UHMWPE Oxidation and Stabilisation during e-beam irradiation

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3rd UHMWPE INTERNATIONAL MEETING

"Polyethylene in total joint replacement systems: Concerns and solutions"

Plan of the presentation

- The e-beam irradiation reaction in vacuum
- The UHMWPE post-irradiation oxidation induced by e-beam
- The UHMWPE stabilisation against oxidation and post-irradiation oxidation.

Physical characteristic of orthopaedic UHMWPE

Molecular mass > 2.000.000

Crystallinity original powder > 75%

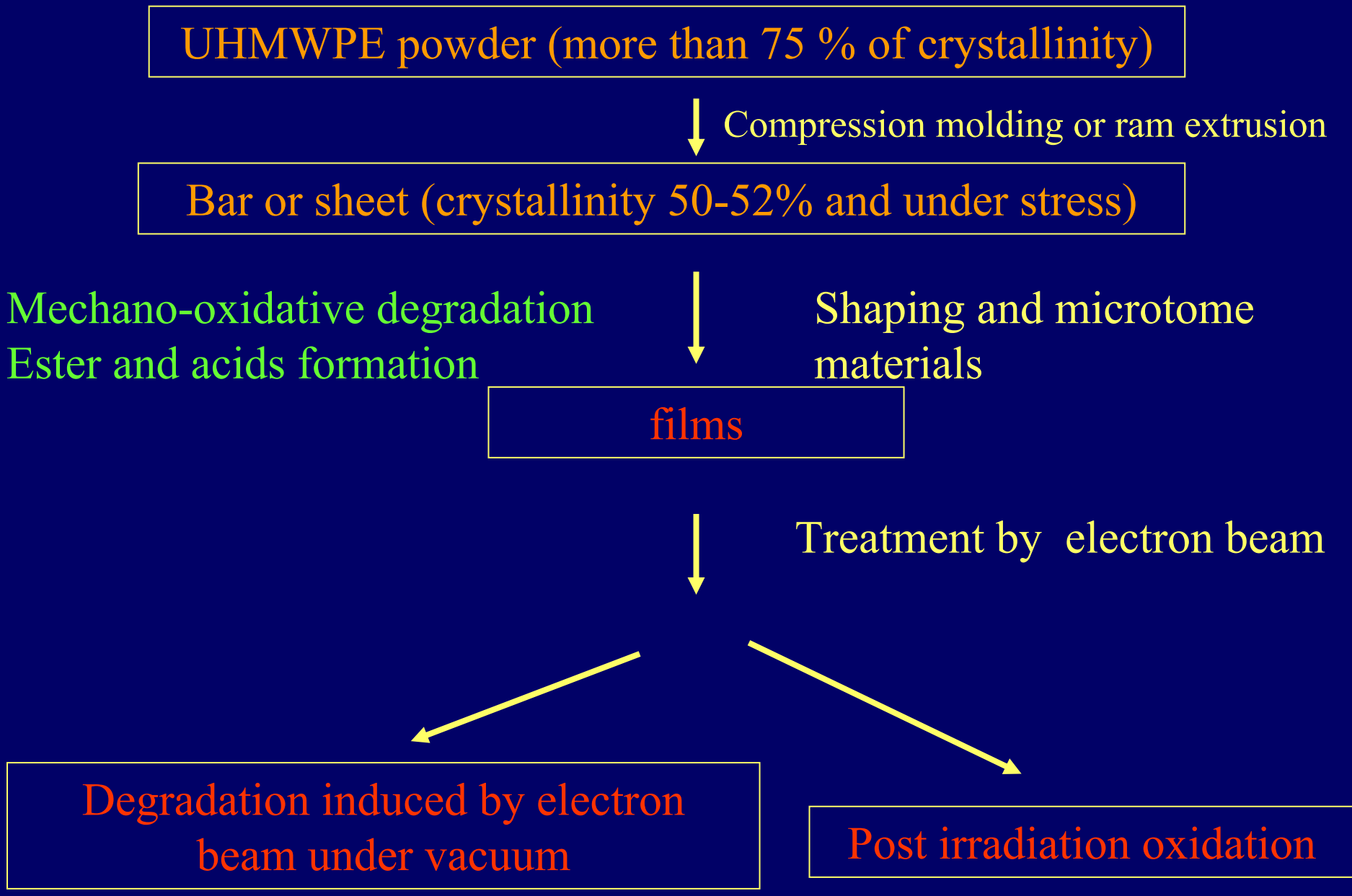
Bar and plate around 50%

Density 0.927-0.944 g/cm^3

Glass Transition -70°C

Melting interval 90°-150°C

Very high viscosity of the melt


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 and microtome
materials
films
Treatment by electron beam
Degradation induced by electron
beam under vacuum
Post irradiation oxidation

