Learning from Mother Nature: Exploiting a Biological Antioxidant for the Melt Stabilisation of Polymers

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Summary: An overview of the antioxidant role of the biologically active form of vitamin E, α-tocopherol, in polyolefins is discussed. The effect of the vitamin antioxidant on the melt and colour stability of polyethylene (PE) and polypropylene (PP) is highlighted. It is shown that tocopherol is a highly effective antioxidant that results in superior melt stabilisation of polyolefins particularly when used at much lower concentration than that needed for conventional synthetic hindered phenol processing stabilisers. As with other hindered phenols, α-tocopherol imparts also some colour to the polymer but this is shown to be reduced drastically in the presence of other antioxidants, such as phosphites, or other additives, such as polyhydric alcohols.

Introduction

The significance of the free radical chemistry responsible for the formation of damaging reactive oxygen species (ROS) *in-vivo* with deleterious consequences, including destructive peroxidation of biological substrates and involvement in various diseases, is well recognised[1]. Peroxidation of lipids occurs during autoxidation of unsaturated fatty acids and in biomembranes where the content of unsaturated fatty acids is relatively high[2]. However, through evolution, mother nature has provided defences for all living organisms to protect against the damaging effect of ROS through the provision of a series of highly efficient biological antioxidants to 'scavenge' ROS. Amongst these, vitamin E (the biologically active form is α-tocopherol, **I**) is the most important fat-soluble biological antioxidant and vitamin C (ascorbic acid) is a major water-soluble antioxidant. Thus, healthy cells with balanced complement of antioxidants will not normally undergo destructive peroxidation due to the outstanding efficiency of these antioxidants. A striking example which illustrates how evolution has provided the ultimate protection against destructive peroxidation in living cells is the finding that more highly oxidisabile edible oils, i.e. those containing higher concentration of polyunsaturates, contain higher concentrations of fat-soluble vitamin antioxidants, particularly vitamin E[3].

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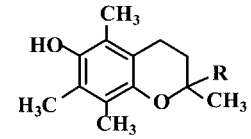


α-tocopherol, I

The importance of the antioxidant role of vitamin E in depressing lipid peroxidation has largely been attributed to its high efficiency in trapping free radicals through a chain-breaking donor (CB-D) mechanism, reactions **1** and **2**. *In-vitro* rate studies on the antioxidant activity of α-tocopherol has shown[4,5] that it is one of the most efficient alkylperoxyl radical traps, far better than the commercial hindered phenols, e.g. BHT, 2,6-di-*tert*.butyl-4-methylphenol. Its efficiency was attributed to the highly stabilized tocopheroxyl radical formed during the rate limiting step, reaction 1.

$$ROO^{\cdot} + Ph\text{-}OH \xrightarrow[CB\text{-}D]{k_{inh}} Ph\text{-}O^{\cdot} + ROOH \qquad (1)$$

$$ROO^{\cdot} + Ph\text{-}O^{\cdot} \longrightarrow \text{Non-radical oxidation products} \qquad (2)$$

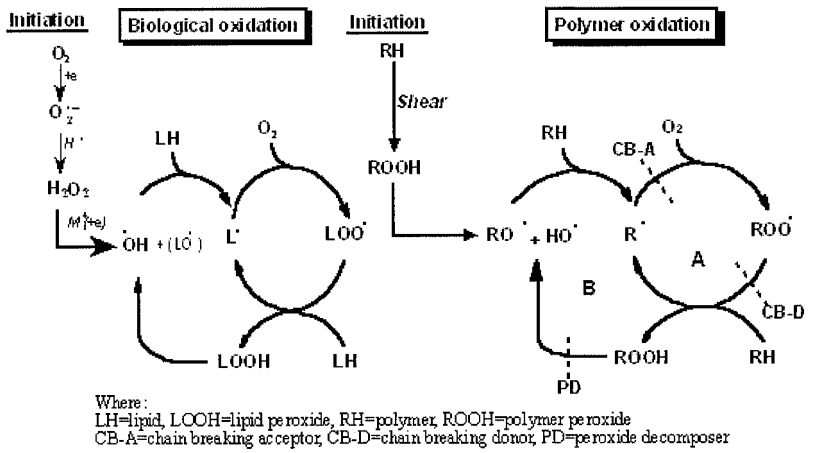
Can we adopt what mother nature has found best *in-vivo* for *in-vitro* applications? To address this question, we have conducted over the last 10 years a detailed experimental programme to examine the antioxidant efficiency of vitamin E (in its synthetic form, the dl-α-tocopherol) in polymers under various conditions with particular emphasis on its action during conventional processing (extrusion) of polymers, and its mechanism of action[10-15] *in-vitro*.

