefins photooxidise readily due to oxygen-containing groups, impurities (metal ions and catalyst residues) and so on.

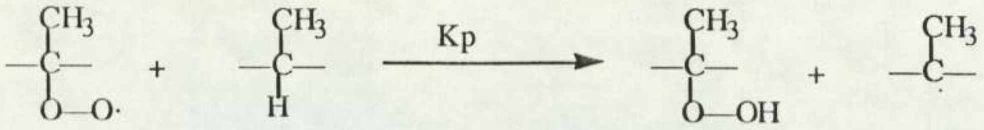


Scheme1.2.1 Alternative reaction of alkyl radicals during high-temperature processing of polyolefins

In section 1.2.1 it is mentioned that during high temperature processing a variety of oxygen-containing groups are formed which absorb UV light in > 285 nm region and cause the photooxidation of polyolefins. When they are exposed to sunlight to generate more hydroperoxides, alcohol and various types of carbonyl groups are generated. The process of photo oxidation is similar to that of thermal oxidation [19]. The carbon centred radicals (R·) in the amorphous regions of the polyolefins rapidly react with oxygen which permeates into the amorphous regions to give peroxyl radicals (ROO·). The peroxyl radicals react quite slowly by hydrogen abstraction from C-H sites on the back bone to produce pendant hydroperoxide groups (ROOH) and fresh carbon centred radicals which restart the cycle of radical generation.

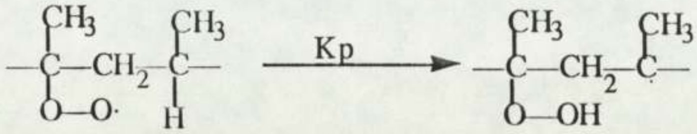
Compared with polyethylene, in PP it is possible that there are two kinds of propagation reactions [20-24]:

(1) Intermolecular propagation:



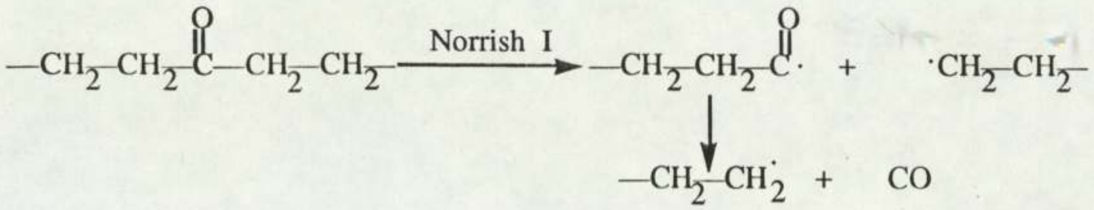
$$-\overset{CH_3}{\underset{O-O\cdot}{C}}- \; + \; -\overset{CH_3}{\underset{H}{C}}- \xrightarrow{Kp} -\overset{CH_3}{\underset{O-OH}{C}}- \; + \; -\overset{CH_3}{\underset{\cdot}{C}}-$$

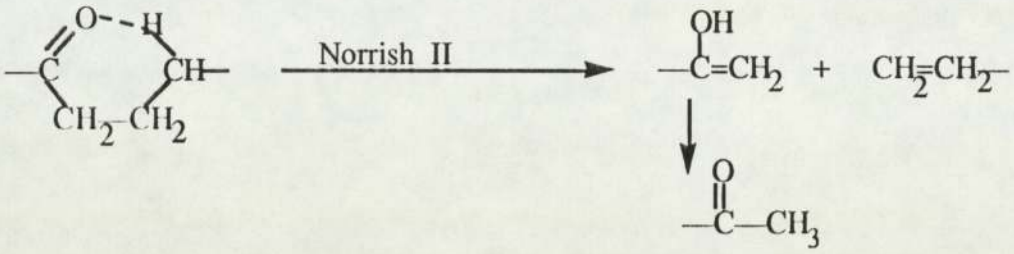
(2) Intra-molecular propagation:



$$-\overset{CH_3}{\underset{O-O\cdot}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}- \xrightarrow{Kp} -\overset{CH_3}{\underset{O-OH}{C}}-CH_2-\overset{CH_3}{\underset{\cdot}{C}}-$$

The rate of intramolecular abstraction is about three times that of intermolecular abstraction[20]. The hydroperoxide group is easily converted to a ketone and alcohol group in polyolefins during the process of oxidation. This kind of ketonic group (carbonyl group in general) is suggested to be the key chromophore which initiates the photooxidative destruction of polyolefins[25-28] because ketonic groups are photolysised to cause chain scission or to give free radicals by both Norrish I and Norrish II cleavage under UV exposure. the scheme shows as follows:





In the first, chain scission occurs adjacent to the carbonyl group to form alkylradical directly. The second is a non-radical reaction which results in chain scission by a way of a six- membered ring transition state yielding a methyl ketone and vinyl unsaturation [29]. The carbonyl and vinyl unsaturate group can be detected by IR which show absorption at 1710-1735 cm^{-1} and about 1640 cm^{-1} respectively. Both absorptions provide evidence to show the extent of photooxidation of polyolefins.

1.3 Morphological Factors Affecting Thermal and Photo Stabilising of Polyolefins

In general polymer oxidation particularly relies on their chemical structure. However, besides the factor of chemical function the rate of oxidation also depends on the polymer morphology (eg. crystallisation degree, orientation, amorphous phase and internal stress). Hawkins and co-workers [30,31] showed that the rate of thermal oxidation of solid PE is markedly affected by the degree of branching of the PE chain molecules. The oxidation rate at 100°C appeared to be roughly proportional to the amorphous fraction. This result suggests that oxidation of semicrystalline PE is restricted to the amorphous region. Michael & Bixler [32] demonstrated that the diffusion constants for gases are markedly dependent on the level of crystallisation of PE, being lower as the crystallinity increase. So the alkylradicals in amorphous phase of PE are easily reacted with oxygen which permeates from the atmosphere, to yield alkylperoxyl radicals and hydroperoxides.

Peterlin and co-worker [33,34] reported that polymer orientation affects to some extent the rate of oxidation. Uniaxial plastic deformation transforms the spherulitic structure of polyolefins into a highly oriented fibrous structure. The high orientation of polymer chains in an amorphous conformation favours closer packing than is possible in completely randomised amorphous polymer. Consequently, the density is higher and hence the fraction free volume is smaller than in an equilibrium amorphous rate. This results in decreasing sorption and diffusion coefficients in polymer and a reduction of segmental mobility. It is therefore to be expected that the rate of thermal and photo oxidation of polyolefins will be markedly affected by polymer orientation. It has indeed been found [35] that when polyolefins are oriented by drawing, the rate of oxidation in general falls considerably.

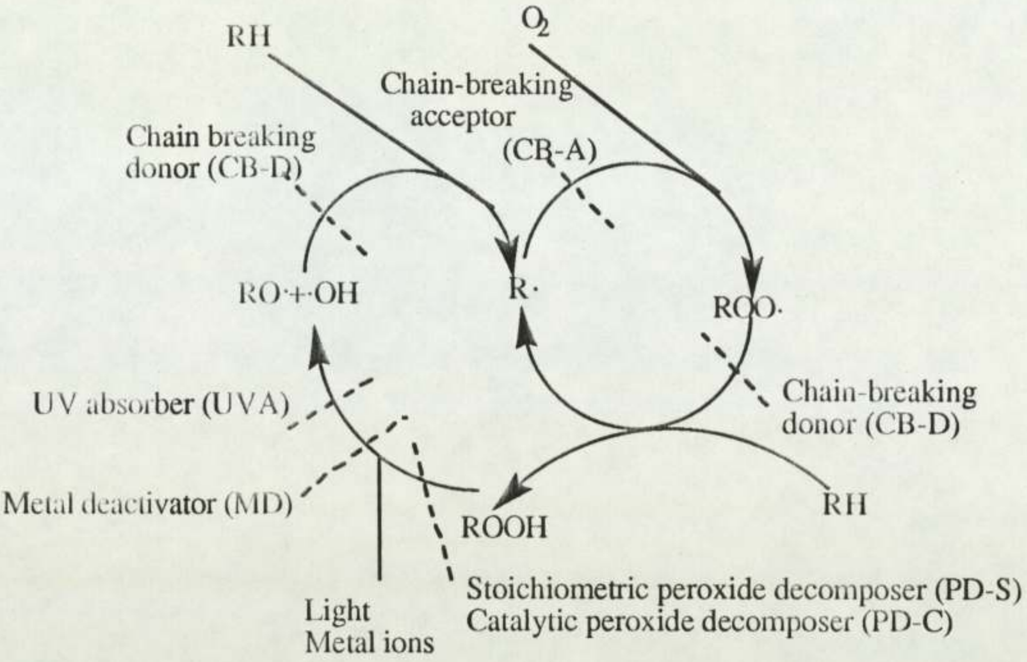
On the other hand, it has been also found [36,37] that PE and PP deteriorate much faster in those areas where they are stressed or have been moulded in strains when exposed outdoor to UV light or ozone. But the effect of external mechanical stresses when they are imposed on polymer during aging is rather complicated because two types of degradation have been considered: mechanical and oxidative. The two processes influence each other. Moreover, the morphological changes in semicrystalline polymers such as PE and PP brought about by applying a mechanical stress, also depend on their original morphology, in particular on their degree of orientation.

1.4 Mechanism of Antioxidant Action

According to the sequence of radical initiation and propagation during oxidation process of polymer given above, antioxidant action processes for inhibition of polymer oxidation can be divided into two fundamental mechanisms: (1) Prevention of initiation (e.g. by decomposing hydroperoxides to form non-radical products, or by absorbing the deleterious energy of UV light to be transformed into heat energy), and (2) Scavenging reactive radicals to terminate the kinetic chain. This involves two interacting cyclical processes. The first is the alkyl/alkylperoxyl chain reaction and the second is the homolysis of hydroperoxides which lead to the chain reaction with new radicals. The two processes are shown as scheme 1.4[38]:

1.4.1 Chain-breaking Antioxidants

Because both alkyl and alkylperoxyl radicals exist in radical oxidation chain reaction of polymer they could be interrupted in two ways by antioxidants shown on scheme 1.4.1[38].



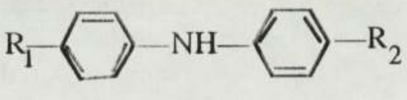
Scheme1.4 General mechanism of antioxidant action

Scheme1.4.1 Redox reaction

The alkylradical can be removed by oxidation process through releasing electron to electron acceptor (CB-A) agent to form unsaturated hydrocarbon product while the alkylperoxyl radical can be reduced to give a hydroperoxide by accepting a electron from electron donor (CB-D) agent.

1.4.1.1 Chain-Breaking Donor (CB-D) Mechanism

Based on the mechanism mentioned above typical conventional hindered phenols and aromatic secondary amines are referred to as chain breaking donor antioxidants despite some of their transformation products function by the chain breaking acceptor mechanism. At an early stage in antioxidant research in the rubber industry it was found that some vulcanising agents had ability to improve long term aging service life of the finished rubber products. They are arylamines and diphenylamines which are considered as the earliest commercial antioxidants shown as follow[39]:

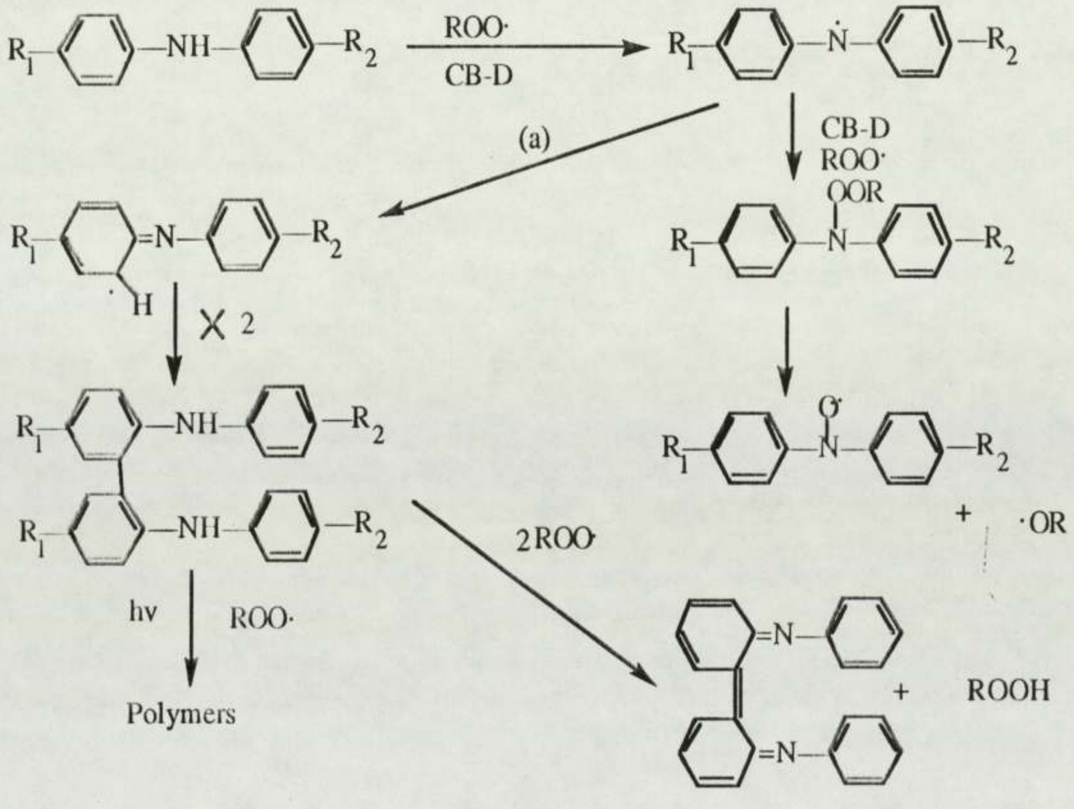


(a) $R_1 = R_2 =$ tOct, DODPA

(b) $R_1 =$ H, $R_2 =$ NHisoPr, IPPD

(c) $R_1 =$ H, $R_2 =$ NHPh, DPPD

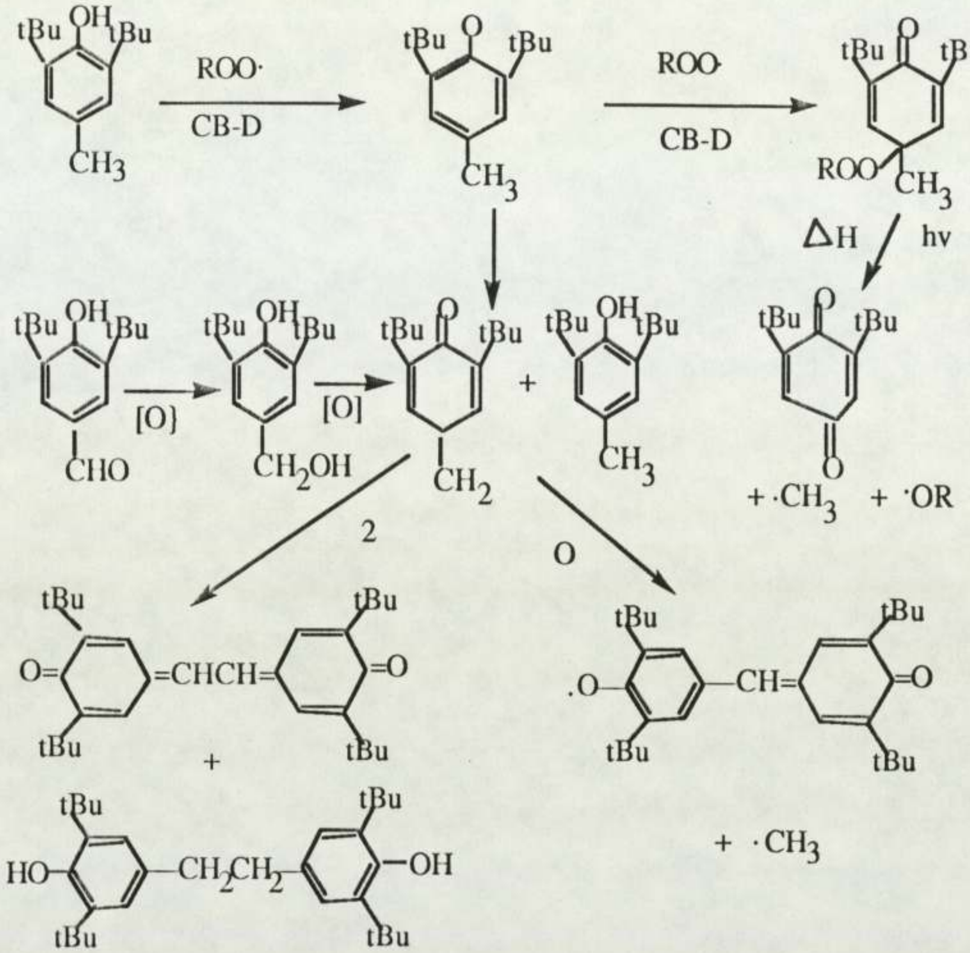
During the process of antioxidant reaction the arylamines are initially converted to highly reactive aminyl radicals by hydrogen releasing. The intermediate products keep reacting in two different ways to give some products which themselves have antioxidant activity. In one way some oligomers and polymerisation would be formed by dimerisation and polymerisation through combination of the aminyl radicals on the carbon atom. These polyoligomers are effective antioxidants like initial arylamine. In other way the nitroxyl radical would be formed by a second CB-D step. This species is a very important CB-A antioxidant. The general chemistry of their oxidation processes shows on scheme 1.4.1.1[39].



Scheme1.4.1.1 General oxidation processe of arylamine

Although arylamines are effective antioxidants in polymers one of their disadvantages is unavoidable. They cause considerable discolouration of polymer to which they are added in because of formation of extensively conjugated quinonoid oxidation product in autooxidation process. Hence, non-staining antioxidants are necessary to meet the variety of demands in some polymer applications. Substituted phenols were found to do this to replace arylamines in white or pastel tinted rubber products. Especially for plastic products, the phenols play a key role against the thermal oxidative degradation of plastics. The simplest, most important member of this class is the ' hindered phenol' 2,-6,-ditert- butyl phenol (BHT) which was originally used in food industry as an antioxidant. Today it is also widely used in polymer materials as a melt antioxidant. The mechanism of phenol antioxidant action in autooxidation condition is summarised in scheme 1.4.1.1a [39].

This is representative of the oxidation chemistry of all hindered phenols. From this scheme it is known that some oxidation transformation products are still effective antioxidants (e.g. stilibene quinone and galvinoxyl) by a complementary CB-A mechanism.



Scheme1.4.1.1a Phenol antioxidant action in autooxidation process

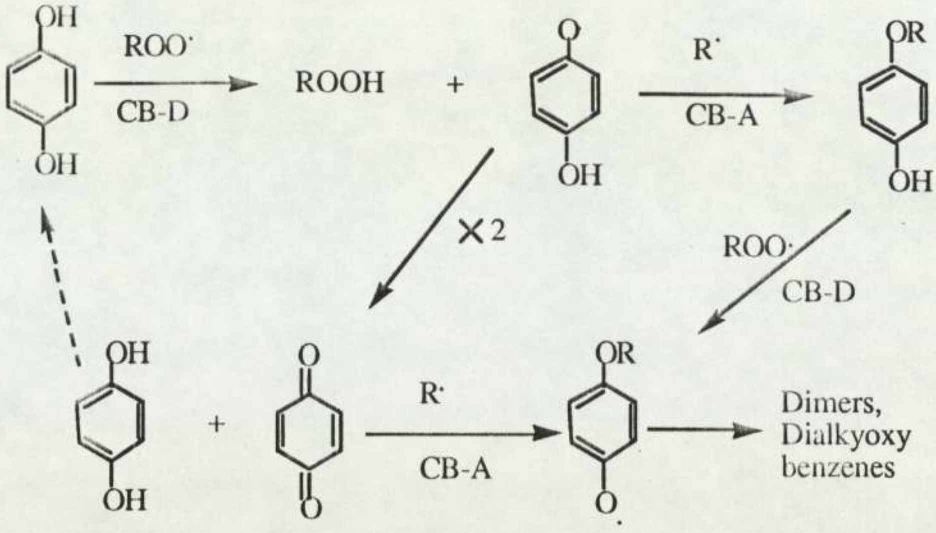
On the other hand, some potential pro-oxidants (peroxy dienones) are formed from phenolic antioxidants at high temperature about 140°C since they are decomposed rapidly to form new active free radicals which make phenolic antioxidants less effective[1]. Therefore, phenolic antioxidants are generally used as heat stabilisers in a synergistic mixture with a peroxide decomposer to increase their effectiveness.

1.4.1.2 Chain- Breaking Acceptor (CB-A) Mechanism

In the absence of oxygen or in the case of a deficiency of oxygen alkylradicals dominate in the process of polyolefin degradation. They are electron donors which are readily oxidised or trapped by electron acceptors (CB-A antioxidants) such as polymerisation inhibitors. In polymerisation the electron trapping agents (CB-A antioxidants) are called inhibitors. They include benzoquinone and aromatic nitro compounds. Benzoquinoid compounds formed from phenolic antioxidants may participate in further processes in a very complex manner. They are able to trap alkylradicals through the system of π-bonds [41-42] and to form donor acceptor complexes. They act as oxidation and dehydrogenation agents[43,44] and oxidise both phenols and amines very readily. In general if a variety of oxidising agents have the ability to remove alkylradicals from an autooxidation system and compete with alkylperoxyl radicals they show evidence of antioxidant activity (CB-A) [45-48].

1.4.1.3 Complementary Mechanism Involving Both CB-D and CB-A

It is known that in the presence of excess oxygen, CB-D antioxidants are the primary antioxidants in the stabilisation of polymers and show very effective activity to react with the alkylperoxyl radicals which are the chain propagating species present in the highest concentration in the system. On the other hand, in the case of oxygen deficiency the CB-A antioxidants take a key role to trap alkylradicals for decrease in the rate of chain initiation against the growth of alkylperoxyl radicals. But in most oxidation processes both alkyl and alkylperoxyl radicals are present to some extents. The CB-D and CB-A antioxidants would be needed at the same time. Some compounds have an advantage that they exhibit both activities effectively (CB-D and CB-A). For instance [40] hydroquinone is best known as CB-D antioxidant, but when it is converted to benzoquinone by CB-D mechanism the transformation product (benzoquinone) plays a role in CB-A mechanism as a very effective alkylradical trap, and may remove many radicals from the system before the final inactive products are produced. The complementary mechanisms involving hydroguinone and its oxidation products are shown in scheme 1.4.1.3[39]:

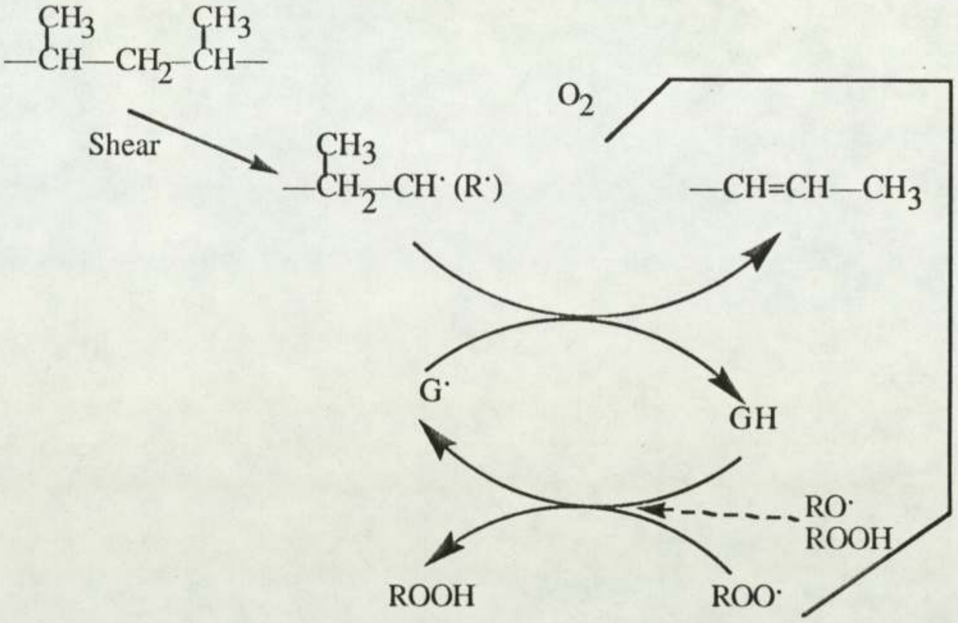


Scheme1.4.1.3 Complementary mechanism of phenol

1.4.1.4 Regenerative Chain-breaking Antioxidant

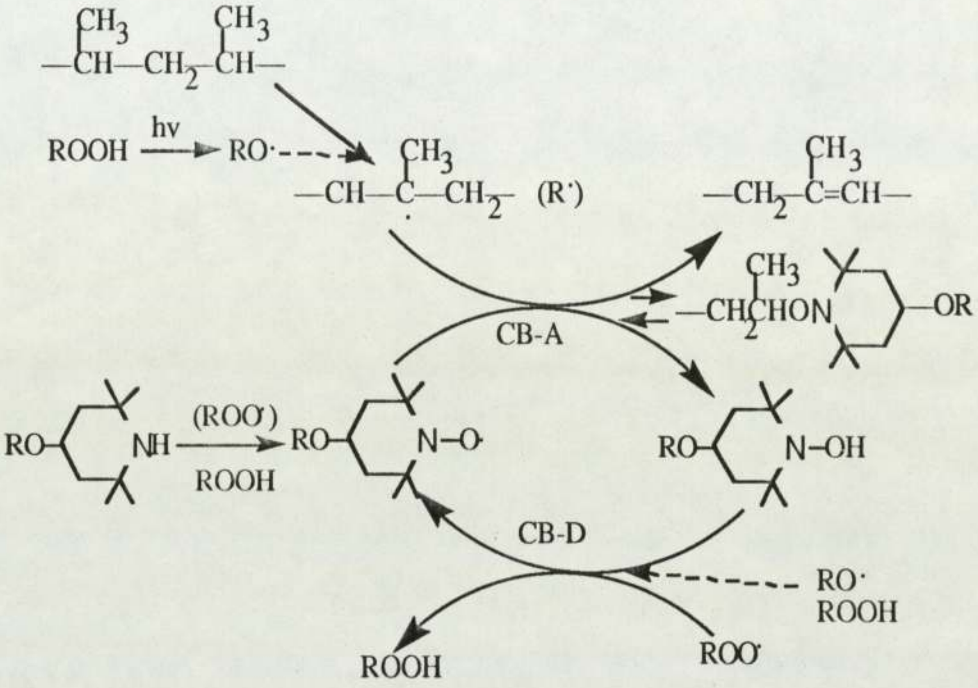
It is found that some chain-breaking antioxidants and their intermediate products have the ability to reverse between oxidised and reduced state. Hence they can be regenerated during the reaction with alkyl and alkylperoxyl radicals which are present at same time in the system. Such as the transformation product (galvinoxyl or G·) of BHT is very effective in melt stabilisation of polypropylene. It would be converted to the parent phenol and hydrogalvinoxy (GH) during first stage by the oxidation of an alkylradical in a CB-A process. On the other hand, GH is also partially re-oxidised to G· (CB-D) by alkylperoxyl radicals. Both CB-A and CB-D mechanisms occur together to exhibit a regenerative cycle shown in scheme1.4.1.4

[38]. Therefore the stoichiometric inhibition coefficient (f) of antioxidant is found to be greater than about 50 [39].



Scheme1.4.1.4 Regeneration of galvinoxyl (G·) during the melt stabilisaton of polypropylene

A similar cyclical regeneration process is also found in the UV stabilisation mechanism of the hindered piperidines which are widely used as commercial UV stabilisers, and are much more effective than other UV stabilisers in PP [49-51]. Unlike the diarylamine, the hindered aliphatic amines are not effective antioxidants, but are transformed to the corresponding nitroxyl radical during the early stage of photo oxidation. The nitroxyl radical is an effective CB-A antioxidant which reacts with alkylradical to be converted to the hydroxylamine. The hydroxylamine in the presence of alkylperoxyl radical may be reoxidised to be the nitroxyl radical following the operation of CB-A and CB-D catalytic cycle process under the condition of oxidation in polymer. The process is shown in scheme 1.4.1.4a [39].



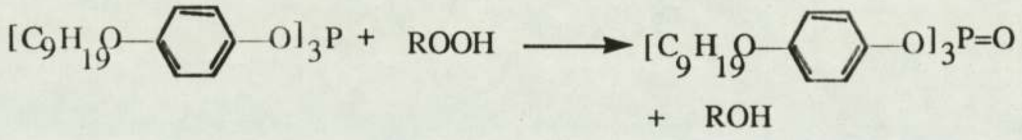
Scheme1.4.1.4a Catalytic role of hindered piperidinoxyl radicals during the photo stabilisation of polypropylene

1.4.2 Peroxide Decomposition Mechanism[38]

The peroxide decomposition mechanism can be divided into stoichiometric reducing (PD-S) and catalytic action (PD-C) for peroxide decomposition.

1.4.2.1 Stoichiometric Peroxide Decomposition Action (PD-S)

PD-S antioxidants should essentially promote hydroperoxides in the oxidation of polymer to be decomposed into alcohols without the substantial formation of free radicals [52]. The typical sample as PD-S antioxidant used in rubber is trisnonyl phenylphosphite for stabilising raw rubber. The reaction process shows as follows:

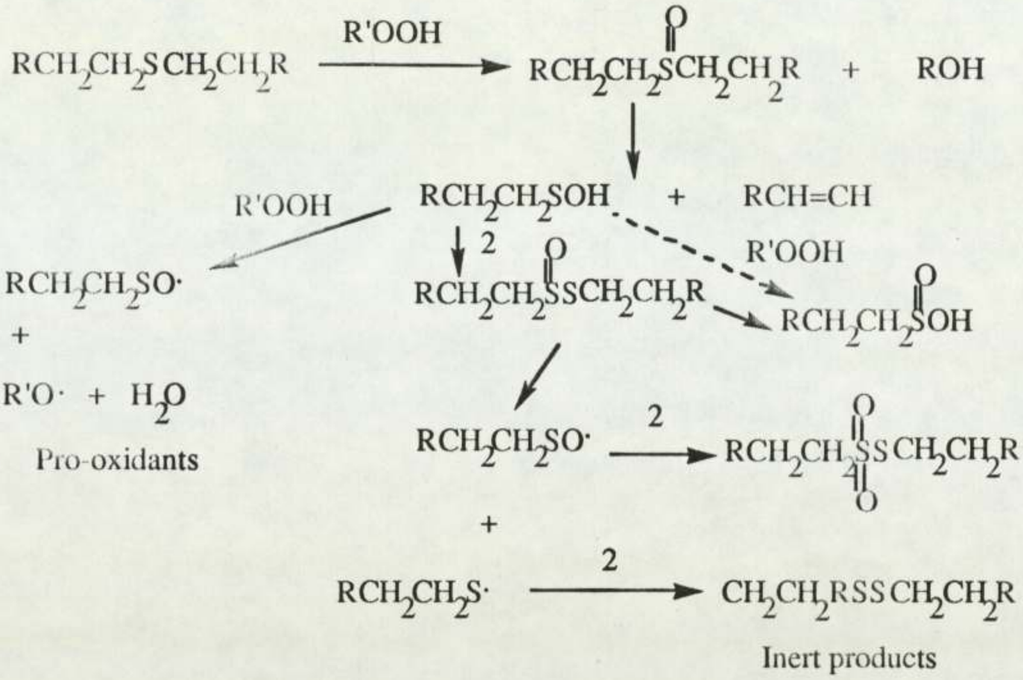


1.4.2.2 Catalytic Peroxide Decomposition Action (PD-C)[39]

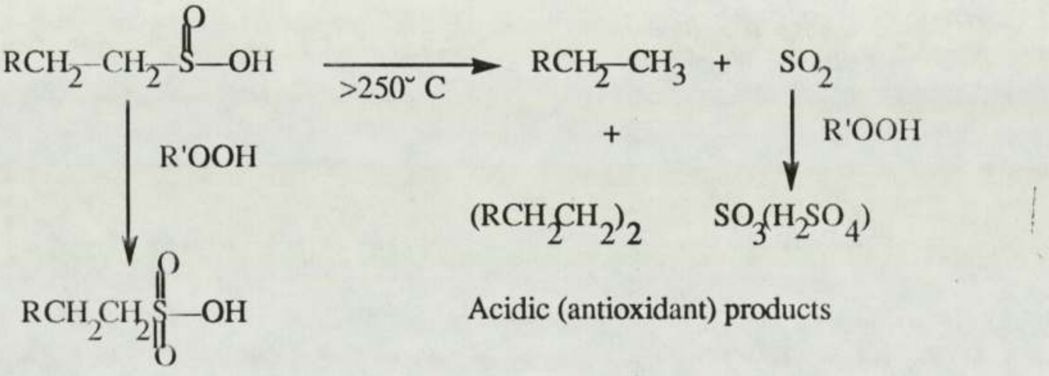
Compared with PD-S antioxidants, considerable initial pro-oxidant effects are normally found in this process. In many cases, the PD-C antioxidant function is preceded by a pro-oxidant stage. The importance of the pro-oxidant stage is a function of the structure of PD-C antioxidants. A wide variety of sulphur compounds fall into this class, such as dialkyl sulphides, thiodipropionate esters, dithiocarbamate, dithiophosphate and so on [53-62]. These compounds are capable of destroying hydroperoxides through the formation of acidic products in a radical generating reaction involving hydroperoxides.

