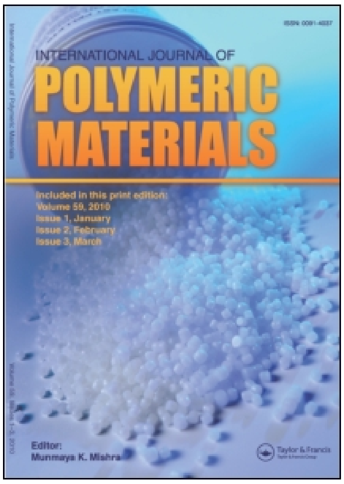

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Some Aspects of Polymer Stabilisation

S. Al-Malaika[a]
[a] Polymer Processing and Performance Group, Department of Chemical Engineering & Applied Chemistry, Aston University, Birmingham, England, UK

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Some Aspects of Polymer Stabilisation

S. AL-MALAIKA

Polymer Processing and Performance Group, Department of Chemical Engineering & Applied Chemistry, Aston University, Birmingham B4 7ET, England, UK

Basic principles of polymer oxidation and the mechanism of action of antioxidants are briefly discussed and applications of different antioxidant functions are outlined. Harnessing the processing operation has contributed to the development of targeted reactive processing methods designed to enhance antioxidant performance and polymer durability.

KEY WORDS Polymer stabilisation, antioxidant mechanisms

1. OXIDATIVE DETERIORATION OF POLYMERS

Hydrocarbon polymers are susceptible to attack by molecular oxygen. Oxidation is the major cause of polymer degradation by the well known free radical process of autoxidation,[1–4] Scheme I. This process normally starts slowly but autoaccelerates leading, in most cases, to catastrophic failure of the polymer product.

The activation energy for the hydrogen abstraction step, c, is much higher than sthat for the oxygen-radical reaction, b, hence reaction c which leads to the formation of hydroperoxides is a rate determining step and is the most important reaction in autoxidation. As the hydroperoxide concentration builds up with the progress of oxidation of the substrate, the energetically more favourable hydroperoxide decomposition becomes the predominent initiating step. The deterioration of mechanical strength and other physical properties of the polymer results mainly from thermal and photolytic breakdown of hydroperoxides and these are further catalysed by the presence of metal ions, reaction 1.

$$2\ \mathrm{ROOH} \xrightarrow{M^{+}/M^{+2}} \mathrm{ROO.} + \mathrm{RO.} + H_2O \qquad (1)$$

$$\begin{array}{llll}
\text{Initiator} & \longrightarrow & \text{R.} & \text{(a)} \\
\text{R.} + O_2 & \longrightarrow & \text{ROO.} & \text{(b)} \\
\text{ROO.} + \text{RH} & \longrightarrow & \text{ROOH} + \text{R.} & \text{(c)} \\
2\text{R.} & \longrightarrow & \text{R-R} & \text{(d)} \\
\text{R.} + \text{ROO.} & \longrightarrow & \text{ROOR} & \text{(e)} \\
2\text{ROO.} & \longrightarrow & \text{Inert Products} & \text{(f)}
\end{array}$$

SCHEME I Autoxidation reactions of polymers.

At normal oxygen pressure, termination occurs via reaction of alkylperoxyl radicals which are present at high concentrations under these conditions,[4] Scheme If, whereas under oxygen deficient conditions, e.g., during polymer processing, uv-initiated oxidation, and during fatiguing of rubbers, alkyl radical concentrations dominates in the oxidising system and termination occurs predominantly by its recombination, Scheme Id and e. The highest concentration radical present in the system is of practical importance as it affects the chemical nature of all ensuing degradation processes, e.g., chain scission or crosslinking, hence the critical nature of the chosen antioxidant.

2. DELETERIOUS EFFECT OF PROCESSING ON POLYMER STABILITY

Manufactured polymers are normally relatively pure materials except for residual adventitious impurities from the polymerisation process, e.g., catalyst residues and unsaturation, in polyolefins. Polymer stored at normal temperature in the dark is stable. However, polymer degradation becomes noticeable under severe processing and fabrication conditions.

