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(Article begins on next page)



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# **Post electron-beam irradiation oxidation of orthopaedic UHMWPE stabilized with Vitamin E**

Costa L.\*, Carpentieri I., Bracco P.

Dipartimento di Chimica IFM and NIS-Centre of Excellence, University of Torino, Via  
Giuria 7, 10125 Torino, Italy

\*Corresponding author: [luigi.costa@unito.it](mailto:luigi.costa@unito.it), Tel +39 011 6707548; Fax +39 011 6707855

## **Abstract**

Ultra-High Molecular Weight PolyEthylene (UHMWPE) has been the material of choice for load-bearing articular components used in total joint arthroplasty in the past 30 years. However, the durability of the whole implant has often been compromised by oxidation of UHMWPE components. Since the use of a suitable, biocompatible stabilizer would minimize this inconvenience, it has been introduced the possibility to use Vitamin E.

In the present work, medical grade UHMWPE was blended with 1.1, 2.3 and 11 mmol/l of Vitamin E and consolidated by compression moulding. Small block of reference and of Vitamin E-blended UHMWPE were then electron beam irradiated at 30, 60 and 90 kGy, both in vacuum and in air. FTIR spectroscopy was used to monitor changes in both the polymer and the additive. Thin sections of virgin and Vitamin E-blended UHMWPE irradiated were aged in air, at room temperature and in the dark and the kinetic of oxidation was followed by FTIR. The reaction between Vitamin E and macro-alkyl radicals or unlikely with peroxy radicals has been demonstrated and a correlation between the decrease of macro radicals and the stabilization effect of Vitamin E has been shown.

**Keywords:** UHMWPE, oxidation, Vitamin E, antioxidant.

## **1. Introduction**

Medical grade UHMWPE, synthesized with Ziegler-Natta catalysis, is a linear polymer with low concentrations of chain imperfections [1,2] and it is generally additive-free, in compliance with ASTM F648-07 [3].

The absence of stabilizing additives for the oxidation process has created problems related to oxidation of the polymer, mainly induced by sterilization with high energy radiation in air [4-7], which often resulted in unexpected and dramatic failures of the whole prosthetic implant. Therefore, the stabilization of UHMWPE has become of primary relevance and, in the recent past, ASTM F2656-07 [8]) introduced the possibility to use  $\alpha$ -tocopherol or synthetic Vitamin E, a natural antioxidant [9,10].

Vitamin E, whose annual production is in the order of 30.000 ton, has a well known stabilizing effect against oxidation and it is already approved by FDA as an additive for food and food packaging. Its stabilizing effect in polyethylene has been studied both during melt processing [11-13] and in solid state after irradiation [14-16].

In both cases, the first step of oxidation is the cleavage of C-C or C-H bonds, with the formation of macroradicals, but the following process can vary considerably between the two scenarios.

Extensive studies have elucidated the mechanism of stabilization during melt processing [17,18], which involves the formation of dimers and trimers derivatives of Vitamin E, due to the high concentration and poor dispersion of the additive and to a higher mobility of the polymer molecules in the melt.

On the contrary, in the case of medical grade UHMWPE, lower concentrations of Vitamin E are usually employed and irradiation is carried out at room temperature.

The study of post-irradiation oxidation of gamma-irradiated HDPE showed that the process leads to the formation of the same oxidation products obtained in thermal-oxidation [19].

Post-irradiation oxidation of UHMWPE has recently been investigated and the oxidation path has been discussed [20].

In this paper the attention is focused on the oxidation process that takes place in electron beam irradiated Vitamin E-blended UHMWPE after long-time ageing in air, in order to verify the effectiveness of Vitamin E as a stabilizer in these conditions. Reactions among Vitamin E and the macroradicals produced by irradiation are investigated and the stabilizing process is discussed.

## **2. Experimental**

### *2.1. Materials*

GUR 1050 powder was blended with 1.1, 2.3 and 11 mmol/l of pharmaceutical grade Vitamin E, corresponding to 0.05, 0.1 and 0.5 w/w%, and consolidated into large slabs, in accordance with ASTM F2965 (Quadrant, Meditech Division, Fort Wayne, IN, USA and Orthoplastics Ltd, Bacup, UK). Compression moulding of the powder was carried out using the temperature, pressure and time usually applied for consolidation of commercially available UHMWPE. The precise combination of these variables remain proprietary, but it is well known that high temperature (higher than 200°C) and pressure must be applied for long times (several hours) in order to assure good consolidation of the powder [1]. Therefore, homogeneous dispersion of Vitamin E can reasonably be assumed. Moreover, FTIR Imaging measurements, recorded with a 6 x 6  $\mu\text{m}^2$  aperture, shows a uniform distribution of Vitamin E into the sample blended with 11 mmol/l of additive.

Commercially available grade GUR 1050 UHMWPE slabs from the same batch were used as reference material.

Thin sections (180 microns) were cut from the blocks by microtoming in air, at room temperature (PolyCuts Microtome, Reichert-Jung, Germany) and were electron-beam irradiated at 30, 60 and 90 kGy both in vacuum and in air. Electron beam irradiation was performed with a 10 MeV accelerator (Bioster, Seriate, Italy), operating at 25 kW power, with a dose rate of  $6 \cdot 10^4$  kGy/h, at room temperature. After irradiation, all samples were kept in liquid nitrogen, until FTIR measurements began. Samples irradiated in air were aged in air, at room temperature and in the dark.