Materials: Gur 1020 or 1050 powder prepared by Ticona and machined by Orthoplastics Perplas or Poly Hi Solidur-MediTECH Division

The film are prepared by microtome in air. The thickness is around 160 micron

FTIR Perkin Elmer 2000, 16 scan. Spectra are normalised at 0.05 A at 2020 cm-1. We work with difference spectra. In this case we have good spectra with absorbance difference of 0.001

Irradiation with e-beam at Bioster 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.

Identification of oxidised species by IR analysis

Alcohols and hydroperoxides were measured at 3630, 3550 and 3420 **cm**

and converted to nitrites and nitrates respectively, by reaction wit
gaseous NO in absence of oxygen.

$$RCH_2OH + NO \rightarrow RONO$$
$$RCOOH + NO \rightarrow RONO_2 \ (1630\ cm^{-1})$$

Carboxylic acids were estimated as acid fluorides after reaction with SF4.

RCOOH + SF4 → RC(O)F (1848 cm-1)

Rif. J. Mallegol, D.J. Carlsson, L. Deschenes PDS 73 (2001) 269

After high energy treatment (gamma or e-beam) in vacuum in function of the dose :

Presence of secondary macroradicals, free to move inside the UHMWPE amorphous phase, less free in the crystalline phase.

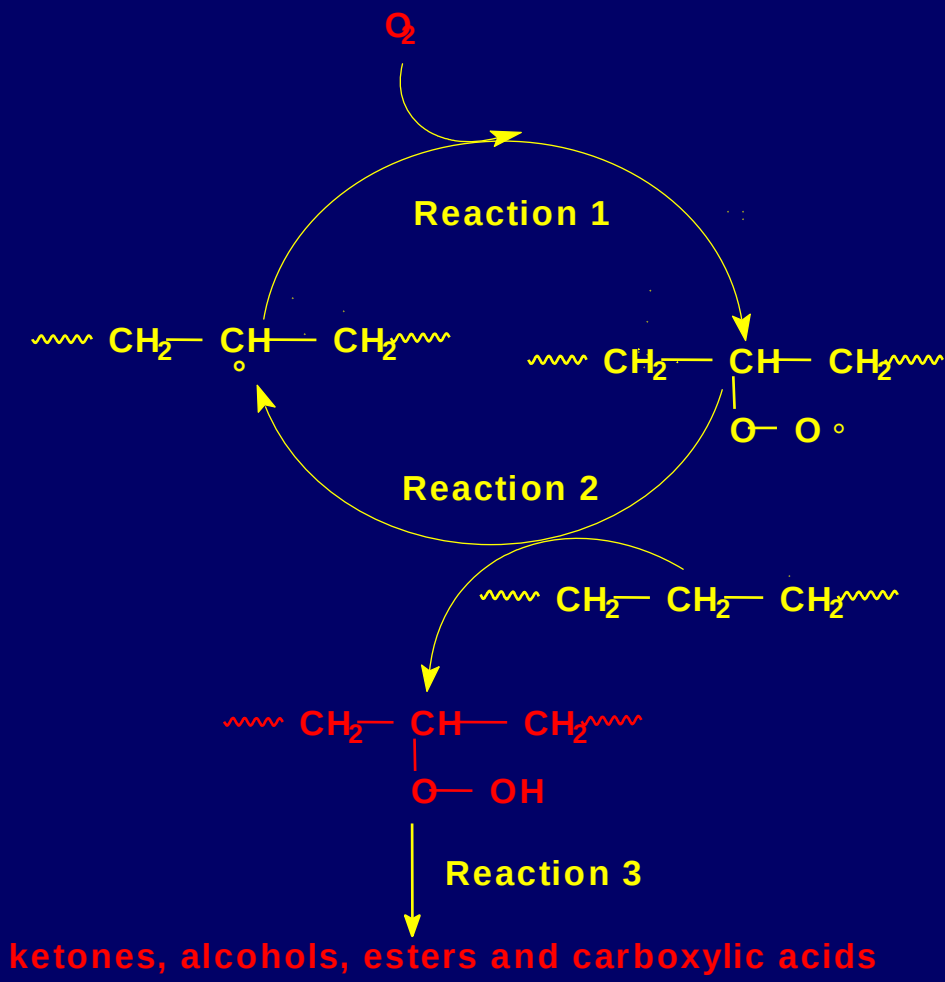
Presence of allylic and probably tertiary macroradicals in amorphous phase