Invariably, polymer conversion technologies involve the use of internal mixers, extruders and injection moulding machines, all of which require the application of shear stress at elevated temperatures to affect polymer/additive mixing and fabrication. Oxygen is inadvertently present in all these operations including the small amount of dissolved or trapped oxygen in the polymer and polymer feed. The combined effect of stress and oxygen at high temperature leads to the formation of oxygenated species, e.g., hydroperoxides and carbonyls, in the polymer with adverse effects on their subsequent in-service performance.[5–7] In unprotected polymer, therefore, the severity of the processing operation determines to a large extent the durability of the finished polymer artifact in-service. The extent of the damage caused depends on the chemical structure of the polymer and its inherent oxidisability, as well as its rheological behaviour.

In certain polymers the deleterious effect of processing can be observed visually such as the case with PVC which discolours severely due to the formation of polyconjugation along the polymer chain.[8] In polyolefins, however, although the damage inflicted by processing is less visual, the build up of hydroperoxide concentration (Scheme Ic) and changes in melt viscosity, (by melt flow index, MFI, and molecular mass measurements) are obvious manifestations of polymer degradation resulting from processing and fabrication. For example, under the limited oxygen atmosphere available in a normal processing operation, polypropylene undergoes chain scission (MFI increases under all conditions, see Figure 1); low density polyethylene undergoes crosslinking (MFI decreases).[6,7,9] In both cases, however, macro-alkyl and alkylperoxyl radicals are intermediates and are ultimately responsible for the formation of hydroperoxides, see Figure 1, which have a profound effect on the service performance of these polymers.

3. ROLE OF ANTIOXIDANTS AND THEIR MECHANISMS OF ACTION

Damage caused by oxidative degradation of polymers, during the processing stage or subsequently in-service, can be minimised or eliminated by the use of efficient

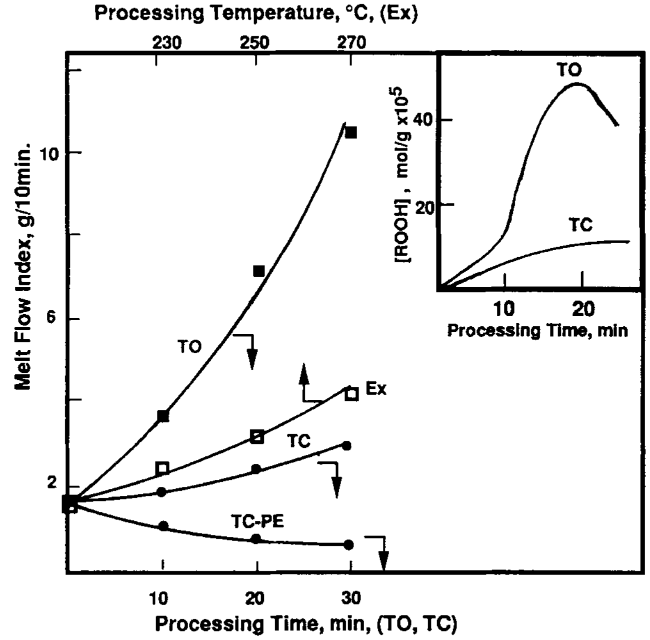
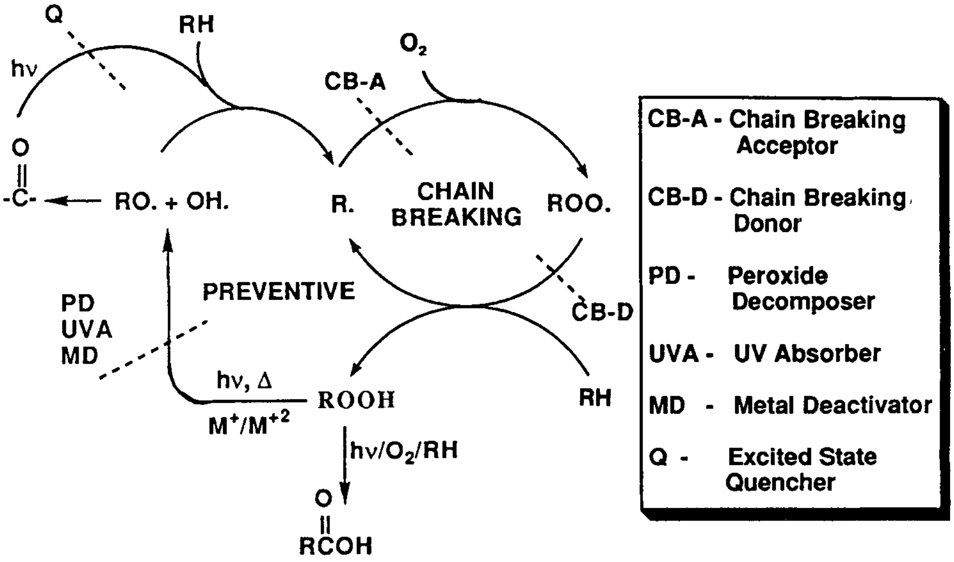


