Chapter 3. Stabilization of irradiated polyethylene by introduction of antioxidants (vitamin E)

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4.1 Introduction

The polymer mechanical properties depend on their macromolecular architecture and processing conditions. In the peculiar case of an UHMWPE hip, the key properties are resistance to wear and delamination. Those materials have aroused a considerable amount of literature showing the changes of wear or impact resistance and fatigue crack propagation with sterilization dose and post-irradiation thermal treatment (annealing or remelting). For example irradiation induced crosslinking improves wear resistance [1,2] but decreases the fatigue resistance properties [1,3] and impact resistance [4], and the crystallinity increase induced by annealing has a negative influence on to impact resistance [5] but improves wear [6] and fatigue [1] and fatigue resistance. Despite this complexity [1], it seems possible to obtain the desired hip properties but the key issue is: ''how maintaining those properties during a time long enough to avoid loosening or wear of hip?".

Polyethylene oxidative stability is actually relatively low: from a general point of view polyethylene undergoes degradation during processing, storage and use. C-H groups of PE react with oxygen to create unstable species leading to chain scissions and subsequent changes in the mechanical properties of polymer materials [7]. For example, at 200°C, a polyethylene without any kind of antioxidant will degrade in less than one minute [8,9], which is considerably lower than the complete processing time of any industrial material. In the field of hips, γ-sterilization provokes only minor direct changes just after the end of are generally low [10] but provokes changes a molecular scale having a negative influence on the long term behavior. For example, results by Costa et coll. [11], and Suljovrujic [12] illustrate well that γ-irradiation sterilized polyethylene structure change as soon as irradiation is finished because of residual irradiation induced radicals.

Thermal treatments above melting temperature allow quenching the greatest part of unstable species [13] but they may induce undesired changes in the polymer morphology (and subsequent changes in properties). Another solution is to add stabilizers able to trap radicals responsible of oxidation. The aim of the present chapter is first to recall the general principles of stabilization. Since vitamin E is particularly adapted in the case of biomaterials, because of its low toxicity, its stabilizing mechanism and performances will be detailed, together with some experimental methods aimed at quantifying residual vitamin E after the complex elaboration process of hip. The existing literature will be reviewed so as to extract the kinetic parameters (rate constants for reactions with radicals, diffusion and solubility coefficients) necessary to perform kinetic modeling for a more complex description of the radio-thermal oxidation of PE + vitamin E. Those data will be compared with data for other common hindered phenols in order to highlight the interest of vitamin E for stabilization of hips. We will also present some practical cases of vitamin E stabilized UHMWPE and some experimental methods to detect and quantity Vitamin E in non-degraded or degraded materials.

4.2 Types of antioxidants

4.2.1. Mechanism of oxidation

Polymers oxidation is an in chain radical reaction involving abstractable hydrogens of polymer, and oxygen which is dissolved in polymer amorphous phase. Mechanisms are quite complex and cannot be extensively presented in this chapter. The main mechanisms are recalled in [14] and we will only present a short summary in this chapter.

Radicals are created whether from:

① γ irradiation: $PH + h\nu \rightarrow P^\circ + 1/2H_2$

The rate is given by: $r_i = 10^{-7} \times G(P^\circ) \times I$

Where:

- r_i is in mol l^{-1} s^{-1}

- G(P°) is the yield of radiochemical initiation, i.e. the number of radicals species absorbed by 100 eV. In the case of PE, G(P°) = 8 [15]

- I is the dose rate (in Gy s^{-1})

② Hydroperoxides (POOH) decomposition. These species, of which origin will be explained in the following, contain a weak O-O bond [16] which is easily cleaved. Hydroperoxides decompose thermally [17]:

- by an unimolecular process:

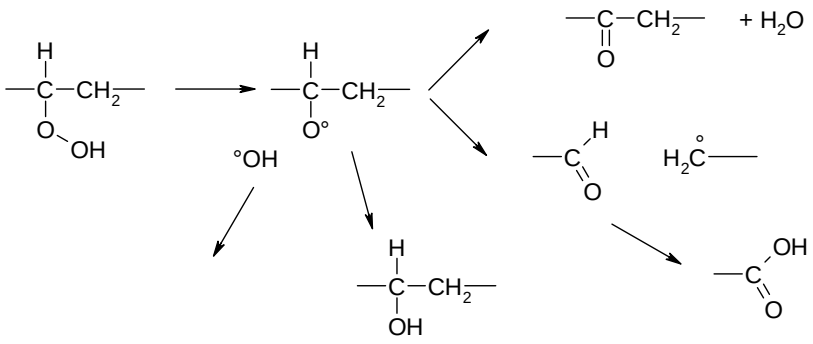
$$POOH \rightarrow PO^\circ + {}^\circ OH$$

- by a bimolecular process:

$$POOH + POOH \rightarrow POO^\circ + PO^\circ + H_2O$$

HO° radicals are extremely reactive and can abstract a hydrogen atom: $HO^\circ + PH \rightarrow P^\circ + H_2O$

Alkoxy radicals PO° are unstable and react by β scission process for example to give carbonyls, chain scissions or alcohols:



It is thus licit to write kinetically equivalent reactions [18]:

$POOH \rightarrow 2P^\circ + \gamma_1 P{=}O + \gamma_2 s$ $\quad k_{1u} = 8.10^{12} \times \exp(-140000/RT)$

$POOH + POOH \rightarrow P^\circ + POO^\circ + \gamma_1 P{=}O + \gamma_2 s$ $\quad k_{1b} = 2.8.10^{9} \times \exp(-105000/RT)$

P=O representing a carbonyl and s a chain scission.

In the absence of oxygen, most of the irradiation induced radicals react to form a crosslinked network but some unreacted radicals exist after the end of irradiation. According to Electron Spin Resonance measurements published by Jahan et al [13,19,20], or Mehmood et al [21,22], their structure could be:

$-CH_2-CH^\circ-[CH{=}CH-]_{m\geq 3}-$

$-CH_2-CHO^\circ-[CH{=}CH-]_{m\geq 3}-$

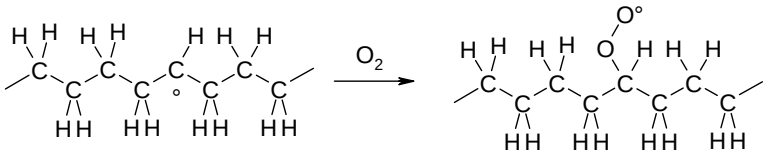
$-CH_2-CH^\circ-CH_2-$

$-CH^\circ-CH{=}CH-$

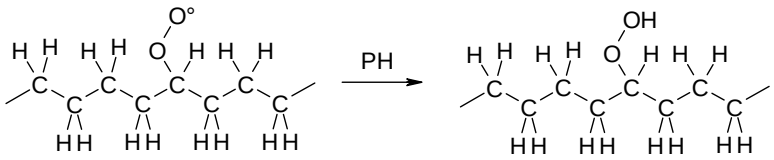
$>CH-OO^\circ$

$>CH-O^\circ$

If they are not quenched by thermal process [13], alkyl radicals can react fast ($k_2 \sim 10^8$ l mol^{-1} s^{-1}) with oxygen:



Peroxy will abstract a hydrogen to yield to a hydroperoxide (see above) and another alkyl radical:



The rate constant at 30°C of this reaction and its activation energy are given by some laws exposed by Korcek et al [23] given here in the case of secondary aliphatic hydrogens:

$$\log_{10} k_3\,(30°C) = 16.4 - 0.048 \times BDE(C\text{-}H)$$

$$E_3 = 0.55 * (BDE(C\text{-}H) - 261.5)$$

Radicals can combine to give non-radical products:

$$P° + P° \rightarrow (1\text{-}\gamma_4)P\text{-}P \text{ (coupling)} + \gamma_4 >C=C< \text{ (dismutation)}$$
$$POO° + P° \rightarrow (1\text{-}\gamma_5)POOP \text{ (coupling)} + \gamma_5 POOH + \gamma_5 >C=C<$$

POO° can also combine to yield to an unstable tetroxide. It was shown that this latter could lead to terminating (formation of carbonyls P=O, alcohols POH, dialkylperoxides POOP) or non-terminating reactions (migration out of the cage of PO° radicals):

$$POO° + POO° \rightarrow POOOOP \rightarrow [PO°\ °OP]_{cage} + O_2$$
$$[PO°\ °OP]_{cage} \rightarrow POOP$$
$$[PO°\ °OP]_{cage} \rightarrow P=O + POH$$
$$[PO°\ °OP]_{cage} \rightarrow 2PO° \rightarrow 2P° + \gamma_1 P=O + \gamma_2 s$$

In the case of pure thermal oxidation, oxidation is characterized by an induction period, which decreases with dose rate (Figure 1):

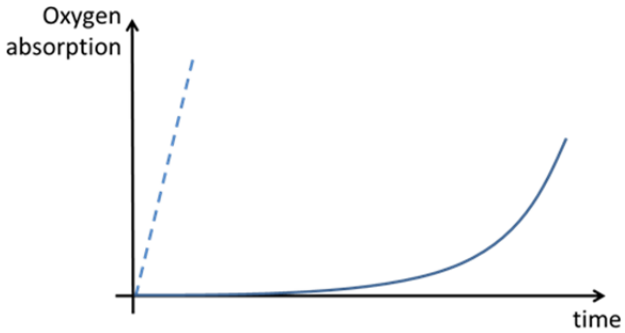


Figure 1. Schematic shape of kinetic curves for thermal (full line) and radiochemical (dashed line) oxidation.

The kinetic chain length may be approximated by:

$$KCL = \frac{\text{propagation rate}}{\text{termination rate}} = \frac{k_3[PH]}{k_6[POO°]}$$

KCL is infinite at the beginning of oxidative ageing and decreases progressively during induction

period. It means that radical species (initially in very low concentration) almost propagate at the beginning of oxidation while they few terminate. Since it is difficult to prevent totally the sorption of oxygen into the polymer, the main strategy for stabilizing the polymer is to quench the unstable species (hydroperoxides, radicals). Since those latter are at very low concentration in the earlier stages of the oxidation process, this can be achieved by antioxidants being added even at low level i.e. without changing the properties of the PE matrix.

4.2.2. General principles of stabilization

There are, schematically, two ways for stabilizing polyethylene against radio-thermal oxidation:

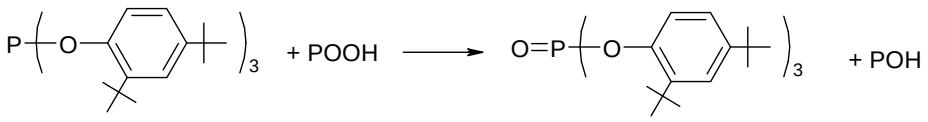
① Decrease the initiation rate, i.e. the rate of radical creation: $r_1 = k_1[POOH]$.
② Increase the termination rate, i.e. the rate at which radicals disappear.

4.2.2.1. Stabilization by decreasing initiation rate

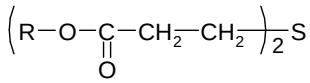
Some polyaromatic compounds [24] may be used in the case of radiochemical ageing to dissipate directly the incident ray energy by some photophysical processes (such as fluorescence). In the case of a hip, there is however no interest to prevent polymer from γ ray effect since γ-radiations improve the mechanical properties of the polymer. It is preferable to limit the side effect of the radiation induced radicals during the in vivo thermal ageing of polymer.

Since alkyls are converted into hydroperoxides (see "4.2.1. Mechanism of oxidation"), and hydroperoxides being the main source of radicals during thermal oxidation [18], it can be first tried to decrease POOH concentration by reducing them into stable products using hydroperoxides reducers such as :

- organophosphorus compounds (phosphites, phosphine and phosphonites). Some controversial mechanisms of radical trapping [25] were proposed. However, the most consensual and reasonable stabilization scheme is [26,27]:



- thioesters fall in the same category [28]:



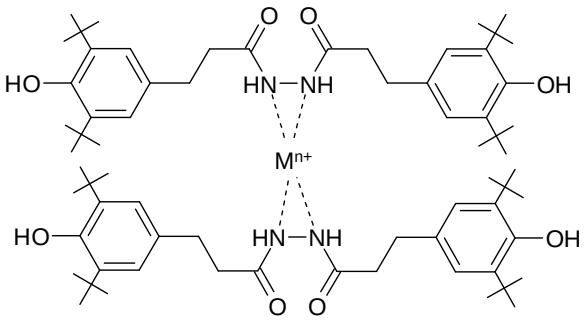
The sulfur yields to a sulfate, which could possibly have a further stabilizing role by successive reactions with POOH [29]:

$$>S \rightarrow >S=O \rightarrow >SO_2 \rightarrow \ldots$$

Since hydroperoxide decomposition is catalyzed by metallic ions [30]:

$$POOH + M^{n+} \rightarrow PO^{\circ} + HO^{-} + M^{(n+1)+}$$
$$POOH + M^{(n+1)+} \rightarrow POO^{\circ} + H^{+} + M^{n+}$$

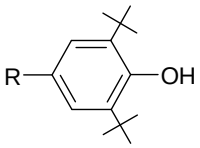
Some stabilizers contain a metal-coordinating functionality [31,32]:



4.2.2.1. Stabilization by increase termination rate

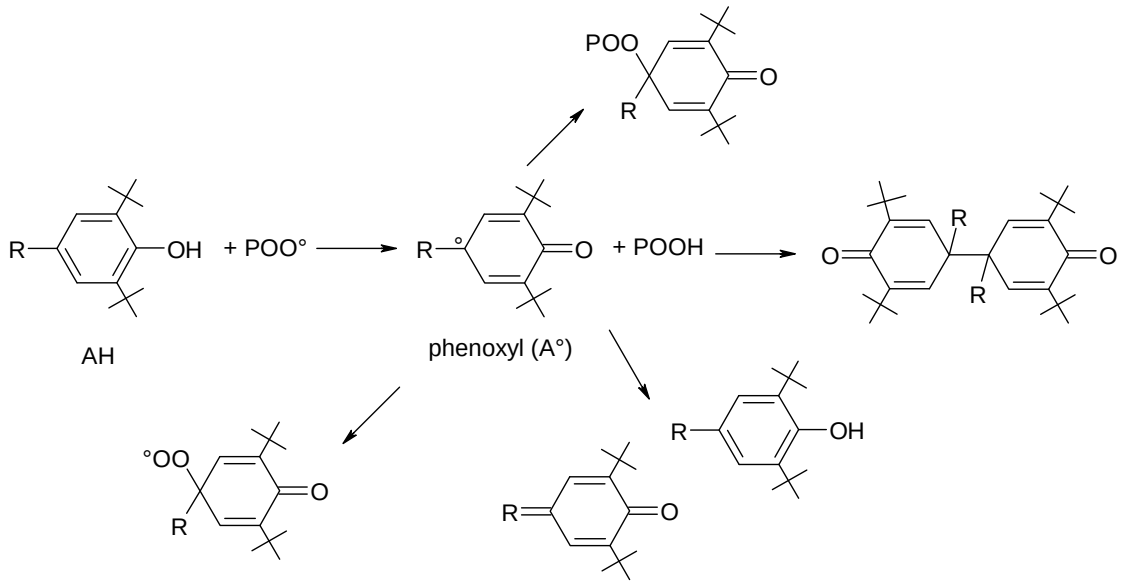
Chain breaking antioxidants fall into this second category of stabilizers strategy. They are all able to react with a radical to give a non-radical species.

