Improving synthetic hindered phenol antioxidants: learning from vitamin E

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Abstract

The efficiency of various commercial hindered phenol antioxidants was studied using differential scanning calorimetry (DSC) to determine the oxidation induction time (OIT) of antioxidant solutions in squalane. It was observed that α-tocopherol has an exceptionally high antioxidant activity. In fact, after normalisation for the molecular weight and functionality of each antioxidant, α-tocopherol was twice as efficient as any of the commercial, synthetic, hindered phenols tested. Through measurements on a series of model compounds, it was possible to identify the aspects of α-tocopherol’s chemical structure that are responsible for its exceptional antioxidant efficiency. The results showed that the para oxygen in α-tocopherol is largely responsible for its exceptionally high antioxidant activity. Most commercial synthetic hindered phenolic antioxidants are based upon 2, 6-di-tert-butyl-4-methylphenol (BHT). We compared the antioxidant efficiency of BHT with that of 2, 6-di-tert-butyl-4-methoxyphenol (BHA) and found that BHA was 94% more efficient. This implies that it may be advantageous to make new commercial hindered phenolic antioxidants that are based in the more effective BHA structure instead of the conventional BHT structure used today. It is expected that addition of a para oxygen (or other electron donating groups) to the aromatic ring of existing hindered phenolic antioxidants would significantly increase their activity. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Hindered phenolic antioxidants are used in both polymers [1–5] and lubricants [2], furthermore, they are probably the most important class of commercial antioxidants. Such antioxidants protect polymers by increasing both their process stability and long-term stability against oxidative degradation [1–5]. Similarly, hindered phenolic antioxidants are used to protect hydrocarbon oils and greases from attack by oxygen, which degrades such materials, especially at high temperatures. The autoxidation of hydrocarbons has been studied for many years and is known to proceed via a series of free radical processes [6,7]. The basic oxidation scheme (BAS), as proposed by Bolland and Gee [6,7], gives an outline of oxidation in liquid hydrocarbons (Fig. 1). It has been pointed out that this mechanism must be applied with caution to oxidation of solid materials such as polymers. For example, polymer oxidation is not expected to occur uniformly, especially in semi-crystalline polymers such as polypropylene [8]. For more recent and detailed information covering the mechanistic and kinetic aspects of autoxidation see the review by Al-Malaika [9]. Despite its limitations, the BAS continues to be useful for describing the oxidation of hydrocarbon materials [10].

In principle, oxidation could be stopped if alkyl radicals could be scavenged efficiently, thus preventing reaction (2). Unfortunately, reaction (2) is extremely fast and so radical scavengers are not effective if there is oxygen present. Hindered phenols act by interrupting this sequence of radical reactions at reaction (3). In the absence of antioxidant, a peroxyl radical (ROO⋅) will abstract a proton from polymer (RH) by reaction (3). The rate-limiting step of the autoxidation [1]. However, when a hindered phenol is added, it provides a more easily abstractable proton than those of the polymer, thus providing a more favourable reaction. The phenoxyl radical formed is sterically hindered and
1 → R-  
(1) Initiation

R + O₂  → ROO-  
(2) Propagation

ROO + RH  → ROOH + R  
(3) Propagation

2R  → R-R  
(4) Termination

R + ROO-  → ROOR  
(5) Termination

ROO + ROO-  → RO + ROH + O₂  
(6) Termination

ROOH  → RO + OH  
(7a) Chain branching

2ROOH  → ROO+ + RO + H₂O  
(7b) Chain branching

Fig. 1. Basic oxidation scheme (BAS) for liquid hydrocarbon oxidation.

this makes it relatively stable so that it does not contribute to further polymer oxidation [1].