## 2.2. FTIR spectroscopy

The FTIR measurements were performed on a System 2000 spectrometer (Perkin-Elmer, Shelton, Connecticut, USA). All spectra were run on thin sections in the transmission mode with a  $4 \text{ cm}^{-1}$  resolution and 16/32 scans per spectrum. The peak at  $2020 \text{ cm}^{-1}$ , a combination band associated with the twisting of  $\text{CH}_2$ , was used as an internal standard, since it can be regarded as unaffected by minor changes in the polymer structure [20]. At the peak at  $2020 \text{ cm}^{-1}$ , all the spectra were normalised at an absorption of 0.05, correlating to a film thickness of ca.  $100 \mu\text{m}$ .

The molar concentration of trans-vinylene and vinyl double bonds was calculated from the respective absorption bands using the molar absorptivity proposed by De Kock and Hol [21].

The degree of oxidation was determined by the ketone absorption at  $1718 \text{ cm}^{-1}$ , the hydrogen bonded hydroperoxide absorption at  $3420 \text{ cm}^{-1}$  and the free hydroperoxide absorption at  $3550 \text{ cm}^{-1}$ . Total hydroperoxides (free plus hydrogen-bonded) were detected after reaction with nitrogen monoxide (NO) for 15 hours in a dark reaction vessel. Under these conditions, hydroperoxides in polyethylene are converted into more easily detectable nitrates. The ROOH concentration was calculated using the extinction coefficient of the absorption at  $1630 \text{ cm}^{-1}$  ( $1933 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), as reported by Lacoste et al. [19].

Carboxylic acid determination was done after derivatization with sulphur tetrafluoride (SF<sub>4</sub>) [19].

The C-OH absorption at 1210 cm<sup>-1</sup> was used to monitor the Vitamin E content [22].

It is important to underline that we mostly refer to IR spectral subtraction; in fact very small variations in the IR absorptions can be detected subtracting the spectrum of the reference, virgin material from that of the irradiated sample. In the present conditions, we are able to detect significant variations of about 0.002 absorbance units (the detection limit of the instrument is 0.0001 a.u.).

The rate of oxidation was calculated by taking the derivative of the oxidation curve with respect to time, using Origin software.

### **3. Results and Discussion**

#### *3.1. Electron beam irradiation in vacuum and in air*

The effect of irradiation on UHMWPE in inert atmosphere has been widely discussed [23].

The feasibility of the reactions taking place in the polymer bulk is governed by thermodynamic and kinetic aspects. The kinetic of the reactions involving macroradicals is not only controlled by the species concentration, but mostly by their statistical probability of collision (i.e. by the pre-exponential factor of the kinetic constant), which depends by the exposed cross-section and by their relative mobility, that is by diffusion itself [24].

Among the most abundant species formed upon irradiation, sec-alkyl macroradicals can migrate with a very high rate [20,23] along the macromolecular chain, via inter or intramolecular H transfer. On the contrary, macro-allyl radicals (obtained via migration of the radical in  $\alpha$  to a trans-vinylene double bond) and peroxy macroradicals (obtained if O<sub>2</sub> is available) are set in fixed positions on the macromolecular chain and the peroxy macroradicals can only spread for propagation of the oxidation process. In the actual conditions, the mobility of the Vitamin E molecule is restricted to the amorphous phase and, even there, it is

quite limited due to the low diffusion coefficient of vitamin E (in the order of  $10^{-5}$ - $10^{-6}$  mm<sup>2</sup>/s) in polyethylene at room temperature.

Figure 1 shows the consumption of the phenol group of Vitamin E in the function of the absorbed dose, for blends with 11 mmol/l of Vitamin E, measured immediately after irradiation in vacuum or in air respectively.

The consumption of the phenol function is proportional to the amount of macro-alkyl radicals produced during irradiation (reaction 5, scheme 1) both in vacuum and in air, with a slightly higher efficiency in vacuum.

This means that macro-alkyl radicals can react with Vitamin E during irradiation in vacuum, thanks to their high mobility [23]. On the contrary, the same migration mechanism cannot be applied to macro-allyl radicals, resulting in a statistically lower chance of reaction for this species.

In the literature, sterically hindered phenols are generally believed to act as chain breaking donor (CB-D) [25,26]. The mechanism of stabilization involves the extraction of hydrogen from the phenol group by a peroxy macroradical.

Our findings show that the interaction between the peroxy macroradicals and Vitamin E does not seem to be the main stabilization mechanism in the present conditions.

In the presence of oxygen, there is a competition between the reaction of the macro-alkyl radicals with Vitamin E (reaction 5, scheme 1) and that with oxygen to form peroxy macroradicals (reaction 7, scheme 1). For this reason, the consumption of Vitamin E is lower if irradiation is carried out in air than in inert environment.

Due to the Vitamin E chemical structure, the hydrogen extraction could involve not only the phenol group position but also the hydrocarbon chain of the molecule of Vitamin E. In any case, at once or through a stabilization of the structure formed, we would obtain a resonance-stabilized  $\alpha$ -tocopheryl radical [27].