The most current chain breaking antioxidants are phenolic antioxidants:



Despite it is non-reactive, the R- group influences strongly the physical properties (solubility [33], diffusion [34], evaporation rate [35]…).

Hindered phenols react by giving a hydrogen atom to a peroxy radical and a phenoxyl radical A°. This one is resonance stabilized. After isomerizing, it can react following several routes (reaction with another POO°, dismutation or coupling, reaction with oxygen…). Some mechanisms are summarized here below:



Some of those "stable" products have a negative influence on the aspect properties (yellowing…) [36]. Some others may have a further stabilizing role [37]. The chemistry of phenol stabilization is actually complex and has hence aroused a considerable amount of literature (see for example [38,39,40]). However, we tentatively showed in recent reviews [41,42] that this mechanistic complexity can well be represented by a kinetically equivalent scheme:

$POO° + AH \rightarrow POOH + A°$ k_{S1}

$POO° + A° \rightarrow POO\text{-}A$ k_{S2}

This haves the main advantage of using a limited number of adjustable parameters for simulating the main features of stabilization by phenols in polyolefins (increase of the induction period with minor – or no – changes on the maximal oxidation rate i.e. the steady state characteristics).

For making short a long story:

- In the absence of stabilizer, a POO° would give an alkyl radical and a hydroperoxide giving two more radicals.

- In the presence of phenols, one POOH is created but 2 POO° disappear which is more favorable for oxidative stability.

- Phenols are efficient stabilizers provided they fulfill the conditions:

$$k_{S1}[POO°][AH] >> k_3[POO°][PH]$$

k_3 being the rate constant of the $POO° + PH \rightarrow POOH + P°$ reaction. Since $[AH]_0 \sim 10^{-3}\text{-}10^{-2}$ mol l^{-1} and $[PH]_0 = 60$ mol l^{-1} [43]:

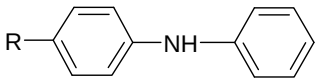
$$k_{S1} >> 10^3.k_3$$

k_{S1} and k_3 are the rate constant for the abstraction of a hydrogen atom by a POO°. They could be approximated by Korcek's law [23] and their difference would originate from the difference between

methylenic C-H and phenolic O-H. Hence, phenols are actually expected to be efficient stabilizers since:

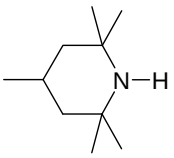
$$BDE(C\text{-}H) \sim 390 \text{ kJ mol}^{-1}$$
$$BDE(O\text{-}H) \sim 340 \text{ kJ mol}^{-1}$$

Aromatic amines have the same behavior than phenols:



The final stable products are hyperconjugated and lead to a strong darkening of samples. Those stabilizers are then rather used in the case of carbon black filled elastomers [44,45].

Hindered Amine Light Stabilizers (denoted by HALS or HAS) are stabilizers derived from 2,2,6,6,-tetramethylpiperidine:



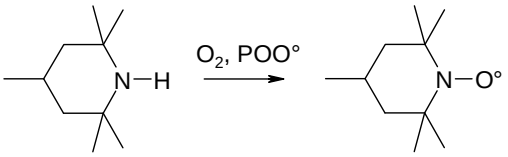
(some alkoxyamine based HAS are also designed for a best resistance to acidic media [46]).

N-H bond is relatively strong and the reaction:

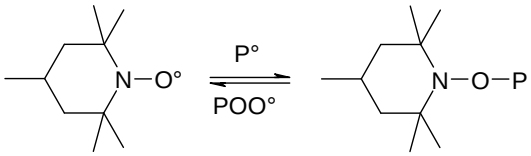
$$POO^{\circ} + >N\text{-}H \rightarrow POOH + >N^{\circ}$$

is henceforward not competitive with $POO^{\circ} + PH \rightarrow POOH + P^{\circ}$.

However, it is well established that >N-H are converted into nitroxy radicals >N-O°, these latter being extremely efficient alkyl traps.



It can be showed that this sole reaction does not explain by itself the great efficiency of hindered amine stabilizers. Denisov [47] has actually proposed a loop mechanism in which nitroxy radicals react with radicals to give an alkoxyamine which regenerates the starting nitroxy by reacting with another radical. The modeling of this mechanism allows an acceptable simulation of stabilization by HAS in PE [48]. This loop mechanism progressively fades because of side reactions deactivating nitroxy radicals or alkoxyamines.



In the case of UHMWPE hip component, vitamin E is the only molecule that can be envisaged because of toxicity concerns. The rest of this chapter will hence be devoted to vitamin E. However, a recent work by Gijsman and coll [49] shows that HALS could be envisaged as radio stabilizers in the case of radio oxidation while not interfering with the crosslinking process (Figure 2):

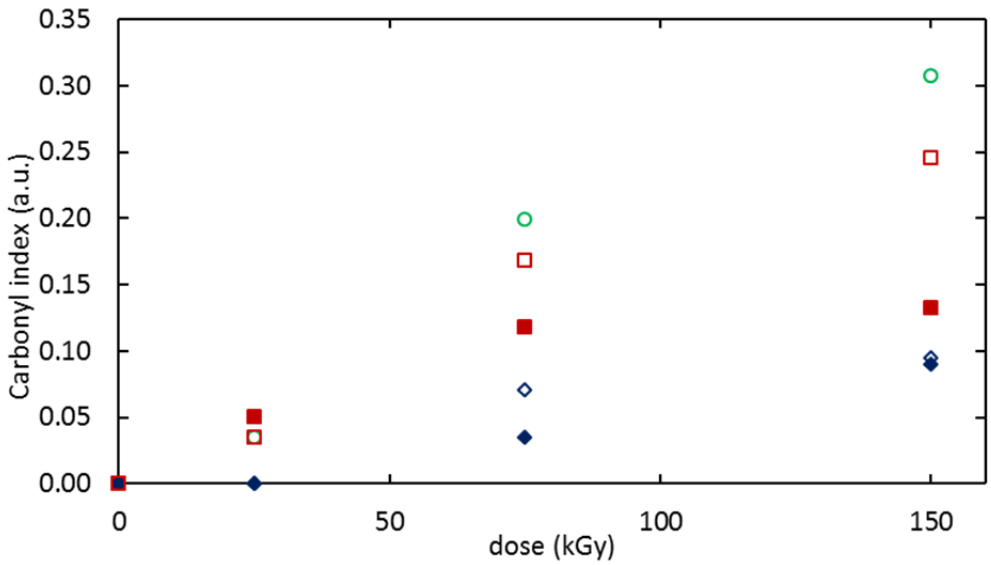


Figure 2. Kinetic curves for carbonyl build up for pure UHMWPE (○), UHMWPE + 0.05% Vitamin E (□), UHMWPE + 0.15% Vitamin E (■), UHMWPE + 0.05% HALS (◇) and UHMWPE + 0.15% HALS (◆).

Figure 2 calls for the following comments:

① Under radiochemical conditions, PE does not display any induction period, contrarily to thermal oxidation [50].

② Stabilization by vitamin E only decreases maximal oxidation rate (related to rate of carbonyl build-up) but does not increase the induction period duration, contrarily to stabilization hindered phenols under "pure" thermal oxidation conditions. Two reasons could be envisaged:
- the structural difference between vitamin E and current phenolic antioxidants (see in the next section of this chapter) which would change its reactivity.
- a difference linked to the source of radical creation and the nature of degradation mechanism, i.e. P° creation by irradiation together with a short kinetic chain length in radio degradation versus P° and POO° creation by POOH decomposition together with a long kinetic chain length in thermal oxidation.

③ HALS are more effective stabilizers than vitamin E. Here also, this is undoubtedly linked to some difference in reactivity towards radicals. However, Figure 2 suggests that there is a certain gain in stability when increasing vitamin E concentration whereas curves for UHMWPE + 0.05% HALS and

UHMWPE + 0.15% HALS are quasi undistinguishable. In other words, one could suspect an effect linked to a maximal concentration above which excess of stabilizer turns to be inefficient. The explanation of such a behavior may be related to the existence of a solubility limit.

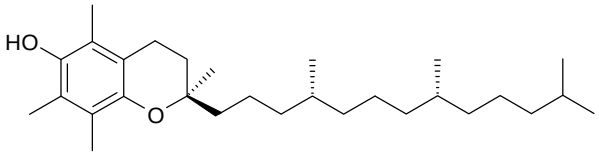
It suggests to describe the efficiency of any stabilizer by:
- its mechanism of stabilization, i.e. the nature of unstable species to be trapped,
- the values of kinetic parameters associated to the stabilization processes,
- the physical behavior of stabilizer (solubility, diffusion…) linked to its structural architecture.

This will constitute the outline of this chapter which focuses on vitamin E.

4.3 Stabilization by Vitamin E

4.3.1 Structure and biological function of vitamin E

Vitamin E (α-tocopherol) is a phenol derivate. It is an antioxidant, having also a noticeable anti-inflammatory action [51,52]. Its structure is:



It is actually close of phenolic antioxidants presented in the previous section. However, there are two specificities of which consequences will be commented in the following:

- Substituents in 2 and 6 positions are methyl. In the case of the most current phenolic antioxidants, which were used for the first implementation of kinetic modeling approaches [41,42], those substituents are *tert*-butyl phenols.

- A linear aliphatic chain making it is actually extremely liposuble. Its low molecular weight (430 g mol^{-1} versus 1176 for AO2 for example) makes it is relatively mobile (high diffusion coefficient).

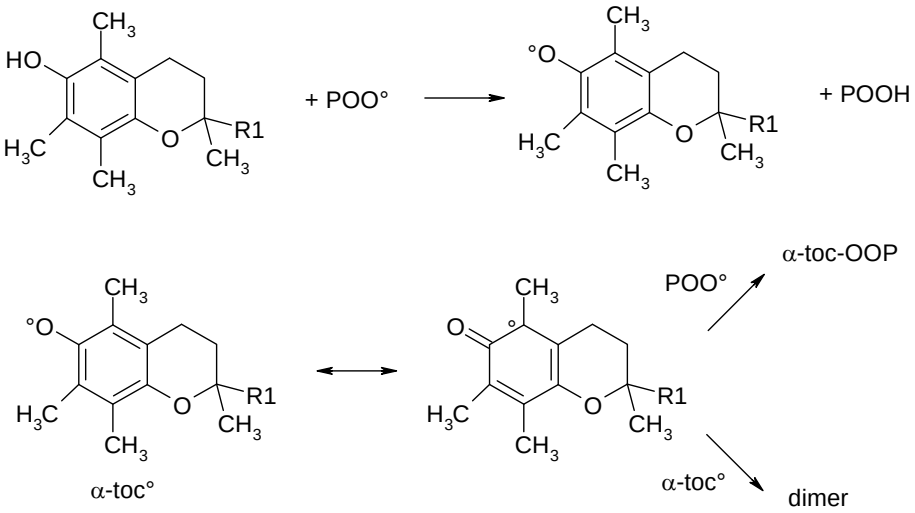
4.3.2 Mechanism of stabilization of vitamin E

Literature reports some comparisons of vitamin E action with some AO (see "Appendix"). For example, Al-Malaika [53] compared the stabilization of a LLD PE with 900 ppm AO1 (ca 16.1×10^{-4} mol l^{-1} in molten polymer) and 300 ppm vitamin E (ca 6.6×10^{-4} mol l^{-1}) and observed a very close behavior, suggesting that vitamin E is, in certain conditions, more efficient than a hindered phenol of comparable structure even at a lower concentration.

Another comparison is the change of Oxidation Induction Time at 200°C [54], expressing the material stability. The changes of OIT with low amount of phenols is here also, more significant for vitamin E than AO2 and AO4.

