Can Incorporation of Vitamin E be an Alternative to remelting of radiation Cross-linked UHMWPE ?

Prof. Luigi Costa

Dipartimento di Chimica I.F.M,

Università di Torino, Italy

UHMWPE powder (more than 75 % of crystallinity)

↓ Compression molding or ram extrusion

Bar or sheet (crystallinity 50-52% and under stress)

Mechano-oxidative degradation
Ester and acids formation

↓ Shaping of the prosthesis

Prosthesis

Degradation induced by γ or electron beam and post irradiation oxidation

↓ Sterilization and crosslinking by γ radiation, e-beam

Ready to implant prosthesis

Shelf ageing and *In vivo* degradation

↓ Life in the shelf and *in vivo*

Retrieved prosthesis

Eto

Sterilization and crosslink treatments induce oxidation in UHMWPE.

Today two systems are used to reduce the oxidation process:

- the first is the heat treatment
- the second is add vitamin E

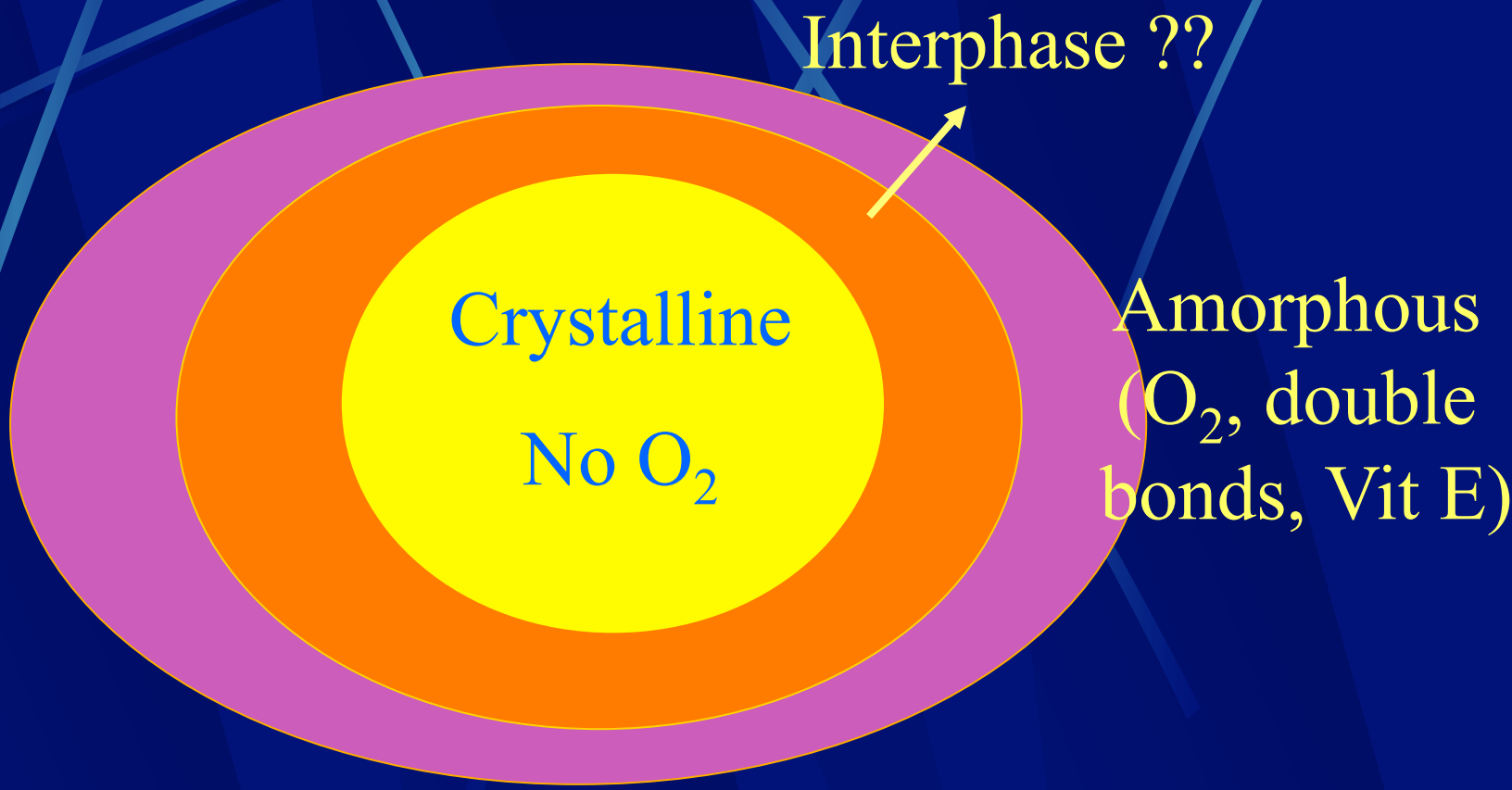
If vitamin E is used, is it possible to eliminate the heat treatment?

Why we wish to eliminate the heat treatment.

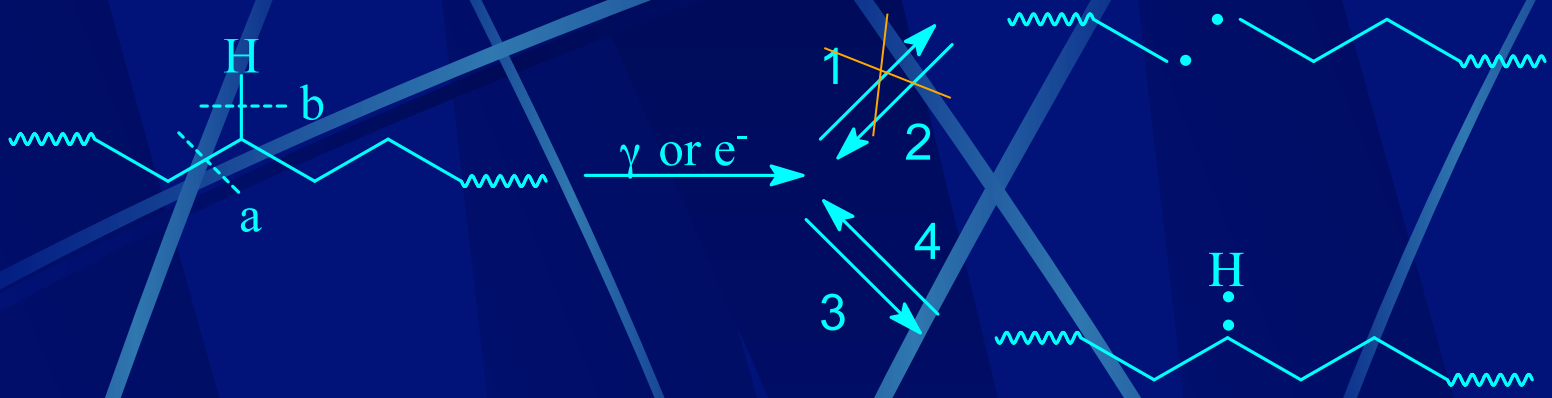
To add vitamin E means: more life for the prosthesis

The mechanical properties, particularly, the fatigue resistance changes, decreases, with the heat treatment.