Less vinyl double bonds and some polymeric chain are crosslinked

New *trans* and *cis* vinylene double bonds

Increase of the crystallinity, from 50% to 54% in function dose

Oxidation in polymer solid state.



R° macroradicals move to O2 and form ROO° fixed in the polymeric chain that can abstract the H and form ROOH and new sec macroradicals free to move

The rate of oxidation process is describe as :

$$V = K\,[R^{\circ}][O_2] \text{ at } T = \text{constant}$$

[R°] measurable only in radiation process

[O_2] depend on solubility of O_2 in the polymer amorphous phase

$K = A\, e^{-Eatt/RT}$

Which is the value of A?

Function of effective collision between the species (Oxygen and Radicals). Any problems in gas phase or in solution. Problems are in solid state.

This concept is valid for all the reaction that happen inside the polymers

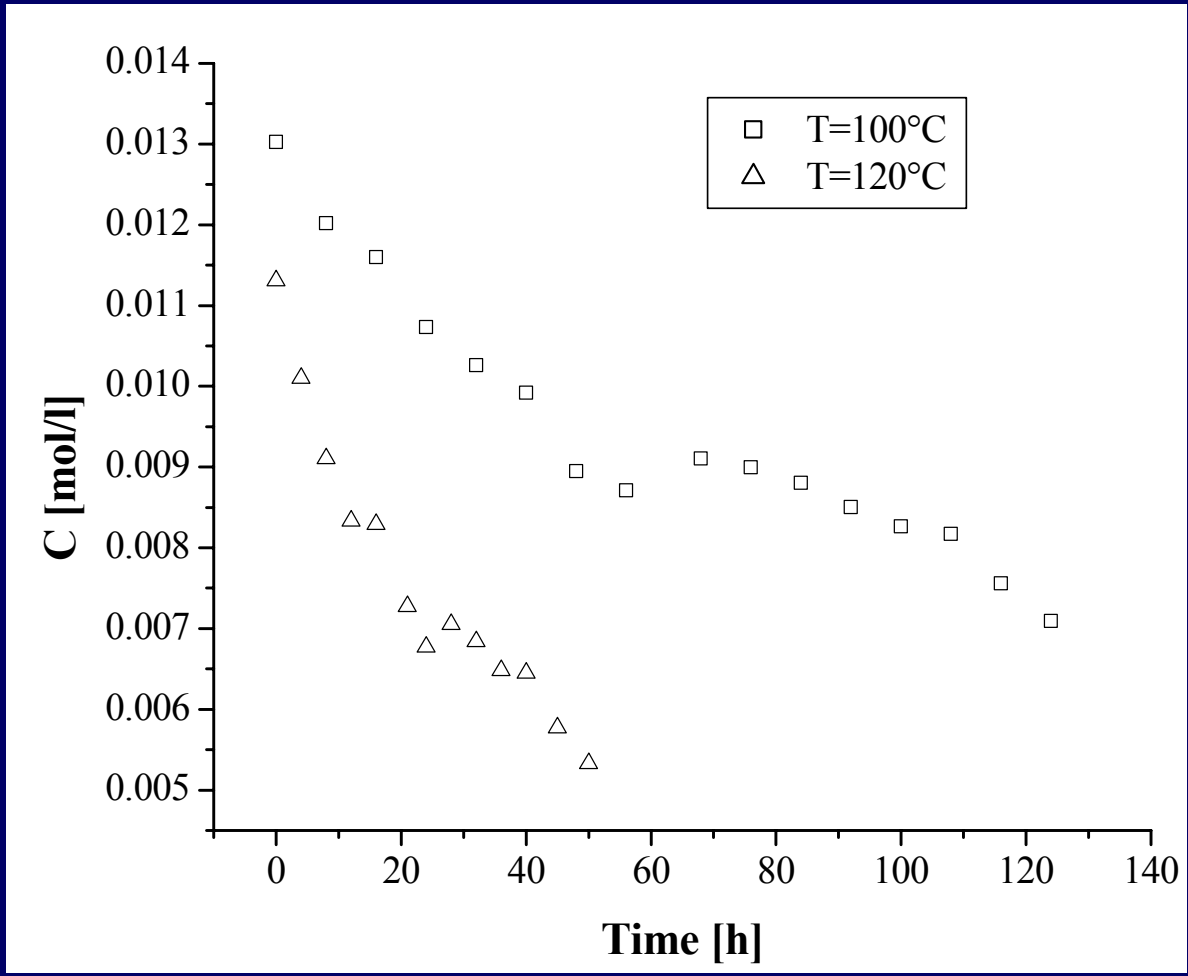
Irradiation conditions with gamma or e-beam