As previously written, one of the peculiarity of Vitamin E is the nature of the two ortho substituents of hydroxyl group, this lower hindrance possibly modifying the stabilization route.

Mallégol [55] supposes its stabilization mechanism is identical to other 2,6-di-*tert*-butyl phenols :



Basing on this mechanism, Lucarini and Pedulli [56] have compiled some rate constants for the reaction between POO° and α (vitamin E), β , γ and δ tocopherol, and some classical hindered phenols such as AO4. In the frame of the above given mechanistic scheme (analytically solved which very often requires using simplifying hypothesis and subsequent mistakes), they observed that:

$$k_{inh} (\alpha, \beta, \gamma, \delta \text{ tocopherol}) >> k_{inh} (AO4)$$

However, they also reported extremely comparable bond dissociation energies values for the O-H group of phenol (about 334 ± 8 kJ mol^{-1}), which is in contradiction with the observed difference between rate constants towards POO° radicals (more than 2 decades).

If the mechanism proposed by Mallégol [55] was true, then vitamin E would not react when polymer is aged in inert atmosphere, typically during the UHMWPE sterilization by γ radiation. It is in contradiction with results obtained by Costa et al [57] according to which vitamin E is consumed when polymer is irradiated under nitrogen, at a (paradoxically) higher rate than when polymer is irradiated under air (Figure 3).

It means that vitamin E has a more complex stabilization scheme than 2,6-di-*tert*-butyl-phenols. This scheme could be:

VitE + POO° $\rightarrow$ POOH + VitE° k_{S1}

VitE° + POO° $\rightarrow$ inactive product k_{S2}

VitE + P° $\rightarrow$ VitE° k_{S3}

VitE° + P° $\rightarrow$ inactive product k_{S4}

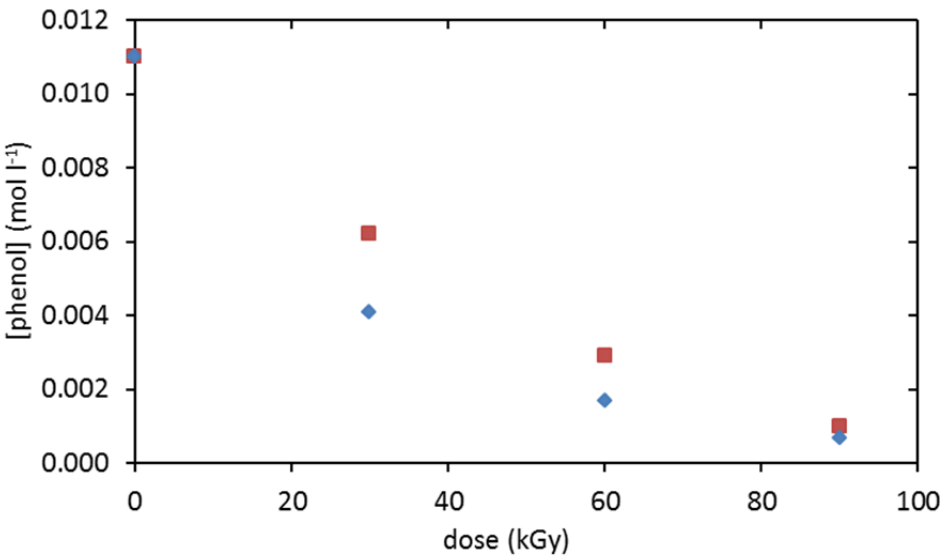


Figure 3. Residual phenol concentration (from FTIR measurements at 1210 cm^{-1}) versus dose for GUR 1050 UHMWPE irradiated under air (■) or nitrogen (◆) at room temperature (NB: 0.011 mol l^{-1} corresponds to ca 0.5%).

k_{S1}… k_{S4} can be estimated by an inverse approach from some ageing experiments identically to what was done for classical hindered phenols [41,42,58]. For that purpose, we will focus first on UHMWPE films thin enough (such those used in [57]) to neglect all diffusion phenomena complexifying the interpretation of experimental results. Vitamin E stabilization reaction can be added to the scheme previously established for additive free PE [15,17] valid at any irradiation dose rate and temperature:

$PH + h\nu \rightarrow P^\circ + 1/2H_2$	$r_i = 10^{-7} \times G(P^\circ) \times I$
$POOH \rightarrow 2P^\circ + \gamma_1 P{=}O + \gamma_2 s$	k_{1u}
$POOH + POOH \rightarrow P^\circ + POO^\circ + \gamma_1 P{=}O + \gamma_2 s$	k_{1b}
$P^\circ + O_2 \rightarrow POO^\circ$	k_2
$POO^\circ + PH \rightarrow POOH + P^\circ$	k_3
$P^\circ + P^\circ \rightarrow \gamma_4 crosslink + (1-\gamma_4) >C{=}C<$	k_4
$P^\circ + POO^\circ \rightarrow (1-\gamma_5)POOP + \gamma_5 POOH + \gamma_5 >C{=}C<$	k_5
$POO^\circ + POO^\circ \rightarrow [PO^\circ\ {}^\circ OP]_{cage} + O_2$	k_{60}
$[PO^\circ\ {}^\circ OP]_{cage} \rightarrow POOP$	k_{61}
$[PO^\circ\ {}^\circ OP]_{cage} \rightarrow POH + P{=}O$	k_{62}
$[PO^\circ\ {}^\circ OP]_{cage} \rightarrow 2P^\circ + \gamma_1 P{=}O$	k_{63}

In which:

- P°, POO°, $[PO°°OP]_{cage}$, POOH are respectively alkyl and peroxy radicals, in cage pair of alkoxy radicals and hydroperoxides.

- P=O, s and >C=C< represents carbonyl compounds, chain scissions, and double bonds.

- k_{1u}, k_{1b}… k_{63} are the rate constant of the mechanistic scheme, expected to display a temperature dependence given by Arrhenius law. We will suppose that the already existing set of rate constants established for HDPE and LDPE, is also valid for UHMWPE since $-CH_2-$ is in each case the reactive site.

For skipping all the mathematics (published elsewhere [41,42,58]), it will just be recalled that this mechanistic scheme is derived into a set of differential equations, of which numerical solution gives changes in P°, POO°, … versus time, absorbed dose, and eventually thickness in the case of bulk materials. For example, in the case of carbonyls:

$$\frac{d[P=O]}{dt} = (1-x_C).(k_{1u}[POOH] + k_{1b}[POOH]^2 + k_{62}[PO°°OP]_{cage} + 2k_{63}[PO°°OP]_{cage})$$

In the case of a PE stabilized with vitamin E, we will focus on the shape of stabilizer depletion curve, and we will try to determine the set of rate constant k_{S1}…k_{S4} describing the stabilization by Vitamin E.

$$\frac{d[AH]}{dt} = (1-x_C).(-k_{S1}[POO°][AH] - k_{S2}[P°][AH])$$

We will implement the following strategy:

- simulations of ageing experiments under vacuum will allow the determination of k_{S3} and k_{S4} (since there is no oxygen, there are no POO° radicals for reacting with vitamin E and simulations turn to be insensitive to k_{S1} and k_{S2}).

- once those two values determined, simulations of ageing under air (or in presence of oxygen), will allow the determination of k_{S1} and k_{S2}.

- given the simplicity of the shapes of oxidation curves or stabilizer depletion curves, several sets of constants could fit without any guarantee on their physical sense. It was published [41] that k_{S2} corresponds to a fast reaction involving two reactive radicals. Its value has only a minor influence on the simulation runs, provided it has a physical sense. k_{S2} was thus fixed from [59]:

$$k_{S2} = 5.10^8 \text{ l mol}^{-1} \text{ s}^{-1}$$

The same assumption can be done for k_{S4} having in mind that P° are more reactive than POO° so:

$$k_{S4} > k_{S2}$$

$$k_{S4} = 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$$

Hence, k_{S3} becomes the only adjustable parameter for simulating results for vitamin E depletion during irradiation in inert atmosphere [57]. This way, we estimated k_{S3} ~ 7.5×10^4 l mol^{-1} s^{-1} (presumably at room temperature, which will be discussed later). Example of procedure of adjustment of k_{S3} is given in Figure 4:

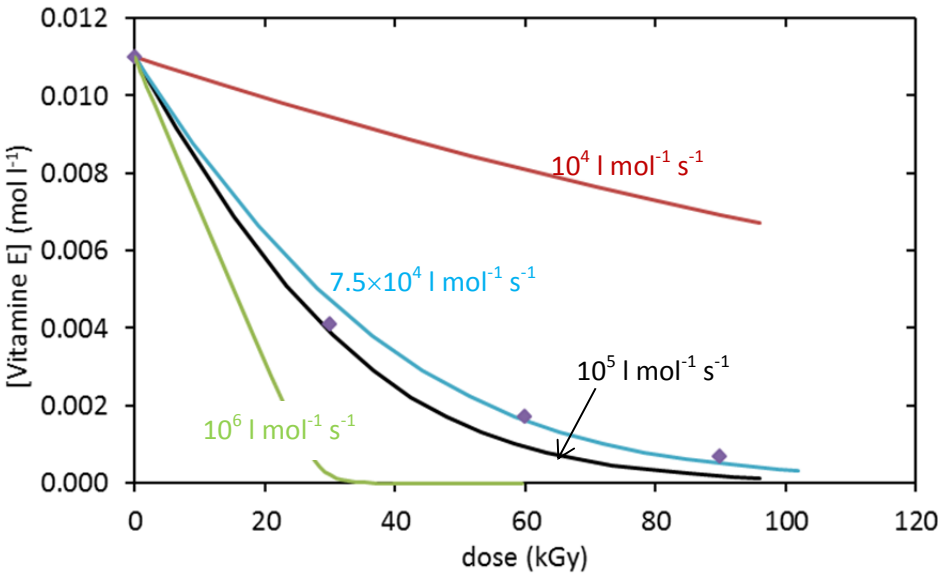


Figure 4. Kinetics of vitamin E depletion during 6 kGy h^{-1} irradiation under inert atmosphere at room temperature (◆) and simulations by the model with several k_{S3} values.

- k_{S1} remains the only adjustable parameter to be determined. We tentatively simulated the results under air [57] with k_{S2}, k_{S3} and k_{S4} previously fixed (see here above). Results are given in Figure 5:

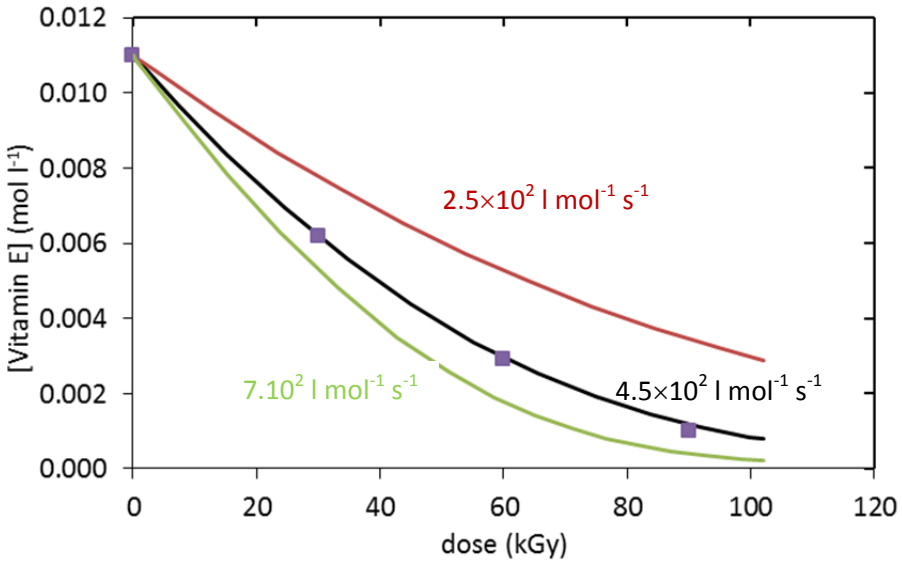


Figure 5. Kinetics of vitamin E depletion during 6 kGy h^{-1} irradiation under air at room temperature (◆) and simulations by the model with several k_{S1} values.

Let us mention that Figures 4 and 5 illustrate the sensitivity of the model (in other word, the aim is not to propose a stiff model which was forced to fit data). Using those values, we tried to simulate other results obtained for irradiation under air:

- comparable results by Bracco par [60], supposing that irradiation conditions are the same than for Figure 6:

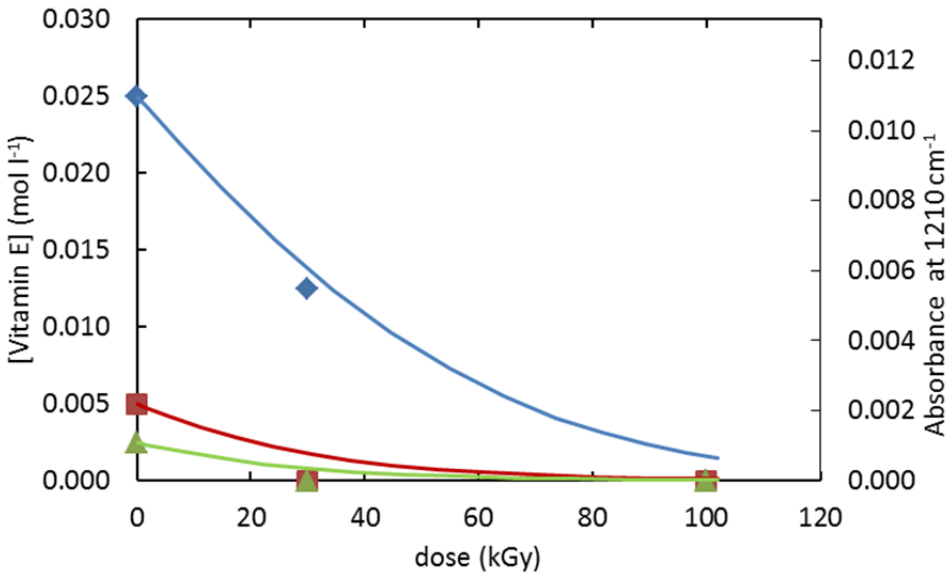


Figure 6. Kinetics of vitamin E depletion during 6 kGy h^{-1} irradiation under air at room temperature (◆ : 0.5%, ■ : 0.1%, ▲ : 0.05%) and simulations by the model with k_{S1} … k_{S4} values given above.