Polymer Oxidation and the Role of Antioxidants

Hydrocarbon polymers are highly susceptible to oxidation by atmospheric oxygen in a process which is responsible for the ultimate irreversible deterioration of polymers. Oxidative degradation of polymers occurs at all stages of their lifecycle that involves polymer manufacture, storage, processing, fabrication, in-service and recycling. An important consequence of polymer oxidation is the loss of useful properties of the polymer; for example, mechanical properties (tensile and flexural strength, elongation to break, impact strength), optical properties and physical characteristics of the surface (reduced transparency, yellowing, chalking, loss of gloss, cracking). It is important to point out,

however, that different polymers vary in their inherent resistance to oxidation depending on their chemical structures and their physical and morphological characteristics.

The free radical chain process involved in polymer oxidation is essentially the same as that responsible for biological oxidation- the main difference is in the nature of the initiation process, see reaction scheme 1. The central feature of this autoxidation mechanism is the peroxidation of the polymer substrate; this occurs through a reaction of the key free radical intermediate, the alkyl peroxyl radical (ROO$^{\cdot}$), with the substrate, leading to the formation of the hydroperoxide (ROOH), which plays an important role in the initiation of the chain reaction[6].



Scheme 1: General process of oxidation of technological and biological systems and antioxidant mechanisms

Most polymers, therefore, require stabilisation to inhibit or retard the process of oxidative degradation throughout their lifecycle, and in particular during the high temperature melt processing and fabrication stages. Antioxidants inhibit the autoxidation process by either interrupting the primary oxidation cycle (cycle A) through the removal of the propagating (ROO$^{\cdot}$ and R$^{\cdot}$) radicals[7], or interrupting the second oxidative cycle (cycle B) by preventing or inhibiting the generation of free radicals[8], see scheme 1. Hindered phenols and aromatic amines are typical examples of chain breaking antioxidants whereas sulphur-containing compounds and phosphites or phosphonites are representative examples of peroxidolytic (peroxide decomposers, PD) antioxidants.

It is well known that under normal conditions of melt processing most antioxidants undergo oxidative transformations during the course of their action[8,9]. The overall stabilisation imparted to the polymer, therefore, depends not only on the initial amount of antioxidants added but, also, on the contribution of their transformation products. This can either be beneficial (when the products are also antioxidants and non-discolouring) or detrimental (when the products exert pro-oxidant effects or/and cause discolouration) to the overall polymer stability. The question is how does the antioxidant behaviour of vitamin E, and that of its transformation products, in polymers differ from that of conventional synthetic hindered phenols?

The Antioxidant Role of Vitamin E as Processing Stabiliser in Polyolefins

The biological significance of the fat-soluble antioxidant vitamin E in protecting living cells from the destructive effect of peroxidation and its exceptional efficiency as a chain breaking antioxidant suggests its potential use in technological media, in particular as a polymer antioxidant. The use of a vitamin antioxidant in polymers is a particularly attractive proposition for human-contact applications due to the ever more strict regulations and costly mandatory toxicity tests imposed in recent years by many governments for clearance of antioxidants.

The melt stabilising efficiency of α-tocopherol in polyolefins has been shown to be outstanding[10-13]. A comparison of the antioxidant efficiency of α-tocopherol during melt extrusion of PE and PP with that of the highly effective synthetic hindered phenol antioxidants, Irganox 1076 and Irganox 1010, respectively, shows clearly the superiority of the vitamin antioxidant, see Figure 1.