In the UHMWPE three phases are present:



First process of macroradicals formations



γ radiation or e^- beam (High energy radiations 10^3 times the energy of C-C): reactions 1 and 3 happen at very low temperature

The macroradicals produced are in solid state (very low mobility of the polymeric chain) therefore the reactions 2 and 4, exothermic process, are possible. Due to the mobility of the H° reaction 4 is less probable

Reaction of secondary alkyl macroradicals. (R°)

Producion of H_2 , sec macroalkyl radicals and vinylen double bonds

Reaction 5: ΔH= -280 kJ/mole ΔS≈0

Reaction 6: ΔH= -28 kJ/mole ΔS≈0

R° = [0.1*10^{-3} moles/kg for 10 kGy]

*Trans v*inylene = [2*10-3 moles/kg for 10 kGy] +
cis vinylene

From the literature:

-The R° are produced in all three phase and are mobile in the amorphous and crystalline phase

-In the amorphous phase the R° lifetime is very short

-In the crystalline phase the R° lifetime is longer (~ 10 hours) and it transfer to the amorphous phase

-During the transfer process of R° allyl macroradicals are produced, more stable then alkyl macroradicals

I. Carpentieri et al" Post-irradiation oxidation of different polyethylene" Poly. Degr. Stab 96, (2011) 624-629

What products are present in amorphous phase of virgin UHMWPE .

Vinyl double bounds [~ 5-10 mmol/l]

tertiary C atom = concentration similar to vinyl double bonds [~ 4 mmol/l]

O_2 [~ 0.5 mmol/l]

Vitamin E [0.1% = 2 mmol/l]

The radical cycle process is described

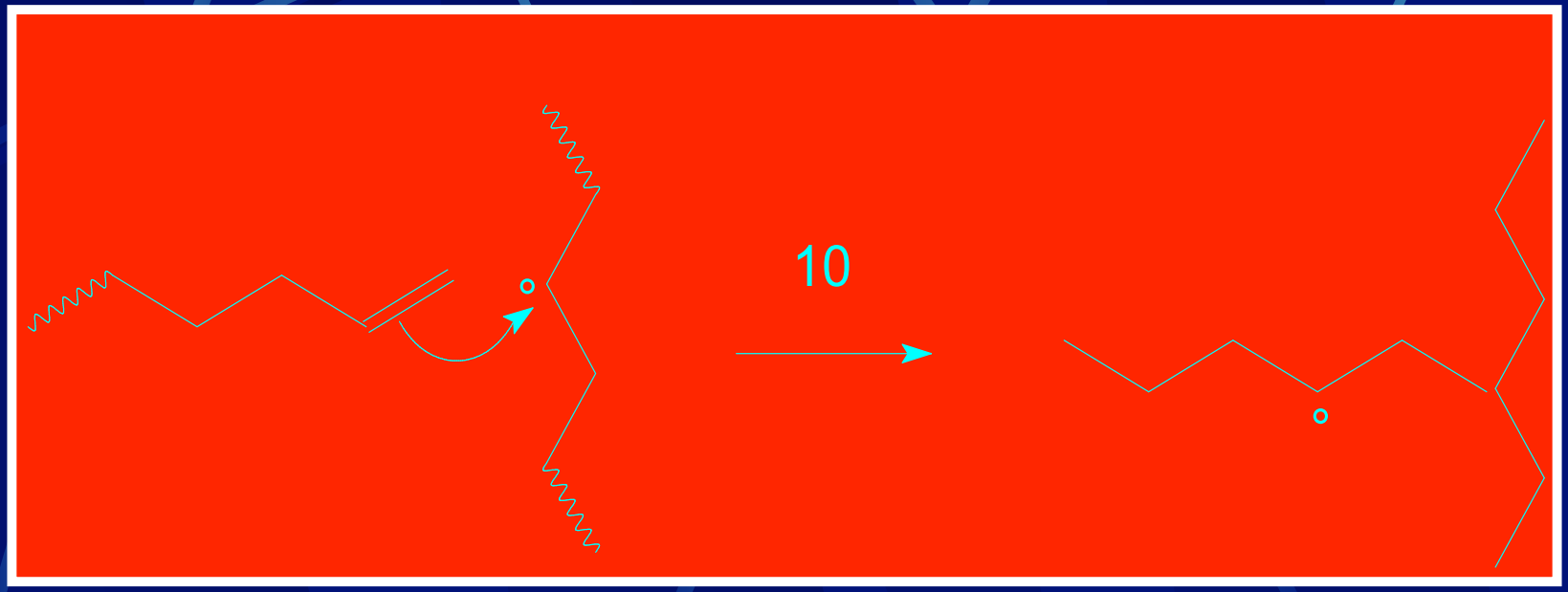
Initiation	Production of macroradicals
Propagation	R° + Species ==> RH + Species°
Termination	????

The rate of propagation reaction is $= K\ [R°]\ [Species]$

$K = \mathbf{A}\ e^{(-Eatt/RT)}$ E_{att} for radicals reaction is very low

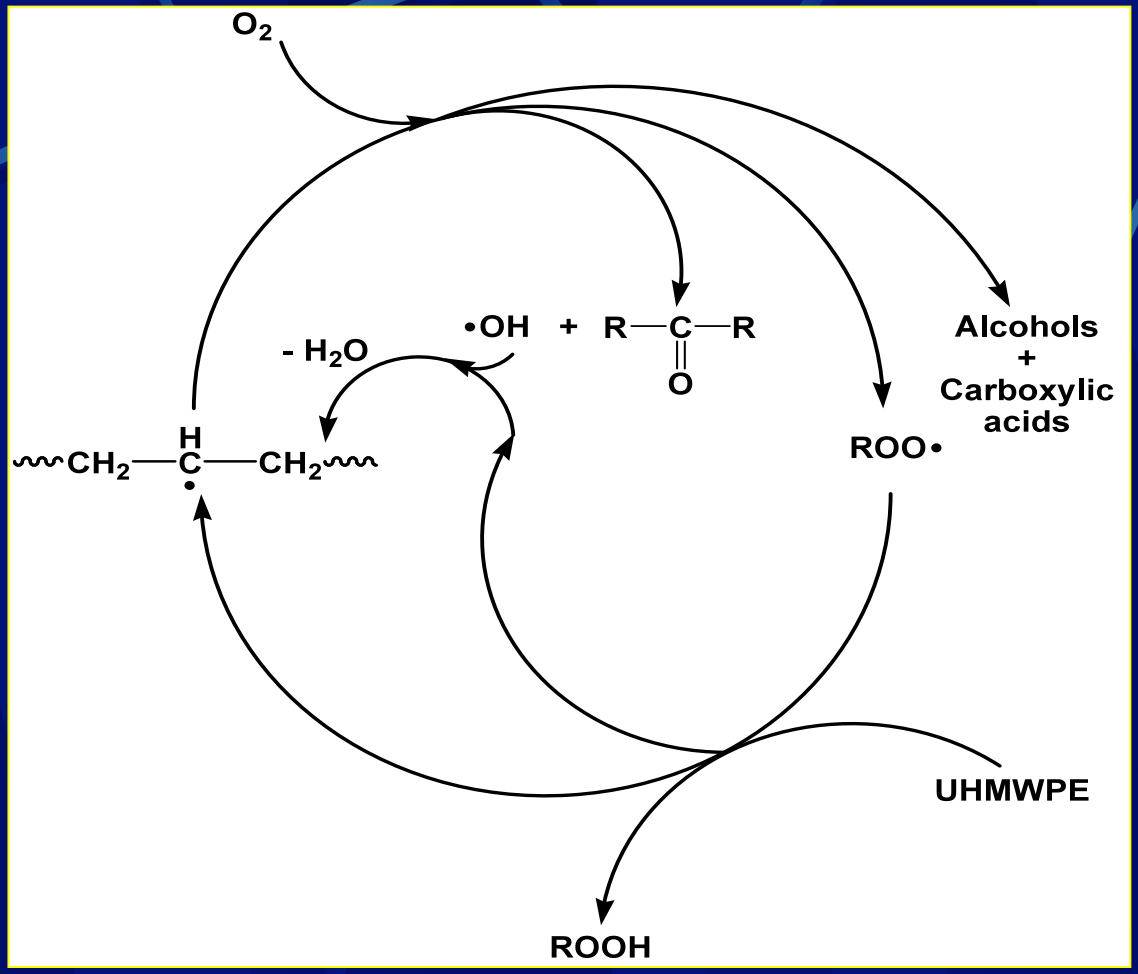
A Pre-exponential factor is relate to the collision facility between the two species