Figure 2 shows the trans-vinylene double bonds concentration before and after irradiation of virgin or Vitamin E-blended polyethylene irradiated in vacuum (a) and in the presence of oxygen (b) at 30, 60 and 90 kGy. It is well known that the amount of trans-vinylene double bonds increase proportionally to the radiation dose [28]. In addition, the present findings show that the trans-vinylene formation is not affected by the presence of Vitamin E, nor by the presence or absence of oxygen. This means that Vitamin E does not influence the reaction of hydrogen extraction, then it can be assumed that this reaction takes place intramolecularly (reaction 2, scheme 1), rather than via H-transfer and encounter of two macro-alkyl radical. This evidence confirms the findings of Dole and colleagues [29].

Figure 3 shows the vinyl concentration decrease during irradiation and how it is affected by the presence of Vitamin E. The simultaneous possibility for the macro-alkyl radicals to react with Vitamin E or with vinyl double bonds results in a lower efficiency of this reaction in the presence of Vitamin E. Thus, the presence of vitamin E reduces crosslinking (reaction 4, scheme 1) [30].

In addition the amount of vinyl double bonds in the presence of Vitamin E is already different before irradiation (figure 3), even if the UHMWPE samples come from the same batch. Commercially, UHMWPE powder is blended with Vitamin E and then compression molded. During processing, radicals can be produced and they can react with vinyl double bonds to form a Y-shaped crosslink. Clearly, vitamin E inhibit this reaction also during processing and, when the concentration is equal or larger than 11 mmol/l, the crosslinking is reduced.

### *3.2. Post electron-beam irradiation oxidation*

Figure 4 shows IR spectral subtractions for virgin and Vitamin E blended UHMWPE films, irradiated at 90 kGy and aged in air, at room temperature for different time, but to the same oxidation level. The two spectra are nearly identical, indicating that even if oxidation takes

longer times to develop in Vitamin E-blended samples, the oxidation products are the same formed in virgin UHMWPE, thus the oxidation mechanism is still the same.

Among the oxidation products, it is important to underline the presence of carboxylic acids, detected after derivatization with SF<sub>4</sub>, and already found also by Carlsson [19]. Acids are produced by scission of the polymeric chain which decreases the molecular mass and lead to a progressive deterioration of the mechanical properties of the polymer.

In figure 5a and 5b ketone and hydroperoxide concentration obtained at increasing ageing time for samples irradiated at 60 kGy with and without Vitamin E are reported. At irradiation doses 30 and 90 kGy similar results were obtained.

It can be observed that the build up of the oxidation products follows the same trend, independently on the presence of Vitamin E, while the total amount differs.

In figure 6a and 6b formation rates of ketones and hydroperoxides are reported. The rates are very high at the beginning of the post-irradiation process, then they decrease very rapidly and they approach zero at 150 hours.

As recently reported [20], the reaction at room temperature between the macro-alkyl radicals formed during irradiation and the oxygen dissolved in the polymer can produce ketones through a mechanism which does not involve thermal decomposition of the hydroperoxides.

Unlike thermo-oxidation processes, in these conditions oxidation is not auto accelerated, but it slow down in short time. Termination reactions are related with the radicals decay, which can form a non radical species through not yet clear mechanisms [23].

Figure 5 shows that the concentration of oxidation products is proportional to that of Vitamin E; in the samples with 11 mmol/l of Vitamin E hydroperoxides were impossible to detect, their amount being lower than the detection limit of the instrument. The rate of formation of the oxidation products (figure 6) in the presence of Vitamin E is lower than that of the virgin sample.

Figure 7a and 7b show how the maximum concentration of ketones and hydroperoxides, formed after 2390 hours of post-irradiation oxidation, is affected by the radiation dose and by the amount of Vitamin E. These data are correlated with the initial condition of the process: at the beginning the process is slower, due to the effect of the stabilizer, therefore the total amount of oxidation products is proportional to the amount of stabilizer and such amount can be considered as a parameter to evaluate the stabilizing effect, like the induction time in thermo or photo oxidation processes.

The amount of ketones and hydroperoxides formed into virgin UHMWPE during the post-irradiation time is proportionally higher at 30 kGy than at 60 and 90 kGy. In agreement with this behaviour, it has been reported that at doses higher than 30 kGy, the oxygen is the limiting reactant [20]. Not all the radicals produced at doses higher than 30 kGy can react with oxygen in the initial steps of the process.

When UHMWPE is mixed with Vitamin E, this saturating behaviour is reached at higher doses, being the amount of radicals available to react with oxygen lower.

#### **4. Conclusions**

When e-beam irradiation of Vitamin E stabilized UHMWPE is carried out under inert atmosphere, a competition takes place between vinyl double bonds and Vitamin E to react with macro-alkyl radicals formed upon irradiation. If irradiation is carried out in air, the number of reactive species rises to three, including also oxygen. The rate of the reactions is a function of the concentration of these species.

The interaction between macro-alkyl radicals and Vitamin E results in the formation of an  $\alpha$ -tocopheryl radical, kinetically stable (reaction 5, scheme 1), then in a fast decrease of the amount of macro-alkyl radicals. The reaction between macro-alkyl radical and oxygen produces a peroxy macroradical, set in a defined position on the polymer chain, which can only extract an H atom to form a hydroperoxyde and, again, a macro-alkyl radical. In the

presence of Vitamin E, these reactions are inhibited, but not avoided, due to the decrease in macro-alkyl radicals (which react with Vitamin E) and to the reaction of the peroxy macroradical with Vitamin E (unlikely, considering the lower mobility of the peroxy macroradical compared to that of macro-alkyl radical).