The rate and the behaviour of oxidation induced by high energy radiation depend on production of radiation:

- Absorbed dose and dose rate which govern the residence time in the sterilisation cell and the rate of radical generation
- Characteristics of the sterilisation plant
- Temperature of the sterilisation cell
- Sample thickness
- Oxygen concentration

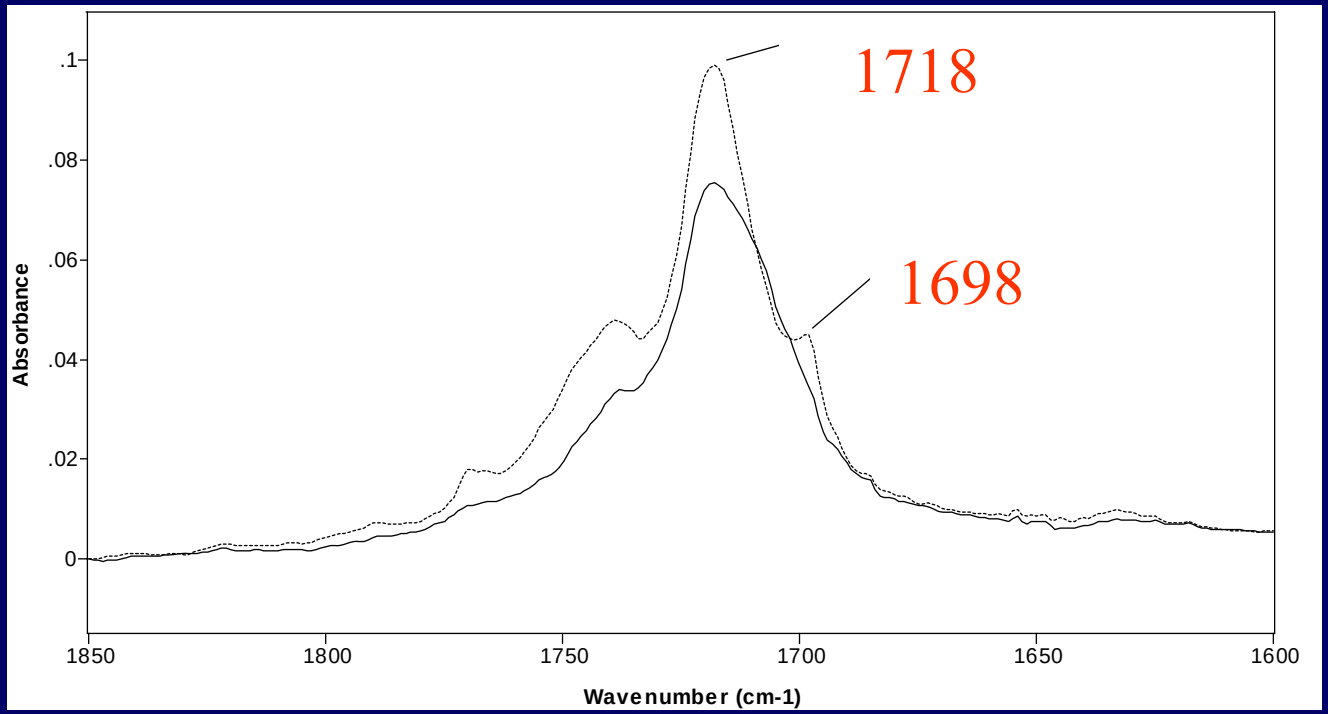
The UHMWPE post-irradiation oxidation at RT induced by e-beam in control condition

Thermal decomposition of ROOH under vacuum



Decrease in hydroperoxide concentration as a function of the decomposition time in vacuum at 100 and 120°C.