Crosslink process



Vinyl double bonds decay and formation of Y crosslinking

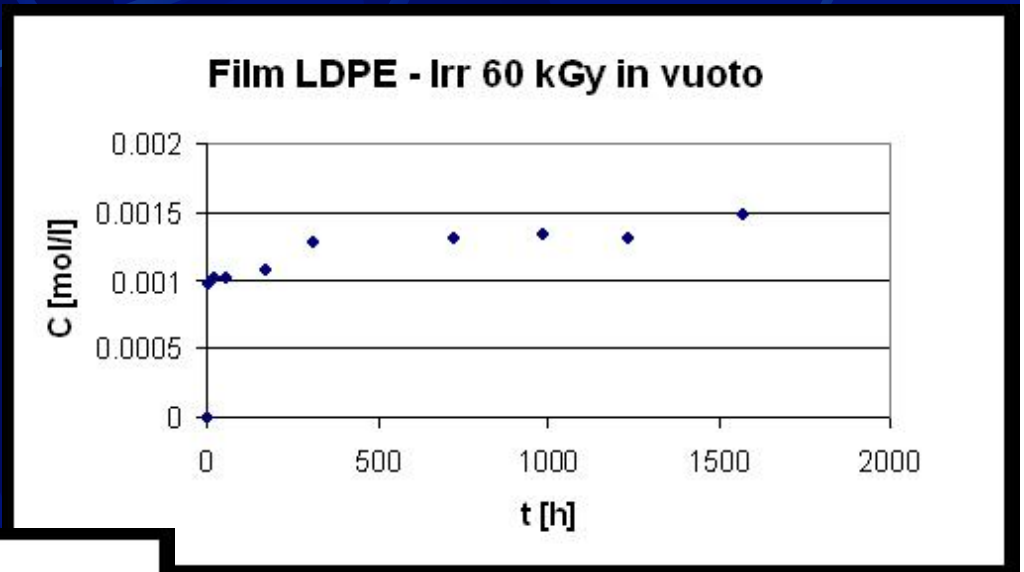
The oxidation cycle (propagation reaction)

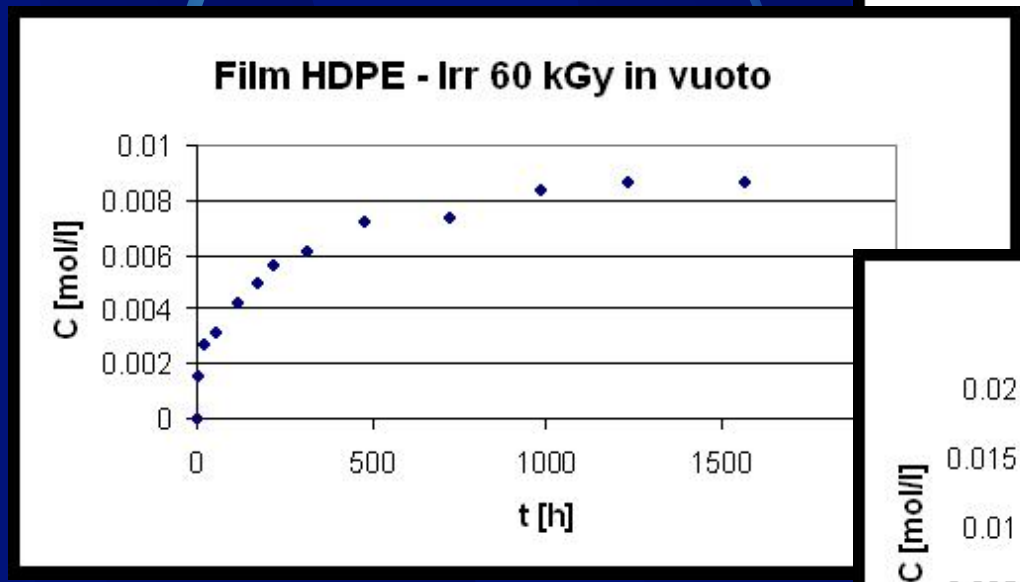


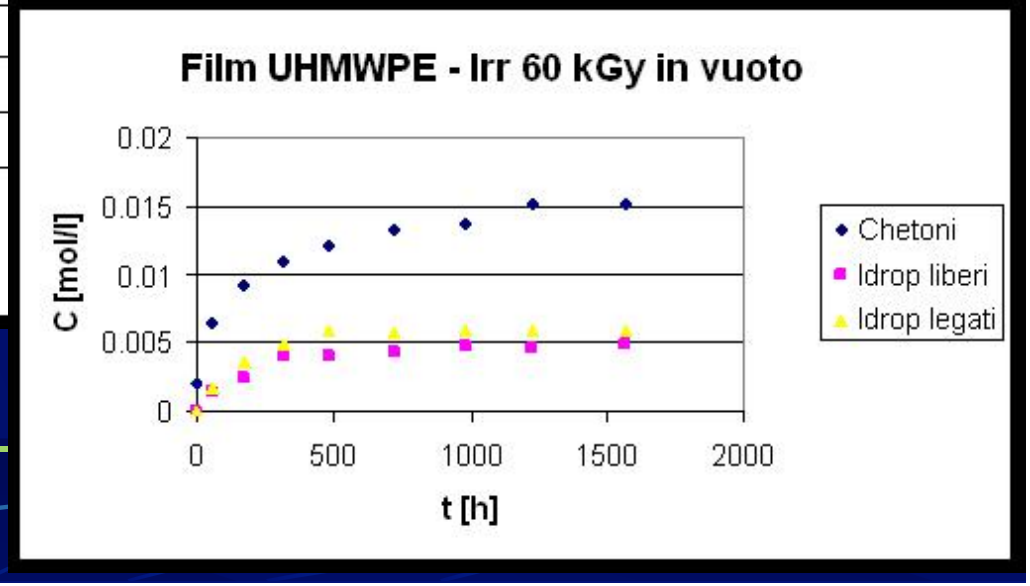
L. Costa I. Carpentieri, P. Bracco, "Post electron-beam irradiation oxidation of orthopaedic UHMWPE", Polym Degr. and Stab. 2008, 93, 1695