- kinetics of thermal ageing at 80°C for PE + vitamin E [55] (Figure 7):

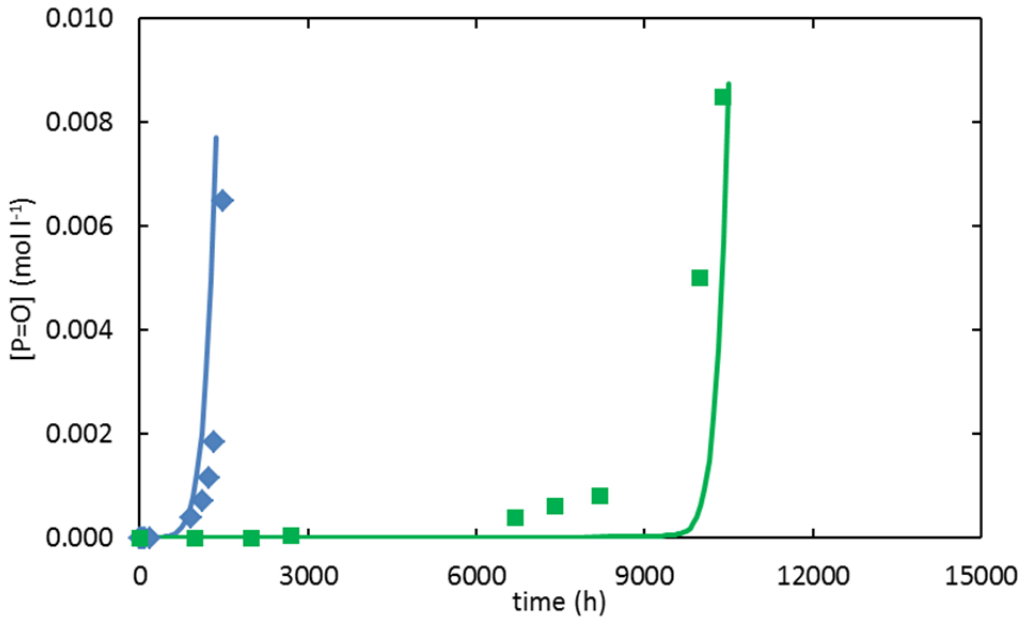


Figure 7. Experimental kinetics of carbonyl build-up during thermal oxidation at 80°C for pure HDPE (◆) and HDPE + 0.016% Vitamin E (■) and simulations by the model with k_{S1} … k_{S4} values given above.

Thus we dispose of a set of k_{S1}… k_{S4} values determined at two temperatures. They are expected to obey to Arrhenius law:

$$k(T) = k_0.\exp\left(-\frac{E}{RT}\right)$$

- k_{S2} and k_{S4} correspond to fast reactions for which activation energy is expected to be close to 0 as already documented in 2,6-di-*tert*-butyl-phenols.

- for k_{S3}, we do not have enough data for plotting a fair Arrhenius diagram. However, the model gave diverging solutions at 80°C for simulations of Figure 9 with $k_{S3} > 10^6$ l mol^{-1} s^{-1} i.e. $E_{S3} > 50$ kJ mol^{-1}.

- last, k_{S1} values of vitamin E were plotted in an Arrhenius diagram (Figure è) together with values determined from AO2 for which a lot of values were compiled in the case of thermal oxidation [42] :

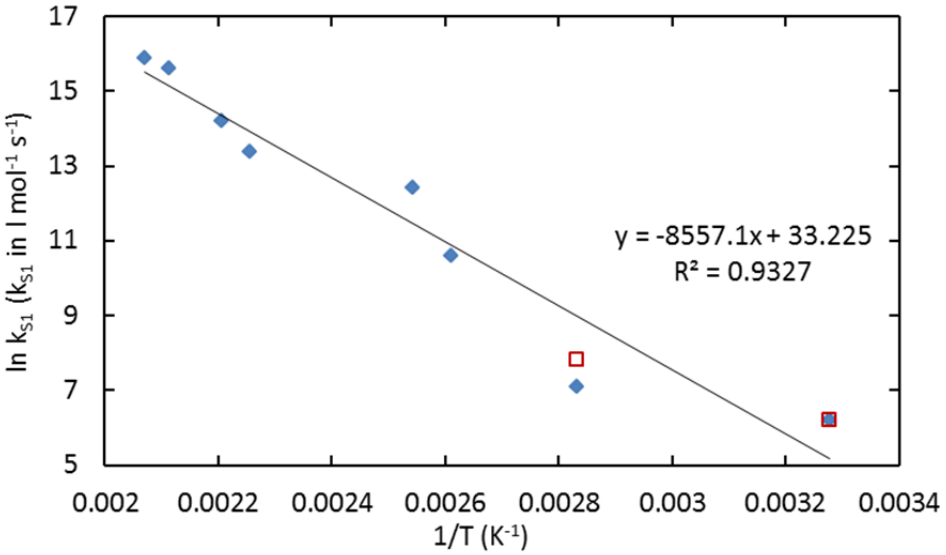


Figure 8. Arrhenius diagram for stabilization rate constant k_{S1} for vitamin E (□) and AO2 (◆).

k_{S1} values for AO2 and vitamin E are actually very close. A slight curvature is observed in the low temperatures range of the k_{S1} Arrhenius diagram. A possible explanation is that those data correspond to irradiation expected to occur at room temperature. However, it is known that irradiation induces a slight heating of sample [61]. k_{S1} values for AO2 and vitamin E would hence correspond rather to values at ca 60°C.

In conclusion, vitamin E and AO1… AO4 displays some commonality because of comparable O-H bond dissociation energy in the phenol group. Then, they have the same reactivity at least for the POO° + AH → POOH + A° reaction. However, vitamin E can also trap P° radical which is not the case of 2,6- -di-*tert*-butyl-phenols, possibly because of a lower hindrance of tocopherols. This can explain why Lucarini and Pedulli [56] reported apparent rate constant for stabilization by tocopherols differing by about 2 decades higher than for AO4.

4.3.3 Methods of incorporation of vitamin E

4.3.3.1. Strategy for adding vitamin E

In the case of many industrial grades of HDPE or LDPE, stabilizers are typically added to the polymer powder just after polymerization process, i.e. prior to its first processing. In the case if UHMWPE, there are schematically two methods for incorporating vitamin E (Figure 9):

- *blending*: it is obtained by blending UHMWPE powder with a vitamin E solution typically in cyclohexane [62] or isopropanol [63], or from a concentrated UHMWPE [6] working as a masterbatch such as those for dispersing pigments and dies. After evaporating the solvent, stabilizer molecules are adsorbed at the surface of UHMWPE grains. After compression molding, this powder leads to a bulk material displaying a constant vitamin E concentration within the whole thickness [62].

- *diffusion* (also named *infusion*): here, a previously molded bulk material is immersed into pure vitamin E. Usual temperatures for infusion range from 100°C to 130°C [64,65,66].

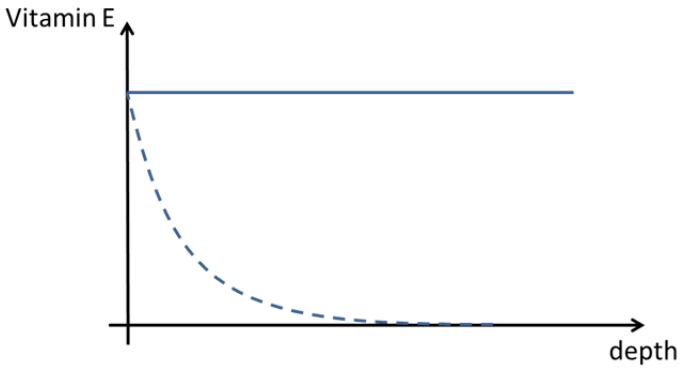


Figure 9. Vitamin E profile in UHMWPE obtained from blending (full line) or diffusion (dashed line).

In the case of infused UHMWPE, the concentration displays a gradient. Further thermal treatment for homogenizing the vitamin E is possible. Whatever the method for incorporating vitamin E, its concentration prior to in vivo ageing depends on:

- Vitamin E solubility at the manufacturing temperature and in vivo,
- Vitamin E diffusivity at the manufacturing temperature and in vivo,
- The time left for impregnation since equilibrium at the sample surface is not instantaneously reached [65] (Figure 10) :

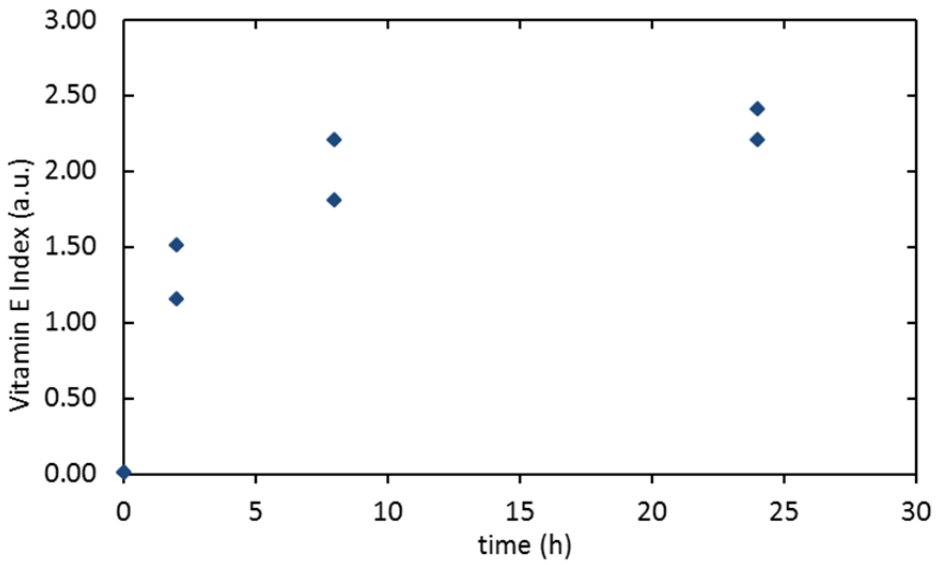


Figure 10. Change of Vitamin E Index at the surface of a UHMWPE material in contact with Vitamin E at 120°C [65].

In the case of infused UHMWPE, the change of Vitamin E concentration with thickness with an « U shape ». Two characteristics may be determined:

- the surface equilibrium Vitamin E Index (VEI_{surf}), related to its concentration (see "4.4 Analysis of the content of vitamin E",

- the thickness at which Vitamin E concentration reaches 0 (z_{max}).

Both depend on temperature (Figure 11).

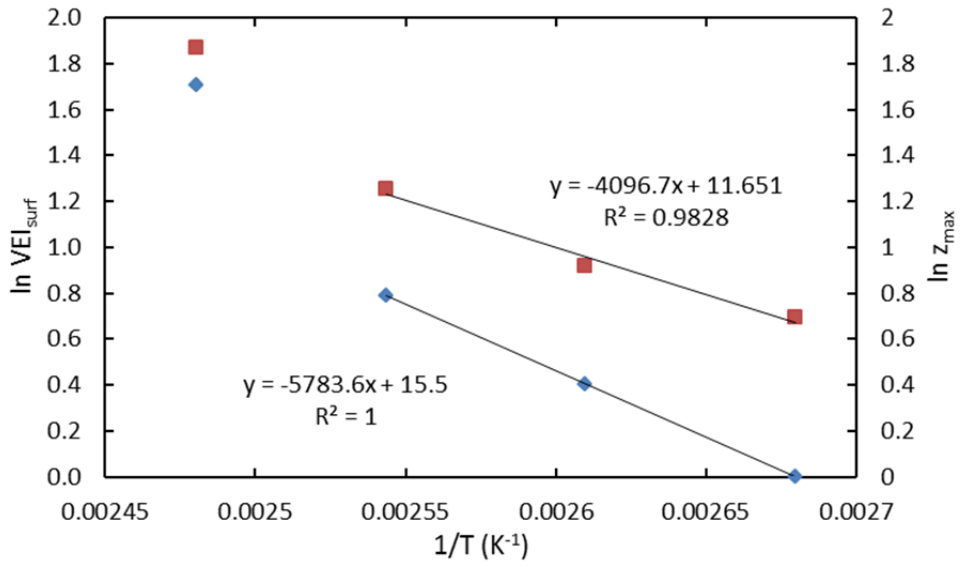


Figure 11. Temperature dependence of Vitamin E Index (◆) and maximal diffusion depth after 24 h (■) in UHMWPE (data at 130°C are neglected for determining the activation energy because of the change in diffusion and sorption induced by the start of melting transition).