The mechanism of action of the mono sulphides has been studied deeply in recent years [63-66]. Scott and AL-Malaika have reviewed the antioxidant mechanism of organic sulphur compounds[64]. Organic sulphides and disulphides used as peroxide decomposing antioxidants in polymer are oxidised to sulphoxides and thiolsulphinate esters by hydroperoxides. These initial oxidation products can not decompose hydroperoxides, but they undergo thermal decomposition to form sulphenic acids (RSOH) and thiosulphoxylic acids (RSSOH) respectively. These reactive intermediates, together with their oxidation and reaction products, decompose hydroperoxides by a catalytic role mechanism. Scott generalises very clearly the action of mechanism of the monosulphides in oxidation process on scheme 1.4.2.2[39].

When thiodipropionate esters are used in polyolefins as PD-C antioxidants, during thermal oxidation aging change from pro-oxidant to antioxidant action occurs as the sulphur acids are produced in the system. The sulphinic acids improve their antioxidant ability not only in their own right as protonic acids but also by conversion to the inorganic acids, SO_3 and SO_4 shown in scheme 1.4.2.2a[39].



Scheme1.4.2.2 Pro-oxidation and antioxidant behaviors during the oxidation of monosulphides



Scheme1.4.2.2a Central role of sulphinic acids in the autooxidation behaviours of sulphides

The effective catalysts for the non-radical decomposition of hydroperoxides are finally protonic acids and acidic products ($RCH_2CH_2S(O)_2OH$). It is also found[67] that the pro-oxidant products which result from some homolytic cleavage of hydroperoxides induced by the sulphur compounds function partly as chain-breaking antioxidants.

1.4.3 Synergism and Antagonism

In principle, antioxidants which function by complementary mechanisms exhibit the phenomenon of synergism. Many antioxidants act by more than one mechanism. Some sulphur compounds are considered in this class. As we mentioned above[39, 55, 56], the important class of thiodipropionate esters involves two complementary mechanisms: peroxide decomposition (PD-C) and chain-breaking (CB- D). But, the chain-breaking function is transient and makes a relatively small contribution to the overall antioxidant function. Hence, many sulphur containing phenols are created as thermal antioxidants which show their ability to both chain-breaking and catalytically destroy hydroperoxides. This function was recognised many years ago by Scott and other scientists[52, 68]. Recently sulphur containing hindered phenols have been studied in more details [69-72]. Compared with non-sulphur containing phenols (e.g. BHT), phenols with the structure $-CH_2-S-R$ have a much higher intrinsic antioxidant activity measured by their molar activity in tetralin. On the other hand, it is also found that a combination of two or more antioxidants shows much more powerful antioxidant effects than either single component alone at any concentration. Such as, the use of the thiodipropinate ester in combination with a high molecular weight phenolic antioxidant improves thermal stabilisation of PP very effectively [73].

However, sometimes it is noticed that the mixture of two different kinds of antioxidants (e.g. hindered piperidine with peroxidolytic stabiliser) shows antagonism in photo stabilisation of PE [55]. The reason might be a fact that the peroxidolytic antioxidant remove the hydroperoxide which would react with the hindered piperidine to produce the nitroxyl radicals, and the intermediate products of the peroxidolytic antioxidant may also react with the nitroxyl radicals to reduce its relative concentration so that the effectiveness of nitroxyl radicals would be decreased by this kind of trapping.

1.5 Stabilisation of Polyolefins to Photooxidation

1.5.1 Antioxidant Mechanisms in The Photostabilisation of Polyolefins

In general, the chemical processes of photooxidation of polymers are similar to those occurring during thermal oxidation[83-85]. The main difference lies in the fact that photoinitiation is much faster than thermal initiation at ambient temperature. Hydroperoxides are formed rapidly in the system which are the common initiators of both processes (thermal and photo oxidation). This leads to higher radical concentration and shorter kinetic chain. The mechanism of photo degradation and stabilisation of polymer are more complicated than that of thermal degradation and stabilisation. Hence, it has been the subject of considerable dispute in recent years. Some workers are only concerned with the carbonyl compounds rather than the hydroperoxides, and have concluded that hydroperoxides could not be involved in this process. But, actually much evidence suggests [75-80] that hydroperoxides are the important initiators for photooxidation during the early stage of the photodegradation of polyolefins. Hydroperoxides are formed during the processing operation, and must be the precursors of carbonyl compounds as a result of thermal and photo decomposition of these primary initiators. The details about this process has been reviewed in the section 1.2.2. It also involves the two main interrelated oxidation cycles: (1) formation of polymer radicals (alkyl and alkylperoxyl); and (2) formation of radical generators. As we know, the most important of radical generators are the hydroperoxides. During thermolysis or photolysis hydroperoxides are decomposed to produce new radicals and further absorbing chromophores (e.g. carbonyl compounds). Therefore, two types of UV stabilisers can interrupt the UV oxidation cycles on scheme 1.4.

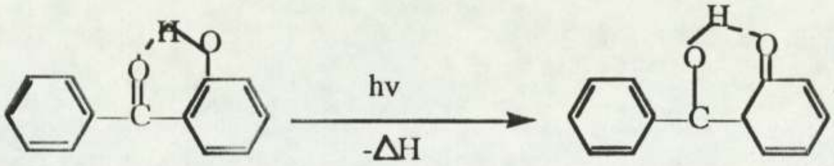
1). Chain-breaking antioxidants [81-83] which interfere with first degradation cycle by intercepting radicals formed during chain propagation i.e. alkyl (CB-A), alkylperoxyl (CB-D) or both; and

2). Preventive antioxidants [84,85] which interrupt the second cycle by removing or stabilising the potential radical generators, hydroperoxides. The effect of this mechanism therefore, is to reduce the rate of chain initiation.

Chain-breaking antioxidants have been mentioned in the section 1.4 and here it is necessary to review the UV preventive mechanisms which include UV screening (UV-S) and absorption (UV-A) agents, excited state quenching and hydroperoxide decomposition agents.

1.5.1.1 UV Screening (UV-S) and Absorption (UV-A) Action

UV absorbers have an ability of absorption of harmful radiation to provide adequate protection against photo initiated oxidation of polyolefins. For example HOBP (2-hydroxyl-4-dodecyloxy-benzophenone) is able to form intramolecular hydrogen bonds to dissipate energy harmlessly via keto-enol tautomerisum in excited state [86] when it



is exposed to UV light. 2-hydrophenylbenztriazole has same function like HOBP for protecting against UV light deterioration of polyolefins. However it is necessary to notice that UV absorption stabilisers like HOBP function most partly by only UV absorption to dissipate harmful UV energy to heat energy, their contributions to the CB and hydroperoxide decomposition action exhibit less effective in the system. They can not effectively inhibit the initiation of alkyl and alkylperoxyl radicals. It is possible that UV absorption stabilisers themselves may be destroyed by hydroperoxides under the condition of UV irradiation [87]. Hence, the effectiveness of UV absorbers in polyolefins must be taken into account the prior thermal oxidation processing history of the polymer (the concentration of hydroperoxides in system).

In addition of UV absorbers some pigments also show UV antioxidant behaviours by UV screening and absorbing function to reflect or absorb the damaging incident light. For example titanium dioxide (TiO_2) in its photochemically inactive form, zinc oxide and carbon black [88-96].

1.5.1.2 Excited State Quenching Action

Excited state quenchers functions through energy transferring from a photo-excited species to a quencher molecule to dissipate the excess energy harmlessly. Many nickel chelates (e.g. Ni complexes of dithiocarbamates, thiobisphenolates and hydroxybenzylphosphonates) show partly their ability to quench photo-excited states of carbonyl compounds in the polymer [97].

1.5.1.3 Hydroperoxide Decomposition Action

Although many compounds decompose hydroperoxides catalytically by non-radical process during thermal oxidation of polymer not all of them are effective UV light antioxidants. For example dialkyl and diaryl sulphides and sulphoxides which are good hydroperoxide decomposers in the processing of polyolefins are somewhat ineffective UV stabilisers for polyolefins [98,99] due to the sensitivity of either original sulphur compounds or their oxidation products to UV light.

So far the most successful UV stabilisers based on the peroxidolytic mechanism are the nickel dithiolate compounds due to their parent metal complex rather than their transformation products which show good responsibility for thermal oxidation stability [100]. Hence, they have a particular advantage as antioxidants under all conditions of polymer oxidation (UV and heat aging). But, their main disadvantage is that they are frequently coloured.

1.6 Physical Loss of Stabiliser from Polymer

The effectiveness of stabilisers depends not only on their chemical structure and intrinsic behaviour but also on their critical concentration in the polymer. For any particular stabiliser its concentration is an important factor in the stabilisation of polymers. Unfortunately the loss of antioxidant is unavoidable during long term service time of polymer. Decrease in concentration of stabiliser may take place in the aging process. The change of its concentration in the polymer may be divided into two processes: (1) chemical reaction of the stabiliser, and (2) physical loss of it from polymer. The former is only dependent on its chemical structure whereas the latter is dependent on its solubility, compatibility, distribution as well as environment factors.

1.6.1 Distribution of Stabilisers in Polymers

To improve their stabilising effectiveness stabilisers should be distributed uniformly in polymers. But most polymers, especially polyolefins, are semicrystalline materials which consist of amorphous and crystalline phases together. In general, stabilisers can be dispersed uniformly in the amorphous polymer which is demonstrated by Frank and Lehner[101] who found a uniform distribution of 2-(2'-hydroxyl-3',5'-ditert-amylphenyl) benzotriazole in atactic polypropylene. In semicrystalline polymers [102-104], low molecular weight stabilisers are concentrated in the amorphous phase, especially at the boundaries of spherulites and in the defect spots of spherulites because the stabiliser is rejected from growing crystallisers during cooling and accumulates in the amorphous phase between the spherulites and non-crystalline regions of the spherulites. Fortunately this distribution behaviour of stabilisers in semicrystalline polymer appears to be advantageous because the amorphous region of most polymers is the part most sensitive to degradation. Hence the non-uniform distribution of a stabiliser in polyolefins (PE, PP) increases its concentration in amorphous phase for protecting them more effectively against degradation.

1.6.2 Stabiliser Compatibility with Polymer

One of the factors which mainly affect the effectiveness and permanence of stabiliser in polymer is compatibility which is relative to the interaction of polymer with additive. According to the theory of solution of macromolecular substances [105-108] in the mixture of polymer with low molecular weight compounds or polymer-polymer blends the compatibility of components is dependent on the square difference of the values of their solubility parameters $(\delta)^2$ which are compared with the maximum values $(\delta)^2_{max}$. The solubility parameter is referred to as the density of the cohesion energy and is equal to the potential energy of a unit volume of a material:

$$\delta^2 = \frac{\Delta E}{V} = -\frac{N_0 \Delta E}{v} \qquad \text{------} \quad (1)$$

Where E is the potential energy, V is the molar volume, N_0 is the Avogadro number and v is the potential energy of one molecule. If the solubility parameters of polymer $(\delta)^2$ and additive $(\delta)^2$ are very close at the same level (or approximately equal), the two components are able to form a homogeneous mixture. They show very good compatibility in the mixture. Generally speaking, the more similar is the character of the components in a system, the better is the compatibility.

1.6.3 Volatility of Stabiliser

Because of thermal motion of molecules the diffusion process of stabilisers in polymer leads to them transport from the bulk of polymer to the surface layer[102]. The stabilisers may evaporate on the surface so that this process results in a decrease in the concentration of stabilisers in polymer. The volatility of stabilisers is affected not only by the properties and structures of polymer and themselves but also by the external physical condition (temperature, air pressure, time and so on). Some scientists found that the effect of temperature on stabiliser volatility can be mathematically calculated by the Ahrenius equation for the thermally activated volatility [109-114], and the rate of evaporation of the stabiliser from rubber [115] or polyethylene [109] is inversely proportional to the thickness of the sample and directly proportional to its surface area.

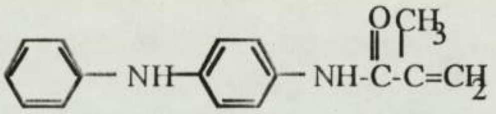
1.6.4 Extractability of Stabiliser

Extraction of stabilisers from polymer is also an important factor for the physical loss of them when stabilised polymers come into contact with water or organic solvents during their service life time. Hence, the extraction process causes a decrease in the real content of stabilisers in polymer, especially in the surface layers which are the most sensitive regions to degradation so that the effectiveness of stabiliser declines definitely.

1.7 Polymer-bound Antioxidant

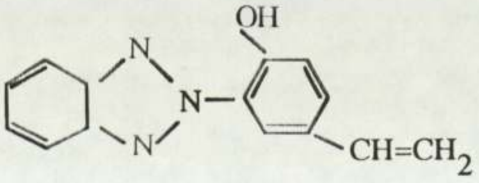
One of innovative methods for improving the efficiencies of themal and photoantioxidants in polymers is to mechanochemically bind antioxidant monomers to the backbone of a polymer to form polymer-bound antioxidants. This has been proposed by Scott[132-133] and several kinds of polymer-bound antioxidants have been made to fundamentally solve the problem of volatilization and exudation of conventional antioxidants from polymers. Physical loss of conventional stabilisers certainly occurs from polymers by volatilisation and extraction which depend on the rate of diffusion. This essentially involves physical behaviours of stabilisers with polymer which include the distribution and solubility of stabilisers in polymer. The solubility are dependant on possible interaction between stabilisers and polymer, cohesion and adhesion energy, volume or surface interaction, and on the intensity and character of interfacial surface force[102]. On the other hand, the concentration of stabilisers, environmental temperature and polymer history also affect the solubility of stabilisers in the polymer. Thus, how to solve this problem has deeply attracted many scientists attention.

Based on traditional methods, one of the ways of improving the solubility of stabilisers in polymer is by modification of the long chain structure of stabiliser molecule similar to the chain structure unit of the polyme[123-127]. But, this methed is not enough to thoroughly solve the problem. In recent years, different methods have been proposed to improve the resistance and permanence of antioxidants in polymers. These include increasing the molecular weight of antioxidants, synthesising polymeric antioxidants, copolymerising antioxidants with polymerisable monomers as well as binding(grafting) of antioxidants to the polymer chain by mechanochemical methods during polymer melt processing. Higher molar mass antioxidants for polymers lead to reduction in the volatility and diffusion rate of antioxidants in pure polymers, but this does not solve the problem of diffusion and migration from swollen polymer since most solvents for organic additives are also good swelling agents for polymers[128]. An alternative measure is required and the only one which offers a satisfactory long term solution to this problem is the chemical combination of the antioxidant with the polymer so that it can not be removed even under the most aggressive conditions. In recent years several groups have investigated the possibility of copolymerising vinyl antioxidants and UV stabilisers at the polymerisation stage. A commercial nitrile-butadiene rubber containing (A) as a co-monomer was marketed by Goodyear[129], and although technically successful, the increased cost of the product has limited its wide application in practice.



(A)

Similar research by Vogel and his co-worker[130,131] has led to the synthesis of vinyl polymers containing the copolymerised monomer(B) and other related UV absorbers. Little information has been published



on the effectiveness of the copolymerised UV stabilisers and no commercial developments appear to have resulted.

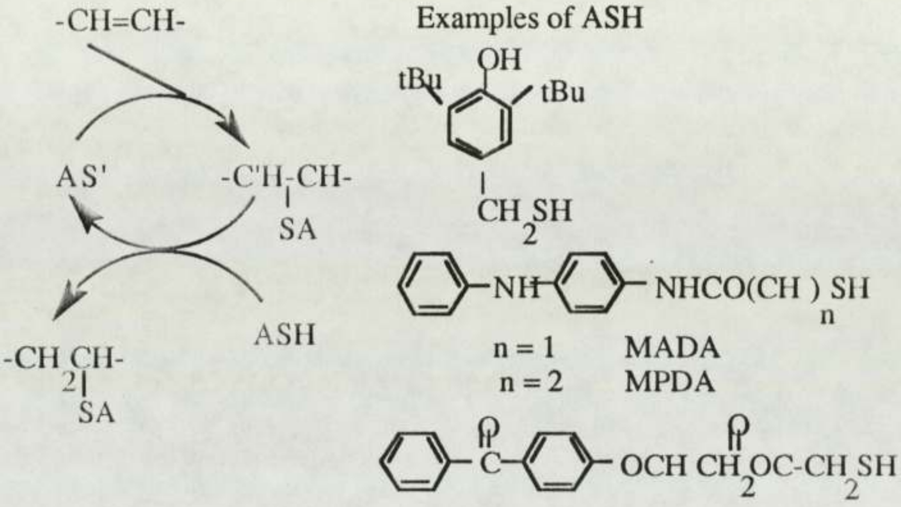
From a practical point of view, binding of antioxidant to the backbone of a polymer by a mechanochemical method during polymer melt processing is one of the best ways to exploit antioxidant-grafted polymers in the potential commercial marketing. Recently, Scott and his co-workers have developed several kinds of polymer-bound antioxidants by mechanochemical method mainly for rubbers[132-140]. Some good results have been achieved in polymer.

The mechanochemistry of polymers has its origins in early days of the natural rubber industry when the process of 'mastication' was used to break long molecular chains in rubber to reduce its molecular weight in the presence of oxygen in order to allow the incorporation of compounding ingredients[142,143]. The mechanism of the mechanochemistry in mastication was very successfully investigated by W. F. Watson and his collaborators during the 1950's[145,146]. Watson showed that macroalkyl radicals produced by mechanochemical scission of the polymer chain could be used to initiate the polymerisation of an added vinyl monomer to form block copolymers[147]. Scott et al. have used the same method to initiate the Kharasch addition of substituted alkyl mercaptans, disulphides and related compounds to olefinic double bonds through the intermediate thiyl radicals (scheme1.7) [135-139, 147-155].

$-CH{=}CHCH_2CH_2CH{=}CH- \longrightarrow -CH{=}CHCH\cdot_2(M\cdot)$ (a)

$M\cdot + ASH \longrightarrow MH + AS\cdot$ (b)

$M\cdot + ASSA \longrightarrow MSA + AS\cdot$ (c)



Scheme 1.7 Mechano-initiated addition of sulphur antioxidants to an unsaturated polymer.

This process is particularly useful for rubbers and rubber modified plastics(e.g. ABS). This reactive processing can be used to make concentrates (masterbatchs) of bound antioxidants in polymers which can subsequently be used as conventional additives during rubber compounding. The extent of binding is in the region of 50-80% for the typical thiol antioxidants, such as MADA, MPDA and EBHPT. High effectiveness of their antioxidant activity has been reported [150,153]. However, it is difficult to achieve binding in excess of 85% due to the formation of disulphide by-products(see scheme1.7) which increase substantially during vulcanisation. These by-products are themselves effective antioxidants, but when contacting with organic solvents they would be removed from rubber products. For some purposes, notably food packing and prostheses, it particularly requires that further generations of polymer-bound antioxidant are up to 100% bound to polymer so that they can not be absorbed by fat, oil and other fluids over a long period of time.

1.8 Object and Scope of the Present Work

In order to solve the problem of physical loss of stabilisers from polymers and therefore to improve the performance of polymers during their service life time many measurements have been taken by scientists. One possible way of overcoming this problem fundamentally is to chemically attach the stabiliser to polymer during its processing operation[132-133]. Scott and co-workers have been successful in grafting a variety of antioxidants to rubbers and plastics in the presence of radical generators or during the vulcanisation. The present work is concerned with three types of bound antioxidants on polypropylene which include reactive hindered amine, UV absorber and hindered phenol derivatives with aryloyloxy groups. Conventional antioxidants normally show a plateau effects on thermal and photostabilisation of polymers with increasing concentration. This has been attributed to the limited solubility of conventional additives with polymers at ambient temperature. How about bound antioxidants in polymers? What exactly happens in bound antioxidant systems? Thus, this study is concerned with:

(1) the relationship between the concentration of the bound antioxidants and their thermal and photo antioxidant activity;

(2) the effects of these bound antioxidants in two or three component synergistic systems; and

(3) the mechanism of acton of nitroxyl radical with hindered phenol in antioxidant system.

Chapter Two

Experiment

2 Experiment

2.1. General Experiment Technique

2.1.1. Materials, Instruments and Equipment

2.1.1.1. Materials

Polypropylene(PP) was supplied in powder form which does not contain any additive under the trade name PROPATHENE HF 22 by I.C.I. It was stored in a freezer.

The parent hindered amine (2,2,6,6-tetramethyl-4-piperidinol) was supplied by Ciba Geigy SA of Switzerland and directly used without further purification. 2,4-dihydroxybenzophenone and 2,6-di-tertbutylphenol were ordered from Aldrich Chemicals Company and directly used without further purification.

The following chemicals and reagents were used for general purpose: methyl acrylate, ethylene chlorohydroxide, potassium tertbutoxide, tertbutanol, paraformaldehydre, acrylic acid, m-choloperoxylbenzoic acid (ex Aldrich chemicals). All other solvents were standard laboratory reagents which include hexane, diethylether, toluene, petroleum ether, dichloromethane, and acetone.

The free radical generator (2,5-bis-tertbutylperoxy-2-5-dimethylhexane) (trade name Triganox 101) was supplied by AKZO chemie company and a multifunctional agent (trisacryloytrimethylolpropane) (Tris) was supplied by Anocomer company and used without further purification.

Three kinds of conventional antioxidants; n-octadecyl-3-(3',5'-di-tertbutyl-4-hydroxyphenyl)proprionate (Irganox 1076) and bis(2,2,6,6-tertamethylpiperidinyl)sebacate (Tinuvin 770) were supplied by Ciba Gelgy, and 2-hydroxy-4-octyloxy-benzophenone(UV531) was supplied by American Cynamid.

2.1.1.2 Instruments

Perkin-Elmer 599 Infrared Spectrophotometer;
Perkin-Elmer 1710 Infrared Fourier Transform Spectrophotometer;
Beckman Du-7 Spectrophotometer.

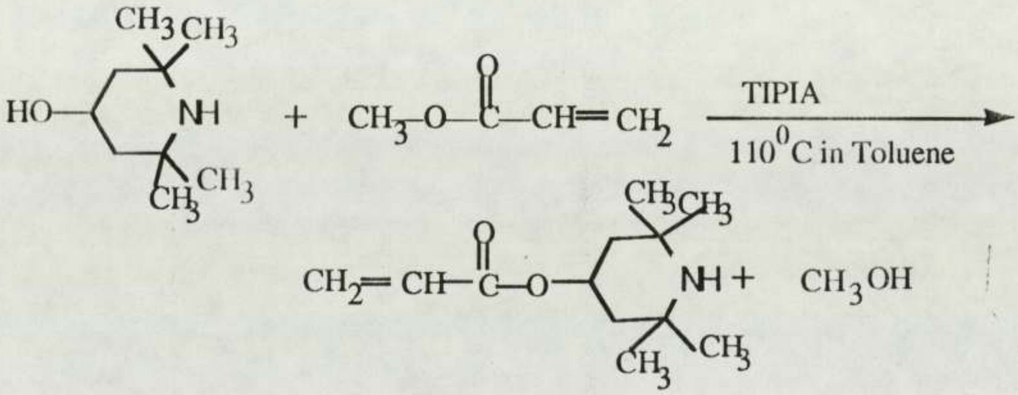
2.1.1.3 Processing Machines

Plasti-Corder Brabender motor fitted within RAPRA-Hampden torque rheometer mixing head was used for polymer processing;

Daniel Electric Press (for film making).

2.2 Synthesis of Antioxidant Monomers

2.2.1. Preparation of 2,2,6,6-tertamethyl-4-piperidylacrylate (AOTP)[117]

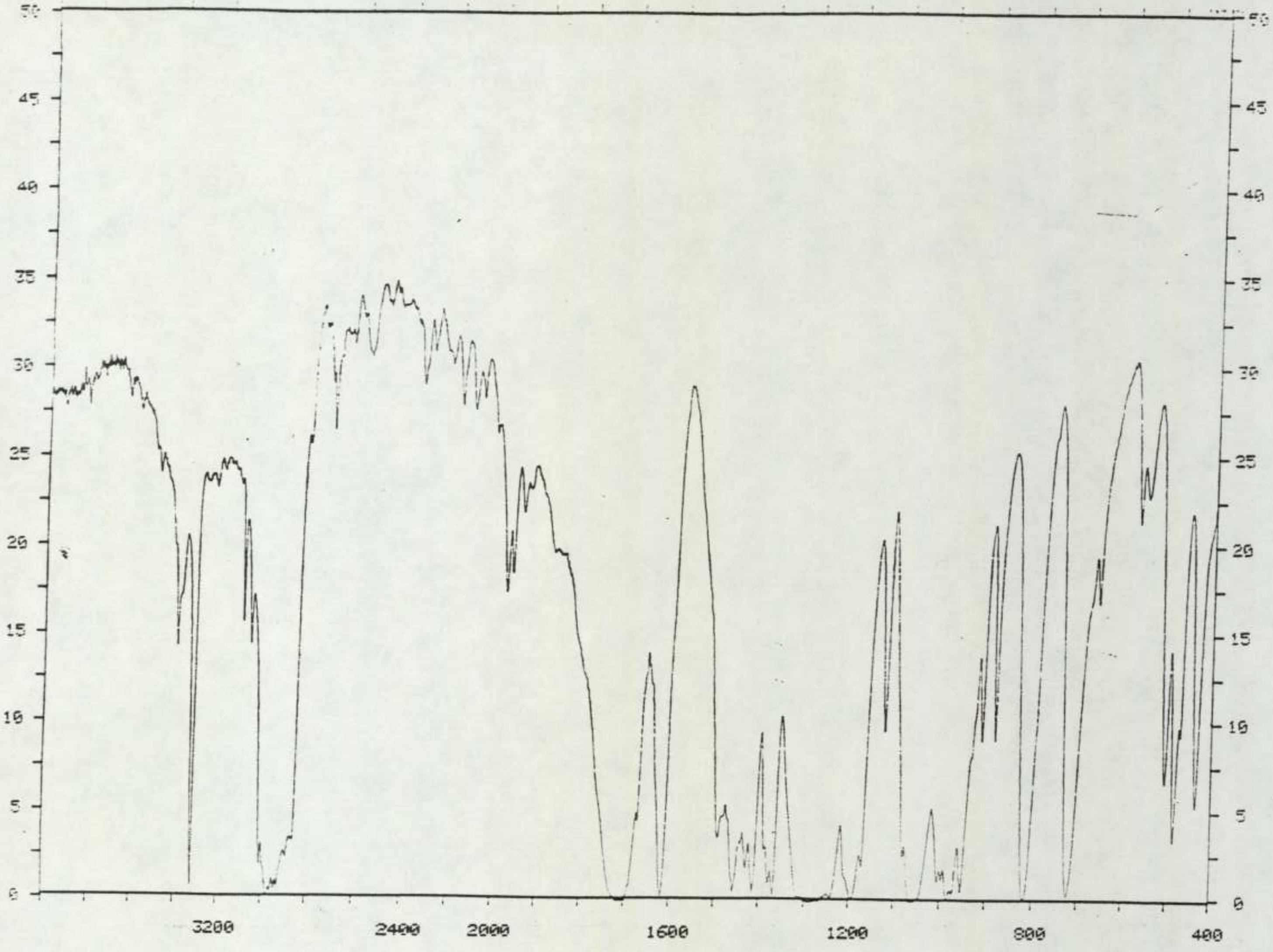


AOTP was prepared according to literature method [117] as follows: 41.6g(0.2mol) of 2,2,6,6-teretamethyl-4-piperidinol, 44.8ml of methyl acrylate(0.533mol) were put into 400ml of dry toluene in a 1l three (or two) -neck flask with condensor and nitrogen inlet tube. The mixture was heated under nitrogen until piperidinol was dissolved completely, then 7.94ml of titanium isopropoxide (catalyst TIPTA, 0.0267mol) was added into the flask and the reaction left for 20-24 hr. under reflux and nitrogen flow. Unreacted methylacrylate and solvent were evaporated until a concentrated yellow liquid was formed. This was then poured into a mixture of 400ml hexane and 500ml of 5% aqueous $KHCO_3$ solution while stirring. The mixture was filtered off and two liquid phases were separated. The water phase was then extracted with 150ml of hexane. Two parts of hexane solution (containing somewhat finely suspended titaniumdioxide) were filtered again througth a filter bed of fine barium sulfate to obtain a clear solution which was evaporated to yield a slightly yellow white solid as the crude product.

The crude product was then dissolved in 150ml of hexane hy warming, and then placed in a freezer for crystallisation. The cooled mixture was filtered quickly and washed with cool hexane (from dry-ice bath) twice, dried in vaccum yielding 27g (50% based on the piperidinol) of white crystalline solid, m.p. 52-53°C (m.p. of 53°C in ref.117).