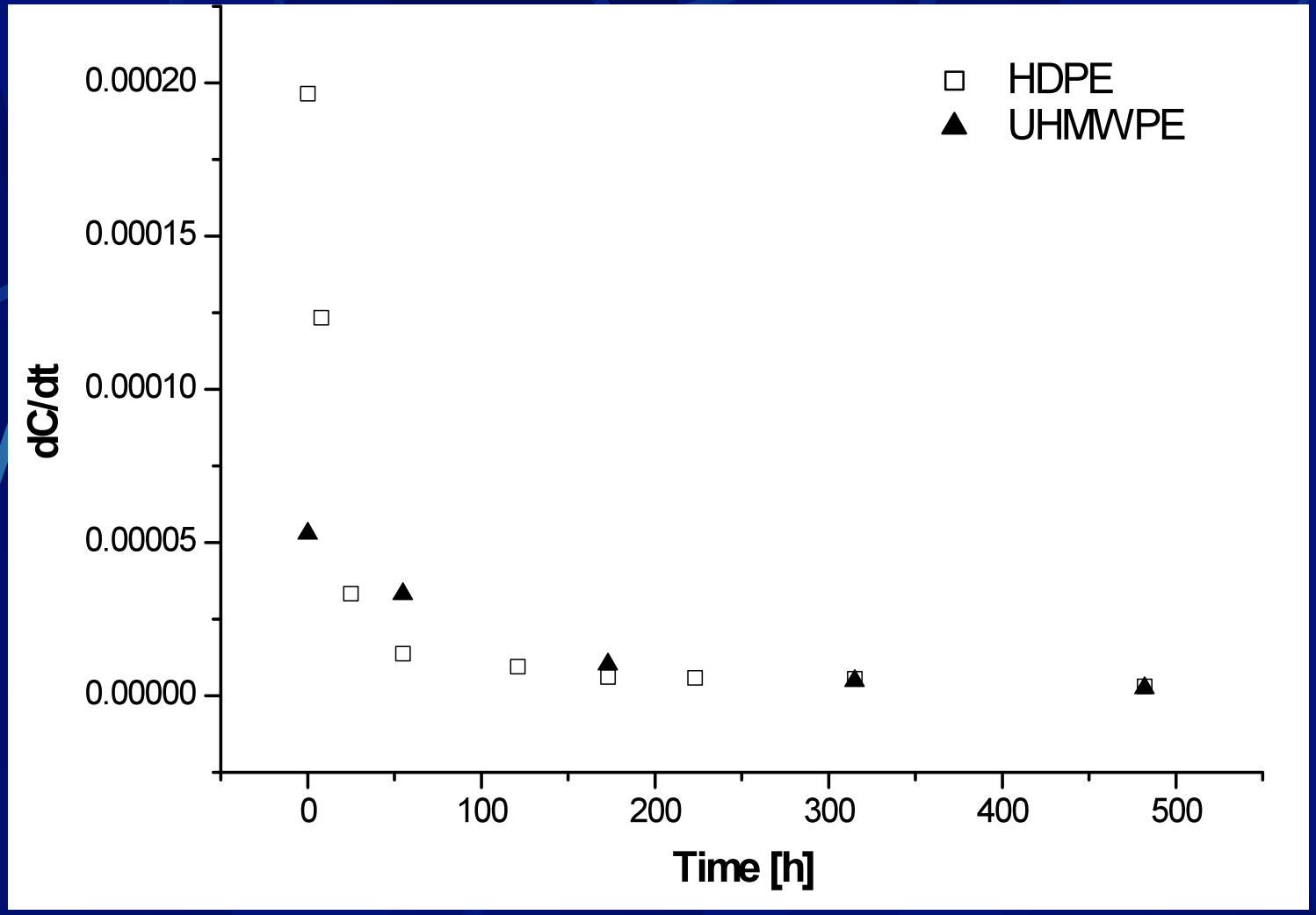
VLLDPE no ox

LLDPE few ox









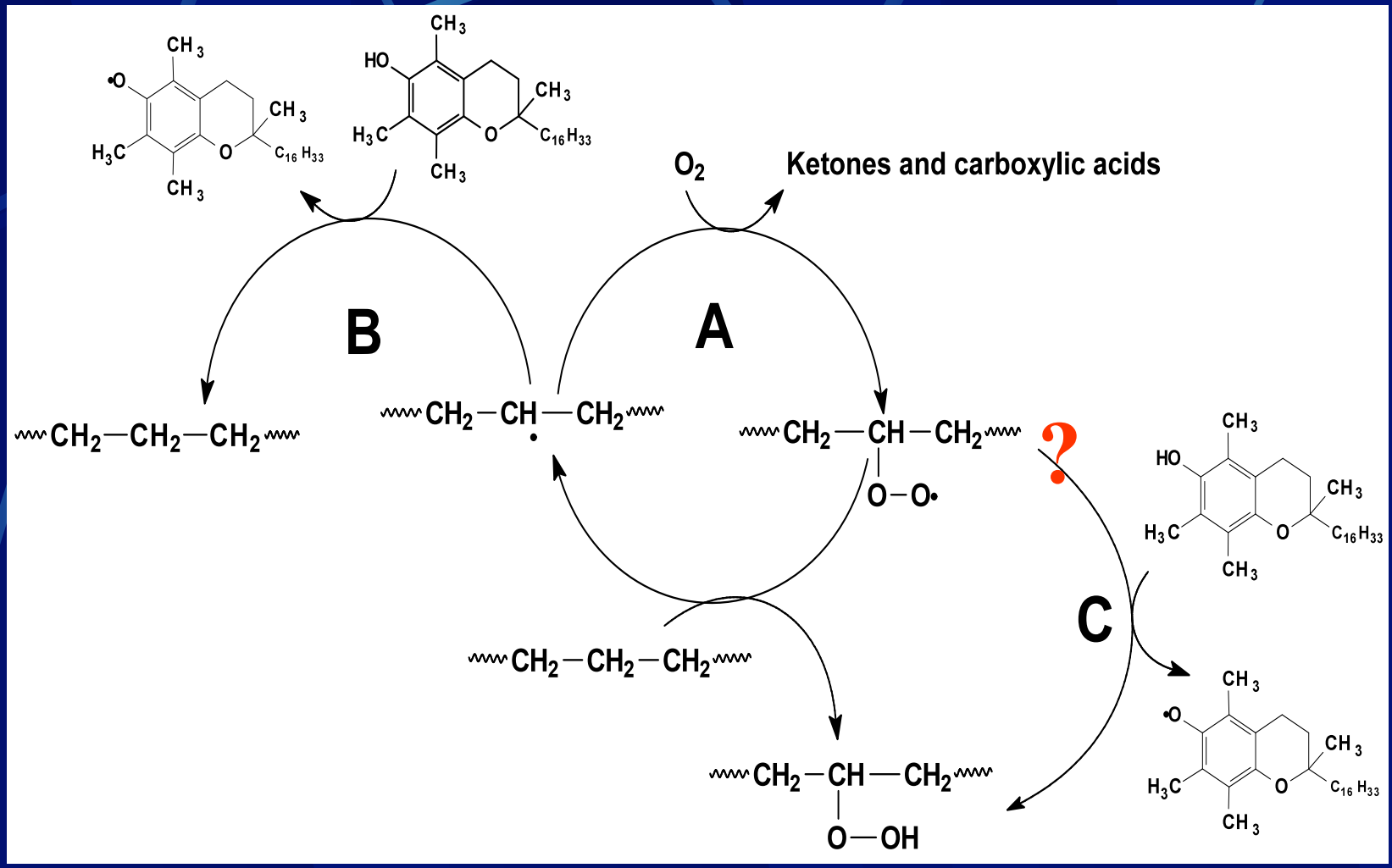
Rate of formation of ketones as a function storage time in air at RT