FIGURE 1 Effect of processing conditions (time and temperature) on melt flow index of PP (and PE where indicated), processed in an open (TO) and closed (TC) chamber of an internal mixer at 180°C and in an extruder (Ex). Inset shows changes in hydroperoxide concentration of PP processed in closed (TC) and open (TO) chamber of the internal mixer.



SCHEME II Oxidation mechanism and role of antioxidants.

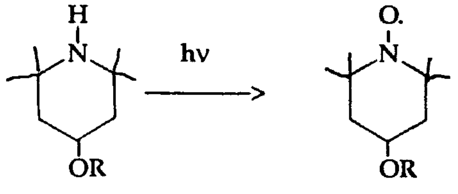
antioxidant systems. Antioxidants, which are used at low concentrations, are able to inhibit polymer degradation by chemically interfering with the autoxidation process (Schemes I and II). They can either interfere with the main oxidation cycle involving R. and ROO. radicals (chain breaking mechanism) or with the second cycle in which the primary product of this process, the hydroperoxides, is formed (preventive mechanism), see Scheme II.

Hindered phenols and aromatic amines (AH) are examples of chain breaking donor (CB-D) antioxidants. Their mechanism of action was one of the first to be investigated in depth[10,11] and involves the reduction of alkylperoxyl radical; these function most effectively when the major propagating radicals in the system are alkylperoxyl. Their reaction with ROO. leads to the formation of a hydroperoxide molecule and an antioxidant free radical, A. (e.g., stable phenoxyl radical in case of hindered phenol), reaction 2. The subsequent oxidation products of the antioxidant radical play an important role in the stabilisation process; they act as antioxidants or pro-oxidants. The chemistry of transformation of hindered phenols and aromatic amines have been extensively reviewed.[10-13]

$$\mathrm{ROO.} + \mathrm{AH} \xrightarrow{\text{CB-D}} \mathrm{ROOH} + \mathrm{A.} \qquad (2)$$