Analysis of Infra-red Spectrum (KBr disc) shown In Fig. 2.1

N-H bond	3317cm^{-1},
Ester carbonyl (-O-CO-)	1713cm^{-1},
Unsaturation (-C=C-)	1616cm^{-1},

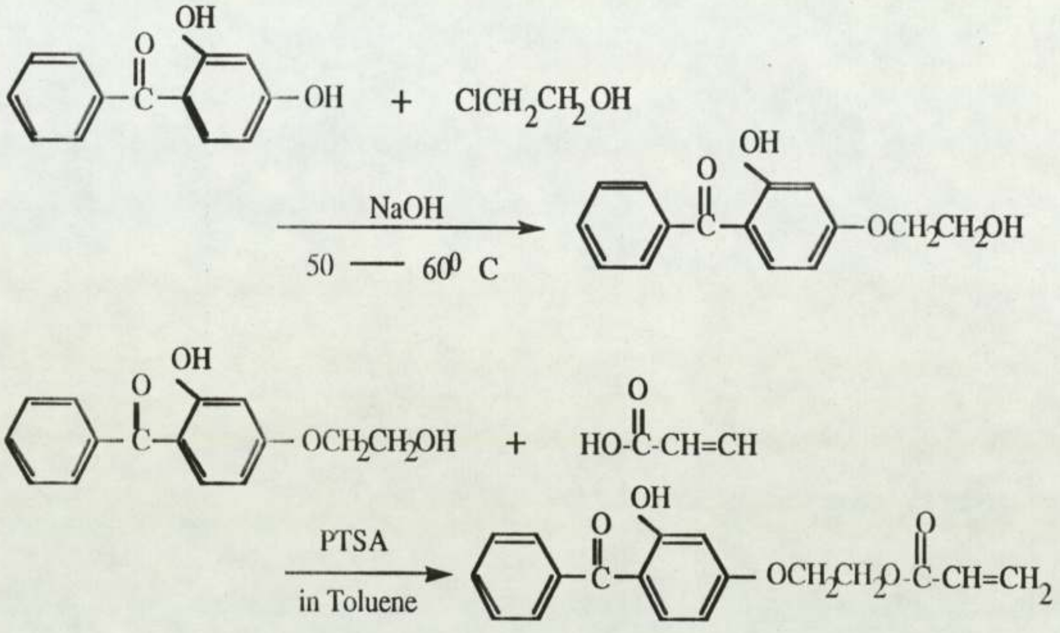


```
PEAK THRESHOLD =  1.00  %T
      CM-1         %T

     3823.0      27.88
     3632.0      28.29
     3394.0      14.27
     3317.0      0.71
     3094.0      15.67
     3059.0      14.40
     3006.0      1.95
     2975.0      0.16
     2710.0      26.52
     2562.0      30.66
     2487.0      33.55
     2335.0      29.09
     2293.0      31.02
     2210.0      30.26
     2162.0      27.95
     2107.0      27.71
     2069.0      28.38
     1973.0      17.47
     1960.0      18.50
     1938.0      21.95
     1713.0      0.01
     1616.0      0.34
     1491.0      3.67
     1456.0      0.60
     1428.0      1.97
     1412.0      0.65
     1367.0      0.43
     1295.0      0.01
     1192.0      0.17
     1123.0      9.63
     1061.0      0.01
      983.0      0.15
      952.0      0.71
      910.0      9.09
      882.0      9.09
      816.0      0.13
      720.0      0.40
      658.0      16.92
```

Fig. 2.1 IR spectrum of 2,2,6,6-tertamethyl-4-piperidylacrylate (AOTP) in KBr

2.2.2 preparation of 2-hydroxy-4-(2'-acryloyloxy)ethyloxybenzophone (HEAB)[118]



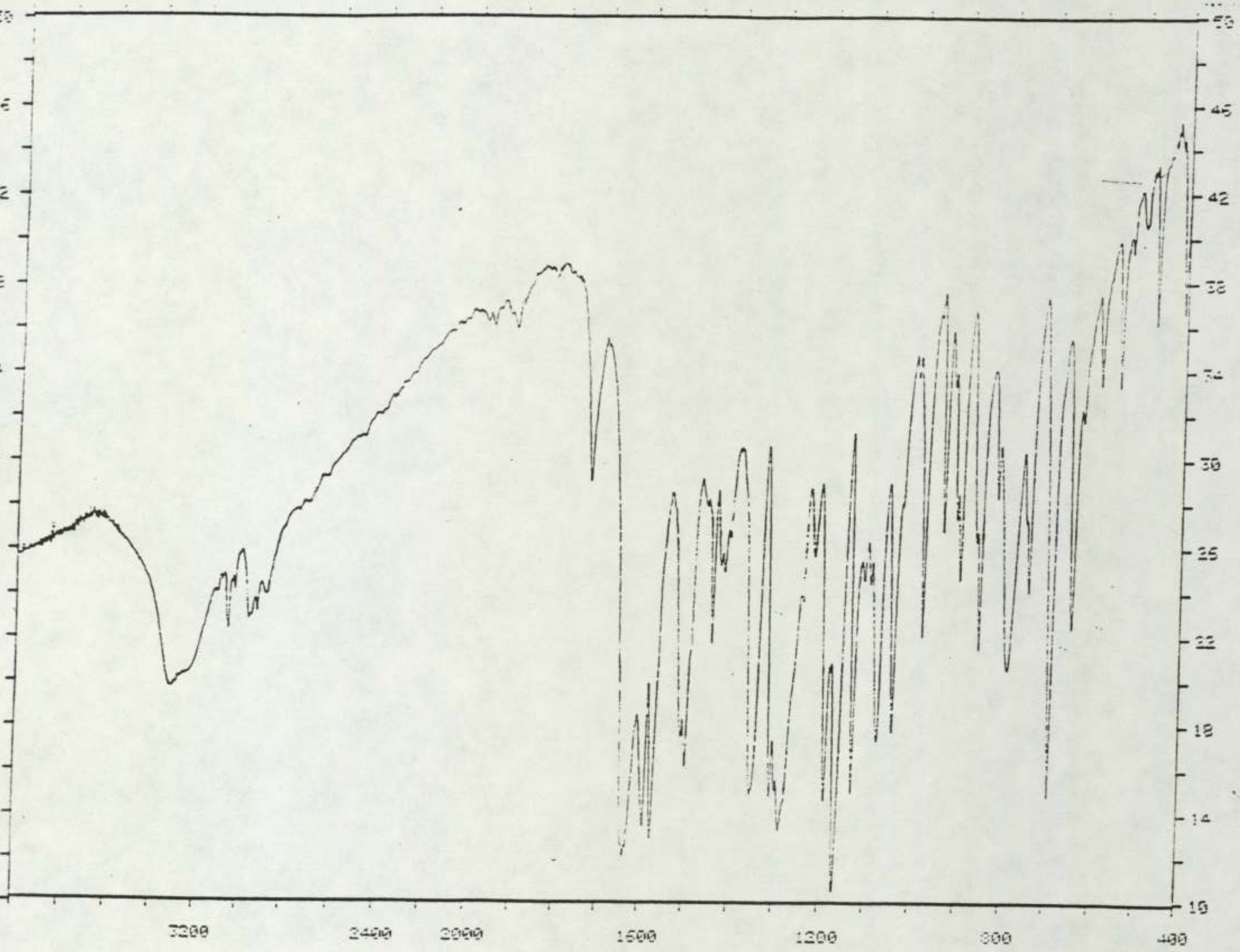
This was prepared by a modified literature method [118] as follows: In the first step, 21.4g(0.1mol) of 2,4-dihydroxybenzophenone and 6g (0.15mol) of chloroethylanol were added together. The mixture was stirred at 60°C for 5 hr., then 125ml of distilled water at 60°C was added. The solution was allowed to stand overnight with stirring at room temperature. The precipitate obtained was washed several times with distilled water and mechanical stirring continued for 5hr. A yellow powder was obtained. The crude product was dissolved in 100ml dichloromethane and placed in a freezer for crystallization. The solvent was removed by filtering, and the filtered product was dried in vacuum oven at 40°C yielding 15g of yellow crystalline solid (I) (2-hydroxy-4-(*B*-hydroxy-ethyloxy)benzophenone), m.p. 88°C(m.p. of 89°C supplied by American Cynamid). In the second stage, 26g of I, 2-hydroxy-4(B-hydroxy-ethyloxy) benzophenone, produced above (0.1mol) and 10.82g of acrylic acid (0.15mol) were added to 200ml of dry toluene in 500ml flask with a Dean & Stark. 0.1g of PTSA(p-toluene sulphonic acid) was added to the flask as a catalyst, and refluxed for 5-6 hr. until 1.8g of water was collected theoretical quantity from the reaction mixture. The solvent was removed from the reaction mixture by rotatory evaporation and the filtered mixture was washed several times with 5% aqueous $KHCO_3$ solution to remove any remaining acid and catalyst, and finally washed with distilled water. The crude product was dissoved in hexane to form a solution which was dried with $MgSO_4$ overnight, then the dry solution was evaporated to remove hexane giving a yellow solid which was crystallised in dichloromethane to give a white yellow crystalline solid, melting point of 65-67°C.

Analysis:

Infra-red spectrum (KBr disc) shown In Fig. 2.2.

Ester carbonyl (-O-CO-): $1726cm^{-1}$,

Ketonic carbonyl(-CO-): $1636cm^{-1}$.

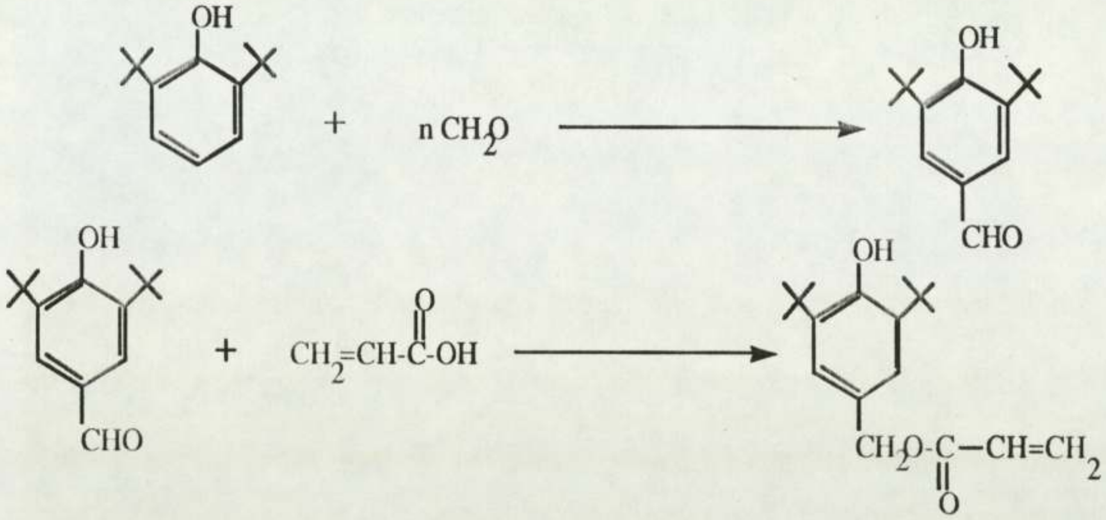


PEAK THRESHOLD = 0.20

CM-1	%T
3313.0	19.77
3052.0	22.44
3023.0	24.33
2957.0	22.87
2918.0	23.21
2879.0	23.97
1957.0	36.12
1904.0	36.00
1814.0	38.32
1725.0	29.12
1636.0	12.33
1592.0	13.59
1574.0	13.95
1511.0	17.55
1500.0	16.31
1444.0	21.91
1427.0	25.35
1418.0	25.97
1353.0	15.11
1310.0	14.95
1287.0	13.48
1220.0	25.81
1191.0	14.75
1168.0	10.55
1131.0	15.08
1109.0	24.59
1095.0	24.50
1077.0	17.45
1043.0	17.91
1000.0	33.32
979.0	22.21
938.0	26.35
920.0	33.42
909.0	27.41
899.0	24.54
854.0	21.54
819.0	28.73
790.0	20.55

Fig. 2.2 IR spectrum of 2-hydroxy-4-(2'-acryloyloxy)ethyloxybenzophone (HEAB) in KBr

2.2.3 Preparation of 3.5-di-tertbutyl-4-hydroxylbenzylacrylate (DBBA)[119]



DBBA was prepared according to literature method[119] as follows: Firstly, a solution of 50g of 2,6-di-tertbutylphenol in 170g of tertbutanol was poured into a 500ml flask, purged with nitrogen. A well dispersed slurry of 8g paraformaldhyde in 100ml tertbutanol was added into the flask which was continuously stirred under ice cooling. A solution of 1.4g patassium tertbutoxide in 28g tertbutanol was then added gradually from a funnel, keeping the temperature below 10°C. Stirring was continued for about 45 min. by which time the mixture had turned into a thick red liquid. the mixture was then poured into a bowl of ice and left in the refrigerator overnight. The yellow crystals fomed were washed with water and then with hexane, giving purplish-white powder which was recrystallised from chloroform and hexane to get white crystals with a m. p. of 130°C (2,6-di-tertbutylhydroxylbenzyl alcohol) (m.p. of 131°C in ref 119).

Secondly, 0.1mol (23.6g) of 2,6-di-tertbutylhroxylbenzyl alcohol was dissolved in 0.2mol (16.23g) of acrylic acid. The mixture was added into a flask and warmed gently on a steam bath until complete solution was achieved, then about 0.1g of p-toluene sulphonic acid (PTSA) was added as a catalyst. The mixture was allowed to stand at 70°C for six hours, and then poured into water. The organic phase was extracted with ether and excess acrylic acid was absorbed with 5% aquous $KHCO_3$ from the organic phase. The ether phase was then dried with anhydrous magnesium sulfate, and filtered. The solvent was evaporated to obtain a concentrated product. The crude product was crystallised twice from petrolum ether to form white crystalline solid, m. p. 64- 65°C(m.p. of 64-65°C in ref.119).

Infra-red analysis (Fig. 2.3):

Hindered phenolic OH (free): 3588cm^{-1},

Ester carbonyl (-O-CO-): 1713cm^{-1},

Vinyl unsaturation (conjugated): 1637cm^{-1}.

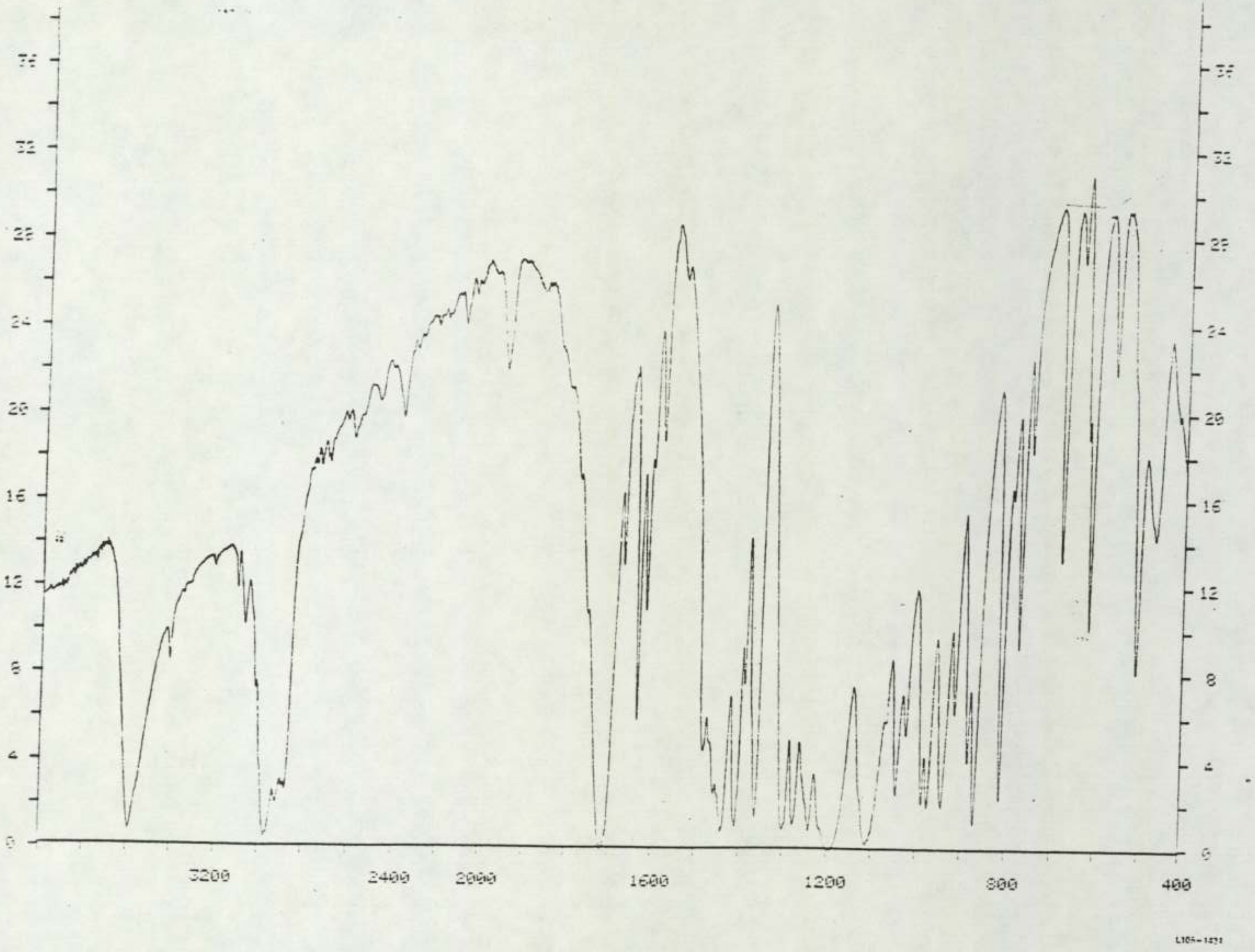
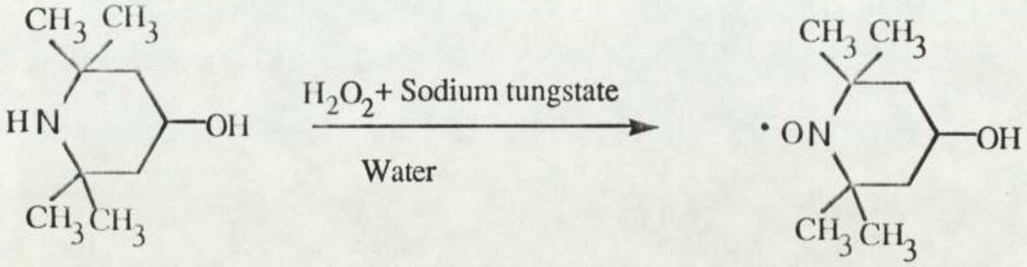


Fig. 2.3 IR spectrum of 3,5-ditertbutyl-4-hydroxylbenzlacrylate (DBBA) in KBr

CM-1	%T
3856.0	12.42
3586.0	0.85
3410.0	8.67
3213.0	12.95
3107.0	11.98
3071.0	10.24
3016.0	7.34
2966.0	0.60
2915.0	2.11
2874.0	2.71
2741.0	17.59
2704.0	17.79
2629.0	19.66
2599.0	19.91
2487.0	20.52
2380.0	19.92
2324.0	22.94
2230.0	24.01
2188.0	24.44
2107.0	24.14
2064.0	25.51
1955.0	22.02
1873.0	25.59
1713.0	0.04
1673.0	13.18
1637.0	5.01
1619.0	11.07
1609.0	17.55
1588.0	18.76
1546.0	25.24
1483.0	4.53
1457.0	2.70
1439.0	0.91
1408.0	1.19
1392.0	7.70
1364.0	1.53
1300.0	1.00
1276.0	1.29

2.2.4. Preparation of 4-hydroxy-2,2,6,6-tetramethylpiperidinel-1-oxy (TMPO)[120]



A mixture of 30g of 4-hydroxy-2,2,6,6-tetramethylpiperidine dissolved in 200ml of water, 40ml of 30% hydroperoxide(H_2O_2) diluted with 200ml of water and 2g of sodium tungstate was left at room temperature for 4 days. The solution was saturated with potassium carbonate and repeatedly extracted with ether. The combined ether extracts were dried with $MgSO_4$. The ether was evaporated and the residue with orange colour recrystallized from a mixture of ether and hexane (2:1). The final product (4-hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl) referred to as TMPO had a m.p. of 71°C (m.p. of 71.5°C in ref. [120]).

Ultraviolet-visible spectrum analysis:

The peak was observed at about 475 nm.

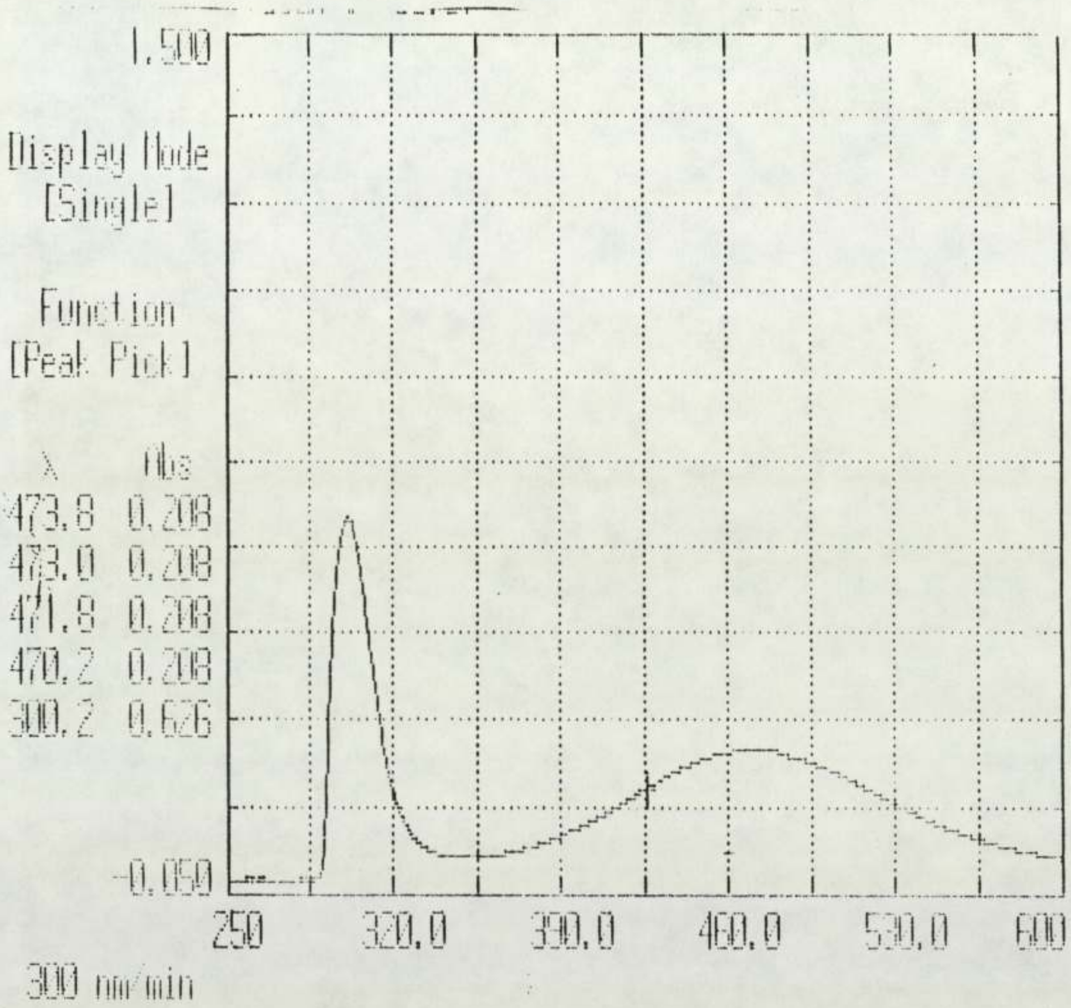


Fig. 2.4 UV/Vis. spectrum of 4-hydroxyl-2,2,6,6-tetramethy-piperidinel-1-oxy (TMOP) in xylene.

2.3. Polymer Processing, Film Preparation and Extraction

2.3.1 Processing of Polypropylene with Additives in Torque Rheometer

In order to mix additives thoroughly with PP, firstly, the additives were dissolved in acetone and added to PP powder by manual stirring. The mixture was evaporated under vacuum to volatilise the solvent completely at 40^0C for 6 hours. The well distributed mixture powder was poured into the torque rheometer which consisted of a given small of chamber with two contra rotating rotators for mixing in various speeds. The speed of rotation was fixed at 65 r. p. m. Other processing conditions, such as, processing temperature and time were varied.

After a given processing time the melt polymeric mixture was removed as soon as possible while the chamber was open, and chilled in cool water to reduce the extent of thermal oxidation of polymer melt.

A full charge of 35g mixture (polymer + additives) was used for each sample processing and the chamber could be open, closed or under inert atmosphere by prior purging with nitrogen or Ar gas and purging again after the chamber was closed.

2.3.2 Film Preparation of Polymer

Polymer films for thermal and UV light aging, or for IR spectroscopic study were prepared by a compression moulding method. An electric press was used which included heating and cooling system for melting and forming of polymer film. The processed polymer sample was placed between two stainless steel glazed plates, and a special heat resistant cellophane film was introduced to prevent the sample from sticking on the moulding plates. Control of film thickness was obtained by a standard quantity of polymer (about 7g) to produce a film thickness of about 1.8×10^{-2}cm (0.007").

The weighed amount of the polymer sample was placed between the plates and inserted into an electric press at 180°C, then pre-heated for 1.0 min. without appling any pressure on it. Pressure of 80kg/cm^2 was then impacted on for a further 1.0 minute. After that, the plates were cooled to about 60°C by running cooling water. A number of films of uniform size and thickness were cut for testing.

2.3.3 Solvent Extraction of Polymer film

In genenal, conventional additives were easily removed from polymer film by using suitable solvent in hot Soxhlet extration during 5-50 hours or less, and a steady stream of nitrogen was bubbled during the extraction period. When extraction was finished the film was dried under vaccum at a maximum temperature of 40°C for 5 hours to remove solvent. This method would be used to investigate the extent of binding of vinyl antioxidants in PP. Dichloromethane was selected as extracting solvent in which the unbound antioxidants were thoroughly soluble.

2.3.4 Thermal and UV light Aging of Polymer Film

2.3.4.1 Thermal Aging of Polymer Film

The accelerated thermal oxidation of processed polypropylene film was carried out in a single cell Wallace oven at 140^0C with circulation of air. Each sample was contained and suspended in a separated cell to prevent cross contamination of additives by volatilization, and was subjected to an air flow of 2.5 cubic feet/hr. (56.7 litres/hr.).

2.3.4.2 UV light Aging of Polymer Film

UV irradiation of polymer film was carried out in an accelerated weathering cabinet consisting of two concentric cylinders. The out cyclinder contains 32 fluorescent lamps: 8 sun lamps and 24 blue lamps which are arranged in symmetrical sequence on a 1 : 3 basis. The testing samples are mounted on the inner cyclinder which rotates around the lamps at a distance from them of 15cm. Temperature inside the cabint with the lights was 30^{0}C ± 1^{0}C. The average intensity of UV irradiation at the centre of drum falling on the surface of film was calculated to be about 5.5 w. h. m^{-2}[121].

2.3.4.3 Measurement of Brittle Fracture Time of Polymer Film

Exposed films tested for embrittlement were of uniform size and thickness (1.8X10^{-2}cm). They were periodically checked during the UV or thermal aging for measuring the embrittlement. The time to embrittlement was determined by a manunal bending of the film to an angle of 180^{0}C. Each measurement of polymer sample was carried out in triplicate for accuracy. The reproducibility of the results was within ± 10%.

2.3.4.4 Spectroscopic Measurement

Rate of thermal and photochemical oxidation were monitored by measuring the formation of the non-volatile carbonyl oxidation products which absorb IR light at about 1710cm^{-1} with a Perkin-Elmer Model 599 Infra-red spectrometer or FTIR M1700 because the degree of degradation (or stabilisation) of polyolefins can be generally related to the extent of carbonyl groups produced during the process of their oxidation. To account for variations in film thinkness and instrument error in intensity measurements, use is made of interal reference band in PP (2722cm^{-1}) which are unaffected by oxidation. A carbonyl index is, therefore, defined as the ratio of the carbonyl absorption at about 1710 cm^{-1} to the appropriate reference band. The carbonyl absorption as well as other functional group absorptions are determined using the base line method[122]. The carbonyl index method is also used for the evaluation of binding extent of active antioxidant in PP because there are ester carbonyl groups respectively in these kinds of bound antioxidants which can be identified and quantified through the base line method with IR.

Most infrared spectrometes measure band intensities linearly in percent transmitance, %T, and therefore logarithmically in absorbance

A. Through this logarithmical relationship of %T with A Slight inaccuracies in the measurement of %T may correspound to very large inaccuracies in the measurement of A. In general, acceptable accuracy in the measurement of A can only be achieved when the band intensity lies between 20 and 80% T. To account for quantitative analysis in change of antioxidant concentration the calibration curve should be established from a wide range of antioxidant concentration.

UV/Vis. spectrometer was used to monitor a change in the concentration of a nitroxyl radical (TMPO) in a solution reaction because the nitroxyl radical has an evident absorption at 475 nm and the absorption intensity is linearly proportional to the concentration of TMPO. The concentration calibration curve is shown in Fig. 5.3.

In order to avoid effects of solvent background on the UV/Vis. absorption spectrum of the nitroxyl radical and minimize the measurement error the absorbance value of TMPO in xylene would be calculated through Net A3 calculation equation[74] rather than directly picking up its absorbance peak at 475 nm. This is accomplished by taking absorbance readings at the beginning and end of the absorption peaks in addition to the maximum absorbtion peak.

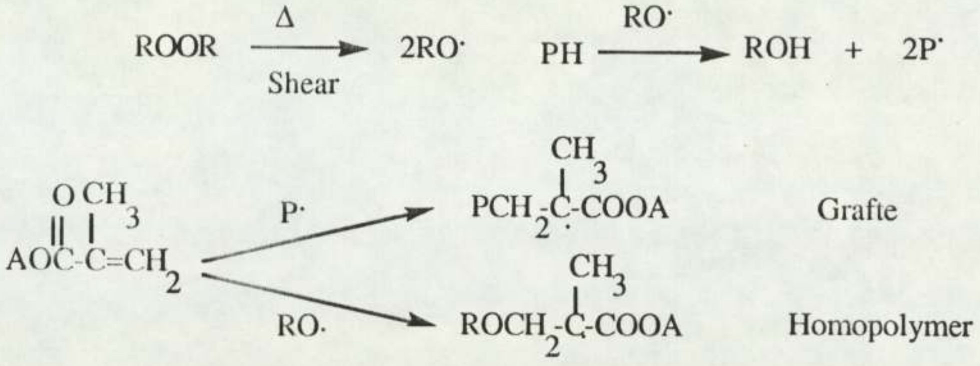
Chapter Three

Preparation of Polymer-bound Antioxidant Concentrates (Masterbatch) and Evaluation of Binding Extent of Antioxidants in Polypropylene

3 Preparation of Polymer-bound Antioxidant Concentrates (Masterbatch) and Evaluation of Binding Extent of Antioxidants in Polypropylene

It is known that many attempts have been reported to graft vinyl antioxidants to polymers [156-164]. Munteanu has reviewed these recently[156] in surface grafting, melt grafting, solution grafting of momomers of antioxidants. This is essentially by free radical chain mechanism. The details of the grafting process is not yet clear because many factors affect the grafting efficiency. In general, grafting appears to be associated with the formation of substantial amounts of homo-polymer(scheme 3.1a)[157] which is generally less effective than fully grafted adducts since the homoplymer tends to separate as a discrete phase which could be removed by leaching or solvent contact. Thus, in this research minimizing the trend of homopolymerisation and increasing the extent of grafting vinyl antioxidants in polymer is an important task so that high performance of polymer-bound antioxidant in photo and thermal stabilising of polymer could be achieved.

Scheme 3.1a Reaction of vinyl antioxidants in polymers(PH)



Different polymer-bound antioxidants were prepared for this study which include one hindered piperidine derivative (2,2,6,6-tetramethyl-4-piperidyl acrylate), one UV light absorber (2-hydroxy-4-(2'-acryloyloxyethyloxy)benzophone) and one hindered phenol (3,5-di-tertbuty-4-hydroxybenzylacrylate). In this work attention is paid to the effects of polymer-bound antioxidant concentration on thermal and photostabilisation and the mechanism of synergism between two and three component polymer-bound antioxidant systems would also be studied.