On the assumption that the maximal thickness of vitamin E penetration is linked to the diffusion coefficient value by the following scaling law:

$$D \sim \frac{z_{max}^2}{t}$$

Then: $E_D = 2.E_{zmax} \sim 68.1 \text{ kJ mol}^{-1}$

It will be recalled in the next sections some structure properties relationships permitting to describe and predict the solubility and the diffusivity of vitamin E in UHMPWE together with some comparisons between vitamin E and some common antioxidants used in polyolefins.

4.3.3.2. On the solubility of vitamin E in UHMWPE

Polyethylene is one of the less polar polymers, in which there are only dispersive (London) interactions. Its solubility parameter is ca 16.5 $MPa^{1/2}$ [67]. Stabilizers generally contain hydroxyl functions, and aromatic groups contributing to increase the stabilizer solubility parameter. Stabilizers are thus expected to poorly dissolve in PE amorphous phase and not at all in crystalline one.

Stabilizers are aimed at increasing the lifetime (or induction time, or any other duration related to the start of visible degradation). The lifetime vs antioxidant curve (see “4.4.4 Thermal methods“, or [68] for example) is characterized by:

- a low concentration domain where lifetime increases linearly with stabilizer concentration,

- a high concentration domain with a concavity and possibly a plateau, meaning that increasing stabilizer concentration is useless.

According to the kinetic analysis of the stabilizer effect, the boundary between the two domains seems to be related to the solubility [27,28].

The issue is thus to choose a stabilizer being at least highly reactive towards a “target” species (radical or hydroperoxide) and being soluble enough in amorphous phase for protecting it against oxidation. When comparing stabilizers of a given “chemical” family, solubility is indeed considered as a key parameter for the prediction of the stabilizer efficiency [69,70,71]. Knowledge of its value and its temperature dependence is therefore necessary for the prediction of polymer long term behavior.

In the framework of the regular solution theory, the solubility of a solid stabilizer into a liquid polymer amorphous phase obeys to a modified Flory-Rehner law [72] describing the equilibrium of free enthalpy of mixing with free enthalpy of stabilizer melting (instead of elastic forces in the classical theory for solvent induced elastomer swelling [73]):

$$-\ln \varphi_1 = \frac{\Delta H_m}{RT} \cdot \left(\frac{1}{T} - \frac{1}{T_m}\right) + 1 - \frac{V_1}{V_2} + \chi$$

Where:

- φ_1 is the solubility limit (expressed as a volume fraction of additive), assumed here to be significantly lower than 1.

- ΔH_m and T_m are respectively the melting enthalpy and melting temperature of the additive.

- V_1 and V_2 are respectively the molar volume of additive and polymer.

- χ Is the interaction parameter, linked to the mixing enthalpy. Under the assumption that dispersive forces are predominant over dipole-dipole and hydrogen interactions, it could be expressed as:

$$\chi = \frac{V_1}{RT} \cdot (\delta_1 - \delta_2)^2$$

δ_1 and δ_2 are respectively the solubility parameter of stabilizer and polymer. They can in principle be calculated from the additive group contributions theory [74].

When studying the mixing of additives in simple solvents, the term V_1/V_2 is non negligible and plays a significant role in the solubility limit (for example the solubility of Irganox 1010 at 23°C is more than 10 times higher in n-octane than in n-octacosane). For small molecules dissolving in polymer: $V_2 >> V_1$ so that this term is neglected [75].

The term $\Delta H_m/RT \times (1-T/T_m)$ expresses the influence of the cohesion in a stabilizer crystal. When the additive is above its melting temperature, or cannot crystallize, the equation is simplified:

$$-\ln \varphi_1 = 1 + \chi$$

For example, the solubility parameters of AO1 and AO4 are found respectively [74] about 18.4 $MPa^{1/2}$ and 21.0 $MPa^{1/2}$ together with molar volume ca 621 $cm^3\ mol^{-1}$ and 220.5 $cm^3\ mol^{-1}$ using the additive group method contribution [74]. Using those values, χ is found respectively equal to 0.78 and 1.64 which gives solubility values close to values reported by Földes [76] for AO1 and Goonetilleke et al [77] for AO4.

Let us now turn to extrapolation of solubility at temperatures below the stabilizer melting point and more generally to the prediction of solubility at low temperatures. Moisan [78] reported the solubility values of stabilizers within a wide temperature range and observed a dramatic temperature dependence: for example, activation energy for solubility would be about 45.4 kJ mol^{-1} above antioxidant melting point, and 72.7 below.

If φ_1 obeys Van't Hoff law, and H_S is the enthalpy of mixing, then:

$$\frac{H_S}{R} = \frac{\Delta H_m}{R} + \frac{\partial \chi}{\partial 1/T}$$

It shows that:

- the changes of solubility with temperature are extremely strong below its melting temperature, with the double contribution from the high values of melting enthalpy (see Table 1) and mixing enthalpy. If stabilizer is incorporated in polymer by an impregnation at high temperature and if the equilibrium is actually reached, a great part of the stabilizer will become insoluble when the polymer will be cooled (which is typically the case of UHMWPE hips) and possibly exudate from the material as observed for AO3 [79]. Given the relatively high cost and toxicity of stabilizers, it arises economical and health issues.

- χ might be tentatively estimated from the solubility values above stabilizer melting points, even if this method has scarcely been employed to our knowledge. Since Vitamin E is actually a liquid in the investigated temperature range (its melting temperature is reported ca 2-3°C [80]):

$$\frac{H_S}{R} = \frac{\partial \chi}{\partial 1/T}$$

Literature reports the effect of temperature on Vitamin E Index (VEI, see part "4.4 Analysis of the content of vitamin E") observed on some UHMWPE impregnated with vitamin E at several temperatures (Figure 11). The data actually well obey Van't Hoff's law. Apparent activation energy is:

$$V_{1m}.(\delta_1 - \delta_2)^2 = 5780 \text{ J mol}^{-1}$$

Since : V_{1m} = 414 cm^3 mol^{-1} [74], then δ_1 ~ 20.2 $MPa^{1/2}$ in good agreement with the value estimated from [74] (19.6 $MPa^{1/2}$).

Using this solubility parameter data for Vitamin E, its solubility at 37°C can be estimated and compared with those of common hindered phenols able to crystallize (Table 1):

	AO1	AO2	AO3	AO4	vitamine E
T_m (°C)	55	123	164	71	-
ΔH_m (kJ.mol^{-1})	65113	68634	36242,1	19300	-
V_1 (cm^3.mol^{-1})	620,7	808	327	220,5	414
φ_1 (37°)	3,9E-02	4,9E-06	1,1E-04	9,6E-03	4,1E-02

Table 1. Molecular parameter and solubility estimated for AO1…AO4 and vitamin E.

Solubility limits in Table 1 are expressed as volume ratio. However, due to the close density of both polymer and antioxidant, they are extremely close to solubility expressed in weight ratio. It is extremely important to emphasize that they are given in amorphous phase. Hence, a 2% solubility

limit (for instance) in amorphous phase would correspond, in a 50% crystalline polymer, to an overall weight ratio equal to 1%. In other words, Table 1 suggests that vitamin E solubility would be about 2%. Some promising results obtained for highly stabilized UHMWPE [3] have to be considered with caution since it is not sure that vitamin E will be retained in amorphous phase at body temperature.

In conclusion, vitamin E is an antioxidant displaying a relatively good compatibility with PE for in vivo conditions, which is a necessary condition for ensuring hip stabilization. This short literature review shows it is due:

- to the long linear alkyl group, ensuring a low χ parameter,

- to its low melting point, since the stabilizer crystallization generally contributes to decrease solubility while increasing its thermal dependence.

4.3.3.3. On the diffusivity of vitamin E in UHMWPE

Since vitamin E (or any other sort of antioxidants) are in low concentration for economic and technical reasons (not lowering the mechanical properties of polymer), it is not expected to change the free volume fraction of the polymer. The diffusion is thus expected to obey Fick's law, with the diffusion coefficient D supposed independent of the antioxidant concentration:

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}$$

This equation was analytically solved by Crank [81] in the case a plate having a 2h thickness such as:

$$c(h) = c(-h) = c_1 \text{ at every time}$$

$$c = c_0 \text{ at } t = 0 \text{ for } -h < z < h$$

The concentration is given by:

$$\frac{c - c_0}{c_1 - c_0} = 1 - \frac{4}{\pi} \cdot \sum_0^{\infty} \frac{(-1)^n}{2n+1} \cdot \exp\left(-D.(2n+1)^2 \cdot \frac{\pi^2 t}{4h^2}\right) \cdot \cos\left(\frac{(2n+1).\pi.x}{2h}\right)$$

And the absorbed mass is hence given by :

$$\frac{m(t)}{m_\infty} = 1 - \frac{8}{\pi^2} \cdot \sum_0^{\infty} \frac{(-1)^n}{(2n+1)^2} \cdot \exp\left(-D.(2n+1)^2 \cdot \frac{\pi^2 t}{4h^2}\right)$$

m_∞ being the absorbed mass at equilibrium, related to the penetrant solubility limit. One can thus simulate the rate of impregnation of an UHMWPE from the estimation of vitamin E diffusivity.

In the field of research on food packaging, some authors from the have investigated the structure diffusivity relationships of antioxidants and have proposed models relating the diffusivity with the molar mass of penetrant and a matrix dependent parameter [82]. Among those models, there are :

- Limm and Hollifield's model [83] : $D = D_0.\exp\left(\alpha.M^{1/2} - K\cdot\frac{M^{1/3}}{T}\right)$

- Mercea, Brandsch and Piringer' model [84] : $D = 10^4.\exp\left(A - 0.13\times M^{2/3} - \frac{10450}{T}\right)$

Where D is expressed in $cm^2\ s^{-1}$, and M in g mol^{-1}. Those equations generally fit rather well the diffusivity of linear molecules [84,85], but overestimate the diffusivity values of branched, star-like, cyclic and polycyclic penetrants [86]. Coefficients are gathered in Table 2:

polymer	K	α	ln D_0	A
HDPE	1760.7	0.819	-0.9	8.8
LDPE	1140.5	0.555	-4.16	10.6

Table 2. Parameters of model used for predicting diffusivity.

For example, the A coefficient expresses the tortuosity linked to the barrier role of crystallites. It is thus not surprising that this parameter is higher in HDPE than in LDPE.

We dispose of diffusivity values published by Oral et al [65] for unirradiated or irradiated UHMWPE. Those Vitamin E diffusivity values are placed in the Arrhenius diagram in Figure 12 together with experimentally values measured for AO1...AO4 (of which structures are given in APPENDIX) :

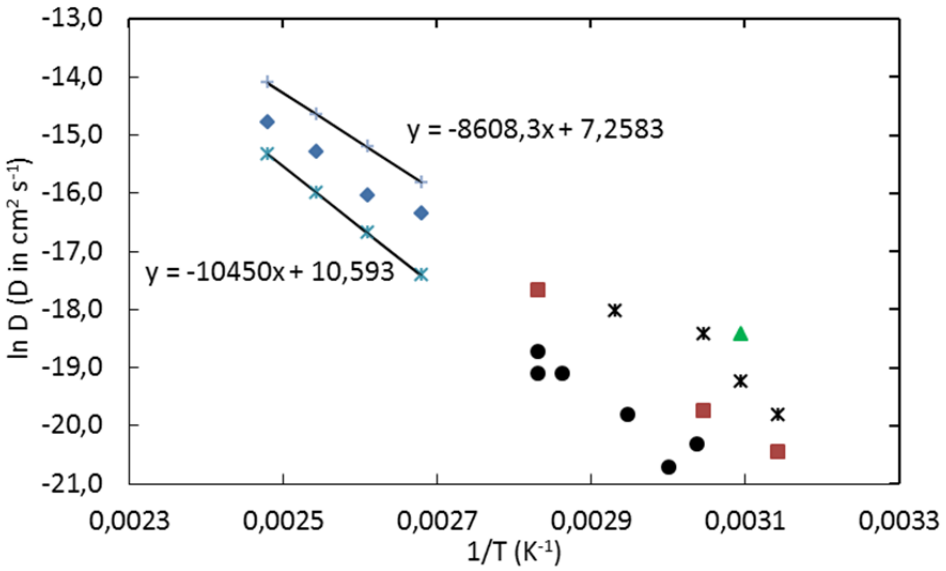


Figure 12. Experimental values of diffusion coefficient of vitamin E in UHMWPE [65] (◆), prediction in LDPE by Brandsch and coll's model (—✳—), Limm and Hollifield's model (—┼—), and experimental values for AO1 (■), AO2 (●), AO3 (-) and AO4 (▲).

Data seem to be fitted by an Arrhenius law as classically observed in literature for penetrants (far) above their glass transition:

$$D(T) = D_0.\exp\left(-\frac{E_D}{RT}\right)$$

Activation energy is ca 68.1 kJ mol^{-1}, in excellent agreement with the value coming from the maximal penetration depth of vitamin E after 24 h (Figure 10). A comparison between this values and prediction by models shows that they are rather well predicted using LDPE parameters, consistently with the fact that HDPE grades are generally more crystalline than UHMWPE and LDPE [11]. In particular, they lead to E_D value of the order of 71.6-86.9 kJ mol^{-1} in good agreement with the experimentally measured value.

Oxidation occurs in a thin surface layer whereas stabilizers are present in the whole thickness of the polymer. When oxidation starts, stabilizer is consumed or lost (by evaporation or migration in the environment media) so that its surface concentration decreases [87]. The diffusion of the stabilizer from the bulk to the surface for maintaining the surface concentration at a sufficient level is thus one of the parameters triggering its efficiency. More precisely, there is certainly an optimal stabilizer molar mass being low enough for permitting a sufficiently high diffusion from bulk to surface but with a limited volatility [88]. Data in Figure 12 were tentatively extrapolated at 37°C (Table 3).