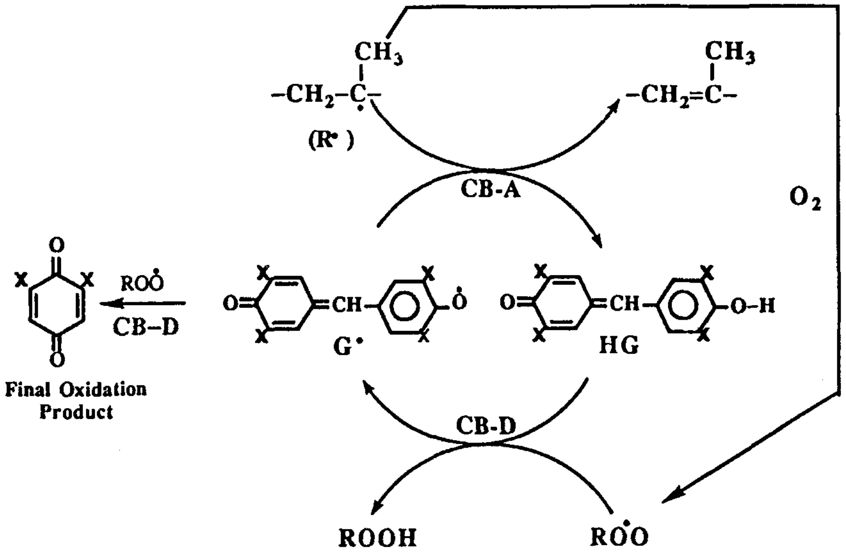
Chain breaking acceptors (CB-A), on the other hand, oxidise alkyl radicals and are most effective when alkyl radicals are the major chain propagating species in the autoxidising system. These include uv-stabilisers, e.g., hindered amine light stabilisers, HALS (via transformation products) and melt processing antioxidants, for example, compounds containing stable radicals such as hindered nitroxyls and phenoxyls. HALS stabilisers which are known to function by oxidising first to the corresponding nitroxyl radical, >NO., see reaction 3[13,14,17-22] are not effective melt stabilisers unlike the nitroxyls derived from them. Nitroxyls and phenoxyls act as catalytic antioxidants alternating reversibly between their oxidised and reduced forms and can, therefore, function under conditions where both alkyl and alkylperoxyl radicals are important, hence are generally good melt stabilisers for polyolefins.[13,14] Scheme III illustrates this catalytic antioxidant mechanism for a stable phenoxyl radical, Galvinoxyl which is effective melt stabiliser for polypropylene.

Preventive antioxidants, most important of which are peroxide decomposers, PD, act by removing hydroperoxides in a non-radical process.[23,24] Peroxidolytic antioxidants are either phosphite esters which act by stoichiometrically reducing hydroperoxides to alcohols, or sulphur-containing compounds, which include thiopropionate ester, I, and metal complexes of dithioic acids, of which dithiophosphates, MDRP, II, and dithiocarbamates, MDRC, III, are typical examples. Ex-



(HALS)

(3)

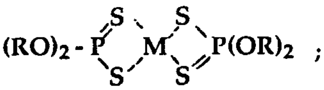


SCHEME III Catalytic antioxidant mechanism for Galvinoxyl, G., involving CB-A and CB-D processes.

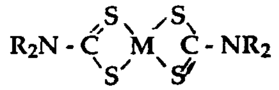
tensive mechanistic studies on sulphur compounds[23–27] have revealed that they undergo a complex series of oxidation reactions involving intermediate free radicals to give sulphur acids which are catalysts for the decomposition of hydroperoxides.

$(ROCOCH_2CH_2)_2S$;

(TP, I)



(MDRP, II)



(MDRC, III)

It was further shown that all metal dithiolate antioxidants exhibit an initial chain breaking activity in addition to their peroxidolytic activity at the later stages of oxidation; contribution of each of these processes varies depending on the nature of the metal complex and the molar ratio of the complex to peroxide.[23,26–28] Peroxide decomposition is a catalytic non-radical process triggered by acids formed by oxidative breakdown of the original sulphur compounds, and as such the original sulphur containing metal complexes are themselves not the true peroxidolytic antioxidants but act as precursors and reservoirs for the effective catalytic species. In the case of nickel complexes of dithioic acids, e.g., NiDRP, NiDRC and nickel xanthate, the initial transformation product was shown to be the corresponding disulphide. Figure 2 shows the changes in concentration of nickel dithiophosphate and the parallel formation of oxidation products (mainly the disulphide and acid products) during its reaction with hydroperoxides at different molar ratios and Scheme IV summarises the main reactions involved in its antioxidant function.[33] These nickel dithiolates were shown[34,35] to be very effective melt and uv stabilisers for polyolefins.