3.1 Designing The Formulation of Compounds in The Binding System

Since grafting of vinyl antioxidants in polypropylene during melt processing is a typical radical chain reaction the chain initiation, propagation, transformation and termination will determine the chemical attachment level and length of grafting chain of vinyl antioxidant in PP. Many variables will affect the above processes. For example, the structure of the polymer, type and concentration of vinyl antioxidant, initiator and the polyfunctional agent used, the processing time, temperature as well as shear rate.

During melt processing the hydrogen on the tert-carbon in PP is easily attacked by free radicals leading to the formation of macroakylradical and peroxylradical, and this results in chain scission of polypropylene at high temperature. In the presence of a radical generator and a certain amount of polyfunctional agent, polypropylene could become crosslinked. Generally speaking, in grafting reactions, if the polymer tends to crosslink a graft structure would result; If the polymer tends to degrade then block-type copolymer would be formed as shown in scheme 3.2[168]. Therefore, to enhance the tendency of vinyl antioxidants to graft on PP, some polyfunctional agent may be added to the mixture.

Scheme 3.2 Possibility of grafting monomers to polymer chain

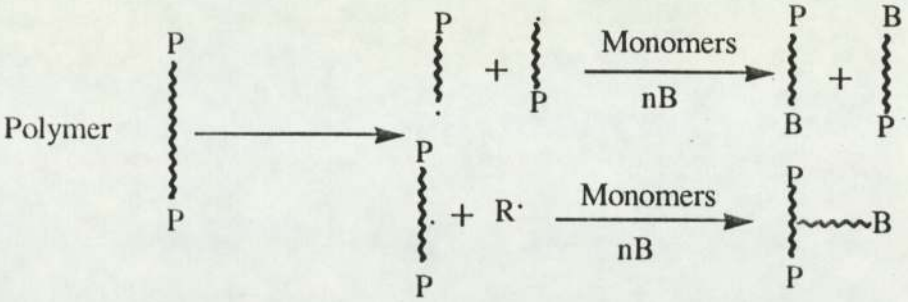


Table 3.1 $L_9(3^4)$ Experimental Designation Table

No	A	B	C
1	A1	B1	C1
2	A1	B2	C2
3	A1	B3	C3
4	A2	B1	C2
5	A2	B2	C3
6	A2	B3	C1
7	A3	B1	C3
8	A3	B2	C1
9	A3	B3	C2

In order to get optimum polymer-bound antioxidant at high extent of binding and to reduce the number of experiments a mathematical statistical method is introduced in formulation designing which is called orthogonal design method[166]. Experimental designation table ($L_9(3^4)$) is selected with three variables and three levels of factors: A----- concentration of antioxidant (% w/w in PP), B-----ratio of initiator to antioxidant (w/w) and C----- ratio of polyfunctional agent to antioxidant (w/w) as shown in Table 3.1

3.2 Analysis of Binding Extent of Antioxidant in Polypropylene

Because all kinds of vinyl antioxidants made in this work contain ester groups (-CO-O-) which had an intense absorption at about 1720cm^{-1} in Infrared, and the ester carbonyl groups are very stable at high temperature both before and after reactive processing and solvent extraction, IR could be used as a semi-quantitative tool. When the IR spectra of polymer-bound antioxidant was compared with that of pure PP resin the difference was most remarkable at about 1720 cm^{-1}. There is a linear relationship of absorption intensity of ester carbonyl compounds to their concentration. Calibration curve is be shown in section3.2.1. Thus IR measurement in the C=O absorption region after extraction of polymer-bound antioxidant was used to assess the extent of binding. In the case of increasing concentration of AOTP (>10%), the carbonyl absorption intensity was very strong and therefore the antioxidant was diluted to 2% where the range of carbonyl absorption intensity falls between 20% - 80% T. In the case of solution, an extract which is diluted down to lower concentration could be examined. Thus, two analysis methods were used for binding measurement; direct testing of PP film with 2.0% concentration of a bound antioxidant diluted from its masterbatch and an indirect solution testing after extraction.

3.2.1 Preparation of Calibration Curve of AOTP Solution

To prepare calibration curve for AOTP, different known concentration of the AOTP was dissolved in dichloromethane(DCM), which was also used as extracting solvent, to form the standard solutions. A linear relationship of carbonyl index ($A_{C=O}/A_{C-Cl}$) with the concentration of AOTP was established as shown in Fig. 3.2.1. A linear equation was obtained as follows:

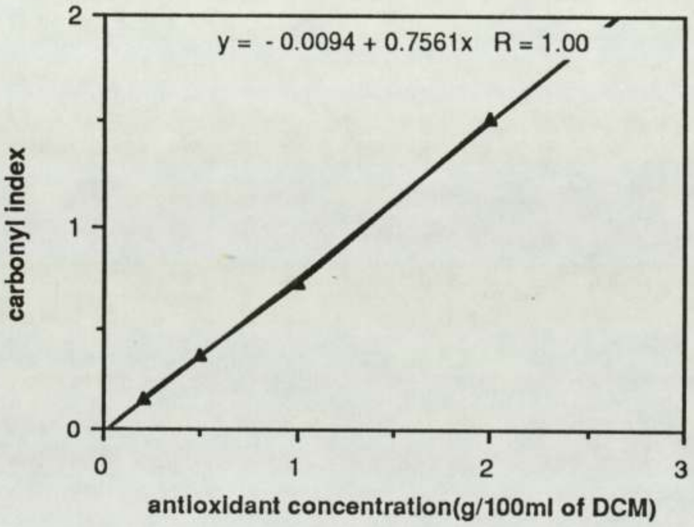


Fig. 3.2.1 Calibration Curve of AOTP in DCM

$Y = c + aX$, Y --- carbonyl index, X --- concentration of AOTP, c and a are constants. Therefore, the concentration of extract in DCM could be calculated by means of the above equation.

3.2.2 Preparation of Calibration Curves of HEAB And DBBA

In addition to ester carbonyl absorptions present in both HEAB and DBBA there are other functional groups such as ketonic carbonyl and -OH which show characteristic absorptions at 1636cm^{-1} and 3588cm^{-1} respectively, and can be quantitatively analysised by IR. Their calibration curves ($A_{1636cm-1}/A_{2722cm-1}$ and $A_{3588cm-1}/A_{2722cm-1}$) were produced as follows:

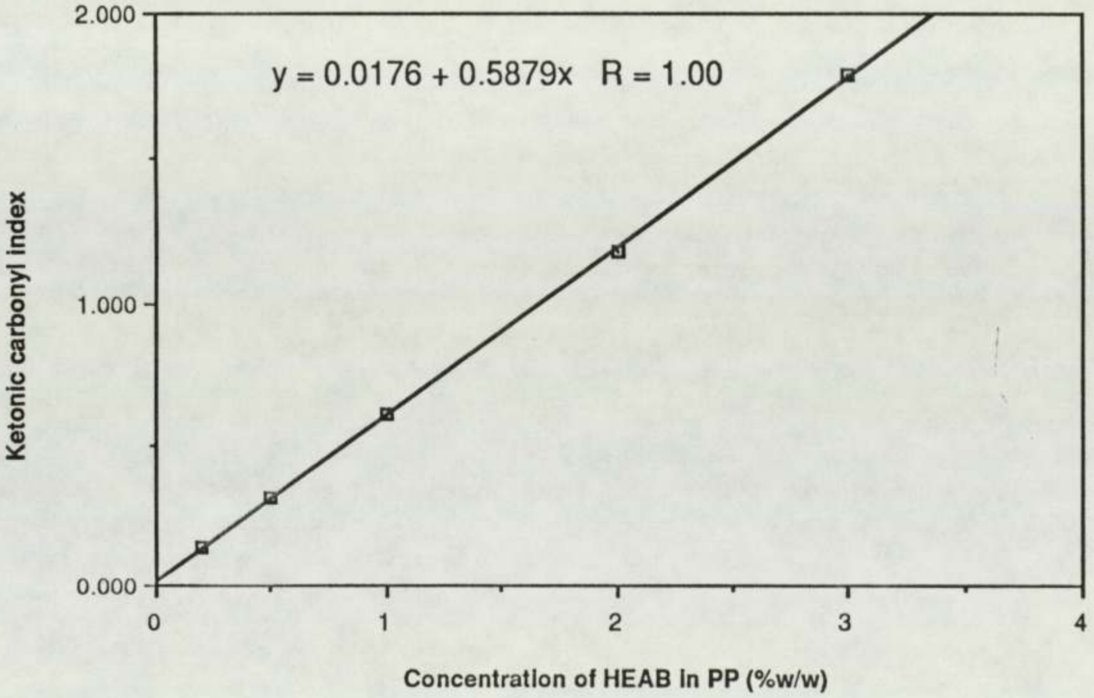


Fig. 3.2.2a Calibration curve of HEAB in PP

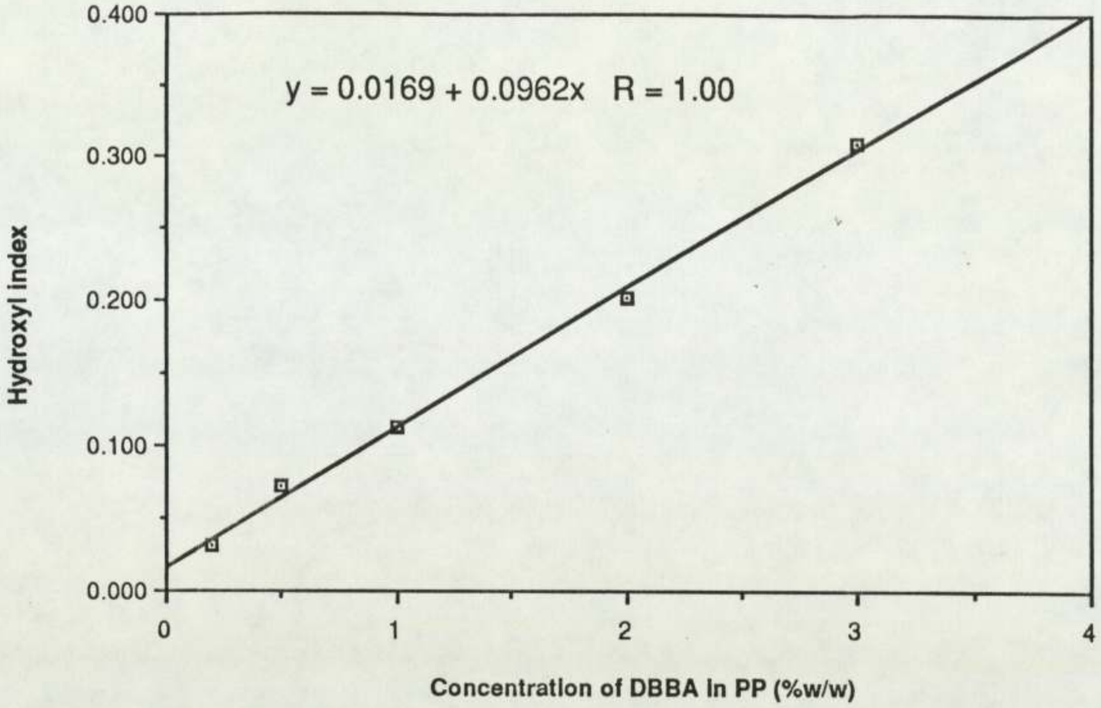


Fig. 3.2.2b Calibration curve of DBBA in PP

This was very useful for more precise evaluation of binding extent of HEAB and DBBA and overcame the problem associated with overlap of ester carbonyl due to the polyfunctional compound (Tris). Therefore diluted masterbatch of HEAB-B* and DBBA-B* at 2.0% concentration was directly chosen for examining the binding degree by checking the change of index in ketonic carbonyl and -OH respectively, and the solution analysis did not need to be done.

3.3 Preparation of Polymer-bound AOTP Concentrate (masterbatch)

Based on $L_9(3^4)$ design table, the formulation of AOTP with other additives in PP was arranged in the experiment shown on Table 3.3.1.

Table 3.3.1 Formulation design of AOTP with other additives in PP

Sample No.	Concen. of AOTP %(w/w)	Triganox/AOTP (w/w)	Tris/AOTP (w/w)
1	5	0.001	0.05
2	5	0.002	0.10
3	5	0.005	0.30
4	10	0.001	0.10
5	10	0.002	0.30
6	10	0.005	0.05
7	20	0.001	0.30
8	20	0.002	0.05
9	20	0.005	0.10

Note: Processing Temperature = 180°C, Processing Time = 10 minutes.

Firstly, AOTP, Triganox101 and Tris were dissolved in acetone to form a homogeneous solution, which were then sufficiently mixed with PP powder and the acetone was completely volatilized. The treated PP was poured into the chamber of TR for chemical grafting by a melt-mixing method, then the polymer-bound AOTP concentrate was obtained at a given processing condition. The binding extent of samples were measured by the IR method illustrated in former section. According to the results of sample No. 1-9 some supplementary experiments were also carried on for study of processing conditions shown on Table 3.3.1.1 and the results of binding efficiency under a variaty of parameters were demonstrated on Table 3.3.1.2.

3.3.1 Results and Discussion

3.3.1.1 Effects of Concentration of Additives on Binding Extent of AOTP in PP

3.3.1.1a Concentration of AOTP

Fig. 3.3.1.1a shows that an increase in concentration of AOTP led to an increase in the level of binding which passed through a maxinum and then decreased with further increase in the concentration of AOTP. this seems to indicate that when the concentration of AOTP was less than 10% the free radicials initiated by peroxide (Triganox101) did not easily attack AOTP monomer in the PP melt and chain propagation of AOTP was slow because chain initiation and propagation of AOTP

Table 3.3.1.1 Supplementary Formulation of Binding System in PP

Sample No.	AOTP (% w/w)	Triganox101 (ratio to AOTP)	Tris. (ratio to AOTP)	Temperature ^0C	Time min.
10	20	0.000	0.10	180	10
11	20	0.002	0.00	180	10
12	20	0.000	0.00	180	10
13	20	0.003	0.10	180	10
14	30	0.002	0.10	180	10
15	20	0.002	0.10	170	10
16	20	0.002	0.10	190	10
17	20	0.002	0.10	200	10
18	20	0.002	0.10	180	5
19	20	0.002	0.10	180	20
20	20	0.002	0.10	180	30
21	20	0.002	0.10	180	10

Table 3.3.1.2 Binding Extent of AOTP in PP under Different Conditions

Sample No.	1	2	3	4	5	6	7	8	9	10	11
Extent (%)	64	69	74	80	85	72	92	86	82	45	40

Sample No.	12	13	14	15	16	17	18	19	20	21
Extent (%)	20	88	75	79	87	75	80	85	79	89

Note: The results from the mean values of six specimen from duplicate processing experiments each formulation tested by diluting masterbatch to 2% concentration and they were confirmed by the solution analysis. The relative derivation(RD) was all less than 5%.

were diffusion-controlled by the mobility of monomers. In the free radical chain reaction, the rate of chain propagation was proportional to the concentration of monomer and free radical initially present in the mixer. Thus, the transformation rate of AOTP to graft in PP increased with an increase in the concentration of AOTP. But when the concentration of AOTP increased to more than 20%, the result was reversed due to its plasticising effect in PP which leads to a reduction in the mechanical shearing forces on polymer chains[135]. On the other hand, if a great amount of AOTP monomer existed in the system. all AOTP monomers could not be totally initiated by macroalkyl free radicals to form grafting, and to a certain extent, low molecular weight homopolymer of AOTP would be produced which could be removed by the solvent during extraction so that binding efficiency would decrease.

3.3.1.1b Concentration of Peroxide(Triganox101)

It is shown in Fig. 3.3.1.1b that binding efficiency increased with an increasing in ratio of the peroxide to AOTP, but this curve passed through a maximum and, then slightly declined with further increase of the peroxide concentration. Fig. 3.3.1.1b also shows that if in the

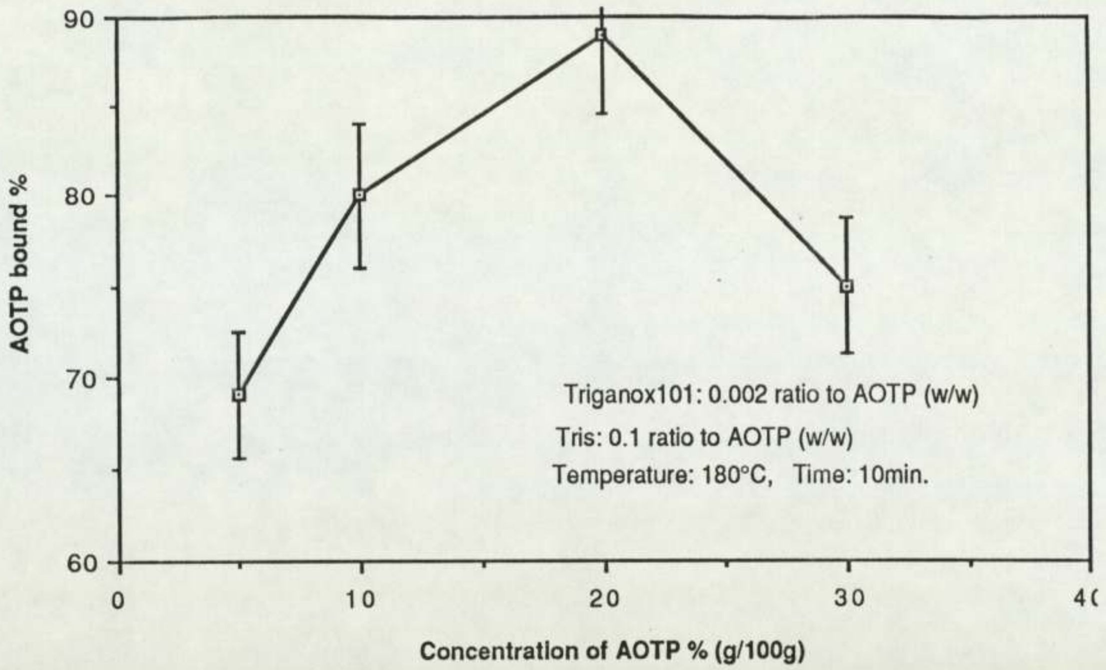


Fig. 3.3.1.1a Binding extent of AOTP in PP as a function of AOTP loading in PP (see table 3.3.1.2).

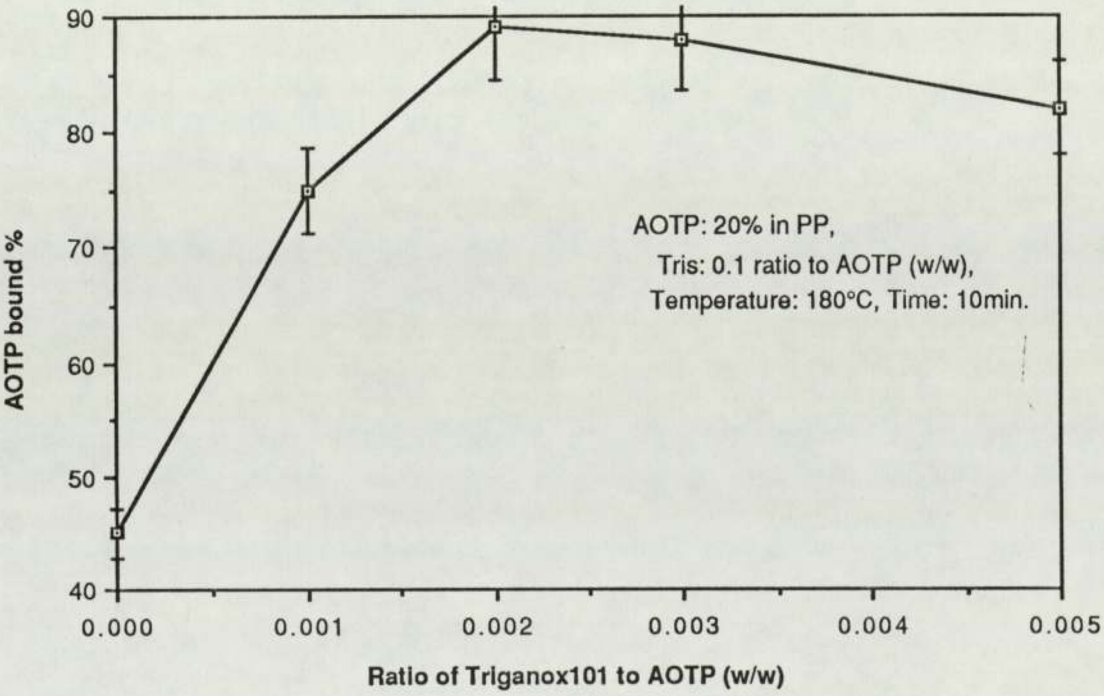


Fig. 3.3.1.1b Extent of binding of AOTP in PP as a function of Triganox101 loading in AOTP(see table3.3.1.2).

absence of free radical generator binding of AOTP is relatively low. From this it seems likely that an increase in concentration of the peroxide leads to an increase in quantity of free radicals in the system so that rate of initiation and propagation of AOTP increased to give more grafts. But, at high concentration of Trigonox101 the decrease in binding level suggested an increase in the number of chain termination reaction between PP chain radicals and primary radicals. On the other hand, with an increase in the quantity of primary radicals the starting reaction of AOTP homopolymer would be promoted. For further details in solution are required to determine the extent of homopolymerisation and, kinetic study of radical reaction in addition to some ESR mesurements is examining the concentration of free radicals in the system.

3.3.1.1c Concentration of Polyfunctional Agent (Tris)

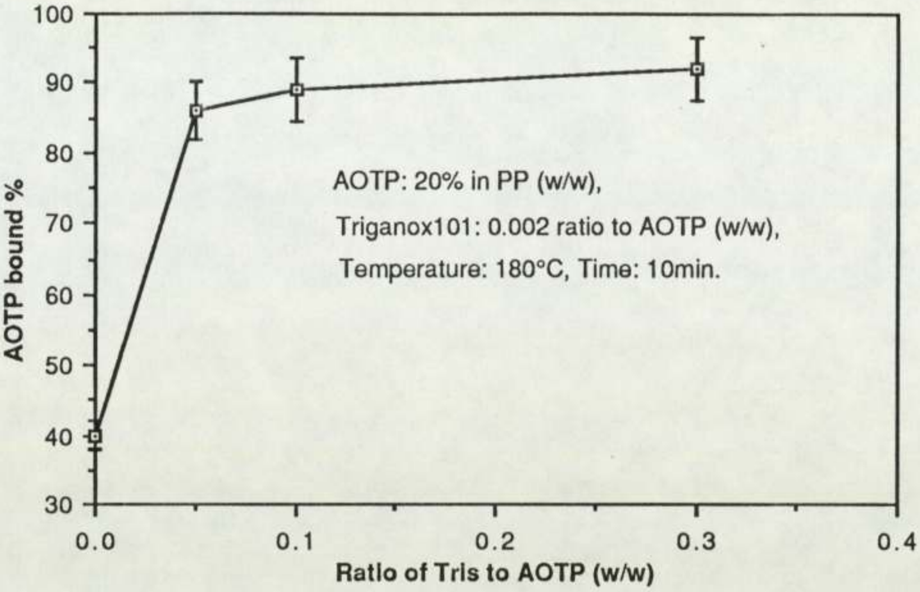


Fig. 3.3.1.1c Extent of binding of AOTP in PP as a function of Tris loading in AOTP(see table3.3.1.2).

It is known[168] that free radicals cause both chain degradation and promote chain crosslinking in polyolefins. the tendency to crosslinking assists in the grafting of active monomers in polyolefin chains. Thus, the use of polyfunctional agent (Tris) must play an important role in promoting the binding of AOTP as a 'bridge' (see Fig. 3.3.1.1c). The extent of binding of AOTP increased with increasing concentration of Tris. It was also noted in Table 3.3.1.2, Fig. 3.3.1.1b and Fig. 3.3.1.1c that if either the peroxide or the polyfunctional agent was not added in the system binding efficiency was much lower; in the absence of both, the binding efficiency decreased to less then 20%.

3.3.1.2 Effect of Processing conditions on Binding Extent

In addition to effects of the additives(AOTP, Triganox101 and Tris) several other processing parameters affect the binding efficiency of additives. During melt processing, the viscosity of polymer determines in part, the rate of macroalkyl radical formation by shear of polymer chain, the distribution extent of additives and the rate of movement of free radicals in melt system. However, the viscosity was itself

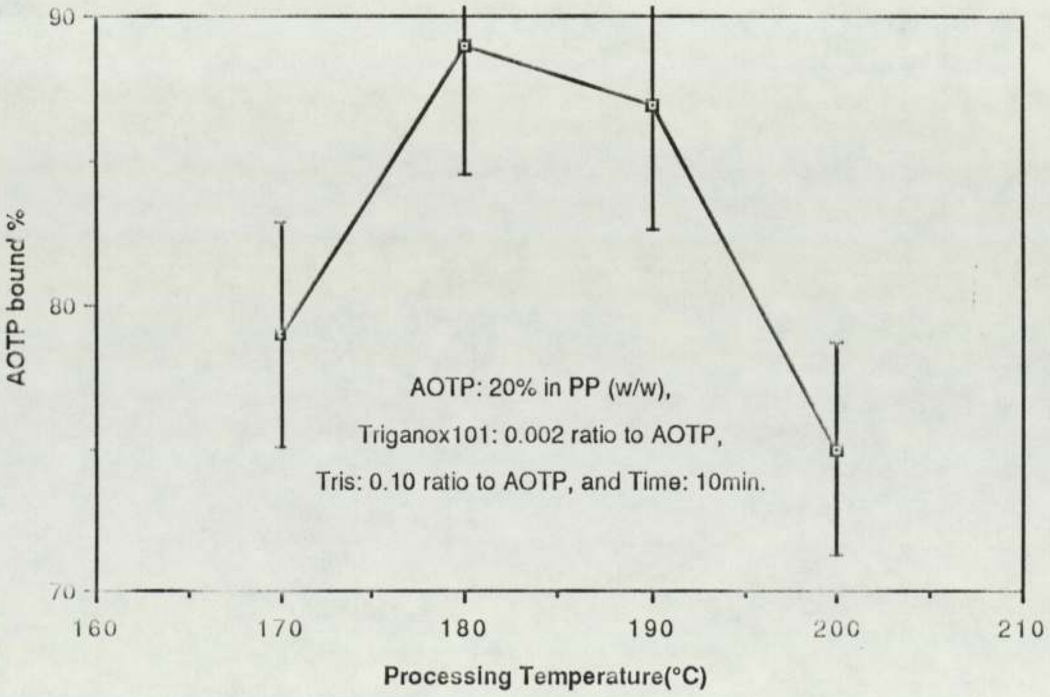


Fig. 3.3.1.2a Extent of binding of AOTP in PP as a function of processing temperature(see table3.3.1.2).

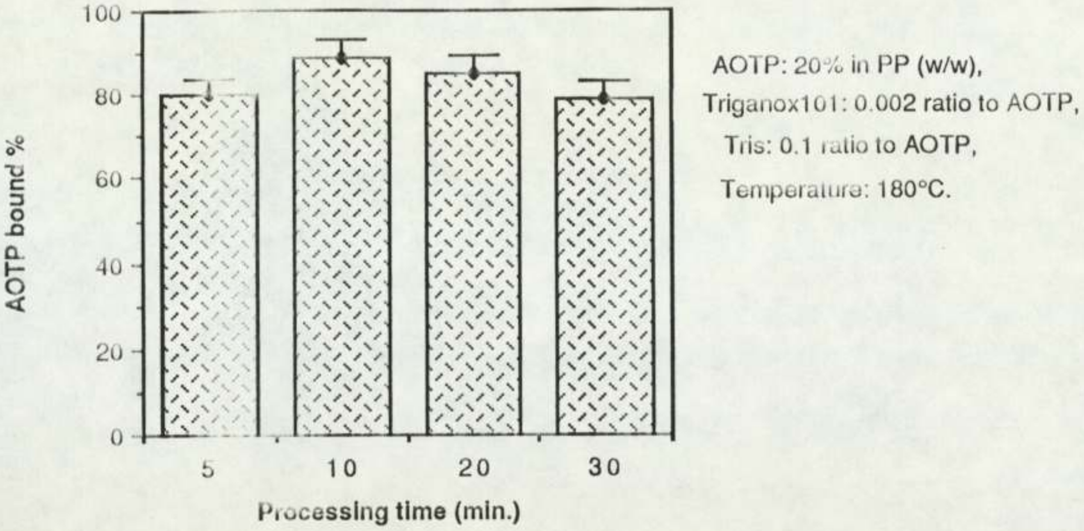


Fig. 3.3.1.2b Extent of binding of AOTP in PP as a function of processing time(see table3.3.1.2).

dependent upon processing temperature and time for all polymers. On the other hand, reaction temperature and time also affected the rate of decomposition of free radical generator, the rate of intiation of monomer and termination of adduct formation. Fig. 3.3.1.2a demonstrates that at a given concentration of additives when the processing temperature was increased, an increase in binding efficiency was observed, followed by a decrease. At about 180 - 190° C the extent of binding was at a maximum. The decrease in binding efficiency at higher processing temperature suggests that the rate of elimination and depolymerisation of grafted AOTP was increased because binding process was a reversible reaction.

Fig. 3.3.1.2b shows that while the amount of initiator, polyfunctional agent and AOTP were kept constant the trend of the binding of AOTP in PP with processing time was similar to the effect of change of processing temperature. An increase in binding efficiency was found when the time was increased up to 20 min., and there after the level of binding declined slightly. The effect of processing time on binding of AOTP was in accordance with that of processing temperature. However, the effect of the temperature was more sensitive than that of time.

From the above results it is clear that many parameters affect the binding efficiency of AOTP in PP during reactive processing. Under the processing condition of 180°C and 10 min. the extent of binding of 20% AOTP to PP was up to about 90% in the presence of 0.002 and 0.10 ratio of Triganox101, Tris to AOTP respectively. This was an optimum level of binding achieved so far in this work. The polymer-bound AOTP concentrate (masterbatch) with 20% concentration (Sample No. 21) were used for studies of effectiveness of polymer-bound antioxidant in thermal and photostabilising of PP in the subsequent work.

3.4 Preparation of Polymer-bound HEAB and DBBA

3.4.1 Polymer-bound HEAB

The essential method for making polymer-bound HEAB was the same as that of making polymer-bound AOTP. From a practical point of view, only one concentration of HEAB in 10% (w/w) was investigated in this work due to the poor solubility of higher concentration of HEAB monomer with PP melt. HEAB in excess of 10% concentration flowed out from the mixing chamber and was partly lost. If the concentration of polymer-bound HEAB was less than 10%, on the other hand, the masterbatch became unuseful for practical application.

It is evident from Table 3.4.1 that HEAB monomer is relatively easily bound on the PP backbone. The extent of binding of HEAB in PP was almostly up to 100%. The effect of Triganox101 (a peroxide) was not as strong as in the binding processing of AOTP. Even without any polyfunctional agent and peroxide compound in the systerm a relatively high level of binding was also achieved up to 65%. After extraction by DCM for about 10 hours HEAB was only partly removed from PP(sample NO.26). The effectiveness of bound HEAB on photostabilising of PP would be discussed in next chapter.

Table 3.4.1 Formulation of Binding of HEAB in PP and Binding Extent

sample No.	HEAB (% w/w)	Triganox101 (Ratio to HEAB)	Tris (Ratio to HEAB)	Binding Extent (%)
22	10	0.010	0.10	> 95
23	10	0.005	0.10	> 95
24	10	0.002	0.10	> 95
25	10	0.002	0.00	> 95
26	10	0.000	0.00	> 65
27	10	0.000	0.10	> 75

Notice: Processing Temperature = 180^{0}C, Processing Time = 10 min.