Thermal decomposition of ROOH under vacuum at 120°C



(—) sample decomposed 0h in vacuum minus reference GUR 1050;

(---) sample decomposed 22h in vacuum minus reference GUR 1050;

Thermal decomposition of ROOH under vacuum

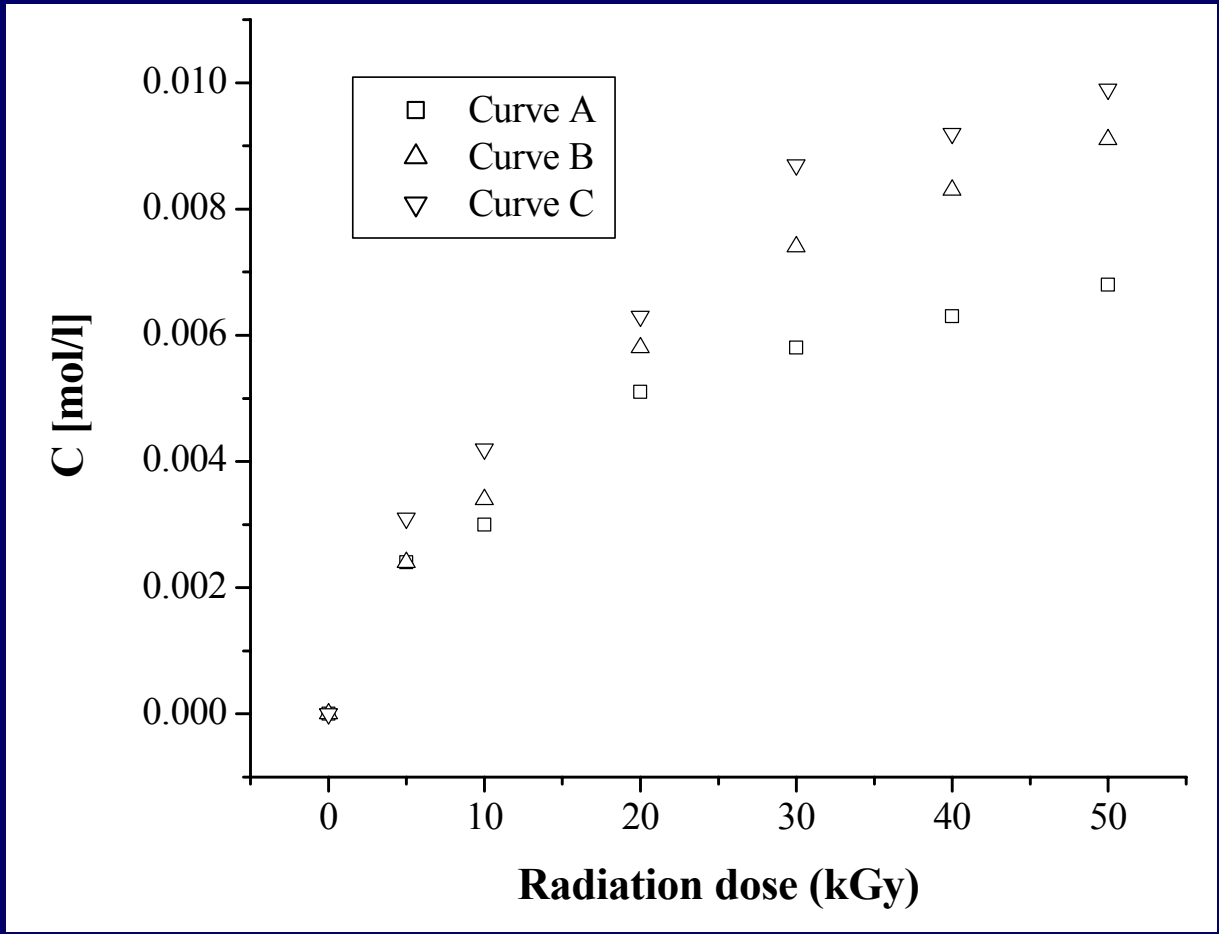
The thermal decomposition of ROOH happen at temperature > 70°C in partial melt state.