It is important to point out that although understanding the chemical mechanism of antioxidant action is of prime importance to the design of effective antioxidants, antioxidant efficiency does not only depend on their inherent chemical activity but

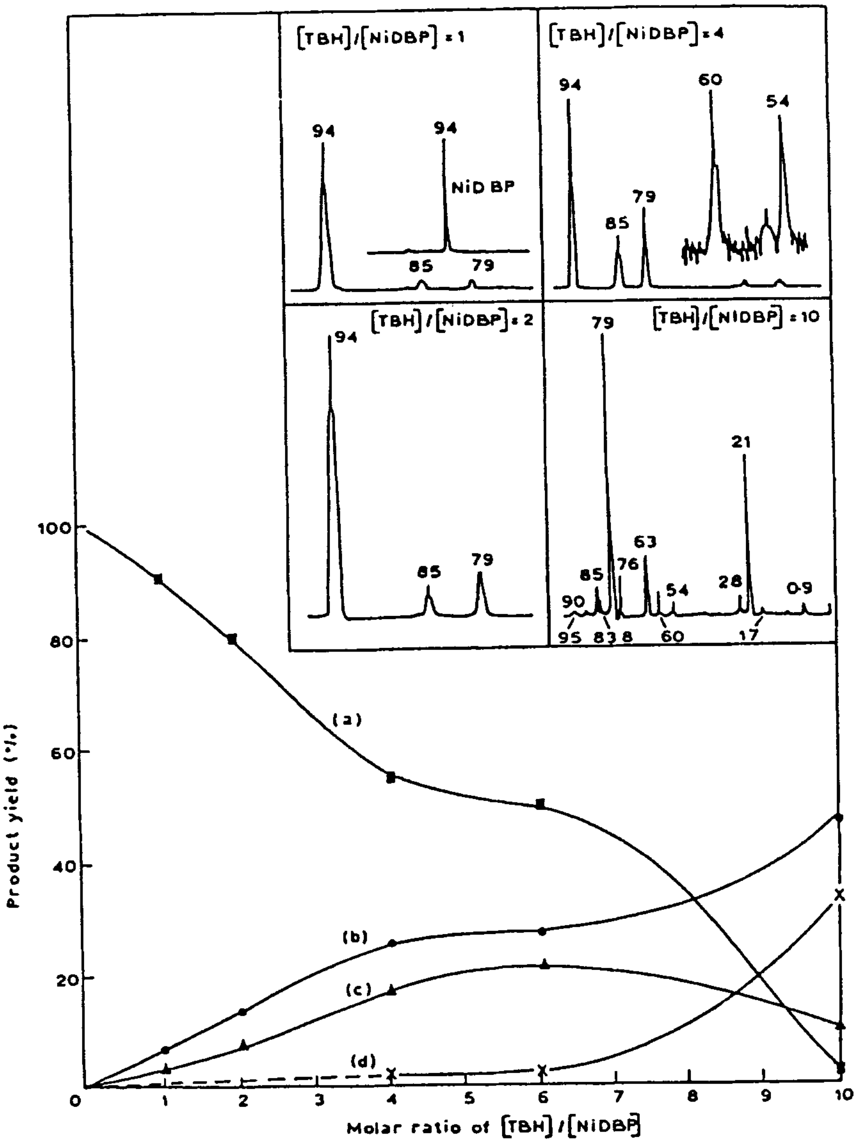
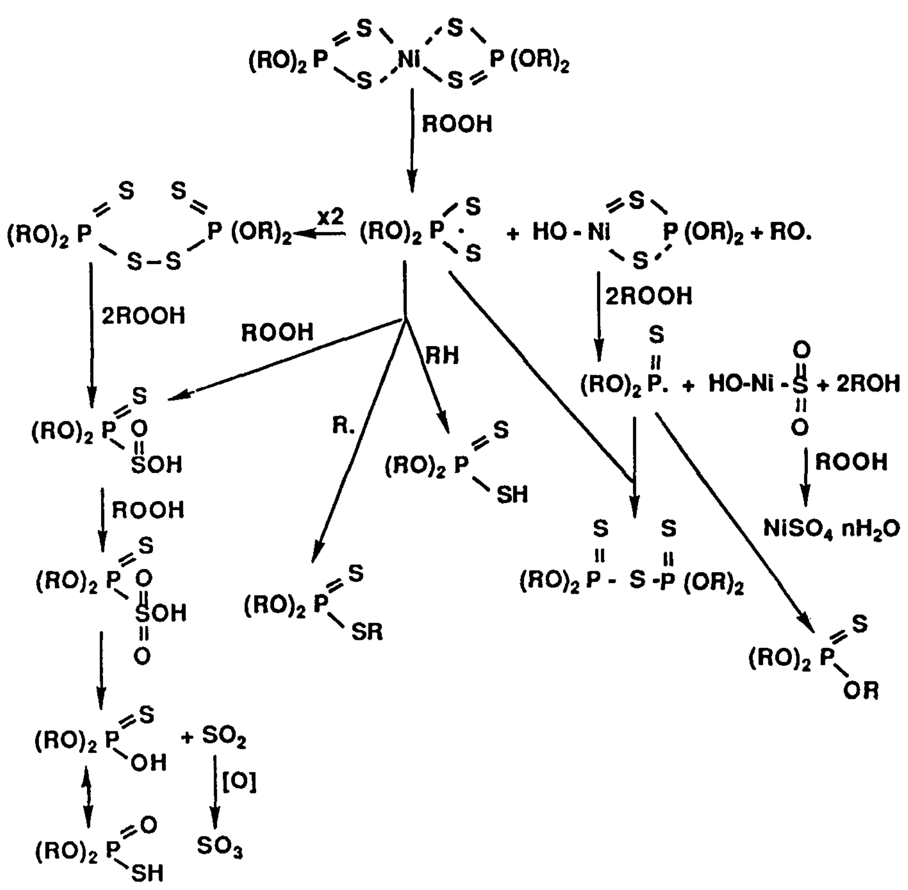