Furthermore, because of the simultaneous possibility of the macro-alkyl radicals to react with Vitamin E or vinyl double bonds, the crosslinking efficiency is diminished.

It must be pointed out that a post-irradiation oxidation process is always initiated, when UHMWPE is treated with high energy radiation, also in the presence of vitamin E and it results in the formation of the same oxidation products. Nevertheless, even if vitamin E cannot completely avoid the formation of the oxidation products, it has a clear stabilizing effect against oxidation of UHMWPE.

It is also important to underline that in the presence of Vitamin E there is a decrease in the crosslinking efficiency, but also a preservation of the material from oxidation and chain scissions, responsible for failures of the prosthetic implants.

## **5. Acknowledgements**

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## Legends to figures

**Figure 1.** Phenol group concentration ( $1210\text{ cm}^{-1}$ ) as a function of radiation dose in a film of UHMWPE + 11 mmol/l of Vitamin E.

**Figure 2.** Trans-vinylene concentration ( $965\text{ cm}^{-1}$ ) as a function of radiation dose: **a)** irradiation process in vacuum; **b)** irradiation process in air.

**Figure 3.** Vinyl concentration ( $909\text{ cm}^{-1}$ ) as a function of radiation dose: **a)** irradiation process in vacuum; **b)** irradiation process in air.

**Figure 4.** Comparison between the oxidation products in GUR 1050 (solid line, oxidation time 215h) and GUR 1050 + 1.1 mmol/l Vitamin E (dashed line, oxidation time 1847h), both irradiated at 90 kGy;

**Figure 5.** Irradiation process in air at 60 kGy: ketone (**a**) and hydroperoxide (**b**) (non-hydrogen bonded plus hydrogen bonded) formation as a function of ageing time at RT.

**Figure 6.** Irradiation process in air at 60 kGy: rate of formation of ketones (**a**) and hydroperoxides (**b**) (non-hydrogen bonded plus hydrogen bonded) as a function of ageing time at RT.

**Figure 7.** Irradiation process in air. Amount of oxidation products after 2390h of ageing time in air at RT as a function of radiation dose: **a)** ketones; **b)** total hydroperoxides (non-hydrogen bonded plus hydrogen bonded).