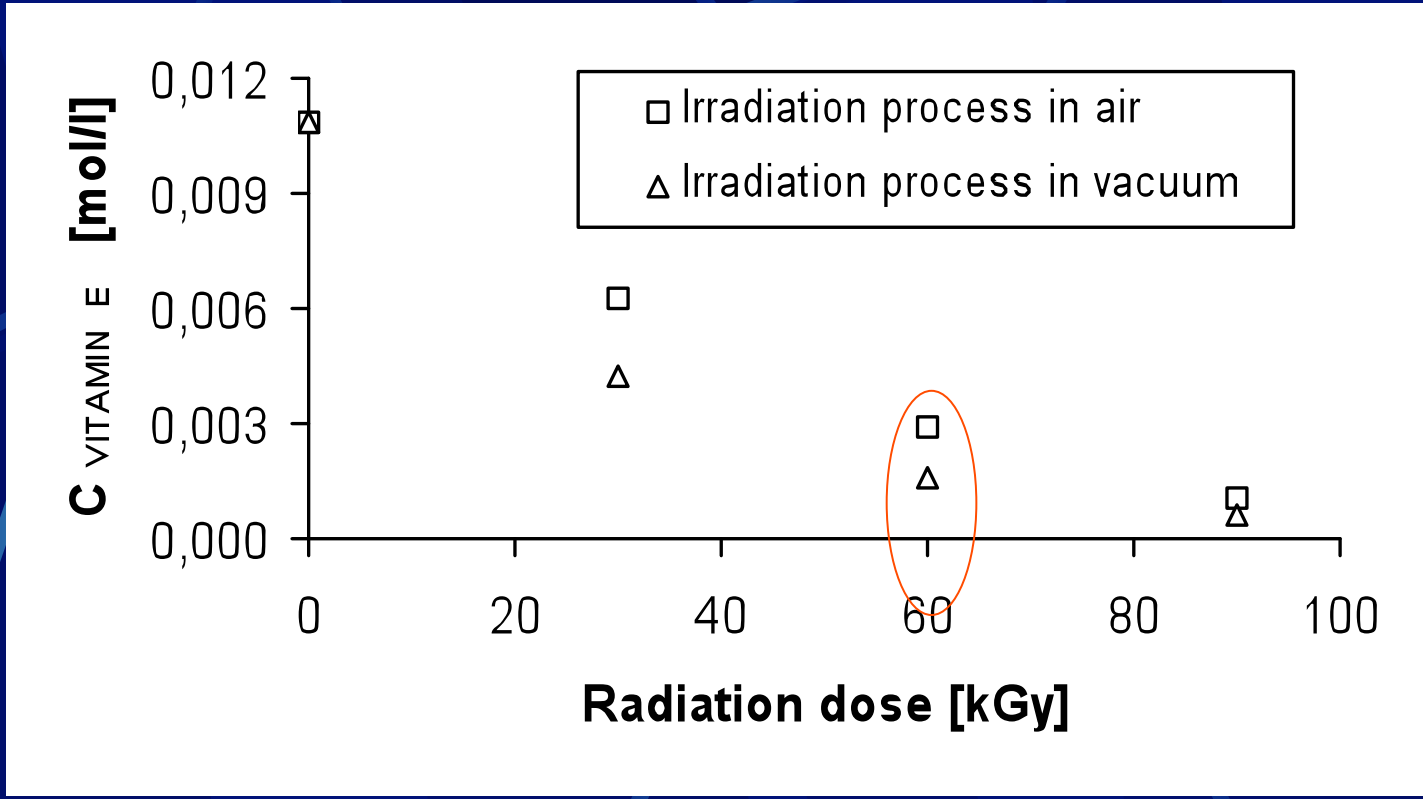
There is a termination reaction:

$$R^{\circ} + ROO^{\circ} \Rightarrow ROOR$$

ROOR is product thermally not stable

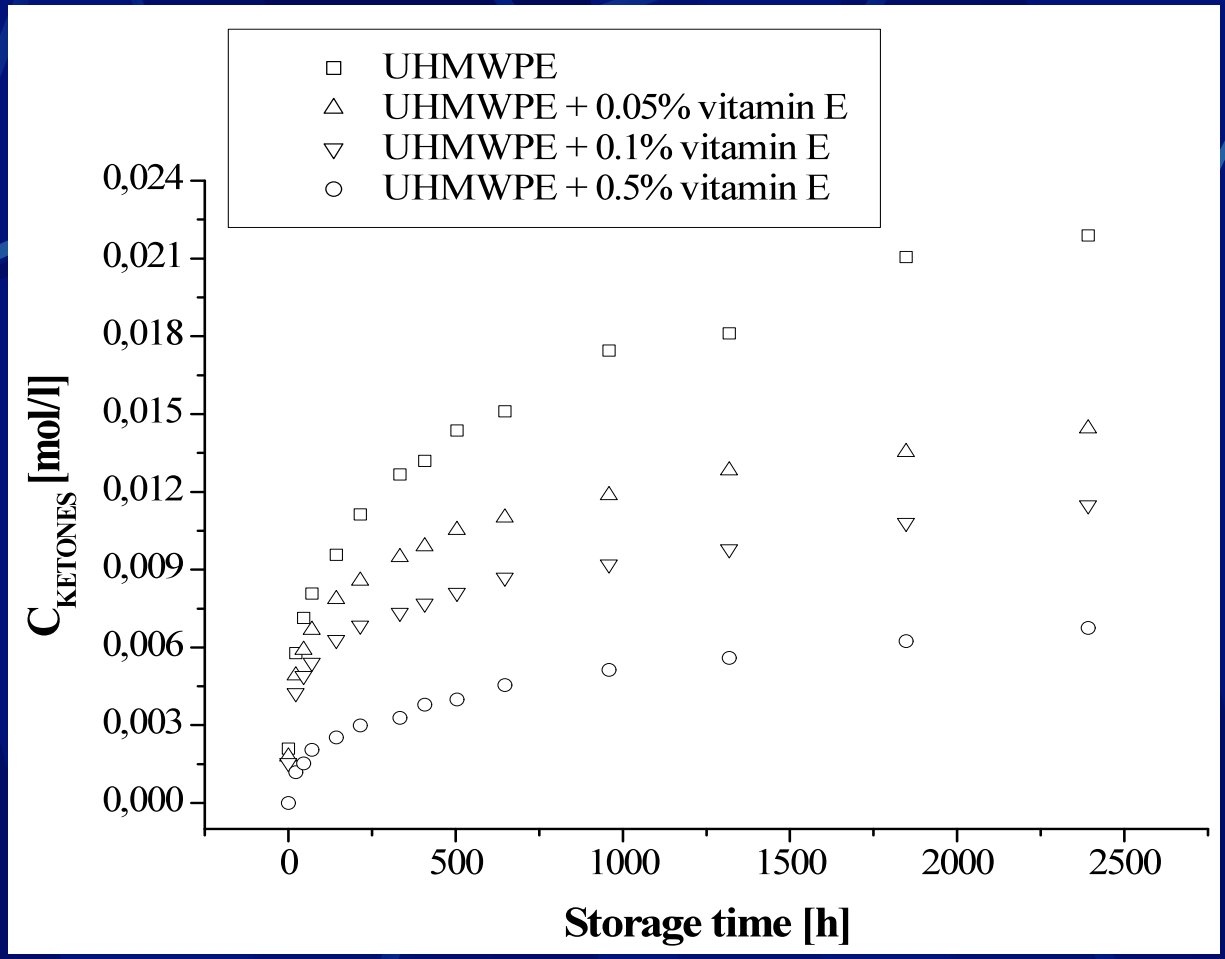
Oxidation cycle in presence of Vitamin E