There are many commercial hindered phenol antioxidants [1] all based on different chemistries for connecting together BHT-like units to a core (BHT is an abbreviation for 2, 6-di-tert-butyl-4-methylphenol). In the past several years, there have been no major steps forward in the field of synthetic hindered phenol antioxidants. Instead, the one major breakthrough has been the commercialisation of a natural hindered phenol antioxidant, α-tocopherol [11,12], which is the major and most active component of vitamin E [13]. The present study was performed on the pure compound α-tocopherol, which has previously been shown to be a more efficient process stabiliser (melt stabiliser) than any other commercially available synthetic antioxidant [14]. There have been several studies to determine why α-tocopherol is such a good antioxidant in vivo [14–18]. However, these studies are not necessarily valid for understanding the high antioxidant activity of α-tocopherol in molten polyolefins at ~150–250°C. This paper continues the investigation to identify the reasons for the exceptional performance of this natural antioxidant. The OIT of model compounds dissolved in hydrocarbon oil at 190°C was measured, as this was considered to be a valid method for modelling polymer melt stabilisation. After finding the reasons behind the high activity of α-tocopherol, that knowledge is applied to suggest how better synthetic process stabilisers and antioxidants can be made.

2. Experimental

2.1. Chemicals

All chemicals were purchased from Sigma-Aldrich Sweden AB, with the exception of the commercial Irganox antioxidants, which were donated by Ciba Speciality Chemicals Inc. Switzerland. The chemicals were used as received without further purification. The α-tocopherol (97% pure) was kept refrigerated in the dark. Squalane, 2,6,10,15,19,23-hexamethyltetracosane (99% pure) was kept in the dark at room temperature in a sealed glass bottle.

2.2. Sample preparation

Stock solutions of the antioxidants were made, since it would have been impractical and inaccurate to weigh antioxidant directly into the DSC pans. Furthermore, by pre-dissolving the antioxidants it was possible to ensure that they had in fact dissolved. Where possible the antioxidant/model compound was dissolved directly in squalane. It was found that all the antioxidants and model compounds except for α-tocopherol and 2,2,5,7,8-pentamethyl-6-hydroxycroman (PMHC) were insoluble in squalane at room temperature. Therefore all the insoluble antioxidants were pre-dissolved in ethyl acetate and then diluted with squalane to give the desired final concentration of antioxidant in squalane. Ethyl acetate was chosen because it was a good solvent for the antioxidants and it was miscible with squalane. Even more importantly, some experiments were performed to check whether the ethyl acetate diluent had any effect upon the OIT results. The OIT of α-tocopherol was measured at several concentrations in squalane with or without ethyl acetate and no significant variation was seen between the two measurements.

2.3. DSC measurements

The OIT testing was performed using a method closely based on ASTM D 3895-95 “Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry”. The instrument used was a Mettler Toledo DSC 821e running Mettler Toledo STAR® software V5.1. The method was programmed into the control software, a sample robot loaded the samples and an automatic box was used to switch gas supply. These measures ensured reproducibility and accuracy in the method.

Some minor changes were made to the ASTM method in order to optimise it for the use of liquid squalane, in place of a solid polyolefin sample, as the oxidisable material. A deeper, larger volume (100 µl) aluminium sample pan was used during this study. It was found that using a standard 40 µl pan gave irreproducible results due to the squalane “spitting” out of the pan during the high temperature (190°C) portion of the measurement method. The use of the deeper pans avoided sample loss and led to improved accuracy and reproducibility of the measurements. The gas and temperature sequence was as specified in the ASTM standard. Initially the sample was held for 5 min at ambient temperature (25°C) under a flow of nitrogen gas (50 ml min⁻¹). This was followed by heating to 190°C at a heating rate of 20°C min⁻¹, still under a flow of nitrogen. After reaching 190°C the sample was held for a further 5 min, after which the gas was switched from nitrogen to oxygen (50 ml min⁻¹).

The sample size used was 30±1 mg of squalane. This was judged to be a suitable sample size because small
variations in sample size in this weight range had no noticeable effect on the OIT measured. Earlier, it had been noticed that for samples of less than 25 mg there was a strong variation of OIT with sample size and so small variations in sample weighing gave errors in the OIT determinations for these smaller samples.

A sample of squalane was also run on a TGA (thermogravimetric analysis) in the same manner as the OIT experiment, i.e., same thermal program, sample size, and crucible, with the exception of only nitrogen gas being used throughout the run, to investigate vaporisation of the squalane. The mass loss due to vaporisation during a 60 min OIT was found to be 4.9%, so it was concluded that vaporisation of the squalane was insignificant.