	AO1	AO2	AO3	AO4	vitamin E
M (g mol^{-1})	531	1178	334	220	431
E_D (kJ mol^{-1})	75.3	104.3	69.5	73.2	68.1
D(37°C)	5.8E-10	5.5E-11	8.8E-10	3.2E-09	1.3E-09

Table 3. Extrapolated diffusion coefficient values of antioxidants at 37°C.

Vitamin E diffusivity at 37°C is ca 1.3×10^{-9} cm^2 s^{-1} (is a decade lower than the order of magnitude reported in [57]). It is one of the highest (apart AO4 which is actually a lowest size molecule). It is thus a rather good choice for protecting the surface of a thick sample polymer.

As it will be seen below, vitamin E can be added before or after irradiation, which arises the issue of the changes of diffusivity with the degree of crosslinking and crystalline ratio. It can be recalled that:

- In the frame of the free volume diffusion theory, diffusivity changes with the penetrant size and the free volume content of the amorphous phase [76,89,90,91]:

$$D = a.\exp\left(-\frac{b}{V_f}\right)$$

Where b is linked to the penetrant size and V_f it the polymer free volume depending on the difference between temperature and T_g of the polymer amorphous phase. Since T_g is not expected to significantly change after crosslinking, it is thus not surprising that D was found to be extremely close in unirradiated and irradiated PE [66].

- D also depends on the presence of crystallites slowing down diffusion. Starting from a classical theory very often used for the diffusion of gases in PE [92,93]:

$$D = \frac{D^*}{\beta\tau} = D_0.\exp(-a.x_C)$$

Where:

- D* is the diffusion coefficient in completely amorphous polymer,

- τ reflects the tortuosity of the path caused by the presence of crystalline entities,

- β is mainly related with the lack of mobility in the amorphous regions close to the anchoring points in the crystals,

- x_C is the crystalline ratio.

Even if it seems more reasonable to propose a linear decrease of D with x_C, diffusion in undoubtedly slower when increasing crystalline ratio. Hence, D are expected to be slower in annealed (thermally treated below melting temperature) than in melted (thermally treated below melting temperature) UHMWPE, in agreement with the observed changes in crystalline ratio [94].

4.3.4 Vitamin E stabilized polyethylenes

First, vitamin E scavenges free radicals propagating oxidation. It is hence not surprising to observe that it significantly reduces the post irradiation effects observed in UHMWPE. Kinetic curves in post irradiation phase always display the same characteristic shape with a maximal increase rate at the beginning of post irradiation (Figure 13).

In the case of unstabilized PE, concentration in POOH or carbonyl reach a pseudo-plateau after ca 1000 h at which [POOH] is on the order of 10^{-3}-10^{-2} mol l^{-1} [11]. This relatively high value can be explained. The concentration in irradiation created radicals is given by:

$$\Delta[P^\circ] = 10^{-7}.G(P^\circ).dose \sim 0.08 \text{ mol } l^{-1}$$

As it will be seen below, 100 kGy irradiation generate an increase in double bonds concentration ca 0.015 mol l^{-1} [15] (in good agreement with the radio chemical yield value G(double bond) = 1.8 [95]). Since G(crosslinking) = 2 [15], , the increase in crosslinking density is expected to be ca 0.02 mol l^{-1}. Since two P° are needed for having a new crosslink or a new double bond, it means that there is a relatively high level of unreacted radicals. It is thus not surprising that the quantity of formed POOH is on the same order than the quantity of unreacted radicals i.e. on the order of 0.01 mol l^{-1}. Basing on the respective reactivity of involved species, the possible mechanism of post-irradiation could be:

$P^\circ_{unreacted} \rightarrow POO^\circ$

$POO^\circ + PH \rightarrow POOH + P^\circ$

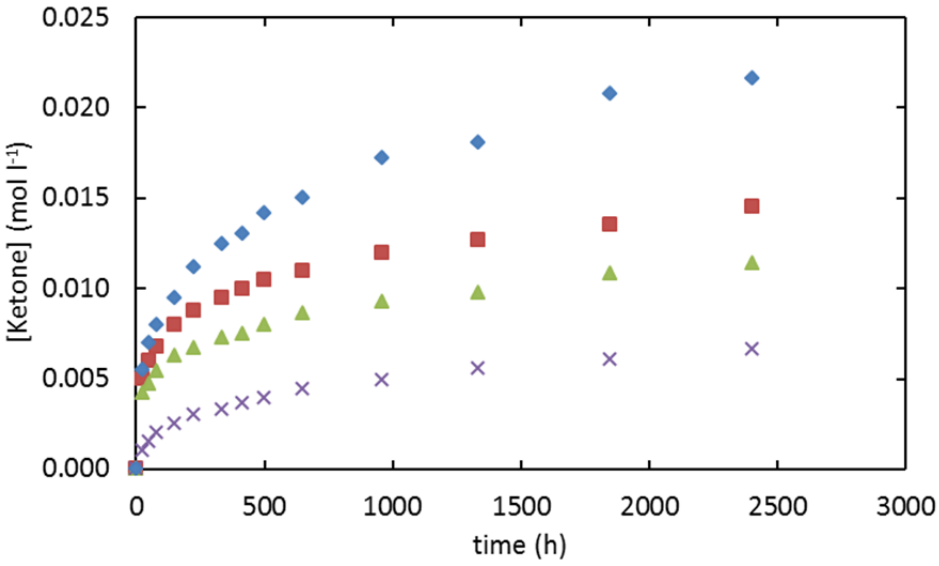
$\delta POOH \rightarrow \alpha P^\circ + \beta POO^\circ + \gamma_1 P{=}O$ (slow)

$POO^\circ + POO^\circ \rightarrow POOOP \rightarrow [PO^\circ{}^\circ OP]_{cage} \rightarrow P{=}O + POH$ (fast)

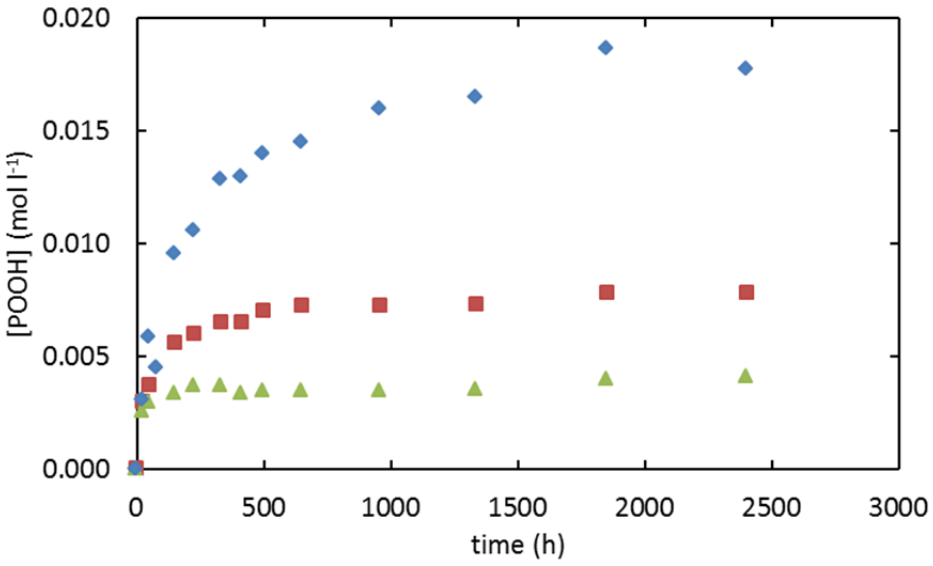
$POO^\circ + POO^\circ \rightarrow POOOP \rightarrow 2PO^\circ \rightarrow \gamma_1 P{=}O + \gamma_2 s + 2P^\circ$ (fast)

Chain scissions s are responsible of the partial destruction of crosslink network, and subsequent loss of wear resistance.

An increase in vitamin E concentration leads to a decrease of both stable ketones build up and hydroperoxides as well (Figure 13), these latter being the precursors of carbonyl products as observed in [57,62,96] and a decrease of intermediary unstable radicals as observed by Mehmood et al [21].



(a)



(b)

Figure 13. Carbonyls (P=O) and hydroperoxides changes (POOH) during room temperature post irradiation of UHMWPE 60 kGy irradiated under air: pure UMWPE (◆), UHMWPE + 0.0011 mol l^{-1} vitamin E (■), UHMWPE + 0.0011 mol l^{-1} vitamin E (▲), UHMWPE + 0.011 mol l^{-1} vitamin E (×) [57]. (NB: 0.0011 mol l^{-1} corresponds to a weight ratio of 0.05%).

Both unreacted P° radicals and the POO° they can form are trapped by vitamin E. However, if vitamin E is added prior to irradiation, the gain in thermal stability is accompanied some undesirable side effects because P° radicals are responsible for the crosslinking aimed at improving wear resistance. In other words, Vitamin E is expected to compete with irradiation induced crosslinking, which is well illustrated by some experimental results [57] in Figure 14:

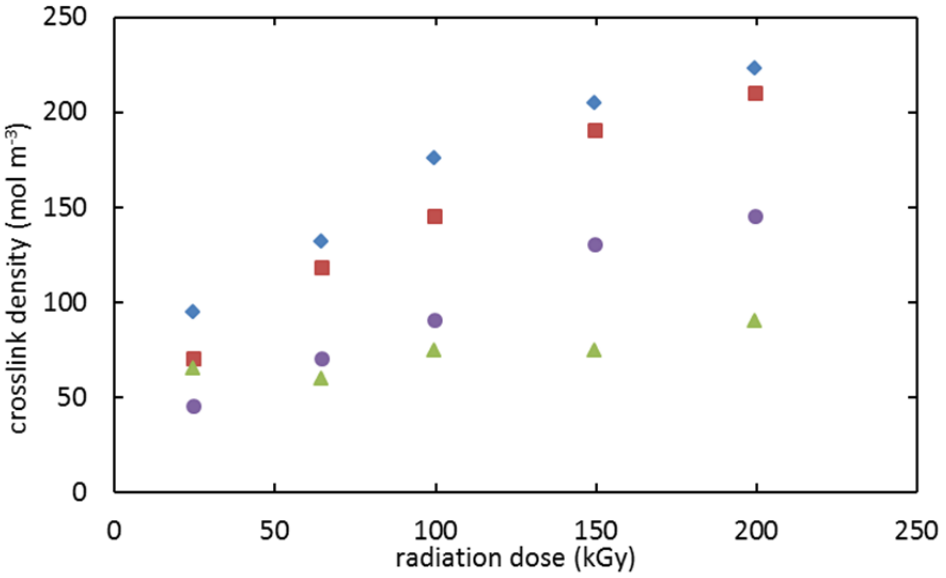


Figure 14. Crosslink density versus irradiation dose for several UHMWPE stabilized by vitamin E: 0% (◆), 0.1% (■), 0.3% (●), and 1.0% (▲).

Kinetic analysis (see previous paragraph) suggests rather that 100 kGy would create 0.02 mol l^{-1} of crosslink, but the question of the absolute value of crosslink density is out the scope of this chapter. The plot of crosslinked density versus vitamin E content for several irradiation doses [63,97,98] in Figure 15 confirms that adding vitamin E prior to irradiation inhibits the UHMWPE crosslinking:

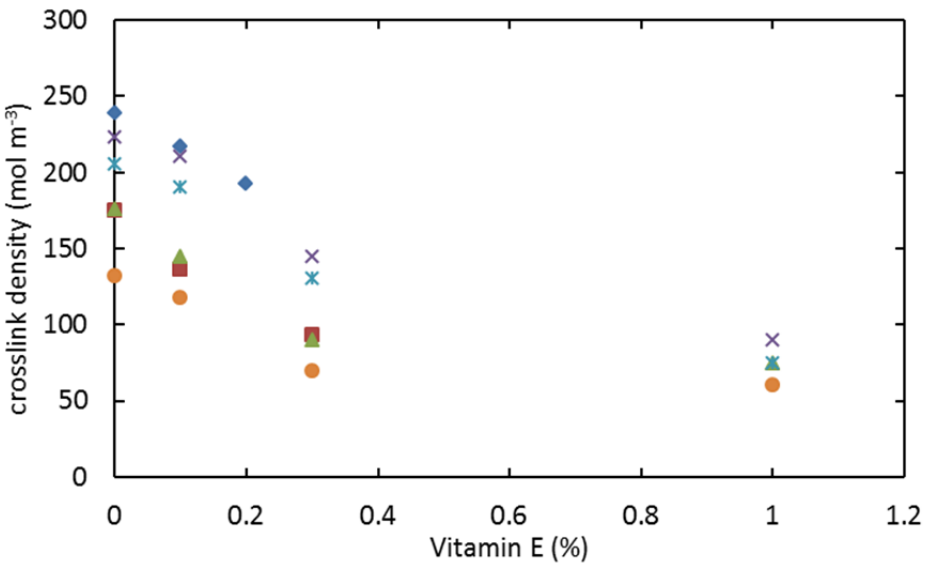


Figure 15. UHMWPE crosslink density versus vitamin E weight ratio for absorbed doses of 65 kGy (●), 100 kGy (■,▲), 150 kGy (✳,◆) and 200 kGy (×).