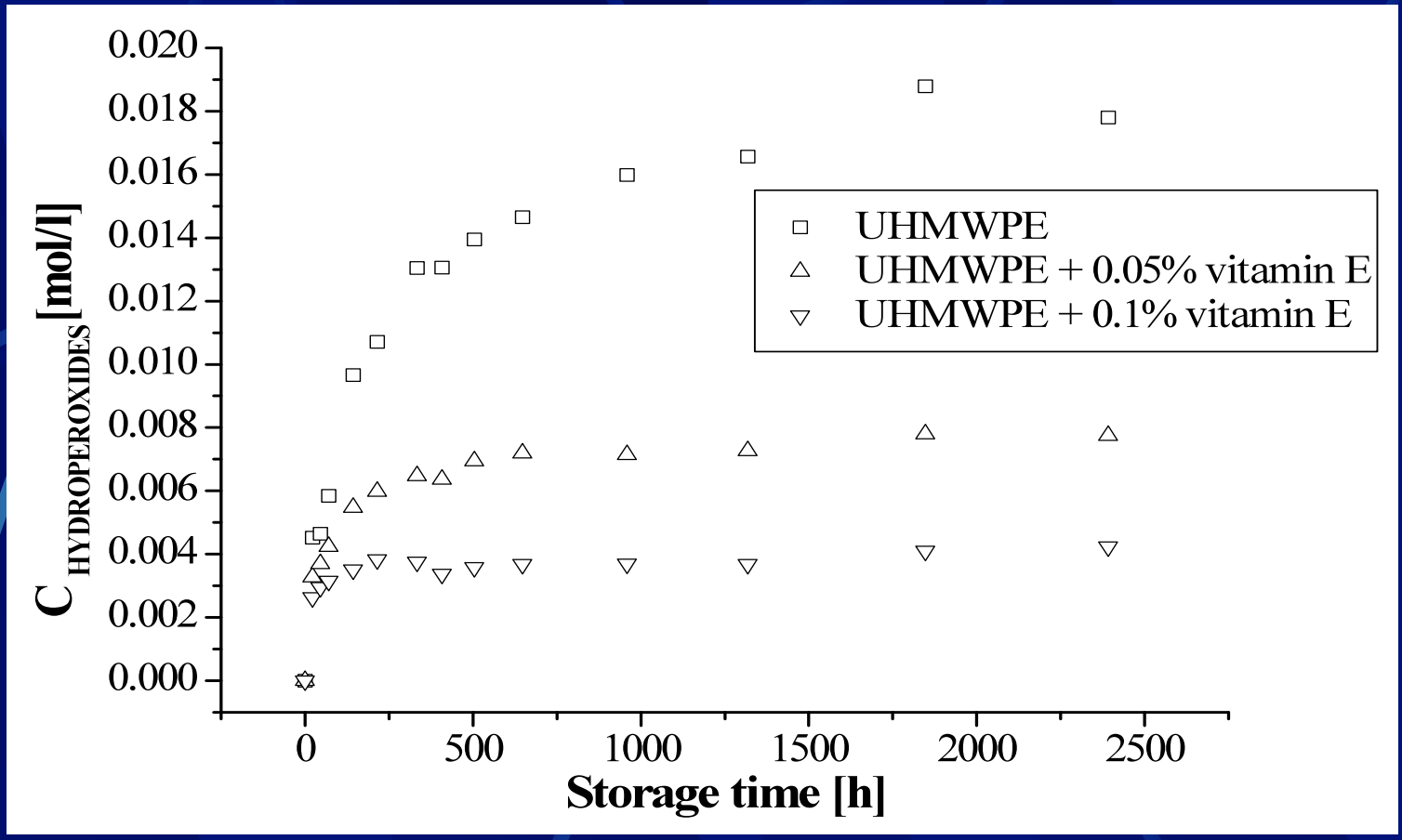


The Vitamin E consumption is 1 mmol/10 kGy

Film of UHMWPE + 0.5% vitamin E: vitamin E consumption of OH species as a function of radiation dose.