The oxidation of the sample was observed as a sharp increase in the energy flow due to the exothermic nature of the oxidation reactions. There are various ways to analyse the curve to determine the onset of oxidation. The ASTM method mentions that there are usually significant errors in manual evaluation of the OIT. Therefore, a new method was chosen, and this was found to be very reproducible as it is not dependent upon human interpretation of the oxidation onset point. The computer was used to calculate the second derivative of the enthalpy versus time curve and the first peak in this curve was taken to be the onset of oxidation. The values obtained using this method were numerically similar to those for the standard method of manually determining the onset point although the second derivative method gave data with noticeably less scatter.

OIT data is notoriously irreproducible and so each concentration of antioxidant was run three times and the average value and the 95% confidence limits of the OIT for each concentration were plotted. Even after these steps, there were still unacceptable variations in the OIT values, so a further measure to reduce errors was introduced. After every set of three runs, a “burn-out” under oxygen was performed at 600°C. This was done in order to remove any oxidation residues that may have built up in the cell during the OIT measurements. It was found that the burn-out step significantly improved the reproducibility of OIT measurements and the combination of improvements led to rather low variability in the results.

The curves of OIT versus concentration of hindered phenol groups were created by fitting a linear fraction equation, \[ \text{OIT} = \frac{A[\text{phenol groups}] + B}{C[\text{phenol groups}] + D} + E, \] to the data. There was no theoretical basis for the use of this particular form of equation, it was chosen purely because it gave a good fit to the data for all antioxidants.

However, this approach has serious disadvantages in that such studies are expensive, time-consuming and potentially inaccurate. In the present study, the above mentioned complications were avoided by the use of a model liquid, squalane (Fig. 2), instead of polyolefin as the oxidisable material for OIT. The use of oils for comparison of antioxidants by OIT is well known [2]. In this study, squalane was chosen as it has a chemical structure very similar to that of polypropylene and the two materials are therefore expected to oxidise via similar mechanisms. Using squalane resulted in a faster and cheaper sample preparation, as it was easy to dissolve the antioxidants at room temperature. Furthermore, because the antioxidants could be dissolved at room temperature, there was no need for compounding and the samples were of accurately known antioxidant concentrations. Samples were prepared at several different antioxidant concentrations. By plotting the full curve of OIT versus antioxidant concentration, a more informative and accurate picture of the antioxidant performance was obtained as compared to single point measurements.

The OIT method is widely used, but some care must be taken when interpreting the results. Firstly, it is not recommended to use OIT to try to predict the performance of hindered phenolic antioxidants in terms of their ability to impart long-term stability to polymers. Studies have shown that it is far better to use other methods such as oven ageing [19] or oxygen-uptake, which are performed at lower temperatures so that the polymer is in the solid state and extrapolation of the results to room temperature is more accurate. However, OIT has been used extensively to evaluate antioxidant performance in oils and in molten polymers [1,19]. OIT is well suited to study antioxidant performance for materials used at high temperature because OIT measurements are conducted at high temperature. So, the authors do not claim that the results can be extrapolated to reflect antioxidant performance at room temperature. Instead, it is believed that the OIT measurements are more indicative of the performance of antioxidants in polyolefin melts during processing and in hydrocarbon oils used at elevated temperature.

Another important point is to consider how to plot the OIT data. Often OIT results are plotted versus the concentration of antioxidant, expressed in ppm [1]. Clearly, this is not appropriate in the present study, as it does not reflect the efficiency of the antioxidant per unit concentration of active –OH groups. That way of

3. Results and discussion

Usually, studies of antioxidant efficiency are performed on polymer samples containing antioxidant.
plotting the results is biased in favour of low molecular weight antioxidants and antioxidants with more than one hindered phenolic group. It was therefore decided to express the antioxidant concentration on a molar basis and to normalise the concentration to allow for the number of hindered phenol groups per antioxidant molecule. Thus, the results presented in this study are plotted as OIT versus the molar concentration of hindered phenol groups. This shows the relative efficiency of the specific type of hindered phenolic groups in each antioxidant. Plotting the results in this way enabled the structural differences in the antioxidants to be correlated with their efficiencies.