3.4.2 Polymer-bound DBBA

It is well known that hindered phenols are efficient radical scaveranging agents. During a free radical initiating polymerisation processing it palys a key role to control polymer molecular weight and terminate the synthetic reaction. DBBA contains a powerful function for trapping free radical as a CB-D antioxidant. Thus, in the case of binding of DBBA to polypropylene, high concentration of Triganox101 peroxide would be required to improve the binding extent. The results on table3.4.2 show that the presence of a high concentration of Triganox101 was actually very important to graft DBBA monomers to the backbone of PP. When the concentration of Triganox101 was less than 0.02 ratio to DBBA (w/w) the binding extent was quite low(about 20%). However, with an increase in the generator concentration to 0.05 ratio or more the grafting degree went up to 70% or higher. But, it was also found that processing with higher than 0.1 ratio of Triganox101 to DBBA led to highly degraded polymer which could not be made into a film at all. The effectiveness of bound DBBA antioxidant on thermalstabilising of PP will be studied in next chapter.

Table3.4.2 Binding extent of DBBA to PP

Sample NO.	DBBA (%w/w)	Triganox101 (ratio to DBBA)	Tris (ratio toDBBA)	Binding Extent (%)
28	10	0.002	0.1	<20
29	10	0.010	0.1	<40
30	10	0.050	0.1	70
31	10	0.050	0.0	60
32	10	0.100	0.1	80

Note: Processing temperature = 180°C, Processing time = 10min.

Chapter Four

Effect of High Concentration of Bound Antioxidant on Stabilisation of Polypropylene

4 Effect of High Concentration of Bound Antioxidant on Stabilisation of Polypropylene

It has been shown by Ibrahim in this group that one kind of vinyl piperidine antioxidant [bis-(2,2,6,6-tetramethylpiperidin-4-yl) maleate, BPHE] when chemically bound to polypropylene gives a linear relationship between concentration and photo antioxidant activity [165,167]. This behaviour differs profoundly from that of conventional antioxidants which normally show a plateau effect with increasing concentration. This has been attributed to the limited solubility of conventional additives at ambient temperature and is an unexpected advantage of polymer-bound antioxidants. However, no further detailed reports have confirmed this behaviour of polymer-bound antioxidants. Therefore, the effect of concentration of bound AOTP(hindered piperidine derivative) and other two reactive antioxidants (HEAB and DBBA) on thermal and photostabilisation of PP are studied in this work. Attention was also paid to the synergism between two or three components of bound antioxidants. Samples were selected generally from the masterbatches of bound AOTP (NO. 21), bound HEAB (NO. 24) and bound DBBA (NO. 30). Any alternative choice of bound antioxidant samples will be noted.

The stabilising effect of these polymer-bound antioxidants was compared with three kinds of conventional antioxidants based on a hindered amine(Tinuvin 770), an UV absorber(UV 531) and a hindered phenol(Irganox 1076). Thermal and photostabilising effects were assessed by mesuring carbonyl index and embrittlement time.

4.1 Photo Stabilisation

4.1.1 Results and Discussion

4.1.1.1 Effect of Bound AOTP on Photostabilising of PP

It is well established that hindered piperidines are firstly oxidised to the corresponding nitroxyl radicals (>NO·) during photooxidation and the nitroxyl radicals are effective inhibitors of the photooxidative destruction of polymers, particularly in polyolefins. Thus, the efficiency of the hindered piperidines in the UV stabilisation of polymers has attracted the attention of numerous investigators [169-175]. But somewhat less attention has so far been paid to effect of high concentrations of hindered piperidines on the UV stabilisation of polymers.

In the present studies, extensive experimental work on the behaviour of bound AOTP on photostabilisation of PP, especially at high concentration was carried out. Although in practice more than 0.5% concentration of antioxidants in polymer is not normally used, for theoretical study it is necessary to know what happens at high concentration in order to understand the antioxidant mechanism of the stabilisers.

The photostabilising effectiveness of the different formulations of bound AOTP was compared with the control samples containing a conventional antioxidant in Fig. 4.1.1.1a. It is clear that bound AOTP was photostabilising PP. Its efficiency increased with increasing concentration, However, the conventional antioxidants (Tinuvin 770) showed a plateau effect with further increase in concentration (>0.5%). It was also found that the conventional antioxidant bloomed out from PP film during UV aging, but this phenomenon did not occur with bound AOTP in PP.

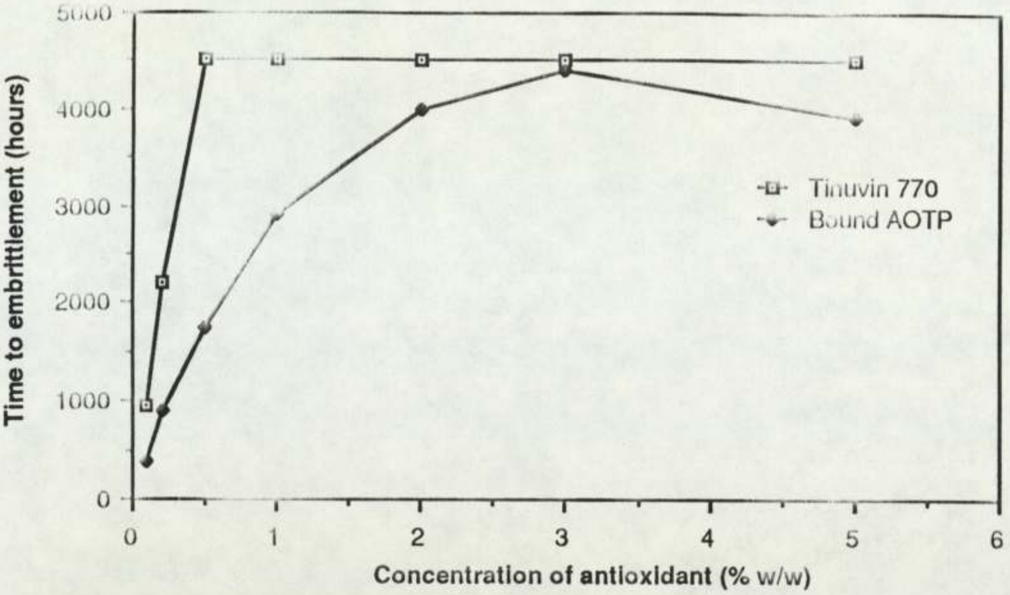


Fig. 4.1.1.1a Effect of bound AOTP concentration on photooxidation of PP in UV light cabinet (Concentration of bound AOTP in PP diluted from its 20% masterbatch (sample NO.21)).

On the other hand, Fig. 4.1.1.1b indicates that conventional antioxidants (Tinuvin 770 and UV531) were easily lost by physical means during UV aging. The intensity of the ester carbonyl absorption at 1735 cm^{-1} in PP film stabilised by 1.0% Tinuvin 770 decreased, evidently with an increase in UV aging time, the behaviour of the ketonic carbonyl absorption of UV 531 at 1630 cm^{-1} was similar to that of Tinuvin 770. But for bound AOTP stabilised sample, the intensity at 1725 cm^{-1} increased slightly before the sample embrittled. It was concluded from these results that the conventional antioxidants could easily migrate and volatilise from the polymer during their service time. This disadvantage could be overcome by using bound antioxidants chemically attached to the polymer chain.

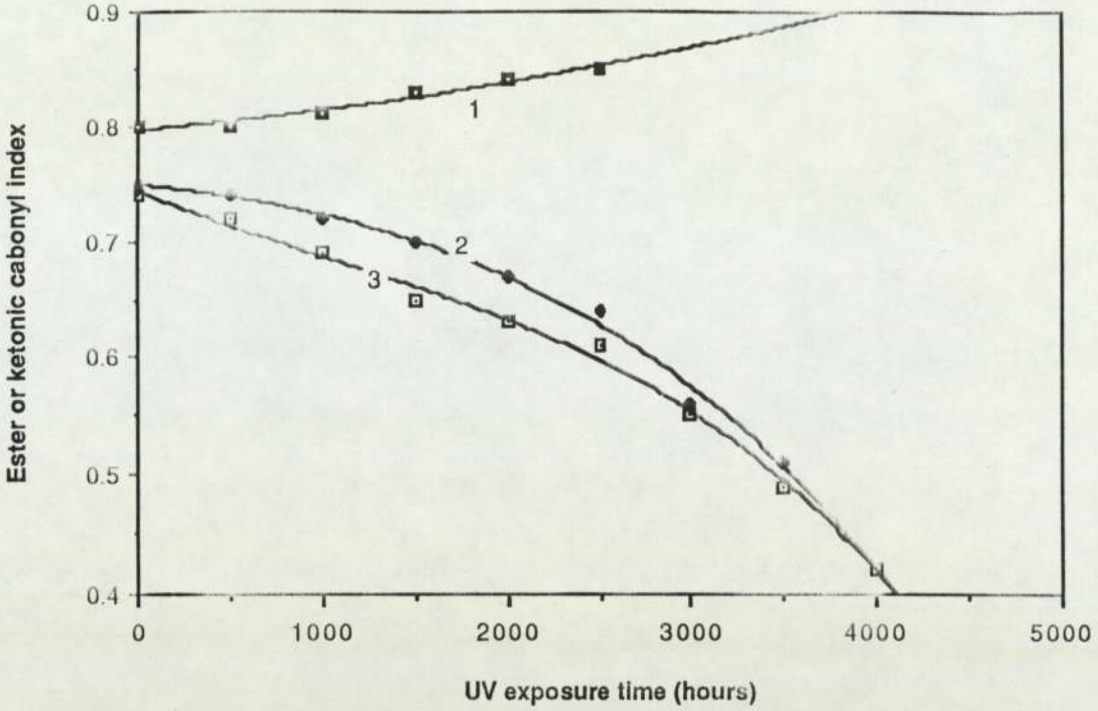


Fig. 4.1.1.1b Change in ester and ketonic carbonyl index of Tinuvin 770, bound AOTP and UV531 in PP during UV aging.
1: bound AOTP(Sample No.21), 2: UV 531 and 3: Tinuvin 770
(note: antioxidant concentration = 1.0% in PP w/w).

But from above two figures it was noted that although bound AOTP was not lost physically from PP the photostabilising performance at very high concentration (3.0%) didn't show firmly an improvement for PP film. On the contrary, a slight decrease in embrittlement time at 5.0% concentration of bound AOTP resulted. It seems that at later stages of photooxidation the structure of AOTP antioxidant itself would be possibly destroyed by radical initiated oxidation, and thus it could not play a role to stabilise polypropylene any more. This may be considered to be a chemical loss.

Table4.1.1.1 shows that at a low concentration of antioxidant PP films stabilised with Tinuvin 770 or AOTP monomer were more stable than with bound AOTP antioxidant. The embrittlement times of PP films with 0.1% Tinuvin 770 or 0.1% AOTP monomer are 950 and 1000 hours respectively. However, PP film with 0.1% bound AOTP embrittled at 350 hours of UV aging. It suggests that during the binding operation in the presence of a peroxide Triganox101 and at a high temperature (180°C), a part of the photostabilising functional groups in the structure of AOTP was destroyed by attack of free radicals initiated by the peroxide to decrease AOTP value concentration in PP, and thus decrease its effectiveness. Another explanation may be that cross-linking and homopolymerising processes are competing with binding reaction, especially at a very high concentration of AOTP up to 20% and in the presence of polyfunctional agent. Thus, bound AOTP antioxidant concentrate could not be distributed uniformly in PP amorphous phase at the situation for which PP film was stabilised with a very low concentration of bound AOTP diluted from 20% masterbatch. The PP film embrittled much more rapidly than with a conventional antioxidant (Tinuvin 770) or AOTP monomer. But after PP films with antioxidants were extracted by DCM the advantage of bound AOTP antioxidant was evidently seen in this investigation.

Table 4.1.1.1 The embrittlement time of PP film with antioxidant

Antioxidant	Concentration Wt %	Embrittlement Time (h) Unextracted	Extracted
bound AOTP	0.1%	350	---
	0.2%	950	500
Tinuvin 770	0.1%	950	---
	0.2%	2100	120
AOTP monomer	0.1%	1000	---
	0.2%	1900	150
No antioxidant	0.0	100	90

Fig. 4.1.1.1c illustrates that PP films stabilised with the conventional antioxidant (Tinuvin 770) extracted by DCM was rapidly broken like unstabilised sample during UV aging no matter how much Tinuvin 770 was added in PP. The embrittlement time was lower than 120 hours. But bound AOTP exhibited a good performance for preventing PP from photooxidation after extraction with DCM. Unfortunately, an unexpected behaviour was found that the photostabilising efficiency of bound AOTP in PP after extraction decreased dramatically compared with that without extraction regardless of the smaller change in quantity of bound AOTP before or after extraction. The reason why the extraction process sharply affects the efficiency of bound AOTP in PP has not been clear so far. Further studies have to be carried out. However it is interesting to note that in the case of 3.0% concentration of the antioxidant in PP the efficiency of extracted bound AOTP was approximately close to that of unextracted bound AOTP.

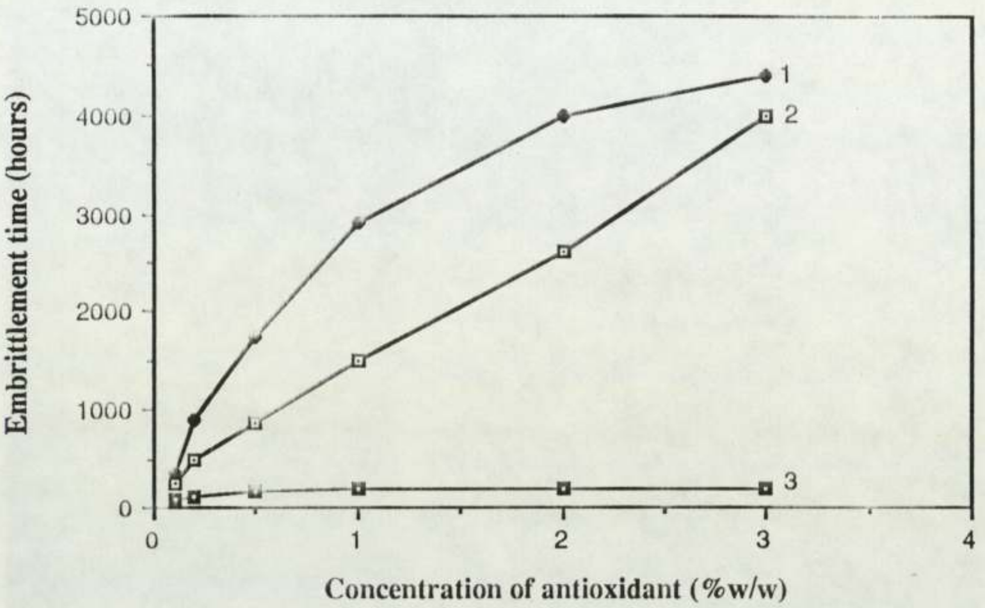


Fig. 4.1.1.1c Effect of solvent extraction on photostabilising of antioxidant in UV light cabinet aging.

Notice: Bound AOTP diluted from its 20% masterbatch No. 21, DCM as extracting solvent.
1: Unextracted bound AOTP, 2: Extracted bound AOTP and, 3: Extracted Tinuvin 770.

4.1.1.2 Effect of Bound HEAB on Photooxidation of PP

HEAB active UV stabiliser with acrylic group is a kind of UV absorber. Its essential functional group for stabilising of polymer is the same as that of UV 531 which dissipates harmful UV light to heat energy and is a very good photostabiliser for polyolefins. But UV 531 can easily be lost from polymer. Therefore, some attempts have been taken to increase the physical resistance of this kind of UV stabiliser to polymer by surface grafting of active UV absorber to polymer[176] or direct polymerisation[131]. few progresses have been made besides some sulphur-containing UV absorber bound on ABS which shows an advantage to stabilise ABS polymer against photooxidation[154]. In this work an attention was paid to investigate the effectiveness of bound HEAB antioxidant on photostabilisation of PP and study the relationship of its concentration with photostabilising efficiency.

In section 3.5 it was shown that the extent of binding of HEAB to PP was nearly up to 100% even though polyfunctional agent (Tris) was not added to the system. Other interesting observation was that even

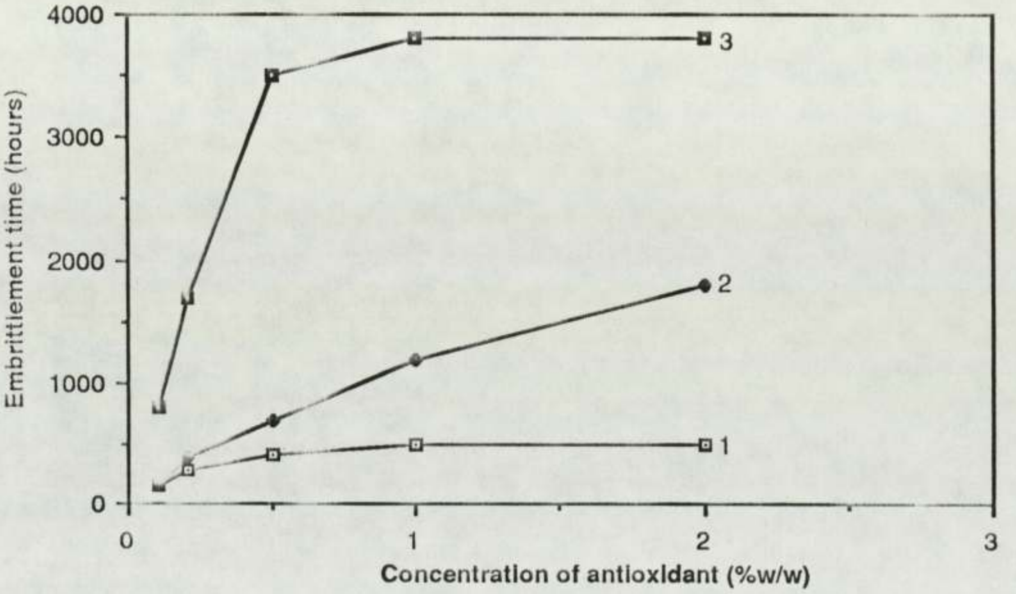


Fig. 4.1.1.2a Effect of bound HEAB antioxidant on photooxidation of PP in UV light cabinet aging.

1: bound HEAB diluted from 10% masterbatch NO. 24; 2: HEAB without Triganox101 diluted from 10% masterbatch NO. 26; and 3: UV 531.

in the absence of peroxide and polyfunctional agent the binding extent achieved was about 65%. Unfortunately, the efficiency of bound HEAB in PP during UV aging was very low and the results was shown in Fig. 4.1.1.2a.

With an increase in concentration of bound HEAB its effectiveness in PP was not increased evidently. The maximum embrittlement time of PP films with bound HEAB was less than 600 hr. no matter how much bound HEAB was added in the range from 0.1% to 2.0%. Compared with that of bound AOTP it was quite ineffective. If 10% HEAB masterbatch (sample No. 26) was directly made without any other additive it played a certain role in photostabilising of PP , at 0.2% and 0.5% concentration the times to embrittlement were 400 and 700 hours respectively. It seems that because HEAB functions as UV absorber like UV 531 which is not effective either as a chain-breaking antioxidant or a peroxide decomposer for polyolefins at elevated temperatures its UV absorbing functional group could be destroyed by attack of a peroxide Triganox101 during the binding process. On the other hand, the binding operation would lead to an increase in the concentration of oxygen-containing groups which accelerate the formation of alkyl peroxyl radicals and hydroperoxide to badly damage the structure of HEAB during UV aging process. This result coincided with some reports that the effectiveness of UV 531 on photostabilisation of PP was dependant firmly on the thermal history of PP processing which was concerned with the formation of alkyl peroxide radicals [78].

Other alternative explanation may be that during melt processing HEAB monomers be very easily homopolymerised to form HEAB homopolymer which could not be distributed uniformly in PP and not easily diffused to the surface of PP. Thus, the antioxidant consumption on the surface layer of PP wold fail to be completely compensated by the diffusion supply from the volumn. The surface layer of PP is easily oxidised during UV aging[181].

Fig. 4.1.1.2b shows that solvent extraction did not distinctly affect UV stabilisation of PP films stabilised with bound HEAB. The embrittlement time was not obviously changed by DCM extraction. This behaviour was different from that of bound AOTP which was sharply affected by DCM extraction and the efficiency of bound AOTP declined dramatically as was shown in Fig. 4.1.1.1c.

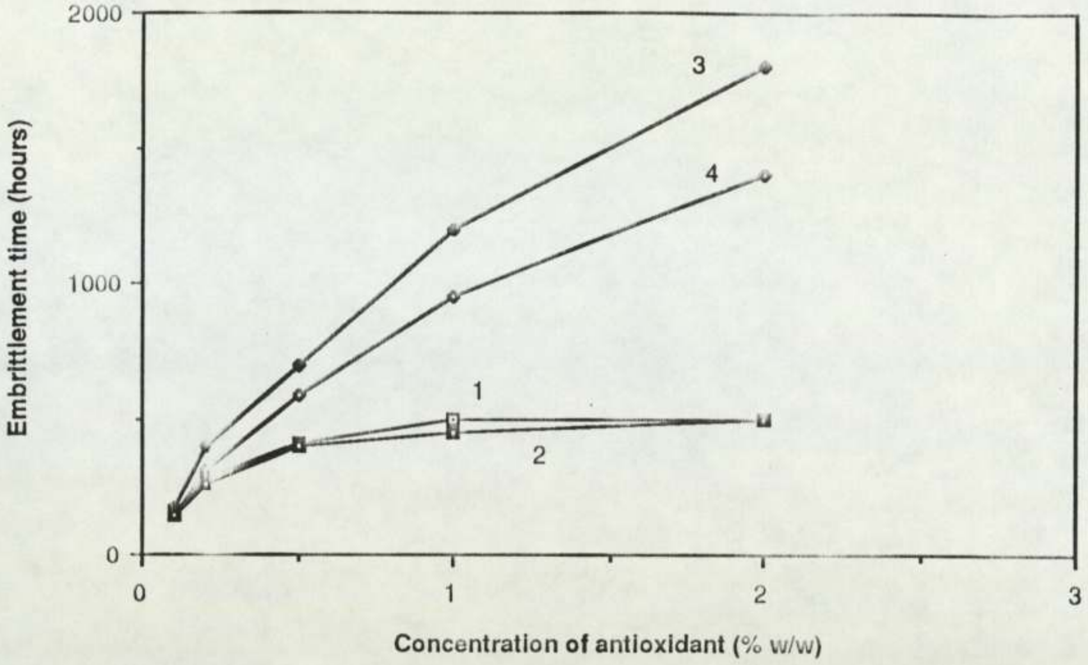


Fig. 4.1.1.2b Effect of solvent extraction on photostabilising action of HEAB in UV light cabinet.

1: unextracted bound HEAB diluted from Sample NO. 24; 2: extracted bound HEAB diluted from Sample NO.24; 3: unextracted HEAB from Sample NO. 26 and 4: extracted HEAB from Sample NO.26.

But it was also found that in the case of lower binding of HEAB in PP (sample NO. 26 without a peroxide Triganox101) photostabilisation of PP decreased after DCM extraction. It seems that part of HEAB stabiliser was removed from PP by DCM solvent and the concentration of HEAB was reduced. Thus, the embrittlement time of PP declined. The above results show clearly, therefore, that binding of HEAB to polymer can improve the physical resistance of antioxidant to polymer, and avoid the solvent extracting and water leaching of antioxidant from polymer. But, due to the presence of a peroxide during binding process and possibly high homopolymerising extent to limit the movement of HEAB in PP the effectiveness of HEAB was affected to decline for UV stabilisation of PP.

4.1.1.3 Effect of Combination of Two Bound Component Antioxidant System

Many reports have been published on the effects of combination of two or more antioxidants on photostabilisation of polymer, especially in systems containing hindered amines in addition to other antioxidant classes. Scott [49] has shown that a peroxide decomposer (e.g. nickel diethyl- dithiocarbonate) reduces the photostabilisation of polyolefins stabilised by HALS (hindered amine light stabiliser) and suggests that the peroxide decomposer, by destroying hydroperoxides, would prevent the transformation of the original amine to the nitroxyl which is converted by the reaction of hindered amine with hydroperoxide and alkylperoxide radical so that photo antioxidant action of HALS would decline. Allen [177,178] has found that the effects of added hindered phenolic antioxidants on the extent of UV stabilisation of PP by HALS show antagonism activity and the photostabilisation of PP was less than that of using HALS alone. On the other hand, different behaviour has also been observed for combination of HALS with UV stabiliser which shows synergistic activity in photostabilisation of PP [179]. For the bound hindered amines and other bound antioxidants very few reports have been published. So in this work the effect of combination of bound AOTP with bound HEAB and conventional hindered phenol

Irganox 1076, and of bound HEAB with Irganox 1076 were examined. Samples were selected from No.21(bound AOTP masterbatch), No.24 (bound HEAB masterbatch) and No.30(bound DBBA masterbatch) without extraction by DCM. The conventional antioxidants were directly added when the bound antioxidant masterbatches were diluted in PP during melt processing.

a. Bound AOTP with Irganox 1076

Figs. 4.1.1.3a & 4.1.1.3b show effects of added Irganox 1076 on photo stabilisation of PP films stabilised by bound AOTP. No synergism was observed over the certain concentration range. In the case of adding 0.04% concentration of Irganox 1076 the results of embrittlement times were almost the same as that of using bound AOTP alone. But, with an increase in the concentration of the phenol up to 0.1% a slight antagonistic activity of phenol was found in photostabilisation of PP stabilised by bound AOTP and it is found to some extent to reduce the efficiency of bound AOTP. The embrittlement times of polypropylene films containing Irganox 1076 with bound AOTP declined slightly during UV light cabinet aging. For example, at 0.2% concentration of bound AOTP alone and with 0.1% Irganox 1076 the embrittlement time of PP film decreased from 950 hours to 800 hours. Changes of carbonyl index as a function of UV cabinet aging on Fig. 4.1.1.3b clearly demonstrated that in the presence of 0.1% concentration of Irganox 1076 the carbonyl index of PP film stabilised by bound AOTP increased more rapidly than that without the phenol with an increase of UV exposure time. This indicates that during photooxidation of PP hindered phenol antioxidants antagonise the stabilising action of hindered amine light stabiliser (HALS). The side effect could result from phenolic transformation products (e.g. active quinone) oxidised by peroxide radical during thermal processing and UV aging. These transformation products may be regarded as photochemically active compounds and be very sensitive to UV light to accelerate the photooxidation of PP film. On the other hand they might react with the nitroxyl radical oxidised from parent amine to consume parts of HALS contributing to photostabilisation of PP.

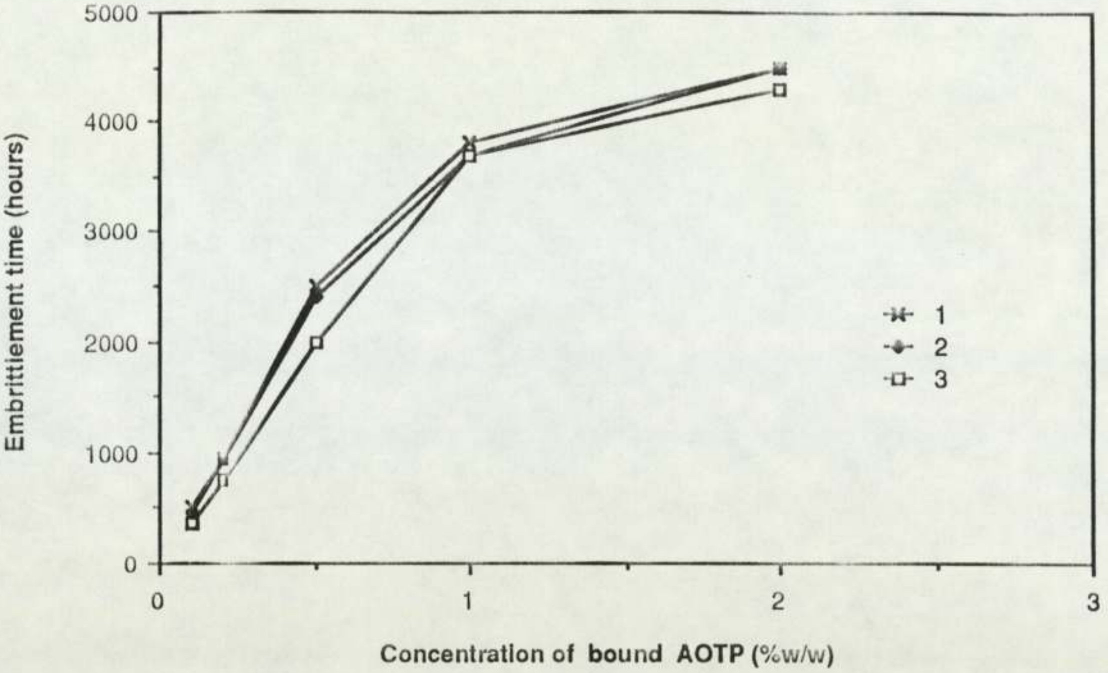


Fig. 4.1.1.3a Effect of Irganox 1076 on photostabilisation of PP stabilised by bound AOTP(No.21).

1: bound AOTP without Irganox 1076; 2: bound AOTP with 0.04% Irganox 1076; and 3: bound AOTP with 0.1% Irganox 1076.

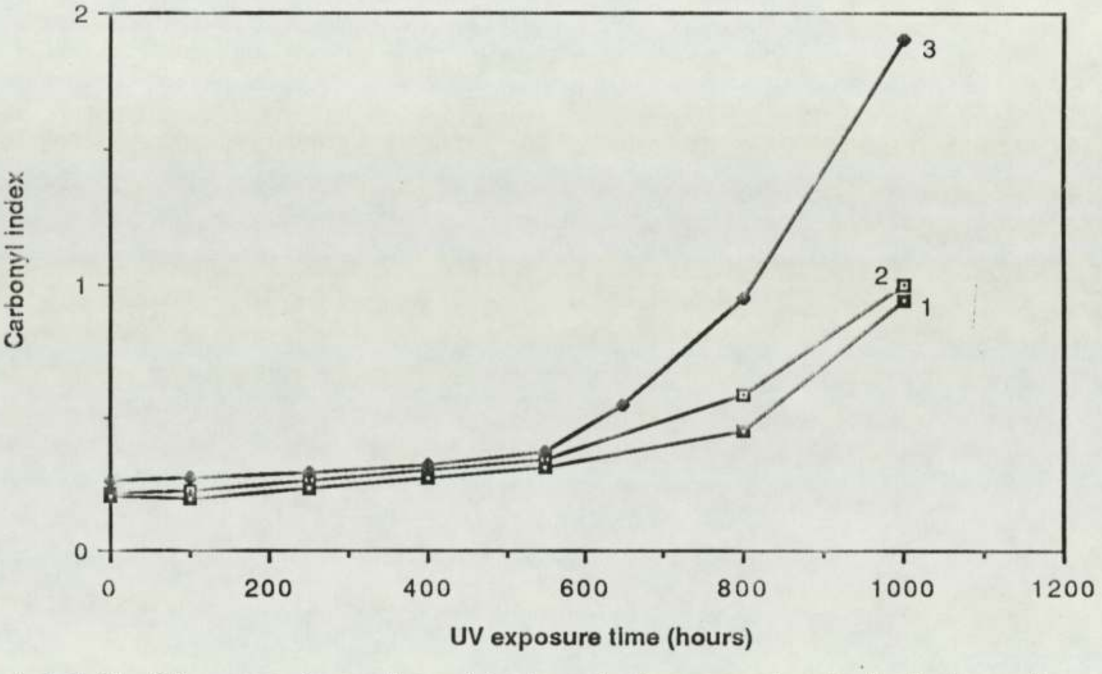


Fig. 4.1.1.3b Changes in carbonyl index during accelerated photo aging of PP film containing 0.2% bound AOTP diluted from No.21.