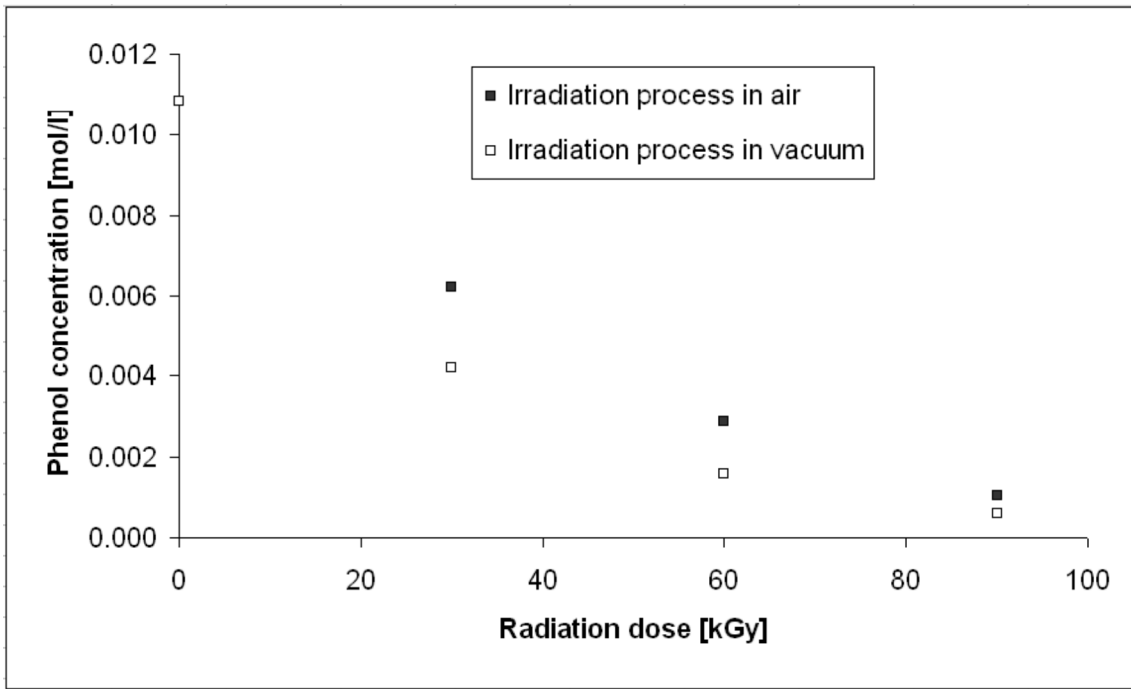


Figure 1

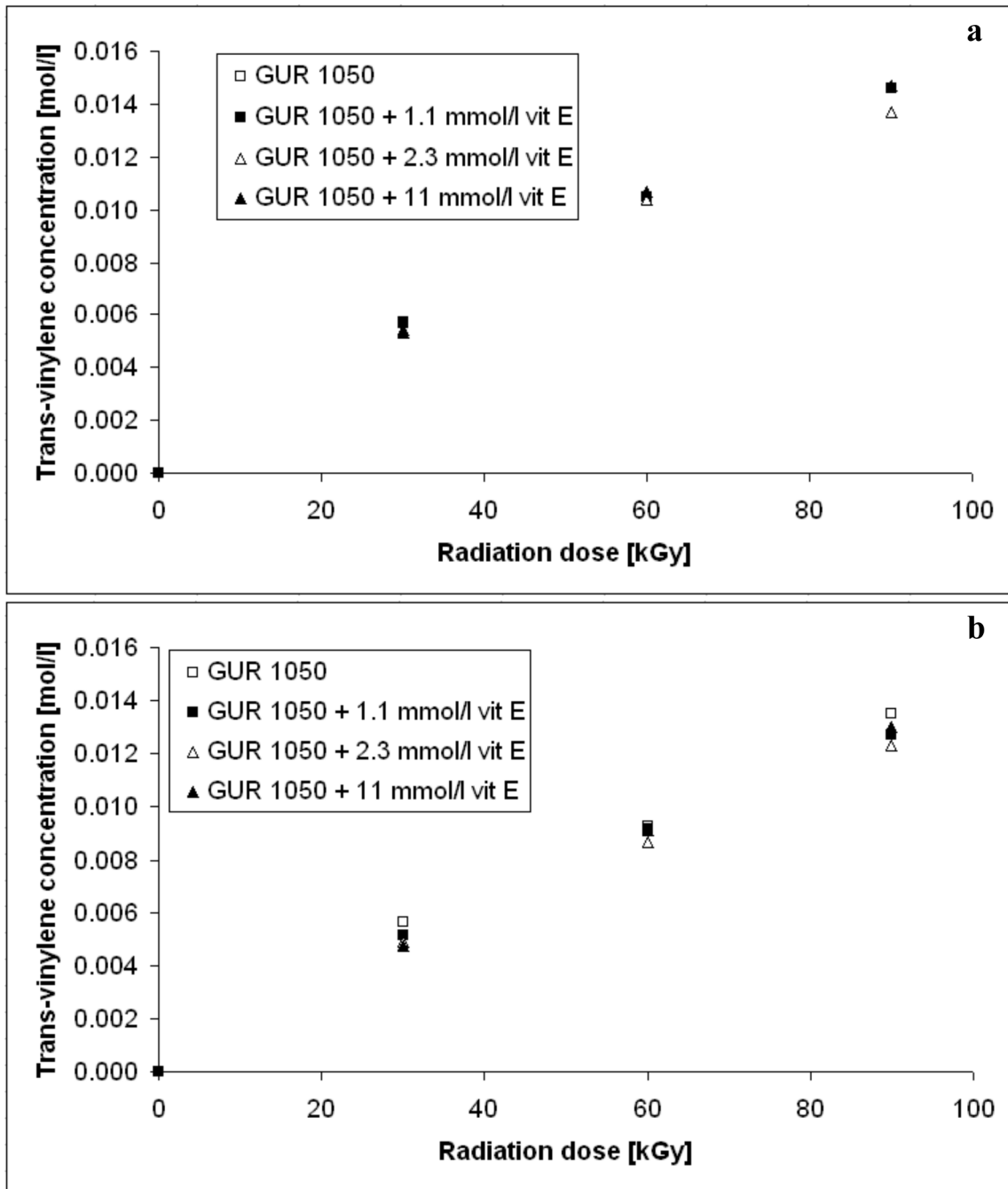


Figure 2

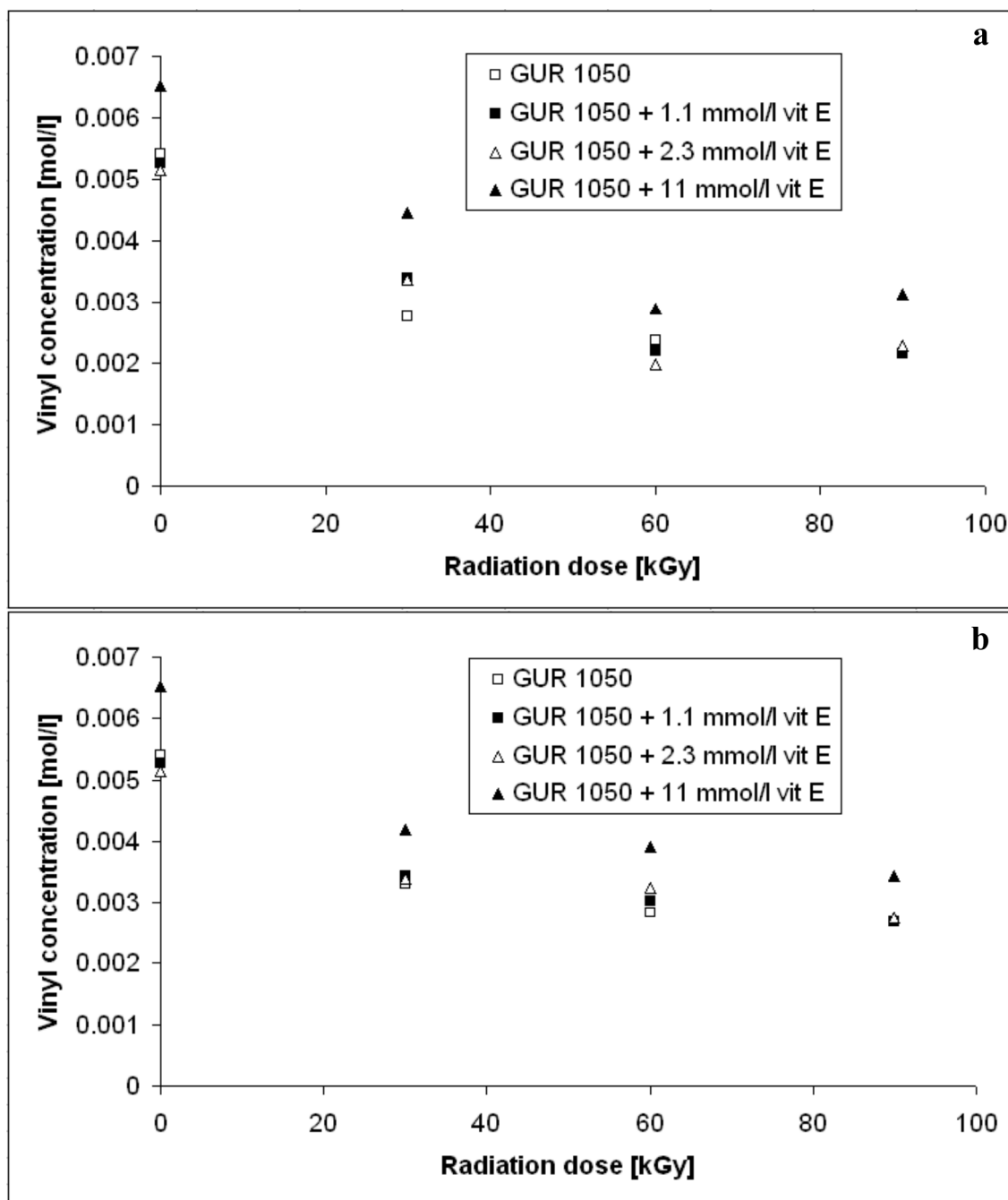