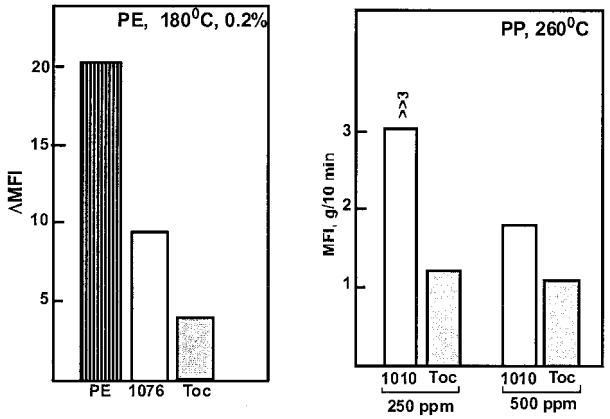


Figure 1. Melt stabilising performance of vitamin E (α-tocopherol), and Irganox 1010 and Irganox 1076 expressed in terms of melt flow index (MFI) and change in MFI (ΔMFI).

Furthermore, the stabilising performance of α-tocopherol is not adversely affected at typical processing temperatures of PE and PP; a drop in stability is observed only at much higher processing temperatures (around 290°C) which is accompanied by a greater "loss" of the antioxidant[12], see Figure 2.

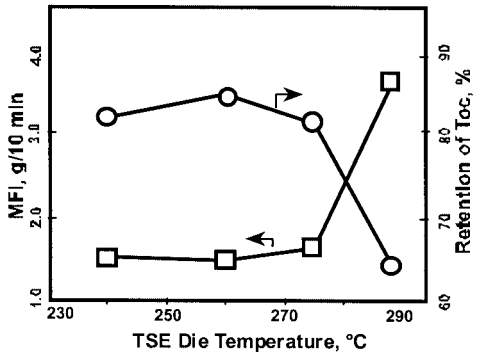


Figure 2. Effect of extrusion temperature of PP containing 300ppm tocopherol on melt stability (monitored by MFI) and on tocopherol (%) retention during twin-screw extrusion (TSE).

The overall migration characteristics of tocopherol from PE into various food simulants are excellent and are quite similar to those of Irganox 1076 (FDA approved for food packaging) with highest migration level observed in olive oil and in the fatty food simulant, heptane, compared to migration into aqueous acidic and alkaline food simulants[11], see Figure 3.

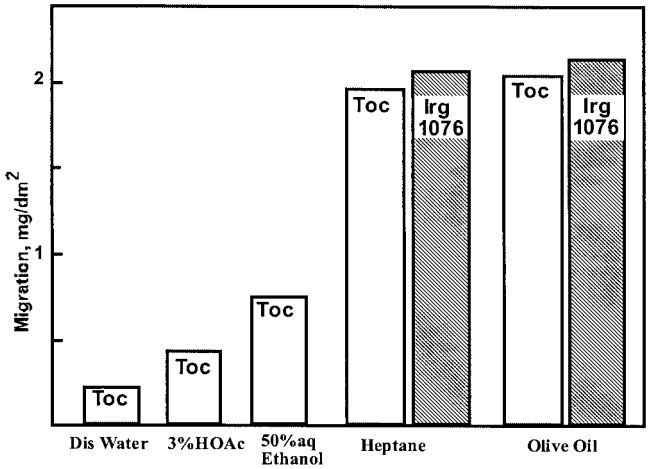


Figure 3. Migration characteristics of tocopherol and Irganox 1076, 0.2% each, from PE (extruded at 180^{0}C) into food simulants using static migration test at 70^{0}C for 2h.

The Effect of Vitamin E on Discolouration of Polyolefins and the Role of Co-additives

Antioxidants generally undergo oxidative transformations during the course of their action and, in the case of sterically hindered phenols, generally results in undesirable discolouration (yellowing) of the processed polymer. The overall extent of discolouration, however, depends on the chemical structure of the parent antioxidant, the nature of the oxidative transformation products and the type and amount of catalyst residues in the polymer. Thus, antioxidant-related yellowing of polymers has been attributed to a number of factors including the formation of coloured oxidation products, e.g. quinonoid structures[16,17], and their interference with metal catalysts[18, 19].