FIGURE 2 Major product yield after complete reaction of NiDRP, with TBH in cyclohexane at 25°C at different molar ratios: (a) NiDBP (δ = 94 ppm); (b) DBMS (δ = 79 ppm); (c) DBDS (δ = 85 ppm); (d) DBTnPA (δ = 63 ppm), DBTPA (δ = 21 ppm) and $(BuO)_2PSH$ (δ = 60 ppm). Inset shows ^{31}P-NMR spectra of products formed at the end of reactions of NiDBP (0.3 M) and TBH at different molar ratios in cyclohexane at 25°C. Numbers on signals are chemical shifts in ppm.

also on their physical characteristics.[36,37] The physical behaviour of antioxidants such as their solubility, diffusion and volatility becomes particularly important when the polymer artifact is subjected to extractive and leaching environments (e.g., hydrocarbon solvents, oils, fats, detergents, in service. A successful design of antioxidants must, therefore, take into account both the chemical and physical behaviour of the antioxidant in the polymer and in the contact media.

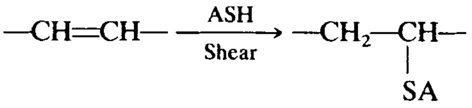


SCHEME IV Antioxidant mechanism of nickel dithiophosphate (NiDRP).

4. POSITIVE EFFECTS OF PROCESSING OPERATION

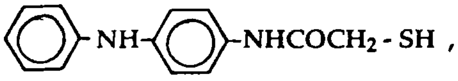
The effects of processing can be made to be put to good use. Chemical reactions can be carried out in the polymer melt using a processing machine as a chemical reactor to achieve chemical attachment of antioxidants to polymer backbone. This approach which is referred to here as 'reactive processing' constitutes an important method to polymer stabilisation since the physical loss of antioxidants is a major cause of premature failure of polymer artifacts in service. Further, loss of antioxidants to contact media especially in food packaging and medical applications, present the added health hazards associated with toxicological effects.