The OIT of α-tocopherol has been measured and compared to the OIT results for commercial synthetic antioxidants such as Irganox® 1010, 259, 1098 and BHT (Fig. 3). In accordance with the literature, it was found that α-tocopherol is indeed a far more efficient process stabiliser than the synthetic antioxidants sold today [14]. A series of experiments were carried out using carefully selected model compounds. The aim was to identify the key structural features that are responsible for the outstanding performance of α-tocopherol and then to suggest how this knowledge could be used to modify and improve upon the existing commercial synthetic antioxidants. It is important to be able to tailor antioxidants to suit individual applications where the antioxidant must have the optimal balance of properties such as; solubility, volatility, extractability, toxicity and price. It was hoped that the synthetic antioxidants could be redesigned to combine the efficacy of α-tocopherol with the versatility of the commercial hindered phenolic antioxidants presently available.

The excellent performance of α-tocopherol must, logically, be linked in some way to its chemical structure. Many synthetic hindered phenol type antioxidants such as Irganox® 1010, 1330, 3114, 1076, 259, 1098 and 3125 rely on the BHT functionality for their antioxidant properties. The synthetic hindered phenols are made by joining BHT units together to increase the molecular weight and thus decrease the volatility and extractability of such antioxidants. It seems reasonable to assume that the efficiency of α-tocopherol is attributable to its chemical structure, therefore there must be some key difference(s) between α-tocopherol and BHT that account(s) for the variation in antioxidant performance. At first glance there are four main differences between the two antioxidants (Fig. 4).

- α-tocopherol has a long aliphatic tail whereas BHT has only a methyl group
- α-tocopherol has methyl groups (rather than t-butyl groups) surrounding the active –OH moiety (at the 2- and 6-positions)
- α-tocopherol has an oxygen para to the active –OH
- α-tocopherol is also substituted at the 3- and 5-positions

There have been some studies attempting to show how the chemical structure of α-tocopherol is related to its efficiency [15–18]. It should be noted that in these studies, the authors aimed to understand the high antioxidant activity of α-tocopherol in vivo. Therefore, they did not consider how this information might be applied to make better synthetic antioxidants for polymers. Howard and Ingold looked at the effects of ring substituents on the rate of reaction of a hindered phenol with a peroxy radical [15]. In this latter work, they found that the reaction was accelerated by a para oxygen, and by the presence of methyl groups, instead of t-butyl groups, in the 2-, 3-, 5- and 6-positions. Penketh also found that a para oxygen was beneficial for the antioxidant performance of hindered phenols [20]. He reported that butylated hydroxy anisole, BHA (Fig. 5), had a relative “antioxidant rating” of 212 in petroleum...
compared to the reference compound BHT, which was defined as having an antioxidant rating of 100.

In later work, Burton and Ingold also attempted to identify why \( \alpha \)-tocopherol is so reactive in vivo [16]. They found that the rate constant for the reaction of a hindered phenol with a peroxyl radical was \( 1.2 \times 10^{-4} \, \text{M}^{-1} \cdot \text{s}^{-1} \) for BHT but this increased to \( 7.8 \times 10^{-4} \, \text{M}^{-1} \cdot \text{s}^{-1} \) for BHA, which has a methoxy group para to the active –OH. Burton and Ingold also investigated the effect of the long alkyl (phytyl) tail [16]. For this they compared \( \alpha \)-tocopherol to the model compound 2,2,5,7,8-pentamethyl-6-hydroxychroman, PMHC (Fig. 5). They showed that, within error limits, PMHC was as reactive as \( \alpha \)-tocopherol. Thus, they concluded that the long aliphatic tail of \( \alpha \)-tocopherol is not responsible for its enhanced antioxidant activity. Instead, they concluded that the activity was due to the para oxygen and the methyl groups in the 3- and 5-positions.