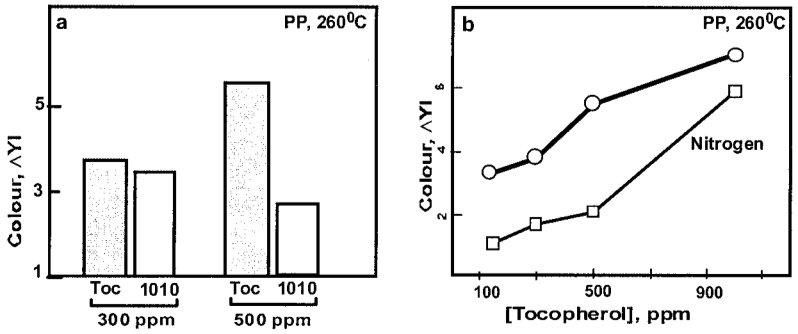
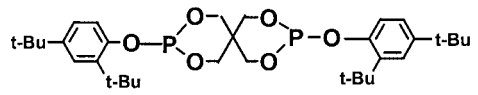


Figure 4. Effect of antioxidant concentation on colour stability of PP extruded under atmospheric conditions and under nitrogen.

Although vitamin E offers excellent melt stability to polyolefins, especially at very low concentrations, it imparts higher levels of discolouration, particularly at higher concentrations, compared to that observed with conventional synthetic hindered phenols, see Figure 4a. It was shown[12], however, that conducting melt processing (extrusion) under a nitrogen atmosphere results in less discolouration (Figure 4b). Studies on the nature of transformation products formed from tocopherol processed in polyolefins have shown[10,13,14] that higher discoloration afforded by the vitamin antioxidant is due, at least in part, to the formation of greater amounts of the more coloured quinonoid-type transformation products of tocopherol[13]. Another possible contribution to the difference in the magnitude of polymer discolouration caused by the use of the tocopherol and Irganox 1076 or 1010 antioxidants, could be based on the difference in their chemical structure, particularly the extent of steric hindrance and their reaction with metal ion impurities from the polymer catalyst. It was shown [21,22] that hindered phenols having

different extent of steric hindrance resulted in different extent of discolouration upon reaction with titanium complexes. Partially hindered phenols, such as tocopherol, gave more colour than the more sterically hindered phenols, such as Irganox 1010.

A general approach to minimising or removing polymer discolouration caused by hindered phenol antioxidants (act by CB-D mechanism), as well as enhancing their melt stabilising performance is through the use of co-synergists based on the peroxidolytic (PD-mechanism) phosphite antioxidants[20]. The use of phosphites, particularly sterically hindered aromatic phosphites, in combination with tocopherol has indeed resulted in both enhanced melt and colour stability [12]. It is clear from Figure 5 that the use of even a concentration (150ppm) of the hindered aromatic phosphites Ultranox U-626, **II**, in combination with 300ppm tocopherol, results in both improved melt stability and pronounced colour suppression together with higher levels of retention of the vitamin antioxidant in the polymer.