An early application in our laboratory of the reactive processing procedure which was adopted to achieve antioxidant permanence involved thiol-containing antioxidants, e.g., IV, in rubbers or rubber-modified thermoplastics.[38] Shear produced by the processing machine initiates radical addition reaction of the thiol function to the polymer unsaturation by producing macroalkyl radicals which react with the thiol function to give a thiol-containing antioxidant adduct, reaction 4. The main advantages of this method is that antioxidants can be located in the oxidatively sensitive part of the polymer where it is most needed such as the case with locating antioxidants in the rubber phase of rubber modified plastics. This is not suitable for saturated polymers and high levels of bound antioxidants are difficult to achieve because of side products (e.g., disulphide).



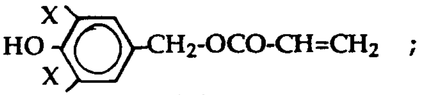
$$\text{—CH=CH—} \xrightarrow[\text{Shear}]{\text{ASH}} \text{—CH}_2\text{—}\underset{\text{SA}}{\underset{|}{\text{CH}}}\text{—} \qquad (4)$$

Where ASH is the thiol-containing antioxidant such as:

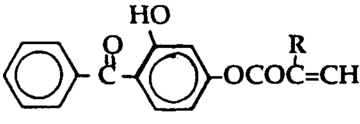


, IV

Another exploitation of the processing operation which has been investigated intensively[38-41] involves the grafting of antioxidants which contain polymer reactive functions, e.g., V, VI, on saturated polymers using a small concentration of a free radical initiator, FRI. It was found that the efficiency of the grafting reaction was low (about 20–30%) while homopolymerisation of the antioxidant, reaction 5b, was high (not normally good antioxidant because of phase separation).

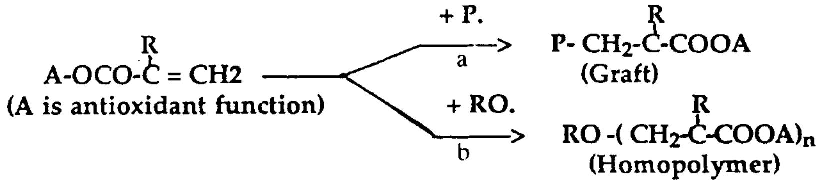


(V) ;



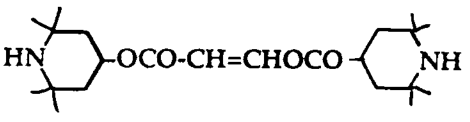
(VI)

$$\text{PH} \xrightarrow{\text{FRI}} \text{P. (Polymer radical)}$$

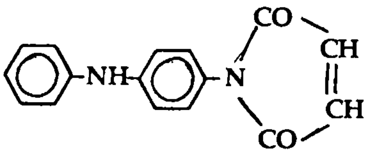


(5)

Higher levels of grafting can be achieved when the polymer melt reaction is carried out in the presence of non-homopolymerisable antioxidants such as bis-maleic esters, VII or amides, VIII.[42] The efficiency of such grafting reaction can be increased to about 90% together with high efficiency of stabilisation.



(VII)



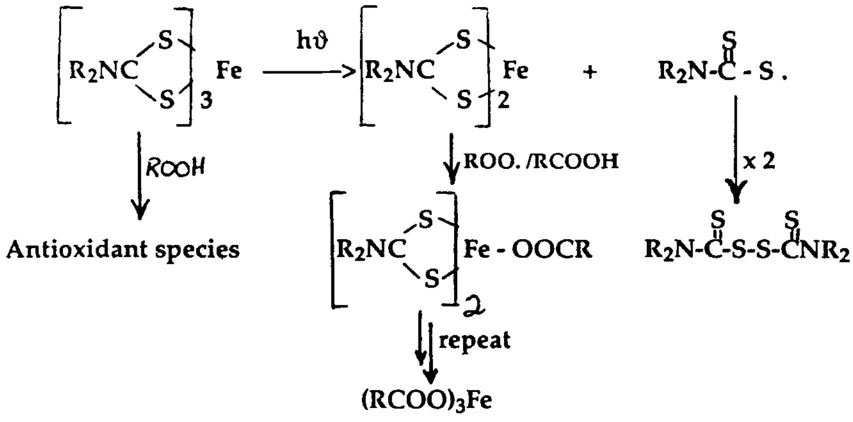
(VIII)