Burton and Ingold calculated that the para oxygen would stabilise the phenoxyl radical through delocalisation of the oxygen lone pair on the benzene ring. In an attempt to verify the importance of the para methoxy group they studied a model compound, TMMP (Fig. 5). Unexpectedly, their model compound, TMMP, was only 9% as reactive as PMHC. They showed by X-ray diffraction that the methoxy group of TMMP was twisted due to steric interaction with the methyl groups in the 3- and 5-positions. This twisting meant that the lone pair of the para-methoxy oxygen was not fully delocalised on the benzene ring, and was thus unable to stabilise the phenoxyl radical in the way they had expected. In contrast, they showed that the para oxygen in \( \alpha \)-tocopherol is able to help stabilise the radical, as the aliphatic ring holds it at a favourable angle, with the oxygen lone pair almost perpendicular to the benzene ring. They concluded that, in retrospect, they had chosen the wrong model compound for their investigation. The methyl groups in the 3- and 5-positions twisted the oxygen lone pair so that it could not contribute to the activity of TMMP. Thus, they were unable to prove or disprove their theory that the para oxygen was the key to the exceptionally high antioxidant activity of \( \alpha \)-tocopherol.

Based on that previous work, it seems that the para oxygen and 3-, 5-methyl groups are the important features of \( \alpha \)-tocopherol that account for its high observed efficiency in vivo. If these findings are also applicable for melt stabilisation of polymers, then it should be possible to design new, much more efficient melt stabilisers based on structures containing a para oxygen and/or 3-, 5-methyl substitution. If this were successful, it would represent a breakthrough in melt stabilisation.

The method used by Burton and Ingold was chosen to model antioxidant performance in vivo. They chose to evaluate antioxidants by looking at the oxidation of styrene at \( 30^\circ \text{C} \) under a pure oxygen atmosphere [16]. They generated radicals at a controlled rate using AIBN dissolved in styrene and measured the rate of uninhibited styrene oxidation using a pressure transducer. Then, a solution of antioxidant in chlorobenzene was added and the new rate of styrene oxidation was measured. By comparing the inhibited and uninhibited oxidation they were able to calculate the efficiency of the antioxidant and also to measure oxidation induction time (OIT) values. The stoichiometric factor (the number of mols of peroxyl radicals deactivated per mol of hindered phenol groups on the antioxidant) for each antioxidant was also calculated. They found the stoichiometric factor was approximately two for all hindered phenols examined including \( \alpha \)-tocopherol, PMHC, BHA and BHT.

As mentioned, these previous studies have already shown the correlation between the room temperature activity of \( \alpha \)-tocopherol and its chemical structure. However, it has been reported that the optimal structure of an antioxidant varies according to the conditions it will be used under. For example, less hindered phenols are generally more effective melt stabilisers than more hindered phenols [1]. Conversely, more hindered phenols are reportedly better than less hindered variants for the long-term stability of polyolefins as measured by oven ageing [1].

As the goal of the present study was to understand the efficiency of antioxidants in polymers, the standard method of oxidation induction time (OIT) determined by DSC was chosen. It was decided to test the efficiency of a new set of model compounds, to see whether the influence of antioxidant structural changes on their ability to stabilise hydrocarbons at elevated temperature could be verified. The model compounds were selected such that only one part of the antioxidant’s structure was altered at a time (Fig. 6). This allowed any changes in antioxidant efficiency to be unambiguously attributed to the chemical differences between the model compounds. Three pairs of compounds were compared in order to examine the influence of specific structural features of \( \alpha \)-tocopherol (Fig. 6). The relative activities of these compounds as antioxidants are presented in Fig. 7.

3.1. The aliphatic tail

The effect of the long aliphatic tail on the efficiency of \( \alpha \)-tocopherol as an antioxidant was examined first. The model compound PMHC can be thought of as
α-tocopherol with no hydrocarbon “tail”. PMHC was found to be slightly more efficient than α-tocopherol (Fig. 7), at concentrations up to about 1000 μM of hindered phenol groups. However, this effect is small and almost within the error limits of the experimental data. Burton and Ingold also reported that, within the experimental limits of their method, PMHC and α-tocopherol were equally reactive towards peroxyl radicals [16].