Ultranox U-626, II

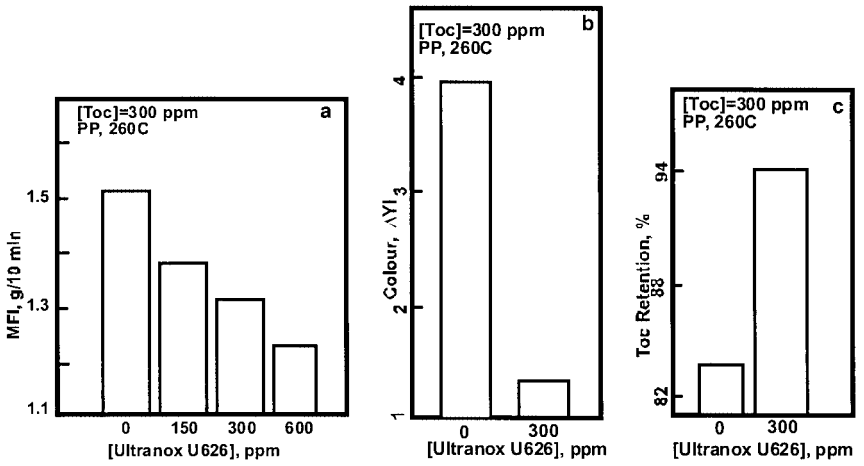
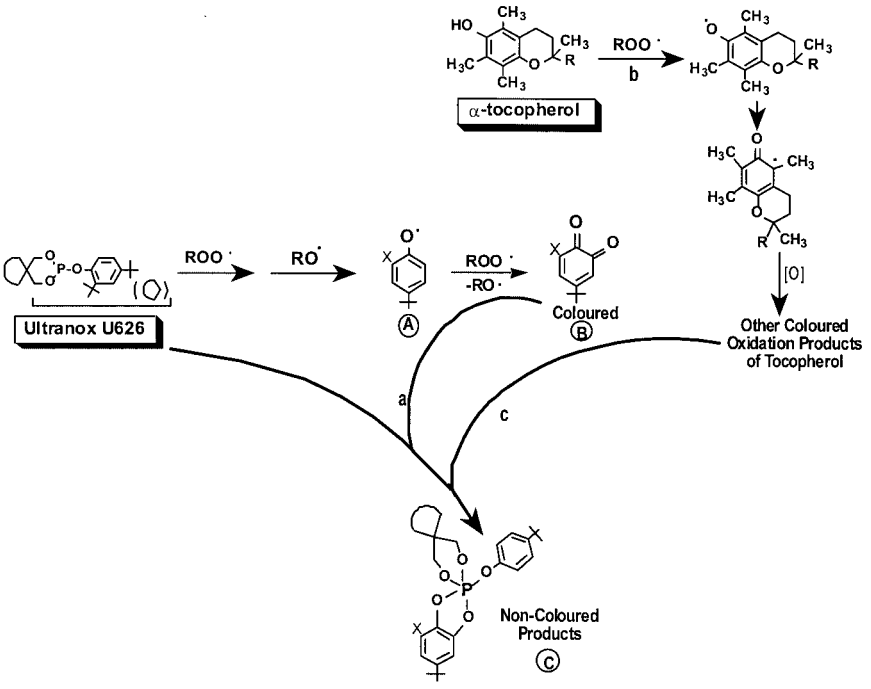


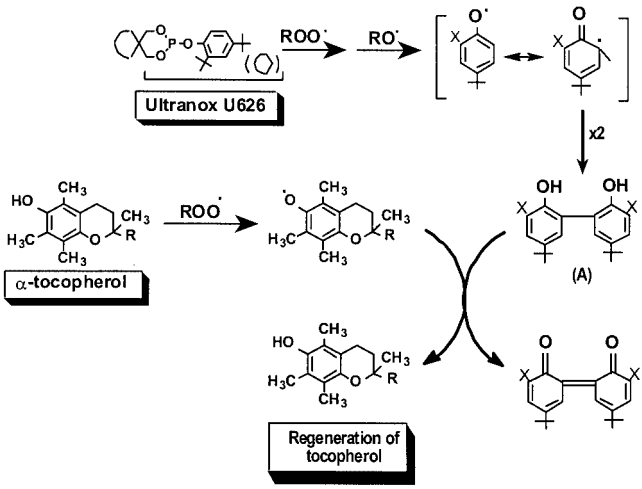
Figure 5. The effect of the phosphite Ultranox U-626, used in combination with 300ppm tocopherol, on melt (MFI) and colour stability of polypropylene and tocopherol retention.