1: bound AOTP alone; 2: with 0.04% Irganox 1076; and 3: with 0.1% Irganox 1076.

b Bound HEAB with Irganox 1076

It is interesting to note in Fig. 4.1.1.3c that the combined behaviour of bound HEAB with Irganox 1076 was definitely different from that of bound AOTP with the same phenol. The embrittlement time of PP film stabilised with bound HEAB increased and was much longer than that of using bound HEAB alone due to synergism[87]. It seems that phenol antioxidants would trap alkyl peroxyl radicals and reduce the formation rate of hydroperoxides which badly damage UV absorbing stabilisers so that the HEAB activity for UV stabilising of PP could remain longer in the system for the protection of PP.

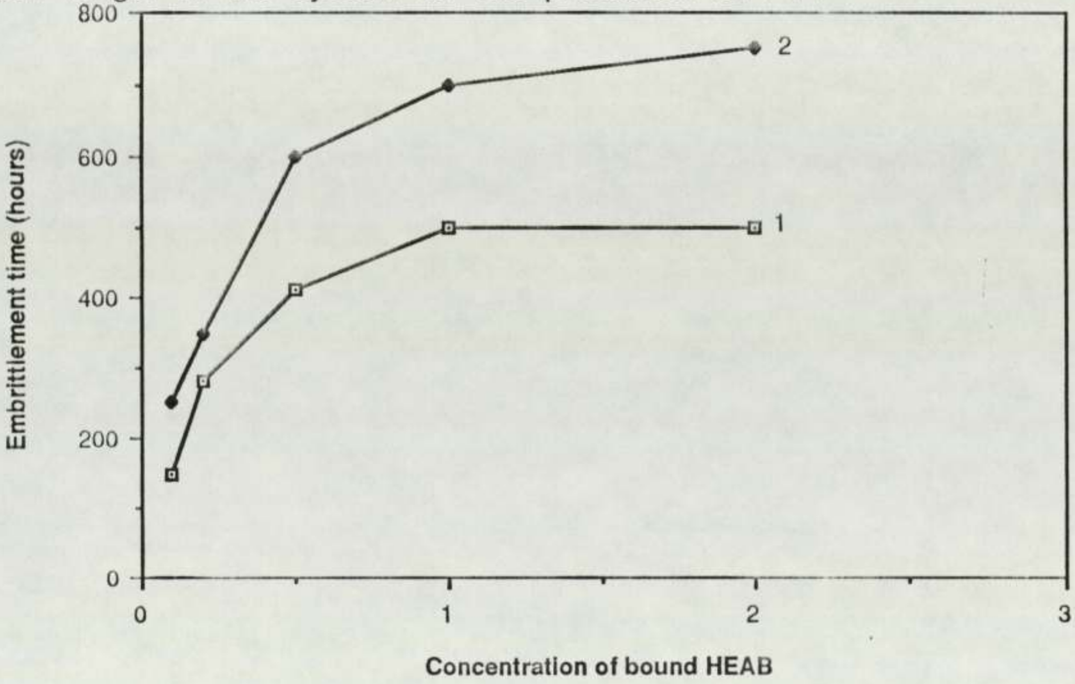


Fig. 4.1.1.3.c Effect of phenol Irganox 1076 on photostabilisation of PP film stabilised by bound HEAB diluted from No.26.

1: bound HEAB alone and 2 bound HEAB with 0.04% Irganox 1076.

c. Bound HEAB with Bound AOTP

The results in Fig. 4.1.1.3d display the combination effects of bound AOTP with bound HEAB. A strong synergistic behaviour was found in the system and the efficiency of bound HEAB on photostabilisation of PP was improved evidently by adding bound AOTP with 0.1% or 0.2% concentration. This behaviour of combination of the two bound antioxidants (AOTP and HEAB) was similar to that of both analogous conventional antioxidants (Tinuvin 770 and UV 531) which have been reported by many scientist [177, 180]. The improved photostabilisation of polypropylene by the combination could result from the combined effects of inhibition of the polypropylene photooxidation through the separate mechanisms of radical trapping by hindered amine (AOTP) and UV absorption by UV absorber(HEAB). The UV absorber should inhibit degradation of the hindered amine by reducing the rate of photolytic reaction of the nitroxyl and the nitroxyl should protect the function structure of HEAB from attack by peroxyl radicals by the mechanism of radical trapping. Unfortunately, although the synergistic photostabilising effect of bound HEAB and AOTP was marked the photostabilisation of PP film did not improve more with the further increase of concentration of bound HEAB. This may be related to the high extent of homopolymerisation and poor mobility of polyHEAB in PP. If this hypothesis is correct avoiding homopolymerisation whilst obtaining graft polymerisation of the antixoidant monomers on polymers is a very important further objective.

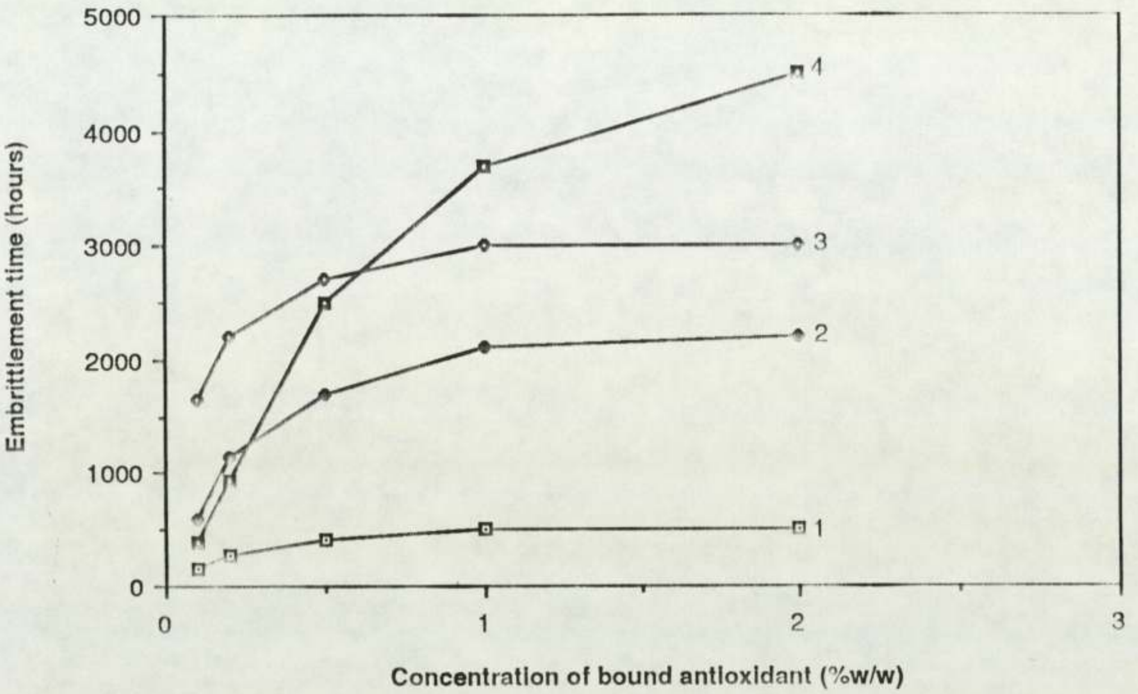


Fig. 4.1.1.3d` Combination effect of bound HEAB with bound AOTP on photostabilisation of PP film during UV cabinet aging.
1: bound HEAB alone; 2: bound HEAB with 0.1% bound AOTP;
3: bound HEAB with o.2% bound AOTP and 4: bound AOTP alone.
Note: bound HEAB and Bound AOTP were diluted from No.26 and No.21 respectively.

In addition, one interesting behaviour demonstrated the IR spectrum of PP film stabilised by 0.2% bound HEAB and 0.2% bound AOTP (Fig. 4.1.1.3d) is that the carbonyl index in the combination system increased gradually with increasing UV exposure time, especially after about 1500 hours the absorption peak increased sharply and the surface of the PP film became rough and non-transparent. But the film did not embrittle at all.

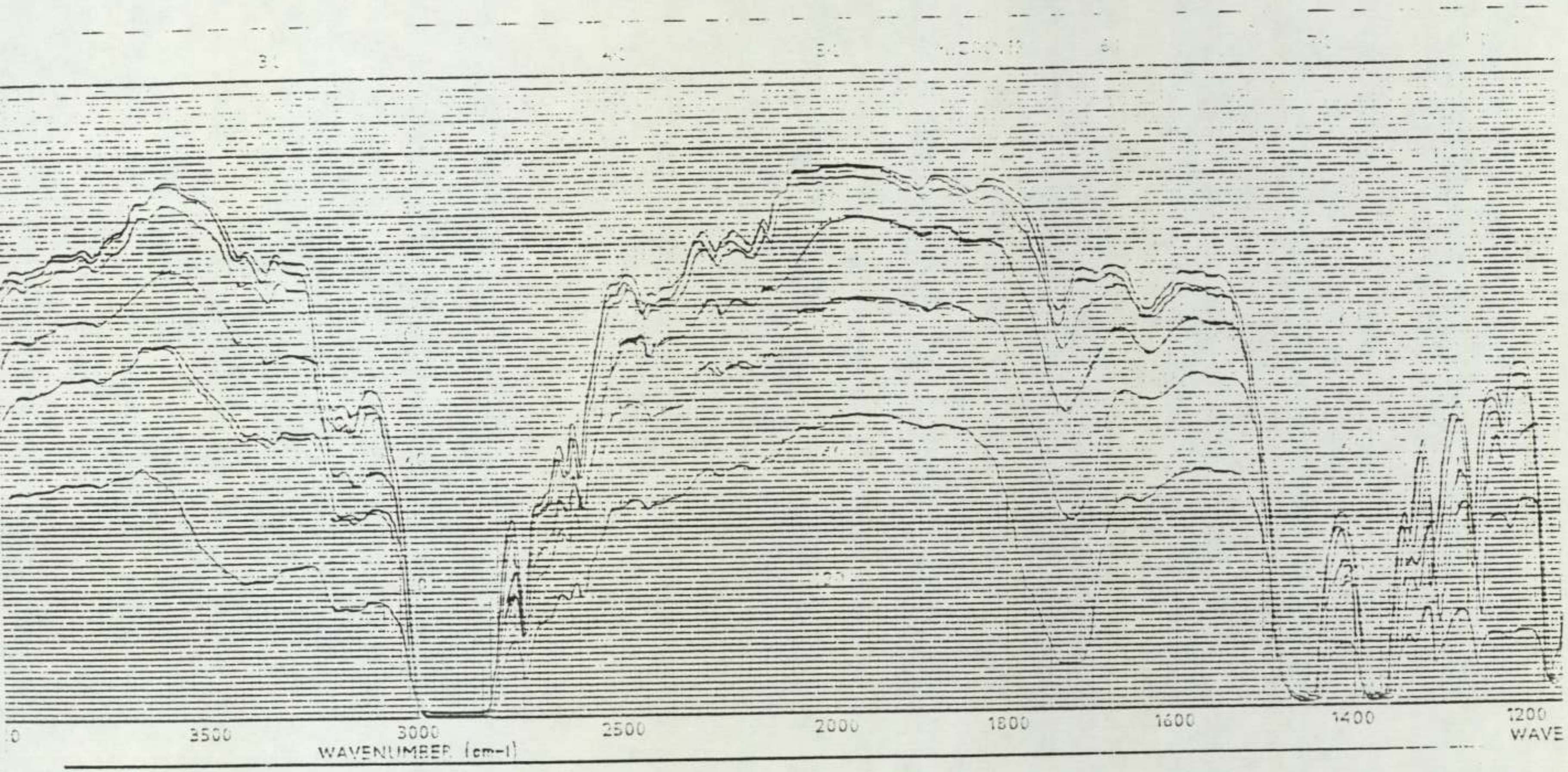


Fig. 4.1.1.3e Change in IR spectrum curve of PP film stabilised by combination of 0.2% bound HEAB and 0.2% bound AOTP with an increase in UV cabinet aging time.
IR testing interval: 0, 500, 1000, 1500, 2000 and 2500 hours.

4.2 Thermal Stabilisation

In this section the investigation was mainly concentrated on the effectiveness of bound AOTP antioxidant in thermal stabilisation of polypropylene. As we know, hindered piperidins are considered to be very effective and important class of photostabilisers for polyolefins. Many scientists have suggested that multiple mechanisms of stabilisation are shown in the action of hindered amines. In general, the nitroxyls converted from parent hindered amines by active oxygen-containing groups (e.g. hydroperoxide and peroxide radical) play an important role as CB-A agents to trap the alkyl and alkoxyl (RO·) radicals forming hydroxylamine and alkyloxylamine (RON<) intermediate products which may be regenerated to give the nitroxyls in a redox reaction. The hydroxylamine and RON< function as CB-D antioxidants show a complementary antioxidant action[39]. But conventional hindered amines do not exhibit thermal stabilising effect in polyolefins during thermal air circulating oven aging at high tmperature (e.g. 140°C). It may be due to the fact that conventional hindered amines (such as Tinuvin 770) rapidly evaporate from the polyolefin film at these high temperatures. The bound hindered amine antioxidant AOTP is a good case to investigate because its bound nature should overcome the problem of volatility at high temprature.

The thermal stabilising effect of bound hindered phenol(DBBA) was also investigated in this study.

4.2.1 Results and Discussion

4.2.1.1 Effect of Bound AOTP Alone

Fig. 4.2.1.1 shows that compared with Tinuvin 770, bound AOTP functioned to some extent as a thermal antioxidant. At 1.0% concentration of bound AOTP the time to fracture of PP film was 120 hours, much higher than that of PP film with 1.0% Tinuvin 770 (10 hours). But the efficiency of bound AOTP on thermal stabilisation of PP was considerably lower than that of Irganox 1076. This confirms that hindered piperidines themselves are not effective thermal antioxidants although their transformation products (>NO' and >NOH) function as CB-A and CB-D agents. From Fig.4.2.1.1 it was interesting to note that with increasing concentration of bound AOTP, lead to an increase in embrittlement time but the curve passed through a maximium, and declined with further increase of bound AOTP concentration.

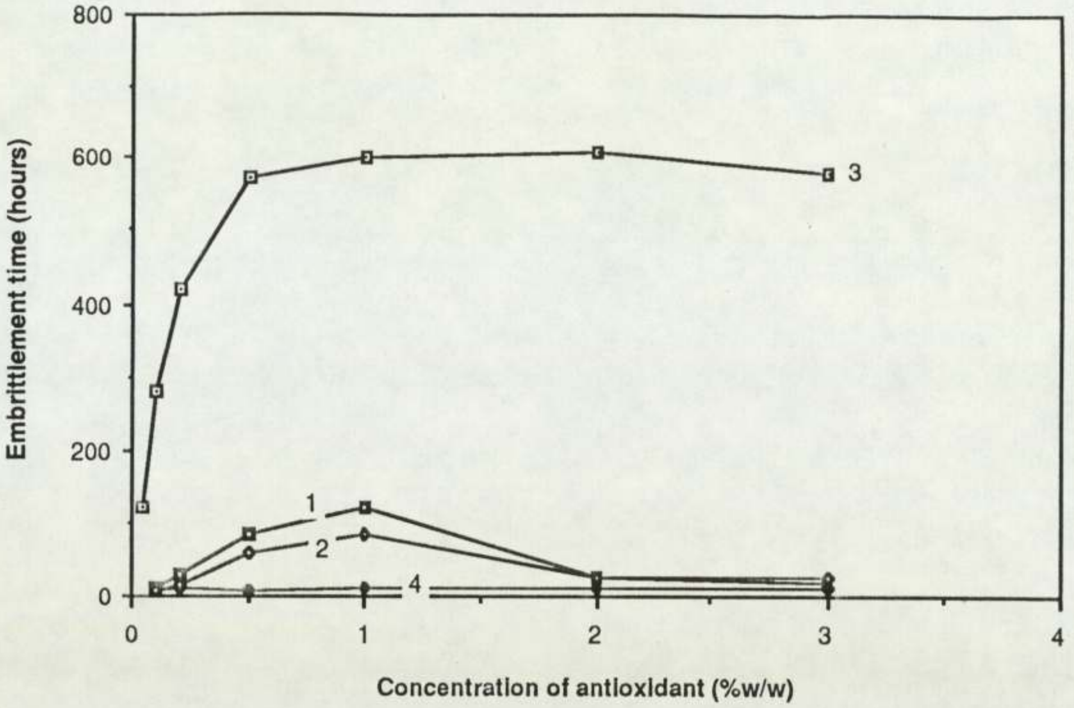


Fig. 4.2.1.1 Effect of bound AOTP antioxidant on thermal stabilisation of PP at 140°C. 1: bound AOTP (unextracted); 2: bound AOTP (extracted); 3: Irganox 1076 and 4: Tinuvin 770.

One possible explanation for the above results is that during the grafting operation of AOTP the small amount of the peroxide(Triganox101) used for promoting the chemical attachment of AOTP monomer to PP chain would lead to some oxidation due to the formation of macro-alkylperoxide & hydroperoxide which are not extracted by DCM solvent. On the other hand, it is known that the rate of thermal oxidation of PP film and the rate of formation of the corresponding nitroxyl from a parent amine would be closely associated with the concentration of oxygen-containing groups[179]. Thus, the presence of macro-alkylperoxide & hydroperoxide should affect both nitroxyl formation and PP oxidation. Therefore, if the concentration of the nitroxyl is not high enough to trap the alkylradicals and to compete with the attack of oxygen from outside, the thermal oxidation process would prodominate in the system so that the PP film would be rapidly embrittled. Otherwise, the nitroxyl converted from bound AOTP would exhibit thermal stabilising effectiveness in PP during the oven aging at 140°C over a critical concentration.

In this work a conventional stabiliser Tinuvin 770 did not display any positive action for thermal stabilisation of PP no matter how much it was added to the system. This result was due to physical loss of Tinuvin 770 from PP (see section 4.2.1.3). It will be shown later (see fig. 4.2.1.1.1) that the effectiveness of a conventional hindered phenol, Irganox 1076 on thermal stabilisation of PP increased from the low concentration range of 0.04% up to 0.5%. But with further increase of its concentration the embrittlement time curve of PP showed a plateau due to its physical loss at 140°C (see section 4.2.1.3).

4.2.1.2 Effect of Bound AOTP with Hindered Phenol

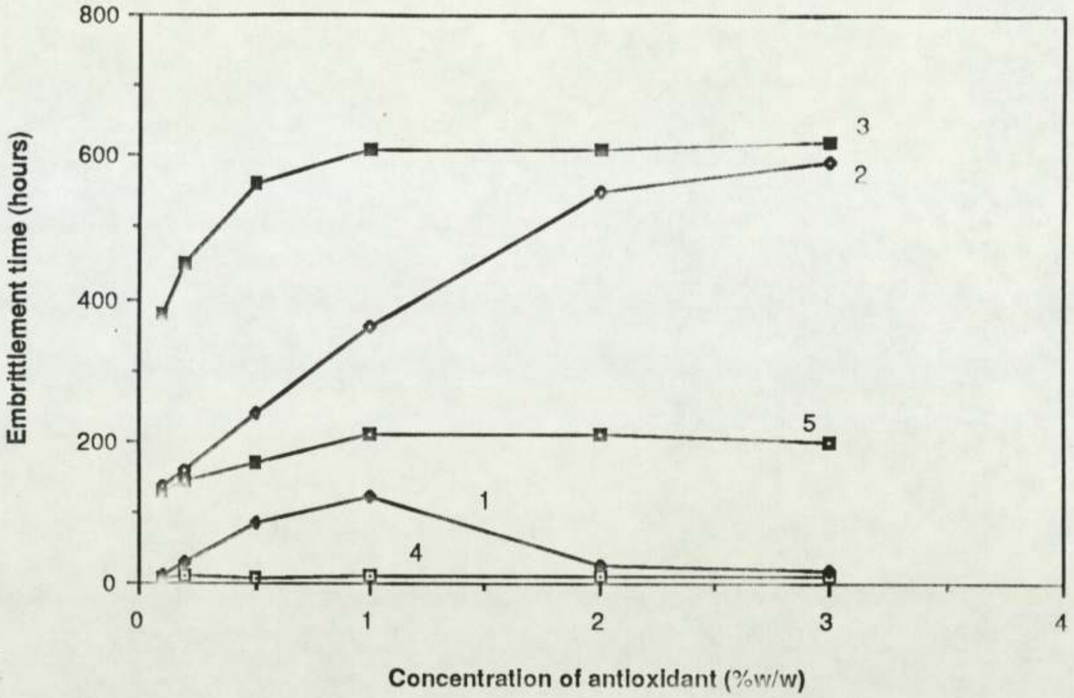
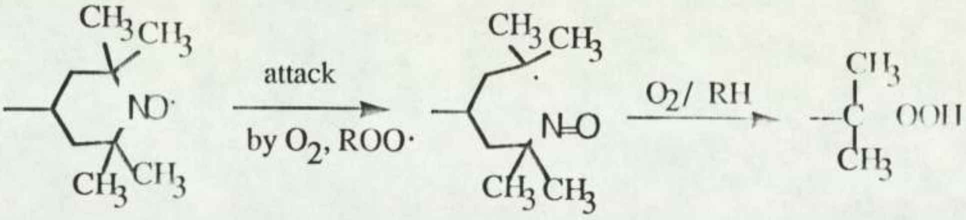


Fig. 4.2.1.2a Effect of combination of bound AOTP with Irganox 1076 on thermal stabilisation of PP at 140°C. 1: bound AOTP alone; 2: bound AOTP with 0.04% Irganox 1076; 3: bound AOTP with 0.1% Irganox 1076; 4: Tinuvin 770 alone and 5: Tinuvin 770 with 0.04% Irganox 1076.

Note: bound AOTP was diluted from No.21. Irganox 1076 was directely added when bound AOTP being diluted in PP during melt processing.

In section 4.1.1.3 it was shown that the combination of bound AOTP with Irganox 1076 showed a slight antagonistic action in photostabilisation of PP possibly due to photo-sensitivity of the intermediate products from the parent hindered phenol to accelerate photooxidation of PP. In this section the effect of a combination of bound AOTP with Irganox 1076 in thermal stabilisation of PP was investigated. Fig. 4.2.1.2a indicates that, the presence of Irganox 1076 with bound AOTP exhibited a dramatic increase in efficiency of thermal stabilisation of PP compared to the absence of Irganox 1076. With an increase in concentration of bound AOTP the embrittlement time of PP increased almost linearly in the presence of 0.04% Irganox 1076 up to about 600 hours. This was much higher than without Irganox 1076. But it was also noted that when the concentration of bound AOTP rose in excess of 1.0% the embrittlement time of PP film increased very slowly or did not rise any more, especially when 0.1% Irganox 1076 was added the embrittlement time curve as a function of concentration of bound AOTP displayed an plateau. This indicates that with increase in concentration, the antioxidant activity of bound AOTP did not increase indefinitely even though AOTP was chemically bound on the backbone of PP to high extent. This phenomenon might result from chemical loss of antioxidant rather than physical loss. Based on the known antioxidant mechanism of hindered phenol and amine this suggests that at the primary stage before the parent amine (bound AOTP) was converted to the corrsponding nitroxyl, the thermal oxidation of PP could be inhibited by the hindered phenol, Irganox 1076, which is a very effective thermal antioxidant in PP. At the same time a part of the parent piperidine (bound AOTP) could be converted into the corresponding nitroxyl thus trapping alkylradicals which will further transformate to hydroxylamine through the redox reactions. The hydroxylamine is an effective CB-D antioxidant by reacting with alkylperoxyl radical, thus preventing thermal oxidation of PP[38]. However, in the absence of Irganox 1076 the rate of thermal oxidation of PP film could be much higher than that of formation of the corresponding nitroxyl so that the concentration of the nitroxyl would not meet the demand of inhibiting the radical progation and the oxidation reaction would dominate in the system to lead to rapid fracture of PP film. Therefore, This indicates that the stabilising activity of piperidine may be closely dependent on the ratio of the concentration of oxygen-containing groups to antioxidant on the aging conditions(temperature, air flow rate) .

Although in the presence of a hindered phenol the performance of bound AOTP was markedly improved the thermal stability of PP and the physcal loss of bound AOTP was not found during oven aging at 140°C, futher increase in the fracture time of PP film did not take place with increasing concentration of bound AOTP as was expected. This result may relate to chemical loss of bound AOTP. With an increase of thermal aging time the parent amine and its transformation products (nitroxyl and hydroxyl amine) might be irreversibly destroyed by reaction with oxygen or alkyl peroxyl, especially at the later stage of thermal oxidation in the case of high concentration of oxygen as follows[188]:



Due to destruction of the chemical structure in bound AOTP it can not any longer behave as a stabiliser.

The behaviour of combination of bound AOTP with Irganox 1076 was discussed above. Fig. 4.2.1.2 also compares a conventional hindered piperidine, Tinuvin 770, with bound AOTP in the thermal stabilisation of PP in the presence and absence of 0.04% Irganox 1076. It shows that Tinuvin 770 alone did not play any positive role in the stabilisation of PP film. But when Irganox 1076 was added to the system, Tinuvin 770 showed some improvement. For example, the embrittlement times of PP stabilised by 0.2% Tinuvin 770 with 0.04% and without Irganox 1076 were about 160 hours and 6 hours respectively. This time (160 hours) was higher than that of PP film with 0.04% Irganox 1076 alone (110 hours). Due to the much more rapid volatilisation of the conventional stabiliser (Tinuvin 770) from PP film its efficiency on thermal stabilising of PP was relatively lower than that of bound AOTP. The investigation of physical loss of antioxidants will be discussed in section 4.2.1.4.

4.2.1.3 Effect of Bound DBBA

Table 4.2.1.3 and Fig. 4.2.1.3 indicate that after DBBA was chemically grafted on PP in the presence of a high amount of a peroxide Triganox101 used for improving grafting extent, its antioxidant activity was dramatically lost compared with the antioxidant activity of DBBA monomer and Irganox 1076. This result might be caused by the addition of a large amount of Triganox101 which is necessary for binding of DBBA on PP. Unfortunately, introducing a lot of a peroxide in the system would cause the oxidation of PP to accelerate the damage of DBBA structure. The concentration of oxygen-containing groups would rise, and since they are chemically linked with the chain of PP they would not be extracted by DCM. Thus solvent extraction hardly removed any oxygen-containing group from PP to improve thermal stabilisation of PP. Otherwise, this process would reduce the relative concentration of DBBA in PP by DCM extraction so that extracted PP film with DBBA was less stable than unextracted one.

On the other hand, it is interesting to note that the combination of bound AOTP with bound DBBA contributed to a positive effect and showed a great synergistic action on thermal stabilisation of PP. In the case of using 0.1% bound DBBA, with an increase in concentration of bound AOTP the embrittlement time of PP increased sharply. But in excess of 1.0% bound AOTP the embrittlement time curve of PP as a function of concentration of bound AOTP showed a slight decline. This result seems closely to be related to concentration of the harmful oxidative products in the PP and the diffusion rate of oxygen (or ratio of alkyl radical to alkylperoxyl radical) in air circulating oven at 140°C.

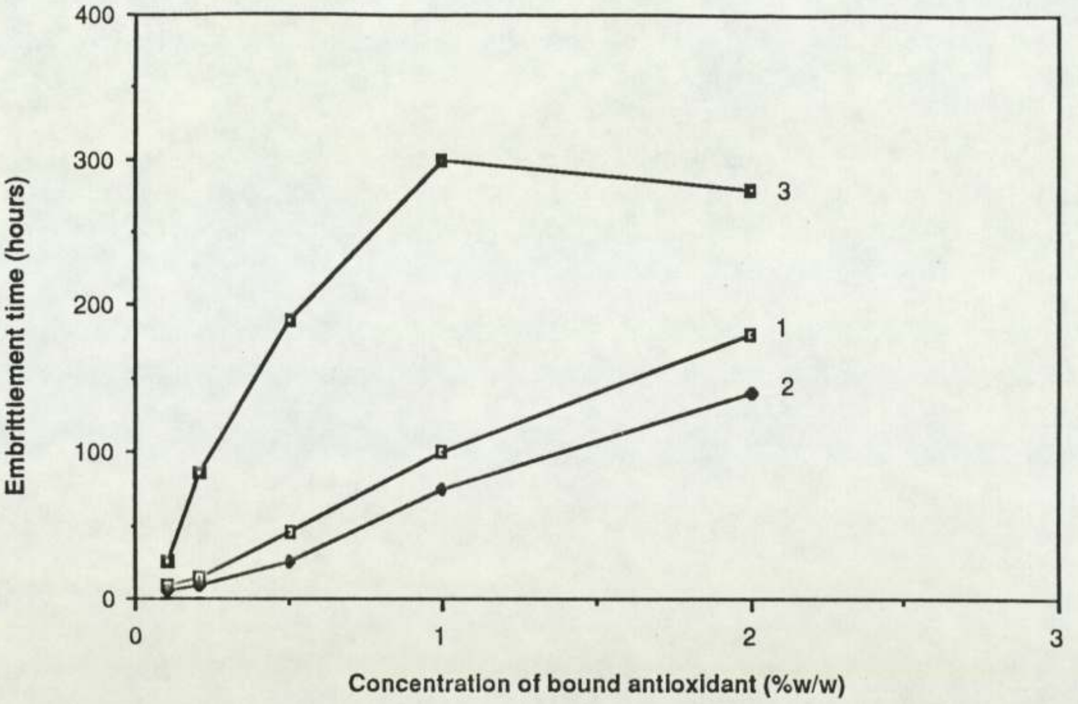


Fig. 4.2.1.3 Effect of bound DBBA antioxidant on thermal stabilisation of PP at 140°C. 1: unextracted bound AOTP; 2: extracted bound DBBA and 3: bound AOTP with 0.1% bound DBBA.

Table 4.2.1.3 Embrittlement time of PP film with different antioxidants in the oven aging at 140°C

Antioxidant	Concentration Wt %	Embrittlement time (h)	
		Unextracted	Extracted
bound DBBA(1)	0.2%	15	10
bound AOTP(2)	0.2%	30	20
(1) + (2)	0.1%(1) + 0.2%(2)	85	---
DBBA monomer	0.2%	330	<10
Irganox 1076	0.2%	420	<10

4.2.1.4 Antioxidant Loss during Thermal Aging of PP

The extent of stabilisation of a polymer depends not only on types of antioxidants and their functional structures but also on their loss through chemical and physical processes occuring during aging of the polymer. Chemical loss of antioxidants results from the destruction of their functional structures by attack of harmful oxidative products and physical loss is mainly caused by their evaporation and extraction from the polymer. In this study it had been found that with further increase of concentration of bound AOTP its efficiency on stabilisation of PP was not increased even though the ester carbonyl index was hardly changed. This suggests the antioxidant function damage of bound AOTP in PP. Contrarily, conventional antioxidants (Tinuvin 770 and Irganox 1076) were both physically lost during both air circulating oven and UV cabinet aging. Fig. 4.2.1.4 shows that with an increase in thermal aging time the ester carbonyl index of the conventional antioxidant decreased. The rate of physical loss of Tinuvin770 was much quicker than that of Irganox 1076. For example, in the case of 0.5% concentration the ester carbonyl of Tinuvin 770 and Irganox 1076 were almost disappeared in about 10 and 300 thermal air circulating aging hours respectively.