Figure 3

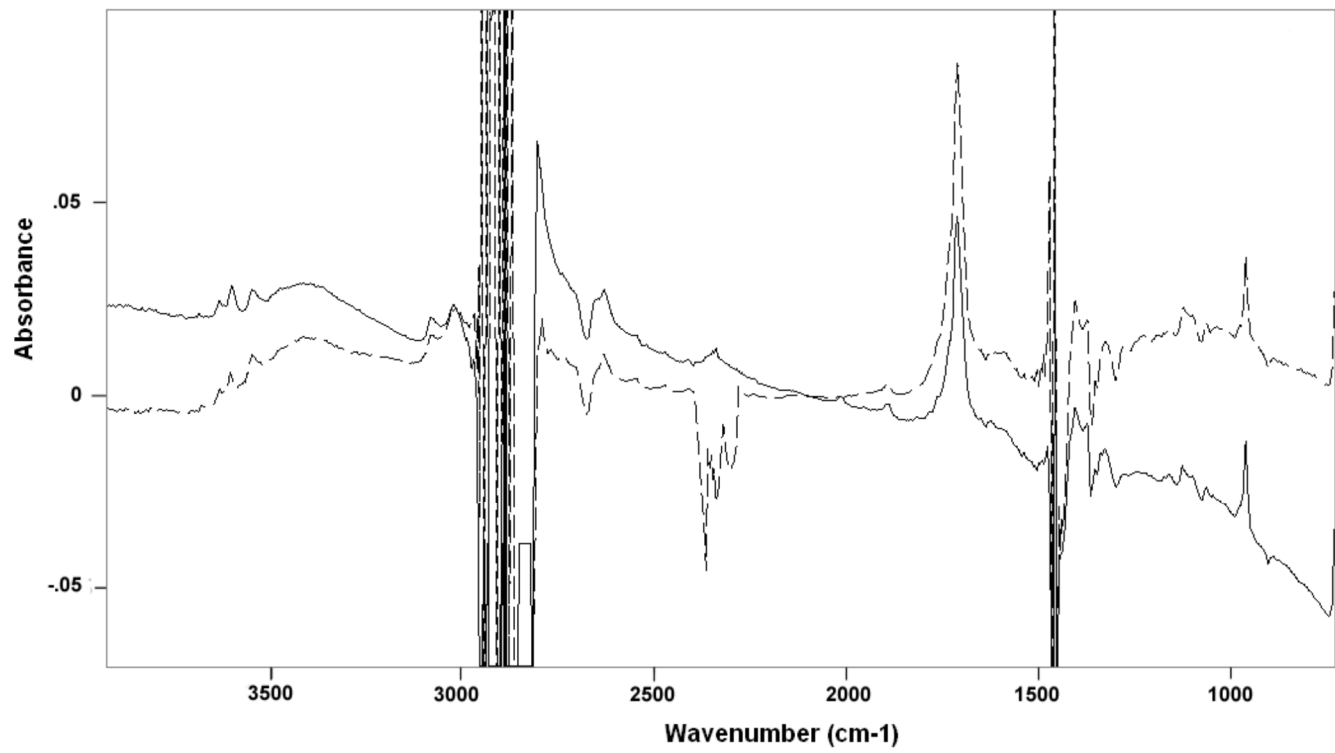


Figure 4

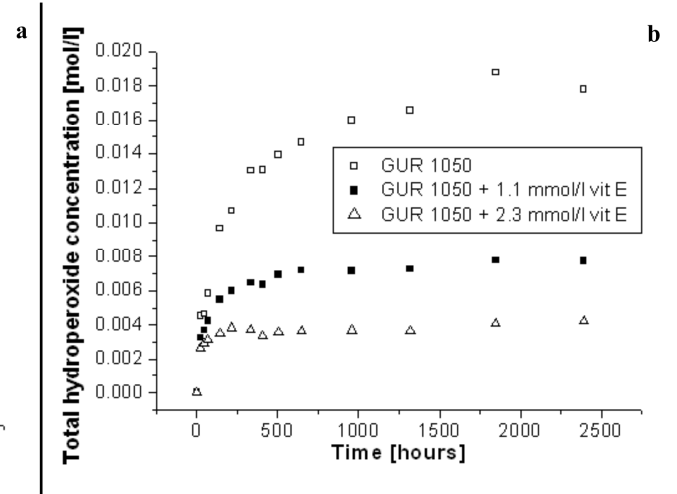