Colour suppression by phosphites is a consequence of their reaction, and/or that of their products, with coloured oxidation products of phenols leading to non-coloured products[12]. Due to the presence of a hindered aromatic moiety, Ultranox U-626 has, in addition to its peroxidolytic activity, a chain breaking activity[23] whereby it can react with the propagating alkylperoxyl (ROO.) and alkoxyl radicals (RO.) giving rise to the formation of a hindered phenoxyl radical, see Scheme 2, structure **A**. This radical reacts with a second ROO· radical to give quinonoid colourd products, e.g. structure **B** in Scheme 2. However, further reaction of such quinone with the parent phosphite U-626 would lead to non-coloured coupled products, e.g. **C**, Scheme 2a. Similarly, reactions responsible for colour suppression may also take place between the phosphite and coloured quinonoid products of tocopherol Scheme 2c, formed from the corresponding tocopheroxyl radical (first product of CB-D reaction of tocopherol with ROO· Scheme 2b) during high temperature processing resulting in further non-coloured products, Scheme 2.



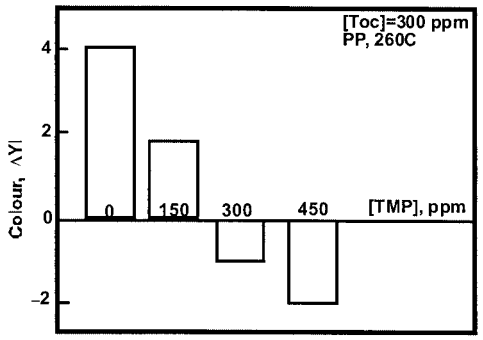
Scheme 2. Some reactions of the phosphite U-626 with tocopherol resulting in non-coloured products.

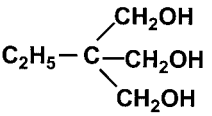
The higher retention of the parent tocopherol antioxidant observed when a small amount of the phosphite U-626 was used, see Figure 5c, has been discussed previously[12]. Firstly, the presence of the phosphite results in a reduction of the amount of tocopherol that is transformed to the more intensely coloured tocopherol transformation products. Secondly, overwhelming evidence[22, 12] points out to a regeneration of the tocopherol in the presence of the phosphite, via a redox-type reaction, through the formation of a phosphite-phenol C-C coupled product, dimer **A**, see Scheme 3.



Scheme 3. Redox reactions resulting in the regeneration of tocopherol.

Another approach to reducing the extent of discolouration caused by vitamin E is to use it in combination with other non-antioxidant co-additives, e.g. polyhydric alcohols[12]. Figure 6 shows that the use of small concentrations of the alcohol **TMP, III**, results in a strong reduction in polymer discolouration, without affecting melt stability. Colour reduction has been attributed to a preferred reaction of the alcohols with metal ion residues to give stable colourless products at the expense of the coloured metal ion phenolates.





TMP, III

Figure 6. Effect of increasing concentration of TMP on colour stability (expressed as ΔYI) of PP extruded in the presence of 300ppm tocopherol.

Conclusion

1. Learning from 'mother nature' has helped us understand the mechanism of action of the vitamin antioxidant *in vitro* and encouraged us to explore its use as an antioxidant in a wide range of polymer substrates, and in particular polyolefins.
2. Vitamin E is a highly effective melt stabiliser for polyolefins and can, therefore, be used cost effectively, at a fraction of the amount of conventional hindered phenols, in a wide range of applications, particularly those involving human contact.
3. The extent of migration of tocopherol from polyethylene into food simulants is similar to that of the FDA-approved hindered phenols, e.g. Irganox1076, for food-packaging.
4. Phosphites, and non-antioxidant polyhydric alcohols, used as co-additives with tocopherol reduce drastically tocopherol-related polymer discolouration.
5. Colour reduction achieved, when tocopherol is used in combination with small amounts of phosphite is due, at least in part, to interaction of products formed during the antioxidant action of the phosphite with coloured quinonoid-type products formed from the hindered phenol giving rise to non-coloured products. The higher degree of tocopherol retention observed in the presence of aromatic hindered phosphite is attributed to a tocopherol regenerative mechanism.

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