Parameters which play a key role in optimising the levels of targeted reactions, e.g., grafting, at the expense of side reactions, during reactive processing procedures include the structure of the polymer reactive function of the antioxidant, the nature and concentration of the free radical initiator and its molar ratio to the antioxidant as well as the processing parameters, e.g., temperature, time. A delicate balance has to be reached between the chemical, physical and rheological characteristics of the reaction components in order to achieve high efficiency of reactions in the melt. Reactive processing procedures and chemical structure of the reactants have, therefore, been altered and a number of uv- and thermal stabilisers and antioxidants have been grafted onto polyolefins to high levels[41–45] using modified procedures. Such antioxidants lead to improved polymer stability especially under extractive and leaching environments.

The advantages of reactive processing approach are three-fold. Firstly, high efficiency of the antioxidant is retained throughout the service performance of the polymer article due to their permanent presence in the polymer hence no problems of toxicity by migration into the human environment. Secondly, in addition to the use of the product to modify the whole polymer system during processing/fabrication (e.g., during extrusion), pre-forming highly modified concentrates can be produced for use as conventional additives in the same or other polymers which adds cost effectiveness and attractiveness. Thirdly, the potential of obtaining site-specific antioxidant grafts for applications which require targeted protection is very great.

5. TIME-CONTROLLED STABILISATION

Fundamental studies on the mechanisms of peroxidolytic antioxidants provided the bases for the design of antioxidant-photoactivator systems based on metal thiolates which offer precise time-controlled stabilisation to polyolefins. These systems, which exhibit an initial photo-induction period, the length of which is controllable, followed by rapid photodegradation, are now in commercial use[46] as photo-biodegradable plastics mainly for agricultural applications. It was shown in section 3 that the peroxidolytic function of thiolates, e.g., II and III, is a consequence of their oxidation by hydroperoxides to sulphur acids, see Scheme IV. The photoantioxidant activity of these metal complexes was shown to vary depending on the nature of the metal ion and their stability to uv-light: nickel is one of the most stable while iron is least stable.[24,47–49]



SCHEME V Antioxidant-photoactivator action of iron dithiocarbamate.

Iron complexes, e.g., FeDRC, III, exhibit unique behaviour at low concentrations it causes rapid photo-oxidation whereas at higher concentrations it gives a well characterised photo-induction period which increases with concentration.[47,48] As previously postulated, a similar to other metal thiolates, a transient dithiocarbamoyl radical is initially formed[50] giving rise to disulphide (as the initial transformation product) and ultimately sulphur acids, which are responsible for the photo-induction period and the high melt stabilising activity. The thiocarbamoyl radical initially produced, is subsequently destroyed releasing free ionic iron (as macromolecular carboxylate), see Scheme V, which is an effective initiator for photoxidation (iron undergoes redox reactions with hydroperoxides leading to free radicals, see rn 1) leading to rapid photodegradation of the polymer.

Commercial polyolefins are not themselves biodegradable and the above method of using an antioxidant-photoactivator system is used to accelerate the rate of polymer oxidation under the effect of sunlight leading to more hydrophilic low molar mass carbonyl-containing oxidation products (most important of which are the carboxylic acids, see Scheme II) which are responsible for the ultimate biodegradation of the polymer through bioassimilation by microorganisms. This system which was developed at Aston in the early seventies continues to be researched in our laboratory to better understand the nature of the final polymer oxidation products of this and other commercial degradable plastics. The application of the reactive processing method is also persued in an attempt to produce bound antioxidant/degradant concentrates that are chemically attached to the polymer backbone hence eliminate health hazards associated with migration of sensitisers into the contact media.

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