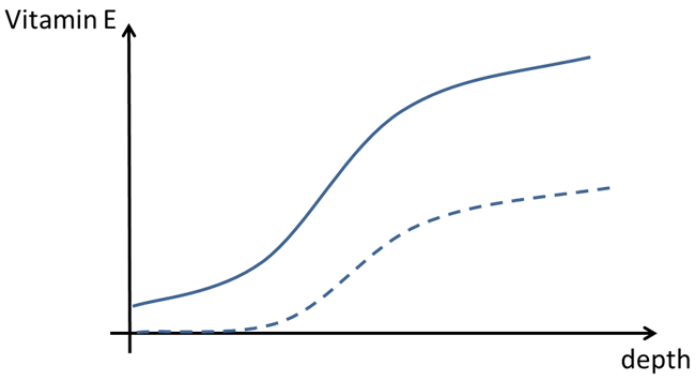
For example, a crosslinked density ca 0.175 mol l^{-1} is obtained for an absorbed 100 kGy dose in the absence of vitamin E. If vitamin E is added prior to irradiation, crosslinked density decreases and plateaus at ca 0.1 mol l^{-1} for a vitamin E content of 0.3% (0.015 mol l^{-1}). The value of this plateau seems independent of vitamin E concentration, and of the order of magnitude of intersect at dose = 0 (Figure 15).

It can be recalled that the irradiation induced crosslink density is given by :

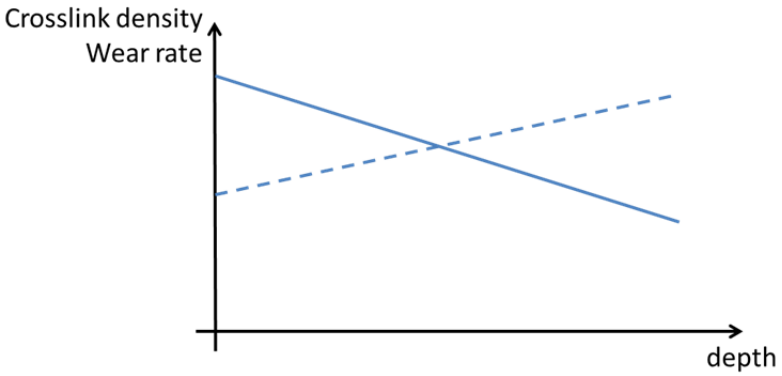
$$x = 10^{-7}.G(x).D$$

where x is expressed in mol l^{-1}, G in mol / 100 eV and D in Gy. For PE, G(x) = 2 so that 100 kGy are expected to increase the crosslink density by 0.02 mol l^{-1}, which is about twice the vitamin E concentration at the beginning of the plateau (0.015 mol l^{-1}), consistently with the fact that vitamin E can trap 2 radicals, and two radicals are necessary to generate a crosslink.

An extremely nice work by Oral et al [92] illustrates this dilemma: an UHMWPE was obtained from stacking a layer of stabilized UHMWPE with another of unstabilized one. Sample was then irradiation crosslinked after homogenization (Figure 16):



(a)



(b)

Figure 16. Vitamin E profile before (full line) and after (dashed line) irradiation (a), and crosslink density (full line) and wear resistance density (dashed line) profiles (b).

It suggests that wear resistance is higher in layers with initially low vitamin E concentration. However, in such zones, thermal oxidation in vivo is also expected to occur faster than in domains where there is a higher vitamin E concentration (see Figure 13).

In other words, stabilizing UHMWPE prior to irradiation is expected to have an adverse effect with the irradiation effect [99]. Vitamin E will be consumed relatively fast during irradiation so that the thermal stability in the post irradiation phase will be low (and even comparable than for unstabilized PE [96]). On the contrary, some promising results on wear and oxidation resistance were obtained by first irradiating UHMWPE, and then infusing vitamin E [64,66,100]. An example is given in Figure 17:

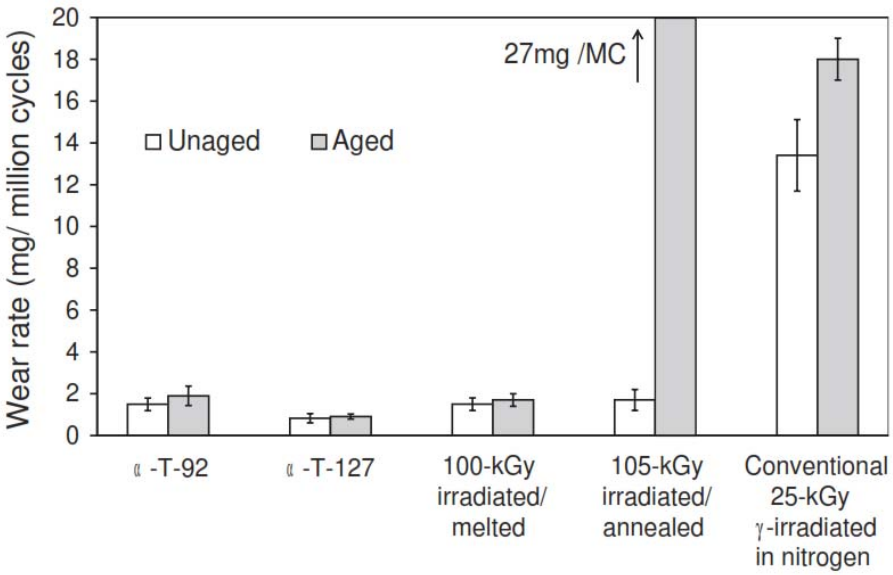


Figure 17. Wear rate of samples before and after thermal aging. α-T-92 and α-T-127: samples stabilized with Vitamin E after 92 and 127 kGy irradiation. Reprinted with permission of Elsevier [64].

- For unaged materials, wear resistance first increases with irradiation dose. Annealing or melting of crosslinked polymers leads to changes in their crystalline morphology, having a second order influence on wear resistance (see for example 100 kGy melted vs 105 kGy annealed vs α-T-92).

- For comparable irradiation doses, melted samples exhibit a better ageing resistance than annealed ones (see 100 kGy melted vs 105 kGy annealed). It is not surprising since the termination of residual radicals [13] and the thermolysis of hydroperoxides [61] are faster when elevating the temperature of thermal treatment.

- Vitamin E stabilized and melted samples display the better oxidative stability. However, the stabilization by vitamin E is possible without changing the polymer morphology i.e. altering some of the other mechanical properties (impact resistance, Young's modulus, fatigue crack resistance…).

In the case of unstabilized UHMWPE, an accelerated ageing test under enhanced oxygen pressure is proposed [100,101,102]. Can such a test be used for assessment of oxidative stability of UHMWPE stabilized with Vitamin E? Shortly, we will recall the existence of a direct phenol-oxygen reaction [58,103]:

$$AH + O_2 \rightarrow A^\circ + HOO^\circ$$

In this reaction, AH is directly consumed without trapping a P° or a POO° radical, and a very reactive HOO° radical is created. Since PE oxidation rate is less sensitive to oxygen pressure than the rate of

this reaction, the tests under elevated oxygen pressure are expected to induce significant underestimations of the effects of stabilizers.

4.4 Analysis of the content of vitamin E

4.4.1 FTIR

FTIR spectroscopy a simple method for detecting stabilizers in polymers [104]. In the case of common antioxidants, the absorption at ca 3650 cm^{-1} can be employed for detecting the unreacted antioxidant [58,105]. However, the partial overlapping with and absorption due to PE matrix prevents to use this absorbance for quantifying vitamin E.

In the case of Vitamin E, absorptions at 1378 cm^{-1} (methyl groups), 1260 cm^{-1} and 1209 cm^{-1} (phenol C-O stretching) and 1090 cm^{-1} (ether group) [60] can alternatively be used for quantifying Vitamin E. Vitamin E Index is currently [62,66] used for measuring the unreacted vitamin E. it is defined as the ratio of two areas:

$$VEI = \frac{Area(1245\text{-}1275\ cm^{-1})}{Area(1850\text{-}1895\ cm^{-1})}$$

The upper term corresponds to vitamin E peak and the lower one to PE matrix peak. As observed by Oral [66], VEI correlates well with the relative mass uptake. Then, the Vitamin E concentration in amorphous phase is calculated from:

$$[VitE] = \frac{1}{1 - x_C} \cdot \frac{\rho_{UHMWPE}}{M_{VitE}} \cdot (w/w)_{VitE}$$

Where:

- x_C is the crystalline ratio.

- ρ_{UHMWPE} is the density of UHMWPE amorphous phase.

- M_{VitE} is the molar mass of vitamin E.

- $(w/w)_{VitE}$ is the vitamin E weight ratio in material.

Some FTIR spectra are shown in Figure 18 for:

- pure vitamin E (a),

- the difference of UHMWPE + vitamin E film with a pure UHMWPE as reference material, which gives the spectra of Vitamin E when dissolved in UHMWPE (b),

- the difference of an irradiated UHMWPE + vitamin E film with a pure UHMWPE as reference material, which gives the spectra of Vitamin E and its degradation by products (c),

- a cyclohexane solution used from removing soluble material from irradiated UHMWPE + vitamin E (d).

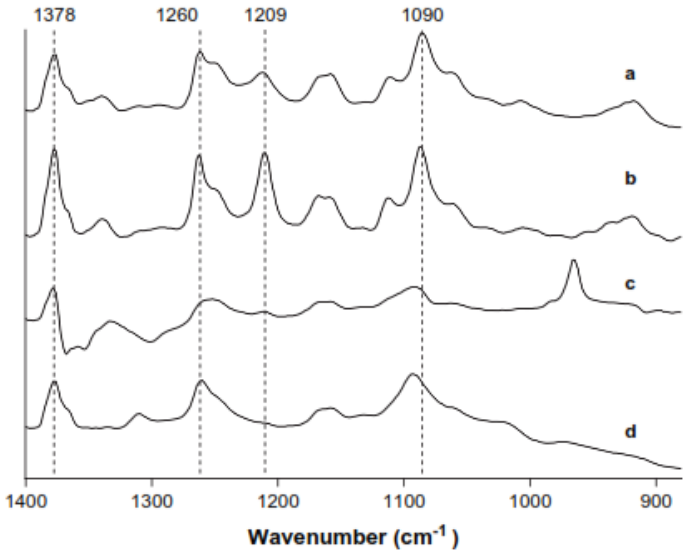


Figure 18. FTIR spectra of pure vitamin E (a), unirradiated UHMWPE + vitamin E (b), irradiated UHMWPE + vitamin E (c), cyclohexane extraction solution of irradiated UHMWPE + vitamin E (d). Reprinted from [60] with permission of Elsevier.

4.4.2 UV

Phenols absorb at ca 280 nm [106,107]. In the case of AO2, molar absorptivity values ca 1500 l mol^{-1} cm^{-1} per aromatic ring were proposed [107] and they seem to fit well with exploitation of results presented in [106] when converting the antioxidant group in nominal phenol group concentration. Since PE does not absorb in this wavelength range, UV spectroscopy allows phenol to be detected. An example of comparison of UV spectra of UHMWPE and UHMWPE + vitamin E is given in Figure 19. The concentration in vitamin E can thus be estimated from Beer-Lambert's law:

$$DO_{280} = \varepsilon.l.[AH]$$

Where:

- DO_{280} it the absorbance at the maxima of the UV signal.

- l is the sample thickness (expressed in cm).

- ε is the phenol molar absorptivity (expressed in l mol^{-1} cm^{-1}).

- [AH] is the phenol concentration (non corrected for crystallinity i.e. if [AH] is determined equal to 0.01 mol l^{-1} from the 280 nm signal, its value in amorphous phase is ca 0.02 mol l^{-1}).

It seems that the maxima of the absorption band is shifted towards longer wavelength, possibly because in the difference of ortho, meta and para substituents between vitamin E and AO1…AO4. However, there is a priori no reason that order of magnitude of epsilon is changed so that UV spectroscopy can be recommended for detecting vitamin E owing to its sensitivity.

It is however complicated to interpret spectra of thermally and/or radiochemically aged PE samples. By-products generated from radical + phenol reaction are generally conjugated structure of which UV absorption partially overlaps with signal of unreacted stabilizers.

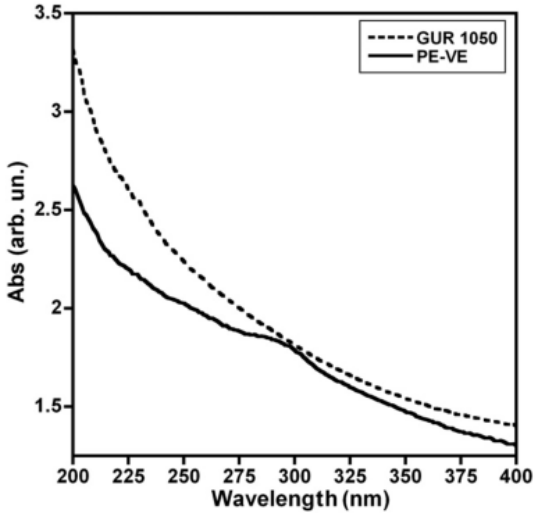
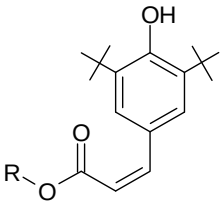
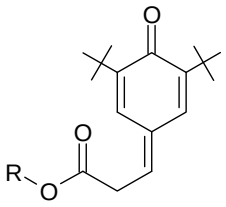


Figure 19. UV spectra of UHMWPE (dashed line) and UHMWPE + vitamin E (full line). Reprinted from [108] with permission of Elsevier.