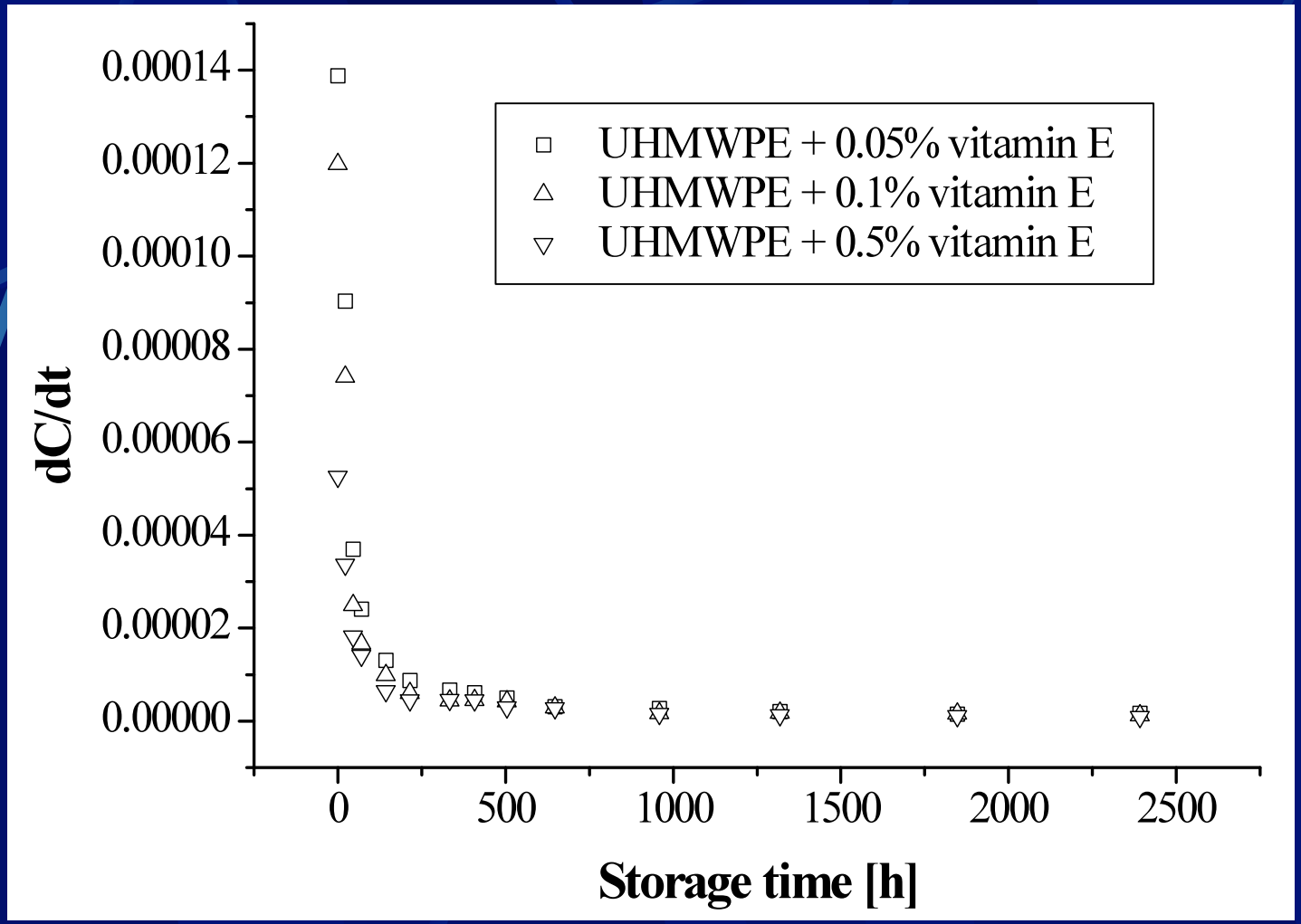


Ketone concentration as a function of amount of vitamin E and of storage time in air at RT. The samples are irradiated to 60 kGy in air.



Hydroperoxides concentration as a function of amount of vitamin E and of storage time in air at RT. The samples are irradiated to 60 kGy in air.

L. Costa I. Carpentieri, P. Bracco, "Post electron-beam irradiation oxidation of orthopaedic UHMWPE stabilized with Vitamin E" Poly. Degr. Stab. 2009, 94, 1542-1547



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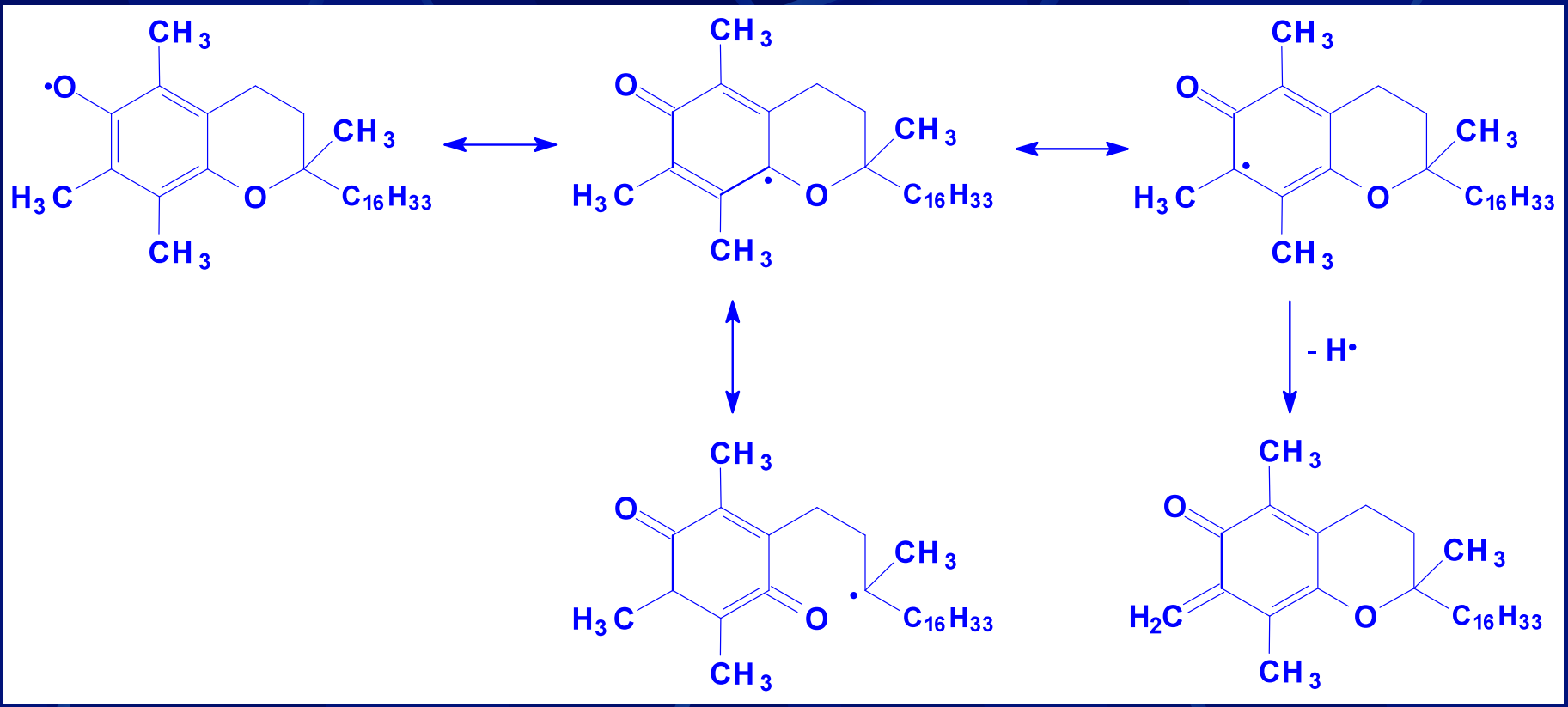
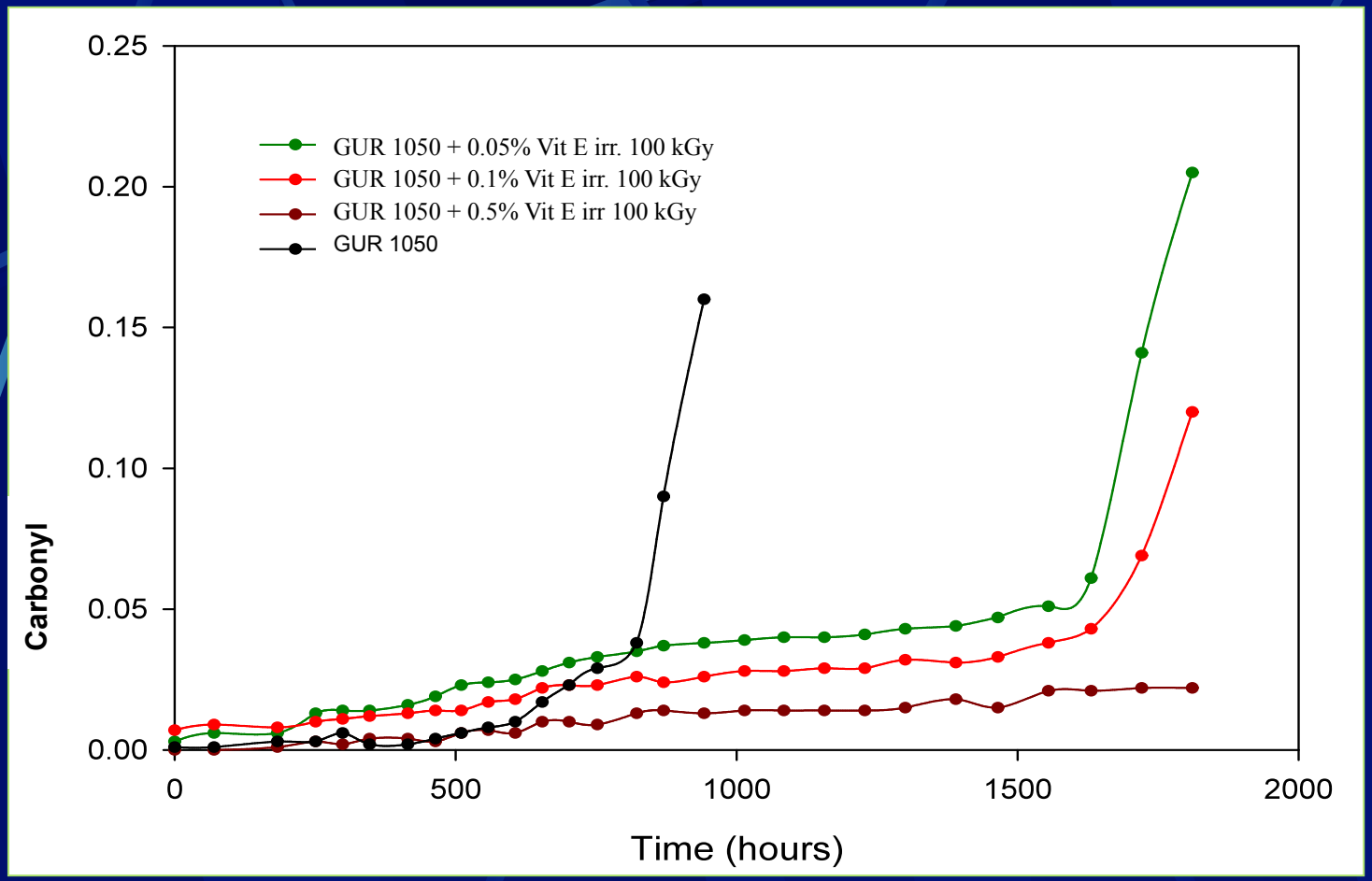