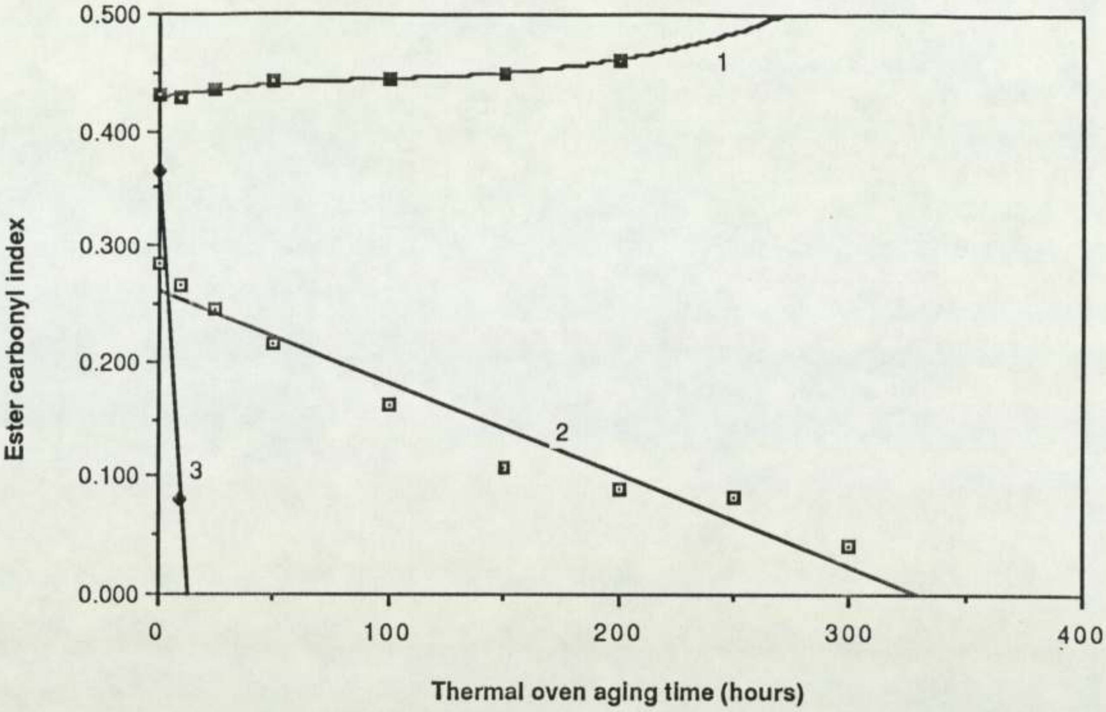


Fig. 4.2.1.4 Change in ester cabonyl index of antioxidants during thermal air circulating oven aging at 140°C. 1: 0.5% bound AOTP with 0.04% Irganox 1076, 2: 0.5% Irganox 1076 and 3: 0.5% Tinuvin 770.

Chapter Five

Mechanism Study of Nitroxyl Radicals with A Hindered Phenol in Thermal and Photostabilisation

5 Mechanism Study of Nitroxyl Radicals with A Hindered Phenol in Thermal and Photostabilisation

5.1 Introduction

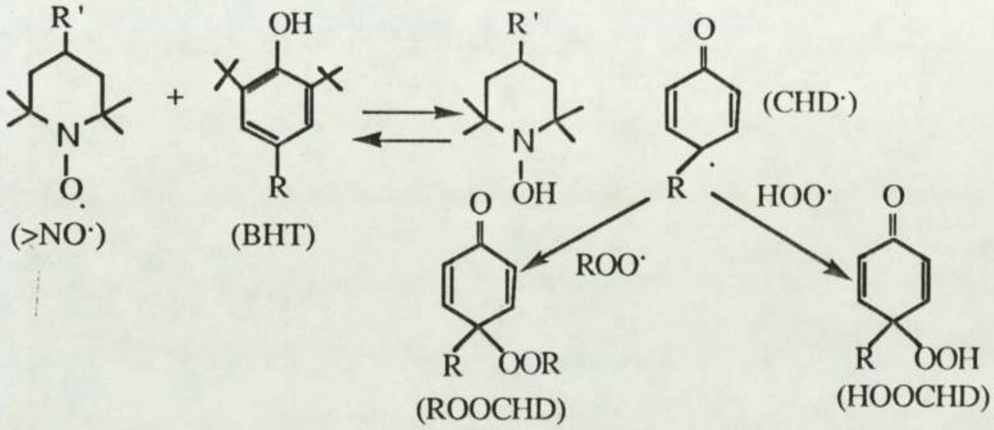
Hindered phenols and amines are very effective antioxidants in thermal and photostabilisation of polyolefins, respectively. Their functions and antioxidant mechanism have been extensively studied in recent years. In the case that macroalkyl and macroalkylperoxyl radicals are present together in a system some hindered phenols acting by a CB-D mechanism, are effective thermal stabiliser and rapidly converted to quionoid oxidation products whilst performing its CB-D function [39] (see scheme 1.4.1.3). However, although hindered phenols are very effective antioxidants in thermal stabilisation of polymers (PP, PE) based on CB action mechanism they do not function as photostabilisers due to their transformation products which are sensitive to UV light hence promote the destruction of polymers during photooxidation.

Compared with hindered phenols hindered piperidines are very effective as UV stabilisers. It has been generally reported that during the UV aging process the parent piperidine is readily converted to the corresponding nitroxyl radical which is a powerful alkyl radical trap(CB-A agent) in the case of limited oxygen, and is transformed to hydroxylamine as a CB-D agent to react with alkylperoxyl radical to be reconverted into the nitroxyl in a redox process. The redox process would be also controlled by the diffusion rate of oxygen or ROO·/R· ratio in the system. This catalytic action is favoured in UV aging process rather than in thermal air circulating oxidation process at a high temperature. But actually it is also found by Scott [85] that the corresponding nitroxyl radicals containing an unpaired electron which can give rise to a 'stable' reduced form can function as melt stabilisers during the processing of PP. The redox catalytic action for chain termination which takes place is similar to that in the UV aging process. This confirms that the nitroxyl radical can play a role in thermal stabilisation of PP under certain conditions. However it is worth noting that the addition of the parent amine is to PP during the melt processing confers no stabilisation of PP[165]. In chapter four it was also confirmed that in the case of stabilised PP by bound AOTP without the combination of a hindered phenol, Irganox 1076, the thermal fracture time of the PP film was low. But in the presence of the phenol bound AOTP contributed an important part to inhibit thermal oxidation of PP. What happens in the system is of some theoretical interests. The transformation of the parent amine to the nitroxyl radical might be an important factor determining antioxidant behaviour.

In this work the bound AOTP (masterbatch No. 21) was selected to be oxidised by a peracid (m-chloroperbenzoic acid) in order to obtain the bound AOTP nitroxyl radical and study its antioxidant behaviour in thermal and photostabilisation of PP.

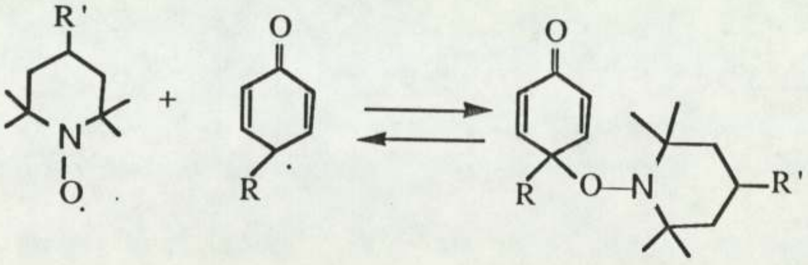
On the other hand a solution reaction containing a nitroxyl radical 4-hydroxyl-2,2,6,6 -tetramethlpiperidine-1-oxyl referred to TMPO and a hindered phenol, Irganox 1076, in the model system was also carried out to investigate the combination effects of the nitroxyl with the phenol.

In recent years during stability tests of polymers some controversial results have been found in combination system of the two antioxidants. Synergistic or antoganistic action may take place on different aging situations. Based on the individual results obtained some interaction mechanisms have been proposed to explain the combination effects of hindered amine with hindered phenols in the thermal and photostabilisation of polymers. Allen et al. [177] studied a phenol antioxidant (BHT) and HALS (Tinuvin 770 and 4-hydroxyl-2,2,6,6 -tetramethlpiperidine-1-oxyl) during the processing of PP with UV, IR and ESR, and suggested that nitroxyl primarily formed in the system, is able to oxidise the phenol antioxidant (BHT) by hydrogen transfer to cyclohexadienonyl (CHD·) via reaction shown as follows:



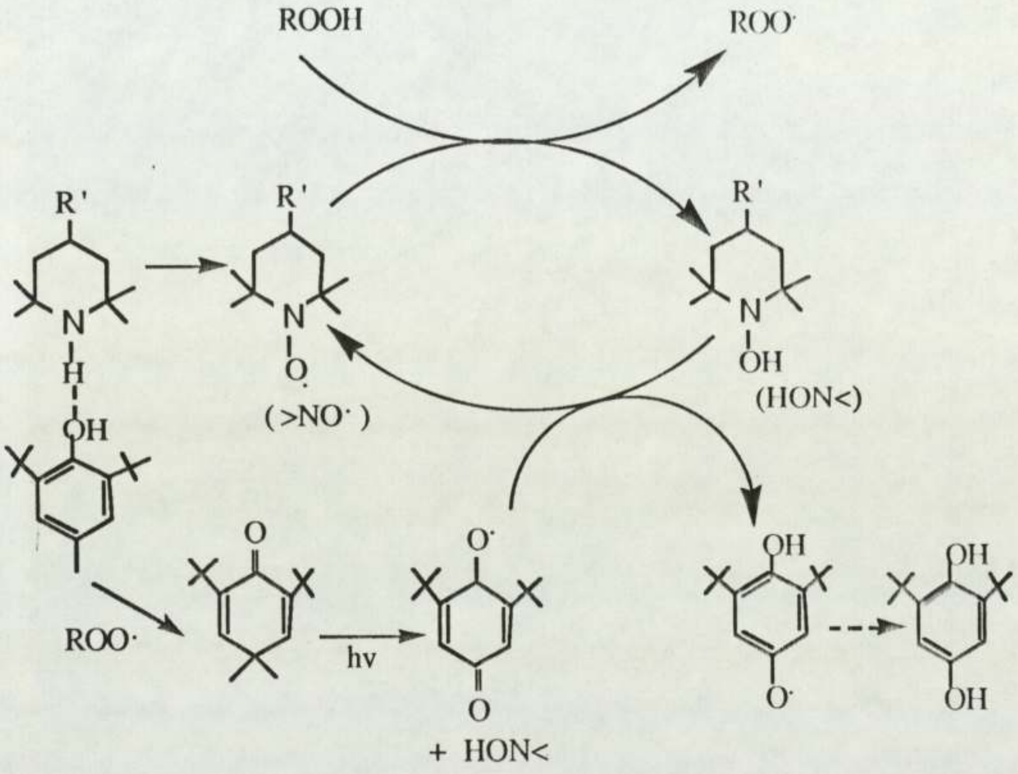
It seems likely from this reaction that the concentration of nitroxyl is diminished and transformation products (ROO-CHD, HOO-CHD) are formed in the stabilised PP so that during UV aging process combination of the two antioxidants would play a negative role for photostabilisation of PP. This antagonism has been proved experimentally. But this suggestion can not completely explain this antagonistic action because the reaction of >NO· with BHT into HON< can be reversible. The concentration of the nitroxyl is not actually lost through this reaction.

On the other hand, based on above reaction proposed an alternative reaction could happen to result in the formation of >NO-CHD as follows[167,183]:



(>NOCHD)

The interaction between radicals generated from HALS and phenol should be a reversible reaction and could contribute to either a synergism or antagonism action which must be concerned in the influences of oxidation free radicals and aging conditions. During thermal air circulating oven process it was suggested [167] that this reaction to explain the synergistic behaviour of combination of bound BPHE (a piperidine amine) with Irganox 1076. There are other complementary mechanisms proposed to explain the synergism between HALS and phenol. Lucki et al.[184] suggest that HALS be able to deactivate ROO-CHD and HOO-CHD generated thermally and photochemically, respectively, from the phenolic antioxidant used. A chemical deactivation like this may eliminate thermolysis or photolysis of the two transformation species, and their initiating efficiency is therefore excluded. Ohkatsu[185] proposed that an interaction between HALS and BHT involved the formation of substituted light excited benzoquinone via the photolysis of ROO-CHD shown as follows:



These mechanistic explanations mentioned above for cooperative phenomena observed under thermal and photooxidation condition could not simply be rejected or accepted, especially for individual results. It is certain that the cooperative effects and interaction between HALS and phenol are very complicated. A lot of work needs to be done to make sure what exactly happens in the system.

In this work the nitroxyl obtained from bound AOTP by oxidation was investigated to confirm its thermal stabilising action on PP in the case of air circulating oven aging at 140°C and combination effect of the nitroxyl with Irganox 1076 was also examined. At the same time attempts were made to study a model solution reaction of an essential nitroxyl radical (TMPO) with a hindered phenol (Irganox 1076) using UV/Vis. spectrometer to detect the change of the nitroxyl radical concentration in xylene under air and N_2 at about 140°C*.

*Note that it was originally intended to use ESR in this study but the ESR machine broke down at a crucial time.

5.2 Effect of Oxidised Bound AOTP on Thermal and Photostabilisation of PP

5.2.1 Formation of Oxidised Bound AOTP

It is generally known that a piperidine can be oxidised by a peroxide to form the corresponding nitroxyl radical. Unfortunately, in this work it may not be possible directly to produce the nitroxyl radical of bound AOTP from AOTP nitroxyl monomer by radical processing because the nitroxyl is a radical trapping agent. Thus, one alternative method was used to oxidise bound AOTP masterbatch by a peroxide.

The detail procedure is as follows:

40g of bound AOTP masterbatch (sample NO. 21) which was added in 200 ml acetone containing 2g of m-chloroperbenzoic acid in a 500 ml flask, was kept in water bath. The mixture was heated at about 40°C and the reaction was kept for 24 hr until it was found that the colour of bound AOTP was changed from white to orange which can confirm formation of the corresponding nitroxide of bound AOTP. The reation was then stopped, the acetone was removed. The oxidised bound AOTP was washed with water three times to remove the residue of m-chloroperbenzoic acid and dried in vacuum. The resulting nitroxyl of bound AOTP with yellow-orange colour was obtained for further studies.

Although the qantitative analysis of formation of the nitroxyl from parent bound AOTP had not been done due to ESR unavailablity it was certain that the nitroxyl radical should be formed in the reaction based on discolouration of bound AOTP masterbatch.

5.2.2 Thermal Stabilisation of PP by Oxidised Bound AOTP

5.2.2.1 Results and Discussion

Fig. 5.2.2.1.a compares changes in the efficiency of oxidised and parent bound AOTP on thermal stabilisation of PP during air circulating oven aging at 140°C. The extent of stabilisation of PP film was improved evidently by oxidised bound AOTP as compared with the parent bound AOTP. with an increase in concentration of the nitroxyl,

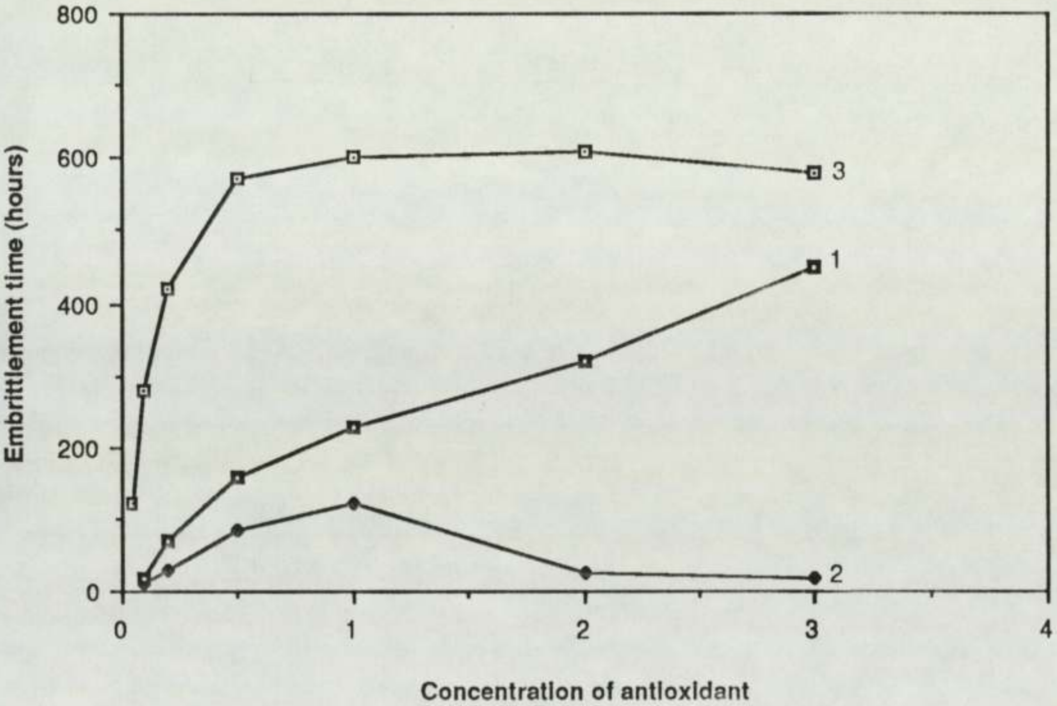


Fig. 5.2.2.1a Change in embrittlement time of PP film as a function of concentration of antioxidant in the case of air circulating oven aging at 140°C. 1: oxidised bound AOTP; 2: bound AOTP and 3: Irganox 1076.

the fracture time of PP film increased unlike the behaviour of bound AOTP in the system. This confirms that the formation of nitroxyl oxidised from parent amine must be a very important process to contribute to the delay in thermal oxidation of PP film and the nitroxyl formation stage determines the bound AOTP efficiency. Because of the presence of a certain amount of nitroxyl over the critical concentration before thermal aging of PP the radical trapping process could compete with that of radical propagation at the first stage of thermal oxidation. But with an increase in thermal aging time the rate of formation of harmful oxidation products would increase more rapidly than the regeneration rate of the nitroxyl in the system so that its thermal stabilising effectiveness would not be comparable to that of its photostabilising on PP and much lower than that of a hindered phenol (Irganox 1076), especially at a low concentration.

It is interesting to note in Fig. 5.2.2.1b and Table 5.2.2.1 that in the case of addition of a small amount of Irganox 1076 the thermal stabilisation of PP film by the nitroxyl of bound AOTP improved dramatically. This indicates that there is actually synergistic action in the combination of the nitroxyl and phenol.

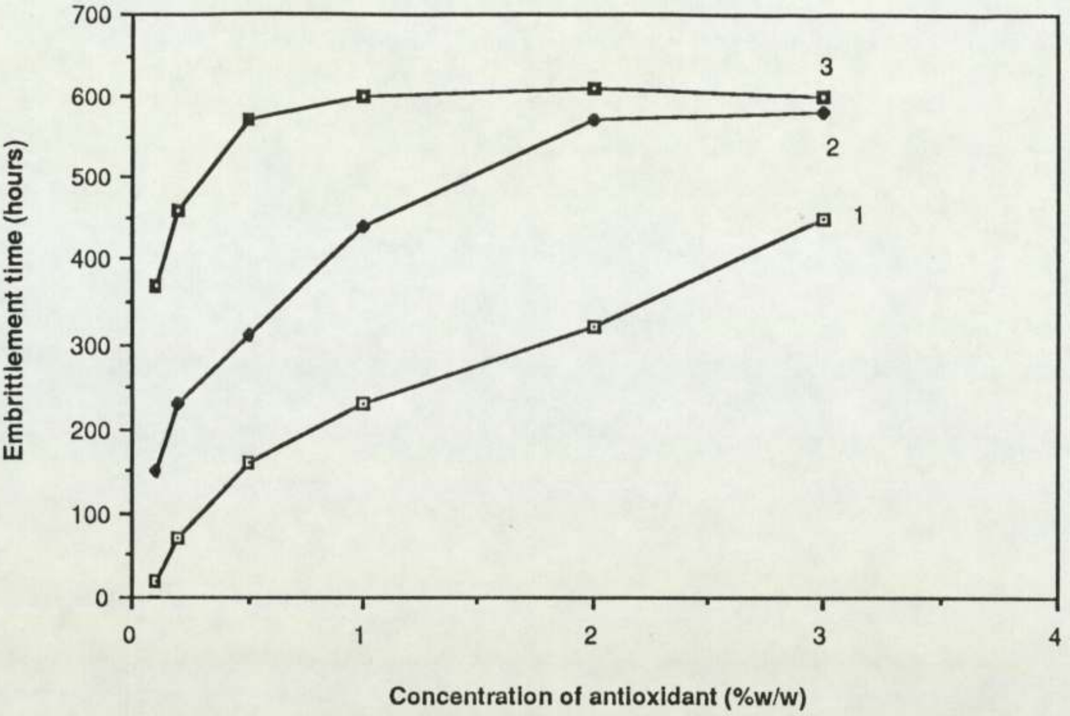


Fig. 5.2.2.1b Cooperative effect of oxidised bound AOTP with Irganox 1076 on thermal stabilisation of PP as a function of oxidised bound AOTP concentration during air circulating oven aging at 140°C. 1: oxidised bound AOTP alone; 2: with 0.04% Irganox 1076 and 3: with 0.1% Irganox 1076.

Table 5.2.2.1 Fracture times of PP films stabilised with different antioxidants in air circulating oven aging at 140°C

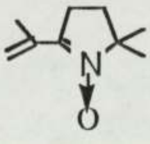
Antioxidant	Concentration Wt %	Fracture time hours
bound AOTP (1)	0.2%	30
oxidised bound AOTP(2)	0.2%	80
Irganox 1076 (3)	0.04%	120
---	0.1%	280
(2) + (3)	0.2% + 0.04%	230
---	0.2% + 0.1%	460

However, it was also found that an increase in the concentration of oxidised bound AOTP in excess of 1.0% with 0.1% Irganox 1076 did not practically increase the fracture time of PP film. This result was consistent with that of original bound AOTP with Irganox 1076 shown in chapter 4 and suggests strongly that at a later stage of thermal aging the formation rate of oxygen-containing products would be very rapid without noticeable regeneration of the nitroxyl so that the bound antioxidant itself would be destroyed by attack of alkyl and alkylperoxyl radicals to loss its antioxidant activity. Unfortunately, a helpful method had not been found to confirm the destroyed function structure of bound AOTP.

5.2.3 Photostabilisation of PP by Oxidised Bound AOTP

5.2.3.1 Results and Discussion

Fig. 5.2.3.1 compares changes in efficiency of oxidised and original bound AOTP on photostabilisation of PP during UV cabinet aging. The oxidised bound AOTP exhibited quite a good performance on photostabilising of PP film. With an increase in its concentration to 2.0% the fracture time of PP film stabilised by oxidised bound AOTP increased steadily. At a low concentration, photostabilisation of PP by the nitroxyl can be seen to parallel closely that of the parent bound AOTP. This is consistent with the role of nitroxyl in the hindered amine photostabilising mechanism. But it was noted that the efficiency of oxidised bound AOTP was between that of original bound AOTP and extracted bound AOTP. Surprisingly in excess of 2.0% concentration the oxidised bound AOTP was less effective than both original and extracted one. These may be concerned with the effect of the formation process using a peroxide (m-chloroperbenzoic acid) which oxidises not only bound AOTP and but also PP chain. Thus, the amounts of macroalkyl oxidants and unsaturated >C=C< groups would be increased in the system (see Fig. 5.2.3.2 showing the IR spectrum of oxidised and original bound AOTP masterbatch) and these harmful groups would accelerate the oxidation of PP film. It has been reported by Moad et al [186] that 2,2,6,6- tetramethylpiperidine-N-oxyl reacts with benzoyl peroxide in solution via a nitroso compound to form the nitrone.



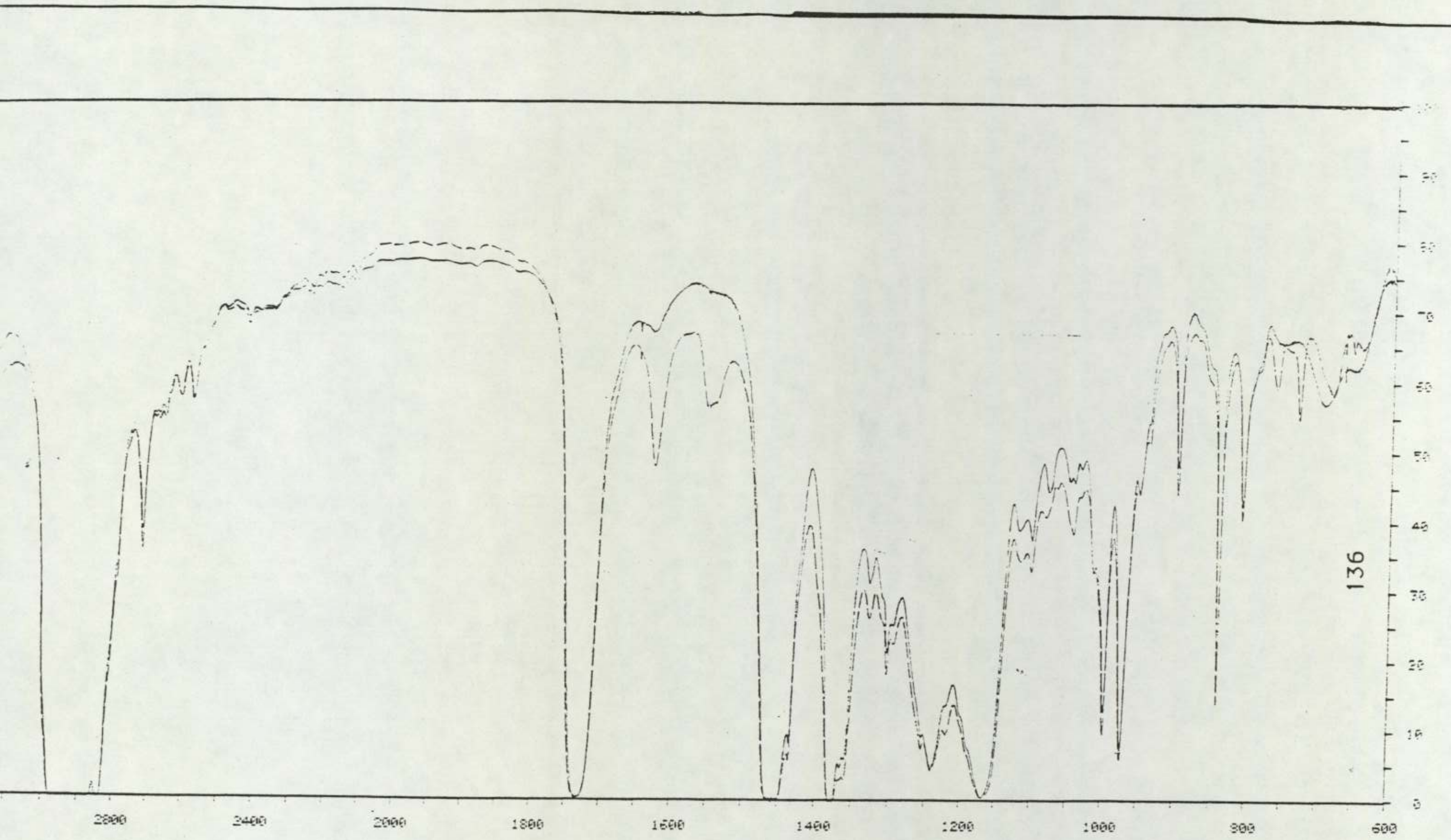
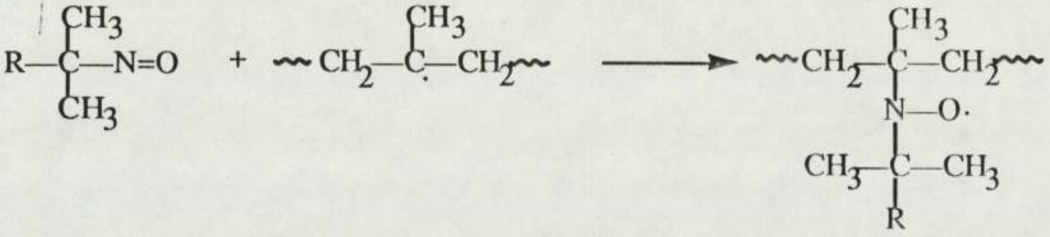


Fig.5.2.3.2 Change in IR spectrum of bound AOTP masterbatch No. 21 after being oxidised by m-chloroperbezoic acid.
----- oxidised bound AOTP and —— parent bound AOTP.

This compound shows IR absorption at 1535 cm^{-1} which could likely undergo relatively rapid secondary degradation reaction. In this work a similar process with the bound AOTP and m-chloroperbenzoic acid could also account for the 1540 cm^{-1} band observed from the bound nitroxyl. The presence of by-products (nitrone) may result in the accelerating oxidation of PP film in the later stage of UV cabinet aging. But, it has been contrary reported[187] alkyl nitroso compounds and nitrones are well known alkyl radical traps and thus would react with PP macroradicals to produce stable nitroxyl.



Therefore, in addition to the regeneration processes of the nitroxyls for stabilisation of PP there might be other positive protection or negative oxidation processes in the system stimulated by some nonidentical side-products formed from production process of the bound nitroxyl.

On the other hand, through the comprising of fracture time curves of PP film stabilised by different antioxidant as a function of the antioxidant concentration it was seen that no matter how much bound antioxidant from 0.1% to 3.0% was in PP the fracture time of PP film was never higher than the maximum value (about 4500 hours) by using a conventional stabiliser Tinuvin 770. This possibly indicates that there may be a maximum or critical value of PP embrittlement time which could not be raised by further increasing of either bound antioxidants or conventional stabilisers.

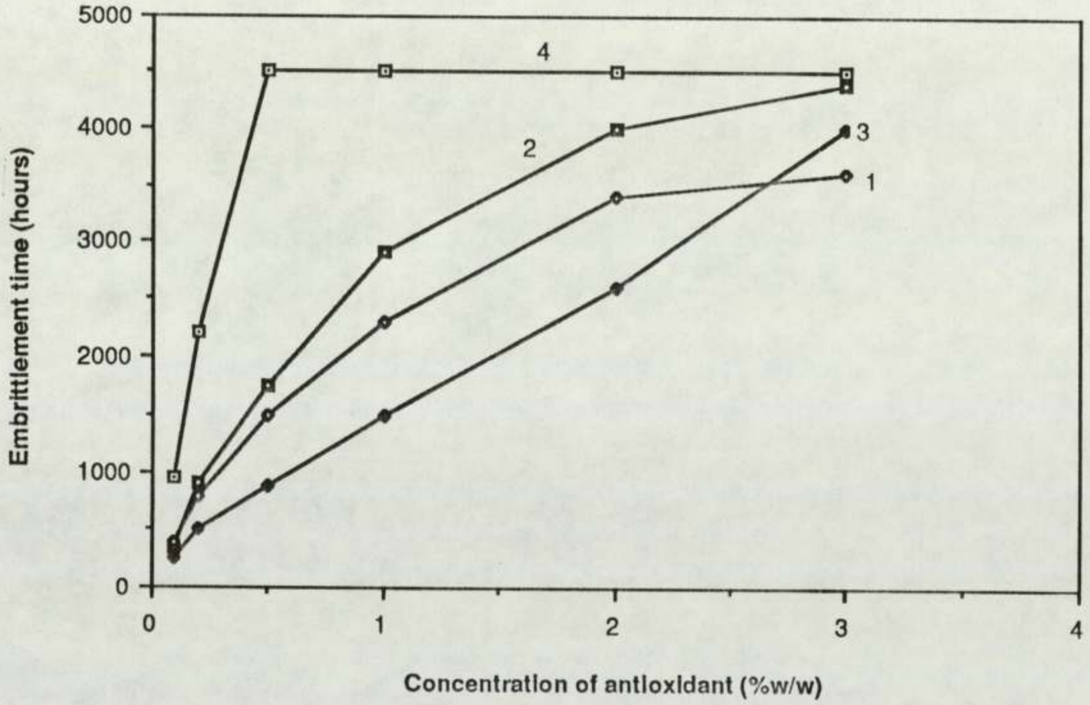


Fig. 5.2.3.1 Comparison of effects of oxidised and original bound AOTP on photostabilisation of PP during UV cabinet aging. 1: oxidised bound AOTP; 2: original bound AOTP; 3: extract bound AOTP by DCM and 4: Tinuvin 770.