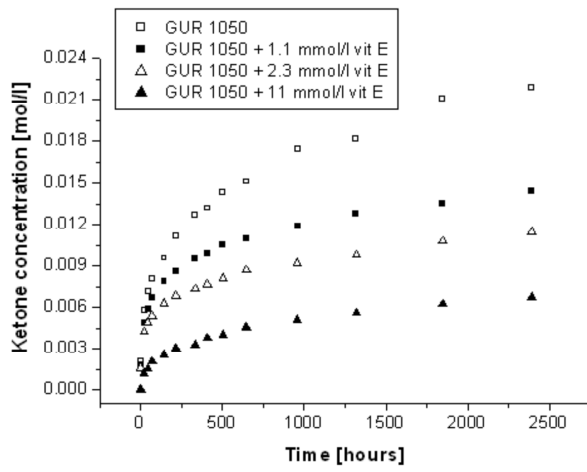


Figure 5

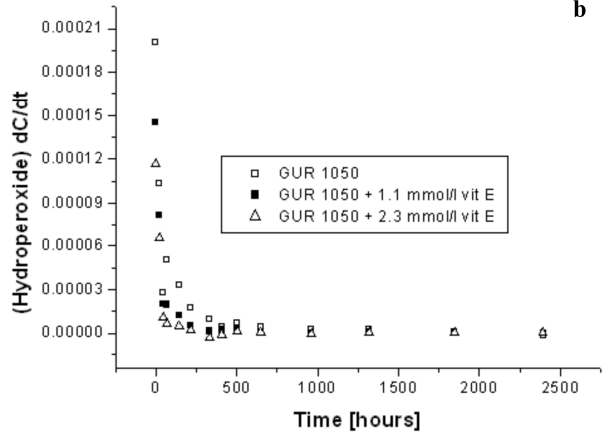
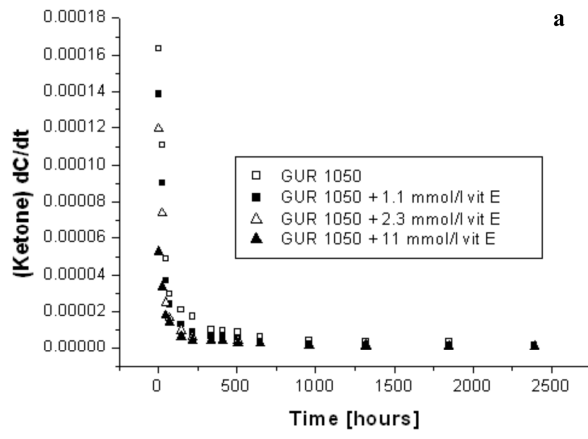