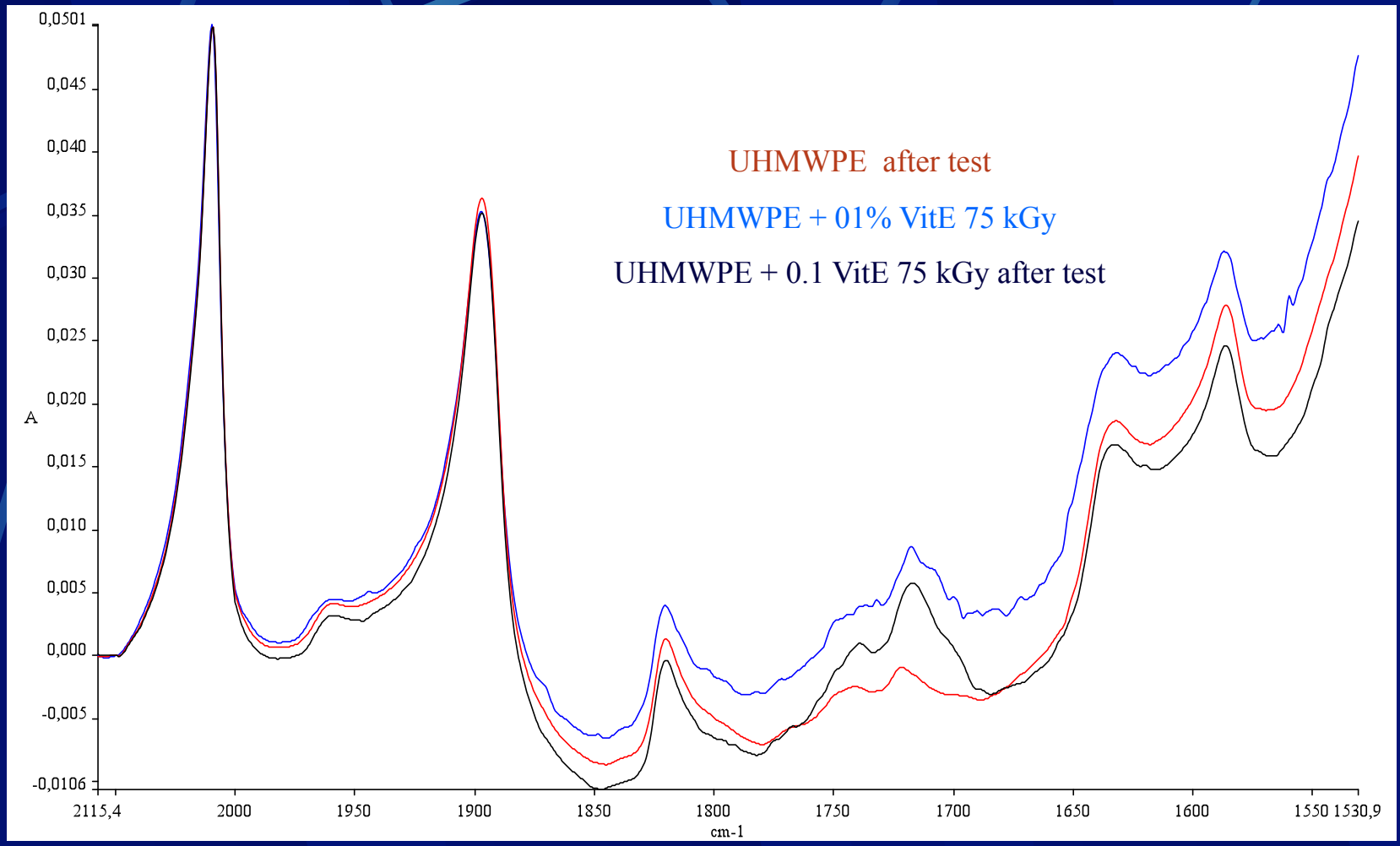
Vit E induces termination reaction, more efficient, therefore it reduces the oxidation process

Thermal oxidation in oven at 95°C



P. Bracco, V. Brunella, M. Zanetti, M.P. Luda, L. Costa, "Stabilisation of UHMWPE with vitamin E ", Polym Degr. and Stab. 2007, 92, 2155-2162.

ASTM F2003-02 after 28 days



The questions was:
Can Incorporation of Vitamin E be an Alternative to remelting of radiation Cross-linked UHMWPE ?

My answer is:

Yes, it can

Acknowledgements

to the students

I.Carpentieri, S. Cordero, A. Pistone, S. Possamai, F. Savognian, D. Elena, Longo, R. Vallero, M. Montechian, E. Carena, A. Romagnolo, F Battaglio, S. Chiaberge, Peditto, F. Fasano, L. Sidoti, E. Demartino, M. Ponchione, G.Murgia, F.Nespola.

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Thank you

At the present time, the use of stabilizers seems to be compulsory for protection against degradation……whose activity can be reduced by using antioxidants as the human body itself produces and uses. For example, vitamin E is certainly biocompatible and could be tested as an antioxidant in PEs

L. Costa, M.P. Luda, E. Brach del Prever, M. Crova, P. Gallinaro "In vivo biotic oxidation of retrieved UHMWPE." Biomaterials, 39 , 1371-1386 (1998)