Fig. 5.2.3.3 points to that the combination of oxidised bound AOTP with a hindered phenol Irganox 1076 hardly showed a synergistic or antoganistic action on photostabilisation of PP. The embrittlement time was not changed practically by combination of Irganox 1076 in either 0.04% or 0.1% concentration.

But in Fig. 5.2.3.4 The growth rate curves of carbonyl groups in PP films stabilised by oxidised bound AOTP and Irganox 1076 as a function of UV cabinet aging time were firmly different from the

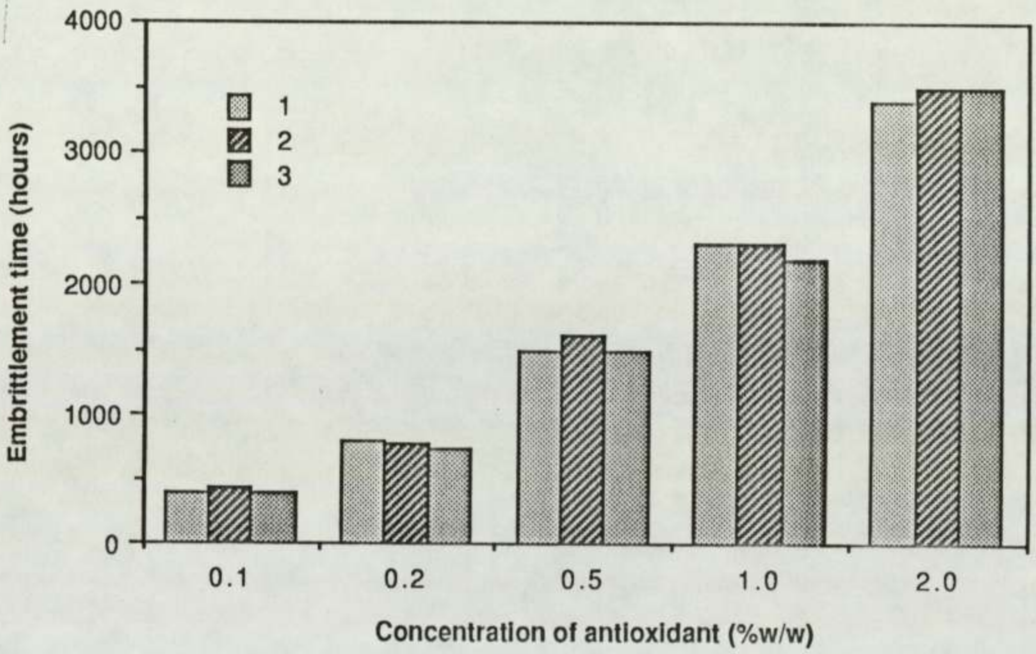


Fig. 5.2.3.3 Combination effect of oxidised bound AOTP with Irganox 1076 on photostabilisation of PP during UV cabinet aging. 1: oxidised bound AOTP alone; 2: with 0.04% Irganox1076 and 3: with 0.1% Irganox 1076.

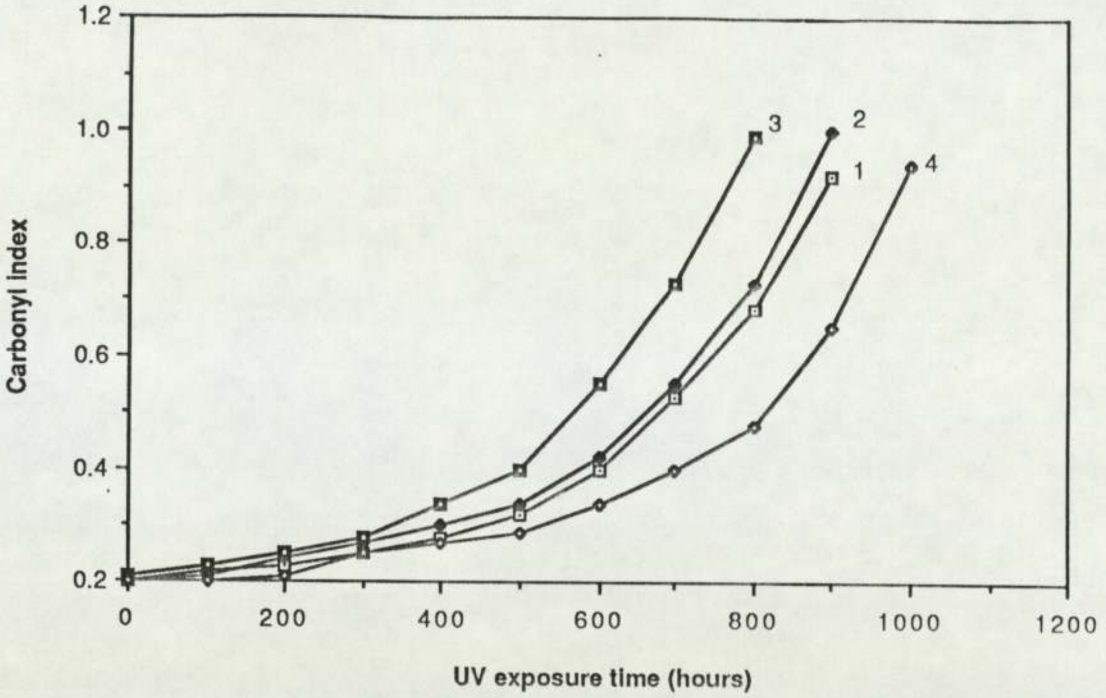


Fig. 5.2.3.4 Change in carbonyl index of PP film stabilised by oxidised bound AOTP with Irganox 1076 as a function of UV cabinet aging time. 1: 0.2% oxidised bound AOTP alone; 2: with 0.04% Irganox 1076; 3: with 0.1% Irganox 1076 and 4: 0.2% bound AOTP alone.

fracture time curves under the same condition. In the presence of 0.1% Irganox 1076 the carbonyl groups in the PP film stabilised by 0.2% oxidised bound AOTP was enhanced rapidly and the growth rate of carbonyl index was obviously faster than in the case of that PP film were stabilised by oxidised bound AOTP alone or with 0.04% Irganox 1076. It was also noted that using oxidised bound AOTP rather than parent bound AOTP promoted the rapid formation of carbonyl groups in PP during UV cabinet aging process. Their growth rate curves were quite distinct.

Comparing of the above two figures it is interesting to note that under these conditions, the measurement in the change of carbonyl index of PP stabilised by oxidised bound AOTP did not exactly correspond to the extent of stabilisation of PP. Moreover, the induction time of photooxidation in PP did not evidently concerned with the growth rate curve of carbonyl index with the increase of UV cabinet aging time. Thus it was difficult to conclude that there was either a positive or negative effect of Irganox 1076 on photostabilisation of PP stabilised by oxidised bound AOTP. Complex reactions could take place in the system concerned with the different intermediates from Irganox 1076 and oxidised bound AOTP as well as alkyl oxidation products. In general, the ratio of the regeneration rate of the nitroxyls to the rate of formation of the oxidation products should be a very important factor to control the extent of stabilisation of PP.

In the next section an attempt will be made to detect the concentration change of essential nitroxyl radical (TMPO) with or without a hindered phenol in xylene at 140°C under air or nitrogen using UV/Vis. spectrometry and to investigate the effect of a peroxide (Triganox101) on the disappearance rate of the nitroxyl radical.

5.3 Kinetic Study of The Rate of Disappearance of Nitroxyl Radicals in A Model System

As mentioned above, the combination of a hindered amine with a hindered phenol showed a slightly antagonistic effect on the photostabilisation of PP and a strongly synergistic effect on thermal stabilisation of PP. The efficiency of the hindered amine is closely concerned with many factors (e.g. concentration of alkyl oxidation products, temperature, air pressure and so on). In this study an attempt was made to use a kinetic method to investigate the effects of a variety of factors on the disappearance rate of 4-hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl (TMPO) in solution. The rate of disappearance of the nitroxyl was considered as a function of solution reaction time followed by UV/Vis. spectrometer using an asorption of the nitroxyl at 475 nm. The concentration calibration curve of the nitroxyl radical in xylene was shown on Figs. 5.3a & 5.3b.

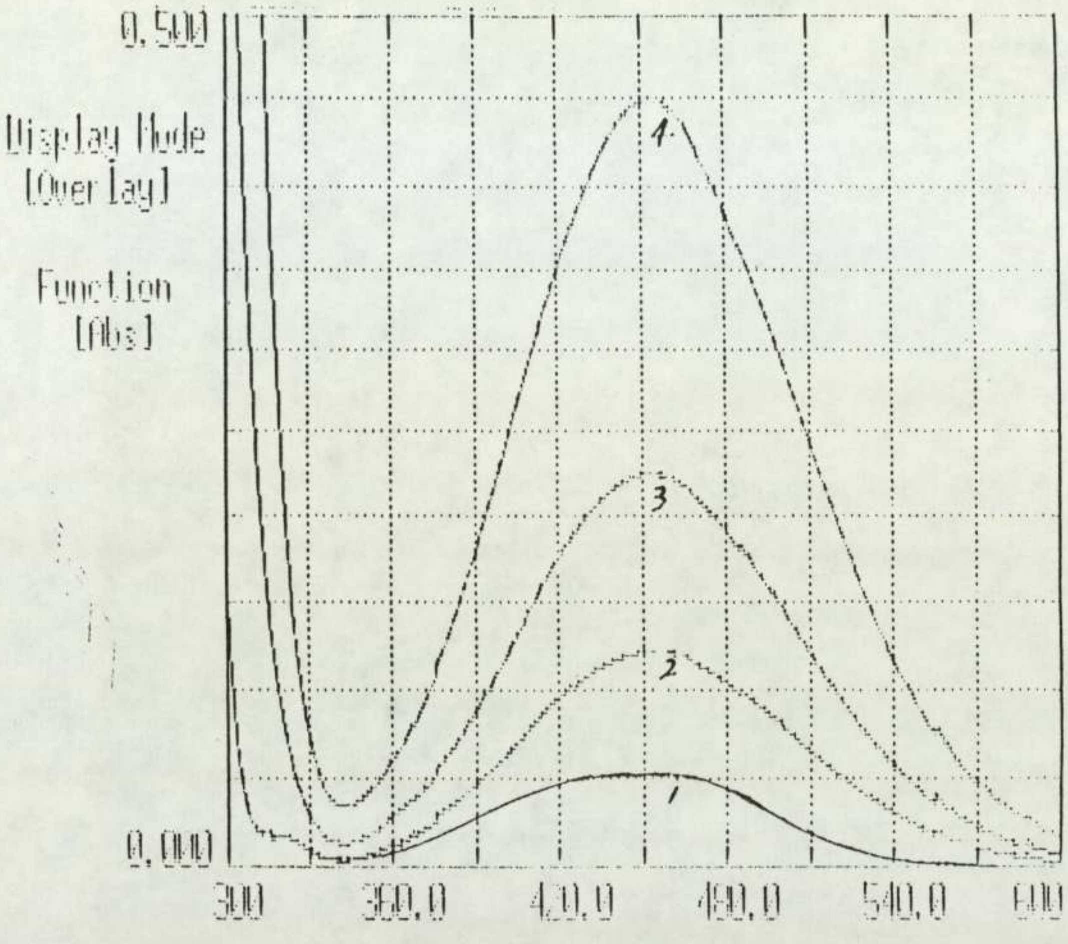


Fig. 5.3a Change in UV/Vis. spectrum of TMOP with increasing its concentration in xylene.
Concentration : 1 --- 0.005, 2 --- 0.010,
(mol/l of xylene) 3 --- 0.020, 4 --- 0.040.

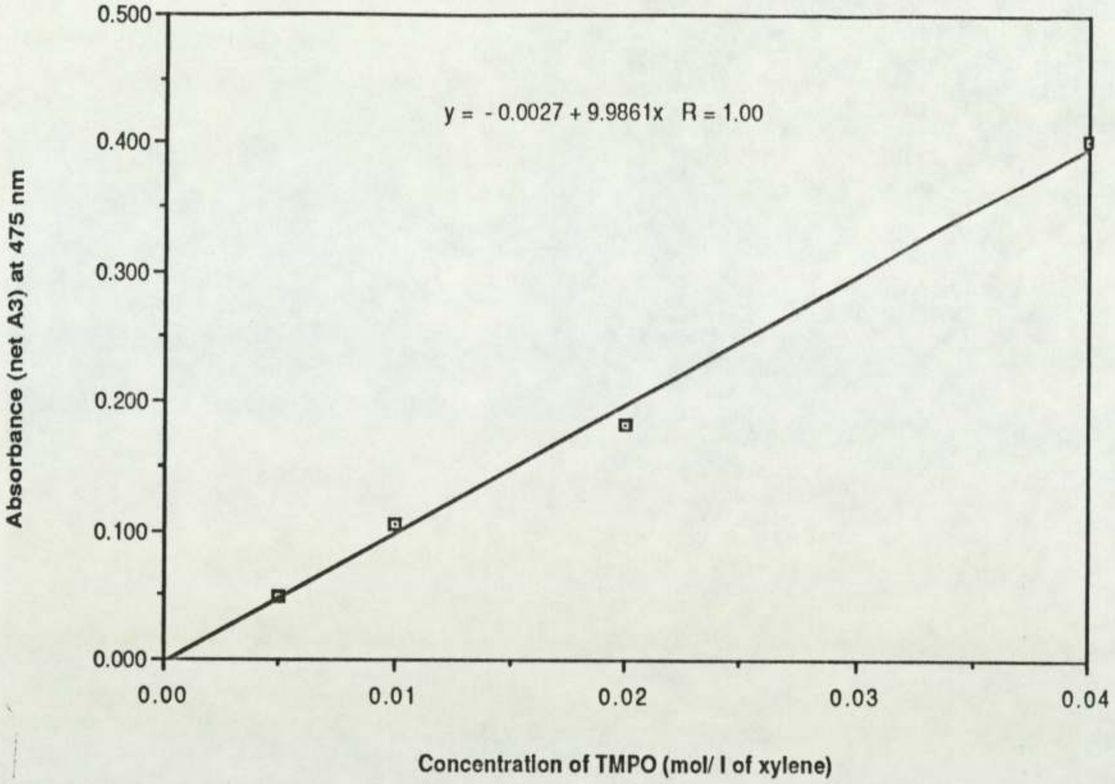


Fig. 5.3b Concentration calibration curve of TMPO in xylene.

It was found that there was a good linear relationship of the absorption intensity of TMPO at 475 nm with its concentration in xylene. Thus, the change of TMPO absorption would be linearly responsive to the change of TMPO concentration during solution reaction.

Details of experimental apparatus and experimental procedure is shown below:

A 50ml three neck flask with a condenser, thermometer and bulb glass tube was used for the study of solution reaction of TMPO with or without Irganox 1076 in xylene under air or nitrogen. In order to avoid oxygen a slow steady stream of pure nitrogen was purged through the solvent and reactants before and during the process of the reaction. The reaction cell was placed in a thermostated oil bath at 140 ± 2°C. 3 ml of sample was normally withdrawn at intervals for testing by UV/Vis. spectrometer.

5.3.1 Results and Discussion

5.3.1.1 Effect of Irganox 1076 on Rate of Disappearance of Nitroxyl Radicals

Fig. 5.3.1.1 compares the change in absorption intensity of the nitroxyl radical (TMPO) (0.02 mol/l) at 475 nm with and without Irganox 1076 (0.01mol/l) in xylene at 140°C as a function of reaction time. It was found that in the presence of Irganox 1076 the absorption intensity of TMPO notably decline with an increase in reaction time and the disappearance rate of TMPO was much faster than in the absence of Irganox 1076 before 5 hours under both air and nitrogen. From curves 3 & 4 it is interesting to note that in the presence of Irganox 1076 the change in absorption intensity of TMPO was little different in the presence and absence of air. Both curves showed almost the same trend during the reaction. But in the absence of Irganox 1076 the shape of curve 1 was quite different from that of curve 2. The disappearance rate of the nitroxyl radical under nitrogen (curve 1) was more rapid than under air (curve 2). Under nitrogen the decrease in concentration of TMPO was almost linearly related to reaction time in xylene at 140°C. By contrast, in air the change in concentration of TMPO was not significant with increasing reaction time until 5 hours. After 5 hours of reaction the presence of air dramatically affected the decay of 475nm baseline due to the serious change of xylene background reference. So in this work only the UV/Vis. spectrometer data of TMPO from solution reaction before 5 hours was recorded and discussed.

5.3.1.2 Effect of Peroxide (Triganox101) on Disappearance Rate of Nitroxyl Radical in The Precence of Irganox 1076

Fig. 5.3.1.2 shows that in the presence of Triganox101 (0.004 mol/l) the loss rate of the nitroxyl radicals was much faster than in its absence. The change in absorption intensity of the nitroxyl radical (0.02 mol/l) at 475 nm in xylene at 140°C decreased sharply with reaction time, especially under air. The disappearance rate of TMPO was linear with reaction time. If there was not Triganox101 (0.004 mol/l) present, a change in the absorption intensity of TMPO at 475 nm was relatively slow between 1 to 5 hours in the system.

These two figures (Fig. 5.3.1.1 and 5.3.1.2) indicate that due to the addition of Irganox 1076 (0.01 mol/l) the reaction between TMPO and the phenol would take place or some complex compounds would be formed to corresponding to the concentration decline of the nitroxyl radical at the early stage of the solution reaction. At the middle stage of the reaction from 1 to 5 hours these intermediate products could be decomposed to re-produce the nitroxyl radical so that the disappearance rate of TMPO would only be slightly changed, unlike that at the early stage of the reaction. On the other hand, due to the addition of Irganox 1076 the disappearance rate of TMPO was hardly affected by air or nitrogen purging. This could result from high antioxidant efficiecy of Irganox 1076 and its high concentration in xylene to prohibit the reaction of TMPO with xylene and alkyl radical. But in the case of absence of Irganox 1076 it suggests the environment factor would affect the regeneration of the nitroxyl radicals so that under nitrogen the absorption intensity of TMPO at 475 nm was declined more rapidly than under air because in the presence of oxygen the alkylperoxyl radical would be formed in the system which could react with hydroxylamine and alkyloxylamine produced from TMPO to lead to regeneration of the nitroxyl radicals.

When a peroxide Triganox101 with a relatively high concentration (0.004 mol/l) was added in the mixture of TMPO (0.02 mol/l) and Irganox 1076 (0.01 mol/l) in xylene, the behaviour of change in absorption intensity of TMPO at 475 nm were quitely different. Due to the presence of oxygen it promote the initiating oxidation reaction in the system so that the rate of formation of oxidative products would be much faster than that of regeneration of the nitroxyl radicals. Therefore, a high amount of peroxide in a system must accelerate autooxidation reaction and destroy the balance of rate of oxidation of alkyl groups and rate of regeneration of nitroxyl radicals. The value concentration of antioxidant would be not enough to prohibit an accerelating oxidation of alkyl groups in a system.

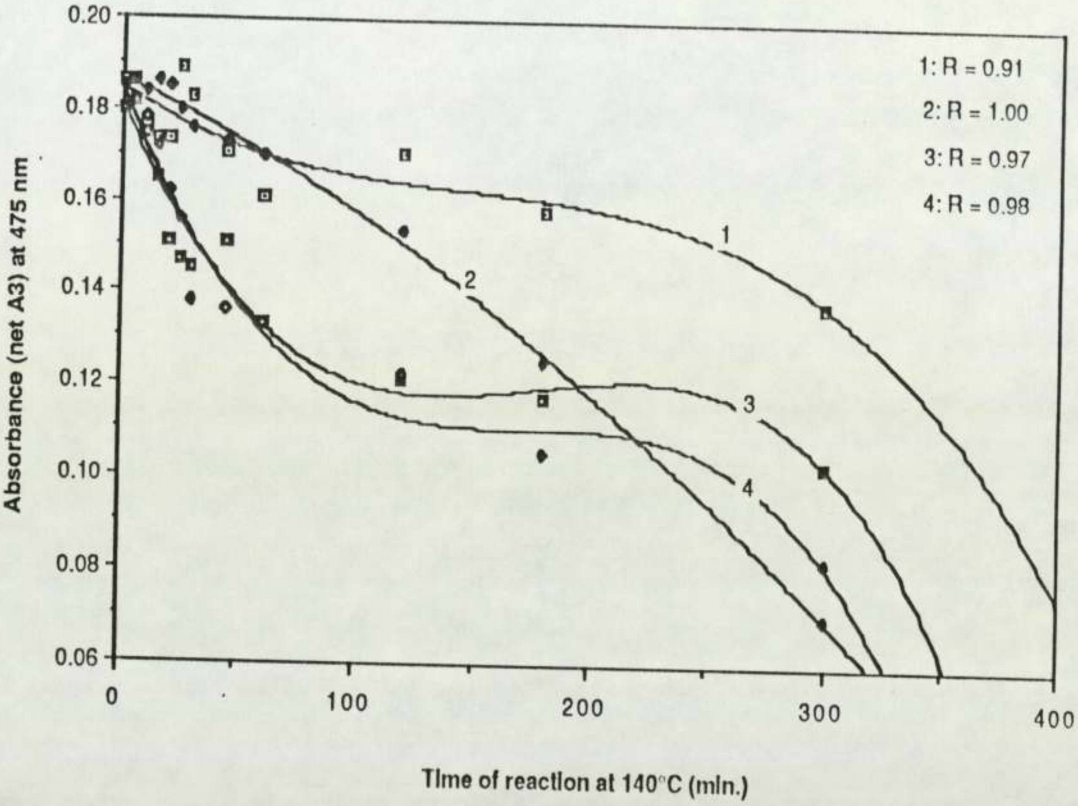


Fig. 5.3.1.1 Change in absorption intensity of TMPO (concentration) as a function of solution reaction time in xylene at 140°C. 1: TMPO alone under air; 2: TMPO alone under nitrogen; 3: TMPO with Irganox 1076 under air and 4: TMPO with Irganox 1076 under nitrogen.

Note: Concentration: 0.02 mol/l of TMPO and 0.01 mol/l of Irganox 1076, R = confidence level and four curves treated by polynomial equation fitting.

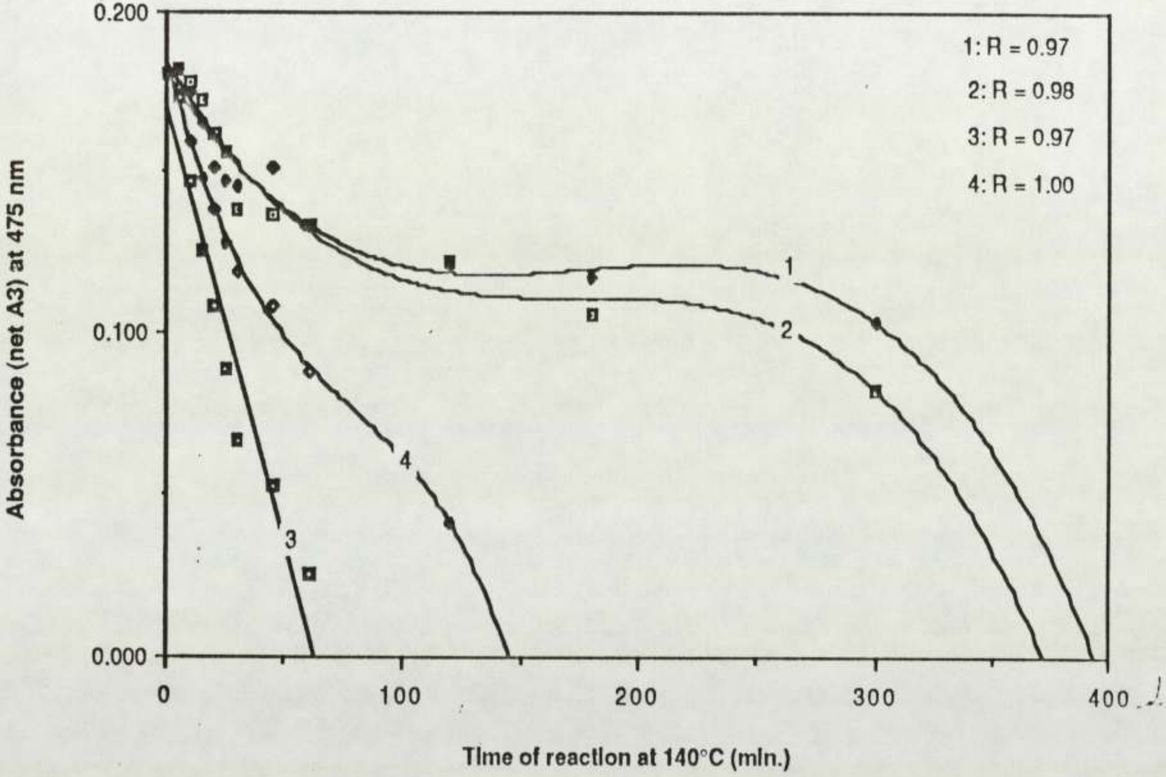


Fig. 5.3.1.2 Change in absorption intensity of TMPO (concentration) as a function of solution reaction time in xylene at 140°C in the presence of a peroxide (Traganox101). 1: TMPO with Irganox 1076 under air; 2: TMPO with Irganox 1076 under nitrogen; 3: (1) with Traganox101 and 4: (2) with Traganox 101.

Note: Concentration: 0.02 mol/l of TMPO, 0.01 mol/l of Irganox 1076 and 0.004 mol/l of Traganox101, R = confidence level and four curves treated by polynomial equation fitting.

Chapter Six

Conclusions and Recommendation for Further Work

6 Conclusions and Recommendation for Further Work

6.1 Conclusions

1). AOTP, HEAB and DBBA antioxidants with acrylic functional groups were able to be grafted on the backbones of polypropylene in the presence of a peroxide (Triganox101) and a polyfunctional agent (Tris). The maximum binding extent of AOTP and HEAB on PP was over 90%. Although DBBA is a hindered phenol antioxidant it was still effectively bound on PP with 80% binding extent by adding a relatively high amount of Triganox101. Generally speaking, the antioxidants with acrylic groups were bound to PP to quite a high level.

2). Bound AOTP was found to be an effective photostabiliser for PP. Its efficiency increased approximately linearly with an increase in concentration up to 3.0% (w/w in PP). Unfortunately, with further incremental increase of bound AOTP, photostabilisation of PP did not improve further as expected even in spite of the fact that no physical loss occured during UV aging. However, conventional antioxidants (Tinuvin 770 and UV 531) were readily lost by physical means from PP due to migration and evaporation, and did not exhibit any resistance to solvent extraction from PP unlike bound antioxidants which were hardly extracted by solvent. This advantage of bound antioxidants would lead to a wide application of polymers with antioxidants in the food and medical industries for avoiding and eliminating the hazards of toxicity and carcinogenicity.

It was interestingly found that bound AOTP oxidised by m-chloroperbenzoic acid was capable of inhibiting thermal oxidation of PP film at 140°C and that its efficiency was proportional to its concentration in PP. However, the parent bound AOTP itself was not an effective thermal stabiliser for PP. This confirms that the oxidised piperidine (nitroxyl) is not only a photostabiliser but also a thermal antioxidant. In the case of combinations of two antioxidant components it was found that the combined effect of bound AOTP with Irganox 1076 was slightly negative on photostabilisation of PP and evidently positive on thermal stabilisation of PP. In the presence of a hindered phenol, bound AOTP had the potential ability to contribute to improve thermal stabilisation of PP in an air circulating oven aging at 140°C, but concentration effects of bound AOTP with Irganox 1076 were quite complicated. A linear relationship of its efficiency with its concentration was not found as expected.

Bound DBBA was found to be very ineffective in the thermal stabilisation of PP. Although a high binding extent of DBBA on PP was obtained This was achieved by adding a relatively high amount of Triganox101 and it seems likely that this had to a large extent destroyed the phenolic function. However, it is interesting to note that a small amount of bound DBBA (0.1% in PP) improved the effectiveness of bound AOTP on thermal stabilisation of PP.

Bound HEAB alone was not an effective photostabiliser. During UV cabinet aging with an increase in bound HEAB concentration its efficiency did not increase notably. But combination of bound HEAB with bound AOTP and Irganox 1076 respectively, exhibited a significant synergistic action on photostabilisation of PP.

3). From kinetic study in solution of reaction of TMPO (nitroxyl radical) at 140°C in xylene, it was found that the disappearance rate of TMPO was closely related to the presence of air, concentration of a peroxide (Triganox101). Irganox 1076 has also affected the disappearance rate of TMPO. In the absence of Triganox101 the disappearance rate of TMPO under nitrogen was much higher than that under oxygen. This confirms that the presence of oxygen promotes regeneration of TMPO in the solution reaction. Otherwise, in the presence of a certain amount of Triganox101 oxygen would accelerate the disappearance of TMPO. This lead to the conclusion that the concentration of peroxide is an important factor to determine antioxidant activity of the hindered piperidine.

6.2 Recommendation for Further Work

1). Comparing bound AOTP with a conventional stabiliser (Tinuvin 770) at a low concentration (below 0.2% in PP), the efficiency of the bound AOTP was much lower than that of Tinuvin 770 in the photostabilisation of PP. This could result from poor distribution of bound AOTP diluted from its 20% masterbatch in PP. On the other hand, it was also found that bound HEAB was a very poor photostabiliser. This could result from homopolymerisation of HEAB (poor distribution) and poor movement of bound HEAB from PP bulk to the surface.

Thus it is necessary to study the morphology of copolymer of the active antioxidant with PP by electron microscopy and thermal analysis methods for observing the distribution of the two components (antioxidant and PP) in the copolymer bulk and change in crystallisation, melting and glassy temperatures to confirm above suggestion. If this suggestion is correct, avoiding homopolymerisation and promoting graft copolymerisation of the antioxidants in PP will be a important task for improving the antioxidant efficiency.

It was found in this work that bound DBBA in PP initiated by a peroxide (Triganox101) was not an effective thermal antioxidant. It seems likely that this had to a large extent destroyed DBBA phenolic function. Thus it is necessary to select other initiators, such as AIBN, for improving the extent of binding DBBA in PP and avoiding the destruction of DBBA phenolic function at the same time.

2). In chapter 4 it was found that the oxidised bound AOTP rather than the parent bound AOTP itself was an effective thermal antioxidant and Irganox 1076 presented synergistic activity with bound AOTP on thermal stabilisation of PP. These results could be contributed from the critical concentration of antioxidants and nitroxyl radical regeneration rate in system. Therefore, ESR analysis could be an effective method to monitor the change in concentration of the nitroxide during the aging process of PP and investigate effects of temperature, air pressure and concentration of the peroxide on regeneration rate of the nitroxide.

3). In order to identify the intermediate products of a nitroxyl radical (TMPO) with Irganox 1076 in solution reaction, HPLC studies wil be needed to separate reaction products and identifying them by MS, NMR and FTIR to confirm the suggested active transformation products. For example >NO-CHD could be produced during the thermal or photooxidation process of PP stabilised by combination of a hindered amine and a hindered phenol.

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