At higher concentrations, however, the α-tocopherol appears to be a more efficient antioxidant than PHMC. This is believed to be due to the long aliphatic tail of α-tocopherol, which makes α-tocopherol significantly more soluble than PHMC. As α-tocopherol and PHMC have similar antioxidant efficiency, it was concluded that the long phytol tail is not responsible for the high antioxidant activity of α-tocopherol.

3.2. Ortho substitution effects

One of the other key differences is that α-tocopherol has methyl groups in the positions ortho to the active –OH group whereas BHT has tertiary butyl groups in these positions. It has been reported that ortho methyl substitution is more efficient for process stabilisers whereas butyl substitution is preferred for better long-term stabilisation of polymers oven aged at high temperature [1].

The results indicate that the methyl substituted model compound, TMP, appears to be a far worse stabiliser than BHT (Fig. 7). However, this may not be a true reflection of the relative antioxidant efficiencies of the two compounds. Instead, it may be that the lower molecular weight TMP (bp 220°C), was lost through volatilisation at 190°C during the OIT measurement. This suspicion was tested by a further DSC experiment in which it was determined that TMP was indeed lost at a significant rate under the OIT experimental conditions. During an OIT run, the sample is held at the OIT temperature, 190°C under nitrogen for 5 min before switching to oxygen. As a test, this holding time was varied to be 1, 5 or 15 min. It was observed that longer holding times under nitrogen gave progressively shorter OIT values. As no oxidation can take place under nitrogen, the reduction in OIT with holding time cannot be attributed to chemical consumption of antioxidant. Thus, it was concluded that the observed reduction in OIT, was due to volatilisation of the TMP. This highlights a disadvantage of the OIT technique; volatilisation of lower molecular weight compounds can make them appear to be less effective antioxidants than they actually are. Perhaps the effects of ortho substitution could be studied using another set of model compounds or, alternatively, the OIT measurements could be performed in a high pressure DSC apparatus to reduce antioxidant volatility.

3.3. Effect of the para oxygen

As mentioned earlier, there has been some work indicating that the para oxygen may be at least partly responsible for the exceptional antioxidant activity of α-tocopherol [15,16]. However, in their study Burton and Ingold concluded that they had chosen the wrong model compound to verify this hypothesis [16]. Their model compound (TMMP) was methyl substituted at the 3- and 5-positions (Fig. 5), these two methyl groups twisted the methoxy group so that the lone pair of electrons...
on the oxygen was not fully delocalised on the benzene ring. In contrast, both PMHC and \( \alpha \)-tocopherol have an aliphatic ring that locks the para oxygen lone pair perpendicular to the benzene ring so that good delocalisation of the lone pair is possible. As a result, the TMMP was only 9% as reactive as PMHC. In the present study, a different model compound, BHA, was chosen, this compound does not suffer the same drawback as TMMP. Butylated hydroxy anisole (BHA) is chemically identical to butylated hydroxy toluene (BHT) except that the former has an oxygen atom inserted in the para position to the active hydroxyl group (Fig. 6). As BHA is unsubstituted at the 3- and 5-positions, there should be no steric hindrance to push the lone pair of electrons on the methoxy oxygen out of plane. Thus, it can be expected that the lone pair can be optimally delocalised on the benzene ring. The results show that the addition of this para oxygen does noticeably change the antioxidant behaviour in two ways (Fig. 7).

Firstly, the BHA is a much more efficient antioxidant than the BHT at the same concentration of \(-\)OH groups. By taking the ratio of the slopes for BHA and BHT, it was calculated that BHA is approximately 94% more efficient than BHT. This is an important finding. It suggests that it may be possible to significantly improve commercial, synthetic, hindered phenol antioxidants by adding a para oxygen to the existing range of antioxidants. Our findings are consistent with the hypothesis of Burton and Ingold who suggested that the para oxygen was able to improve antioxidant efficiency. However, they claimed that the 4-methoxyphenols are typically 5 times as reactive as their 4-methylphenol analogues. Such a large improvement in antioxidant activity for BHA compared to BHT was not seen in the present study, perhaps because of the different experimental conditions and methods used in the two studies.