In the case of AO1, there are for example cinnamates and quinone methides:



Cinnamates



Quinone Methides

absorbing respectively at 320 and 300 nm [109]. In the case of Vitamin E, the absence of an aliphatic structure in para of hydroxyl seems to prevent the formation of such products. However, the wide variety of reported by-products (see 4.4.3 HPLC) undoubtedly also display an absorption in the 300 nm wavelength region which will involve the same sort of difficulty for interpreting spectra of oxidized samples.

4.4.3 HPLC

High Pressure Liquid Chromatography is expected to separate unreacted antioxidants from its degradation by products. For example, phosphite yields a phosphate when reducing a hydroperoxide into an alcohol. Phosphite and phosphate are easily separated by HPLC which allows envisaging the stabilization scheme and its kinetics [27].

Vitamin E is rather not polar and dissolves easily in hexane solutions. In the case of PE stabilized with vitamin E, an example of chromatogram of soluble material removed from PE is given in Figure 20 [110]:

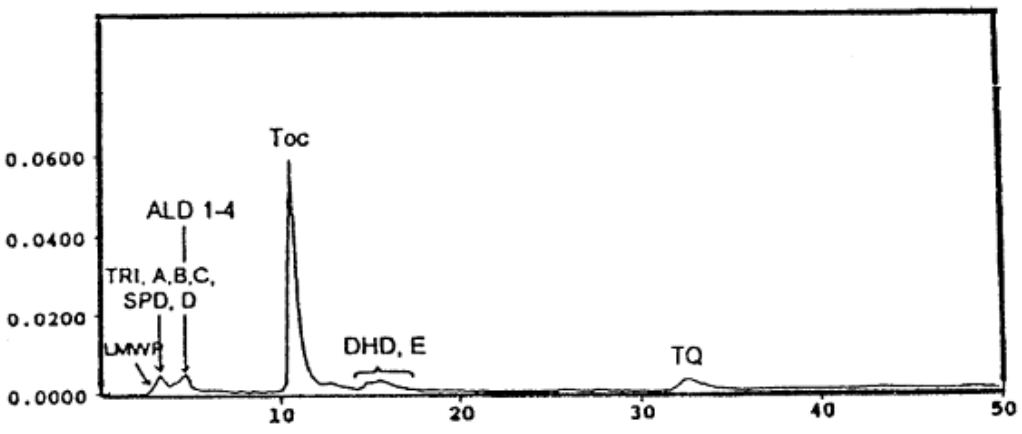


Figure 20. HPLC Chromatogram of vitamin E (Toc) and its by products (TQ, Tri A,B,C …) removed from thermally degraded PE. Reprinted from [110] with permission of Elsevier.

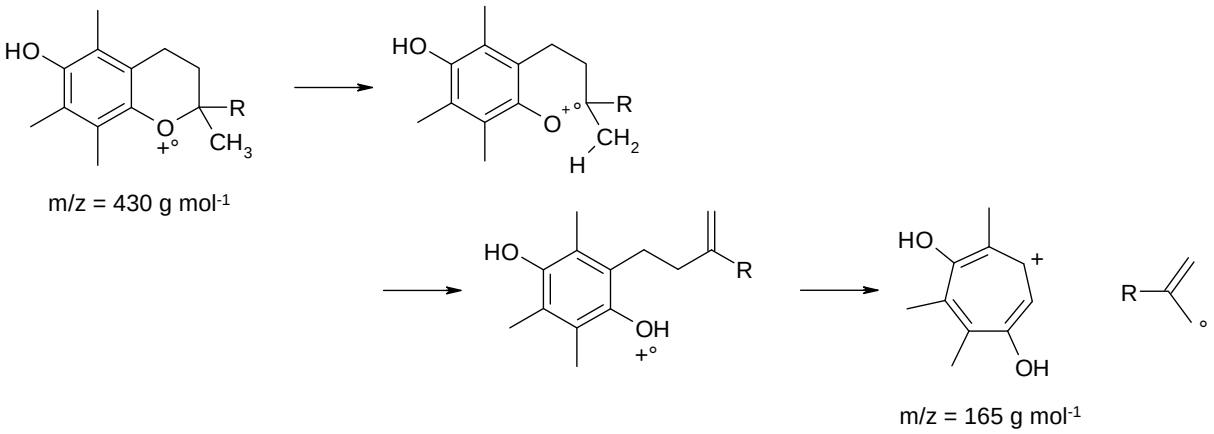
Apart the products analyzed by HPLC, there are also reaction by-products coming from the reaction:

$$POO^{\circ} + vitE^{\circ} \rightarrow \text{inactive products}$$

Which are grafted on the PE chain and cannot hence been removed by solvent extraction.

In conclusion, the use of HPLC is appealing because of brings extremely detailed informations on the stabilizer transformation routes. Furthermore, it permits to efficiently separate unreacted vitamin E from all its derivates, contrarily to UV spectroscopy where all signal overlap at least partially. However, the sampling is sometimes complicated due to the difficulty to totally remove stabilizer and its by-products from a semi-crystalline (and even crosslinked) matrix which is insoluble [111].

In Figure 20, HPLC detection is UV at 290 nm. Mass spectrometry is another possible method for detecting vitamin E [112]. When ionized, vitamin E product a parent peak at m/z = 431 and a main peak at 165 ascribed to the following decomposition mechanism [113]:



4.4.4 Thermal methods

Thermal oxidation leads to some radicals bimolecular combinations which are rather exothermic. When heated above their melting point under air, typically at temperatures ca 170-200°C, lifetime of polyolefins is extremely short. Hence, a exothermal signal is observed by Differential Scanning Calorimetry shortly for sample exposed at 200°C shortly (less than 1 min) after DSC cell is switched from nitrogen to oxygen (Figure 21). It is however significantly increased when stabilizers are added [42,114].

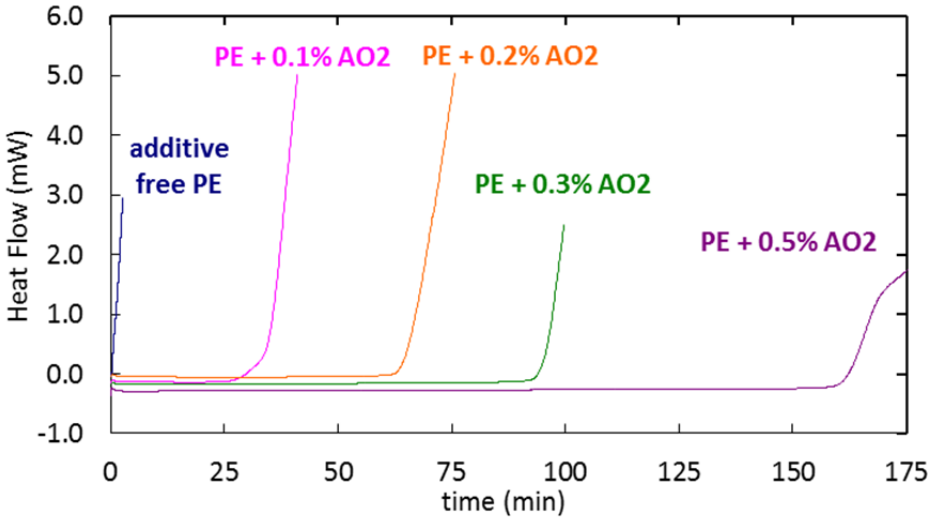


Figure 21. Isothermal part of DSC thermogram at 200°C under 0.1 MPa O_2 for PE + AO2.

There is actually a wide literature on OIT values for PE + AO2 for instance [9,114]. Data are more scarce in the case of PE + vitamin E. However, some results illustrates OIT increase with AO2, AO4 and vitamin E concentration (Figure 22) in a model hydrocarbon liquid [54]:

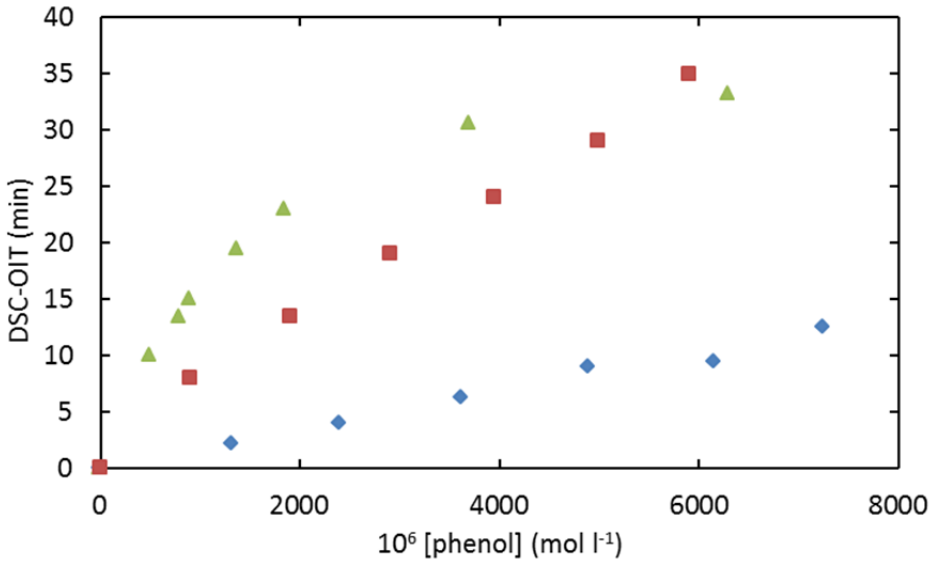


Figure 22. Changes of Oxidation Induction Time à 200°C of squalane with antioxidant concentration (◆: AO4, ■:AO2, ▲: vitamin E).

Curvature in OIT vs phenol concentration (Figure 22) can originate from stabilizer volatile loss [27,28] in the conditions in which DSC-OIT is performed. As a matter of fact, the slope for squalane + AO4 is lower than for squalane + AO2 whereas both stabilizers are expected to display a comparable efficiency in trapping radicals linked of a comparable Bond Dissociation Energy for O-H group.

DSC-OIT appears thus a reliable for detecting stabilizers in virgin polyolefins stabilized with phenolic antioxidants. However, in the case of polymers having previously undergone whether an irradiation or any thermal treatment likely to provoke some thermal oxidation, OIT value expresses the combination of residual concentration in stabilizers and in unstable species generated from ageing. Hence, a distortion between residual OIT depletion and residual phenol depletion is expected [42].

4.5 Conclusions

The elaboration of UHMWPE hips is particularly challenging. As nicely illustrated by Atwood [1]:

- unirradiated UHMWPE have a fair oxidation stability in vivo conditions, but a poor wear resistance.

- irradiation crosslinked UHMWPE thermally treated below polymer melting point (annealed) have an improved wear and fatigue crack propagation resistance. Their resistance to oxidation may be insufficient because some unreacted radicals (after irradiation) did not terminate during annealing.

- irradiation crosslinked UHMWPE thermally treated above polymer melting point (remelted) have an improved wear resistance, and have possibly recovered a great part of the oxidation stability, but display poor crack propagation resistance.

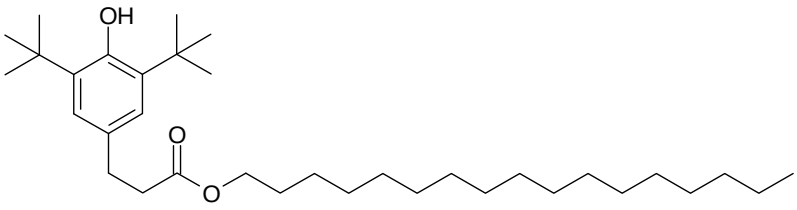
Vitamin E offers the possibility to trap residual radicals and avoid some post irradiation effects. However, it directly competes with crosslinking. It could be an interesting strategy for add vitamin E by an impregnation method in the crosslinked UHMWPE.

However, it seems difficult, at this state of our knowledge, to completely compare the wide variety of methods for designing UHMWPE hips, differing by dose rate, total dose, temperature and time for the thermal treatment, method for incorporation of vitamin E.

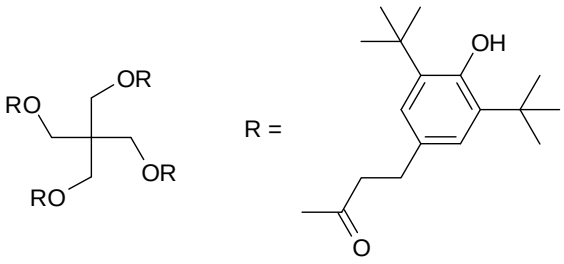
We have then chosen to gather all the physicochemical parameters describing the vitamin E action. We discussed their physical sense by comparing their values with those published for common antioxidants. We dispose now of a numerical tool permitting to describe the stabilization by Vitamin E. We presented in this chapter some simulations in thin films, but they can be adapted in a diffusion- reaction coupling model, which will be finally helpful for discussing the method for designing UHMWPE materials by a non-empirical way.

APPENDIX: Structure of stabilizers

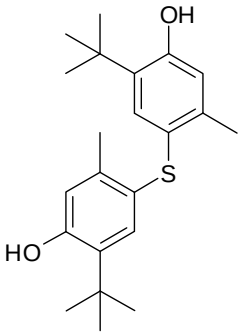
AO1 (CAS NO. 2082-79-3)



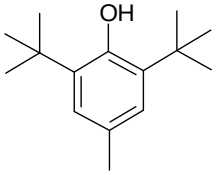
AO2 (CAS NO. 6683-19-8)



AO3 (CAS NO. 96-69-5)



AO4 (CAS NO. 128-37-0)



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