Figure 6

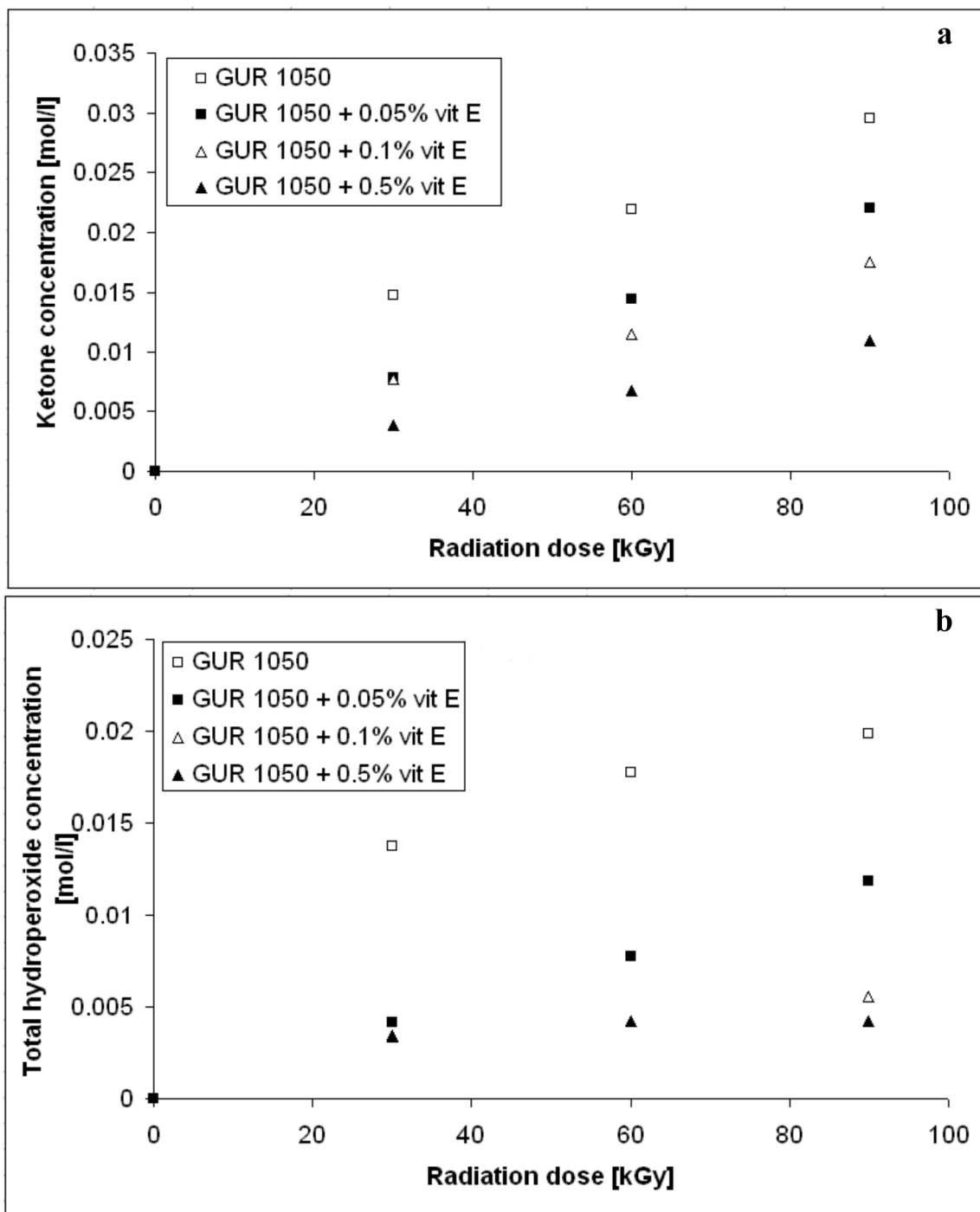
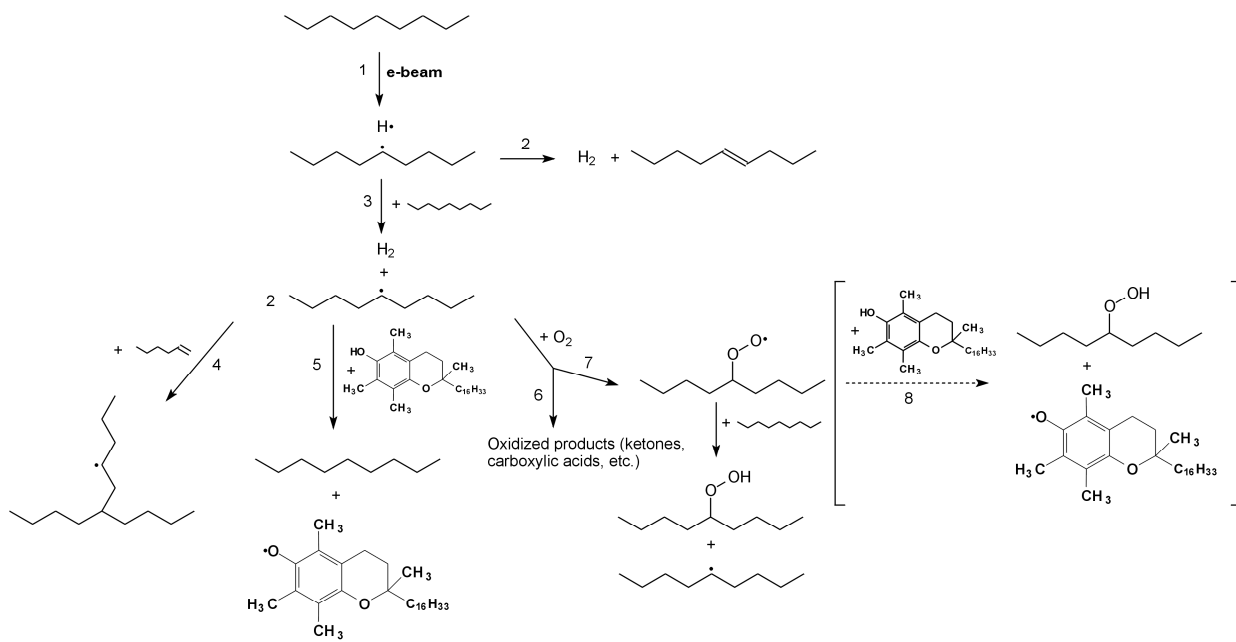


Figure 7





Scheme 1