The other effect of the para oxygen, is that the BHA curve flattens out appreciably at higher antioxidant concentrations. This levelling out is also seen for PMHC and \( \alpha \)-tocopherol, both of which also contain a para oxygen. In contrast, BHT does not show this behaviour. This levelling could, in principle, be attributable to BHA losing solubility at higher concentrations but this is not believed to be the true explanation. Firstly, BHA is expected to have very similar solubility to BHT as the addition of one oxygen atom should not have a large effect on the solubility parameter of such a large molecule. The other reason that solubility is not thought to be the cause of the observed levelling, is that the \( \alpha \)-tocopherol OIT curve levels out even though \( \alpha \)-tocopherol is highly soluble in squalane. Therefore, it is believed that the para oxygen has some more complicated influence on antioxidant activity. Perhaps, at high concentrations BHA and \( \alpha \)-tocopherol molecules can react bimolecularly to form some new species with little or no antioxidant activity. Formation of dimeric and trimeric structures at high antioxidant concentration has been reported in a paper by Al-Malaika et al. [21]. On the other hand, similar levelling of OIT data has been reported by Gugumus for Cyanox 2246 and Irganox 1330 [19] in PE-LLD and neither of these commercial antioxidants have an oxygen para to the phenol group.

4. Conclusions

Using OIT measurements in a test liquid, squalane, it has been possible to quickly and reproducibly measure the relative efficiency of a range of commercial hindered phenol type antioxidants and antioxidant model compounds. The present work confirmed the earlier finding of Al-Malaika, who found that \( \alpha \)-tocopherol is a more efficient antioxidant than the traditional, synthetic antioxidants such as Irganox 1010 [14]. Our main focus was on correlating the exceptionally high antioxidant activity of \( \alpha \)-tocopherol with its chemical structure. Commercial antioxidants are usually based on the BHT moiety whereas \( \alpha \)-tocopherol is also a hindered phenol but with a different chemical structure than BHT.

By studying some model compounds, it was found that the most important structural difference between \( \alpha \)-tocopherol and BHT was that \( \alpha \)-tocopherol contains an oxygen atom para to the active hindered hydroxyl. This para oxygen gives a 94% increase in antioxidant activity for butylated hydroxy anisole (BHA) compared to an analogous compound butylated hydroxy toluene (BHT) that possesses no para oxygen. The implication of this finding, is that it may be possible to modify the commercial synthetic hindered phenol antioxidants so that they too contain a para oxygen as this is expected to significantly improving their activity. However, the introduction of an oxygen in the para position is expected to reduce the stoichiometric factor (defined as the number of radicals neutralised per hindered phenol moiety) of some commercial partially hindered antioxidants [1]. For this reason it might be better to insert the oxygen at one or both ortho positions. This should still increase the antioxidant efficiency as the ortho and para positions are electronically equivalent, but placing oxygens at the ortho positions should not reduce the stoichiometric factor of the antioxidants. Of course, synthesis costs and other factors would determine whether this is a commercially viable option.

Antioxidants containing no para oxygen typically give an approximately linear increase in OIT versus antioxidant concentration, this is in accordance with reports in the literature [1]. However, antioxidants that do contain a para oxygen, all lost a significant proportion of their activity at higher concentration. For \( \alpha \)-tocopherol, the activity does not begin to tail off noticeably until concentrations of approximately 1000 ppm or more.
Therefore, this levelling effect will probably not be significant within the range of antioxidant concentrations used in typical polymer process stabilisation.

It has been reported that methyl substitution is best for process stabilisers, whereas tert-butyl substitution is better for long term stabilisation [1]. α-Tocopherol is methyl substituted in the ortho positions whereas BHT has tert-butyl groups. Unfortunately, the effect of methyl versus butyl substitution could not be evaluated under the chosen experimental conditions because the methyl substituted model compound (2,4,5-methyl phenol) was too volatile under the OIT test conditions.

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References