The main products of thermal decomposition are ketones and some α,β-unsatured ketones

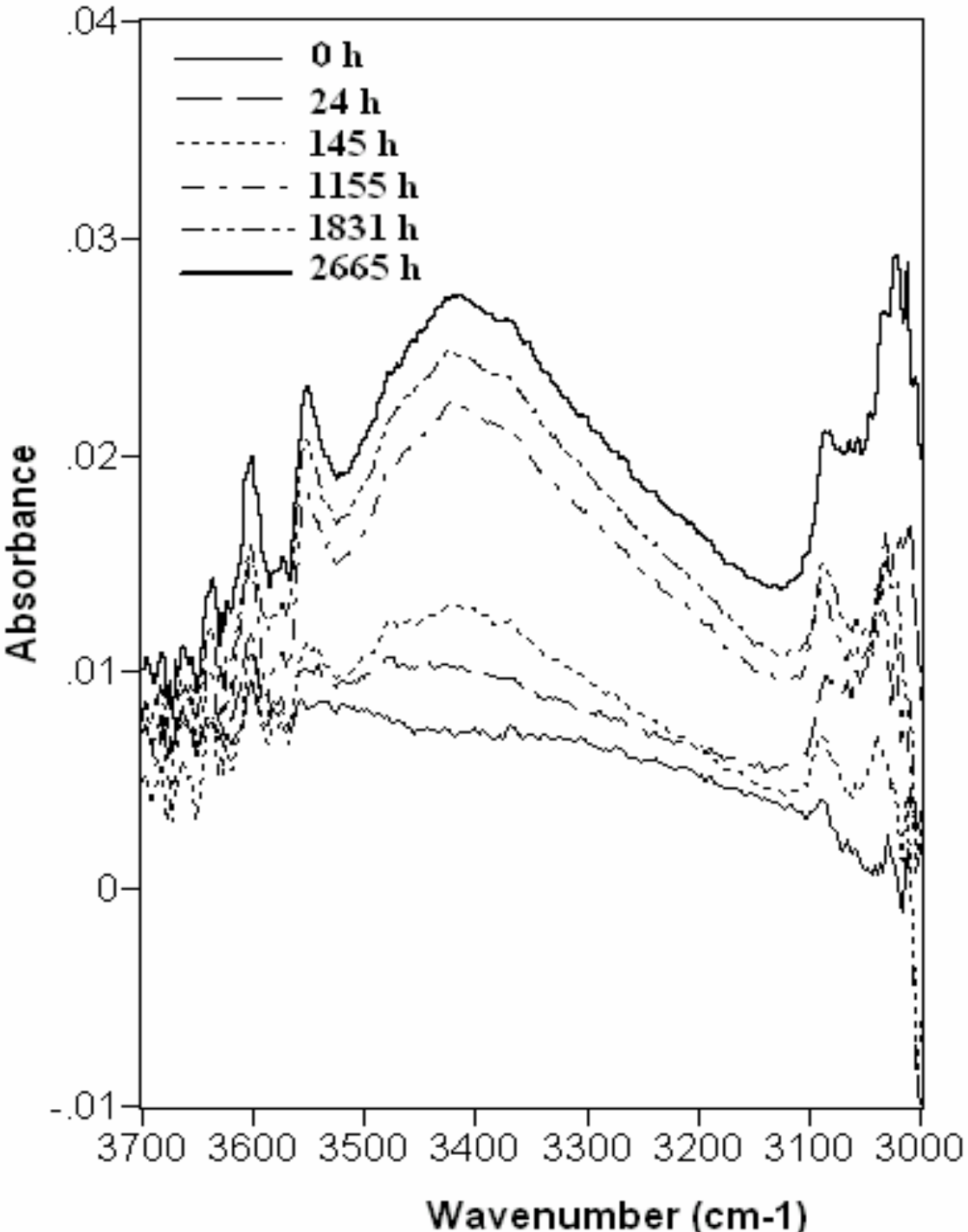
$$ROOH \longrightarrow R_2C{=}O + H_2O$$

But ketones are formed also during the e-beam post-irradiation

Hydroperoxide total concentration after NO treatment as a function of radiation dose in air and of storage time in air at RT. Films 40 microns

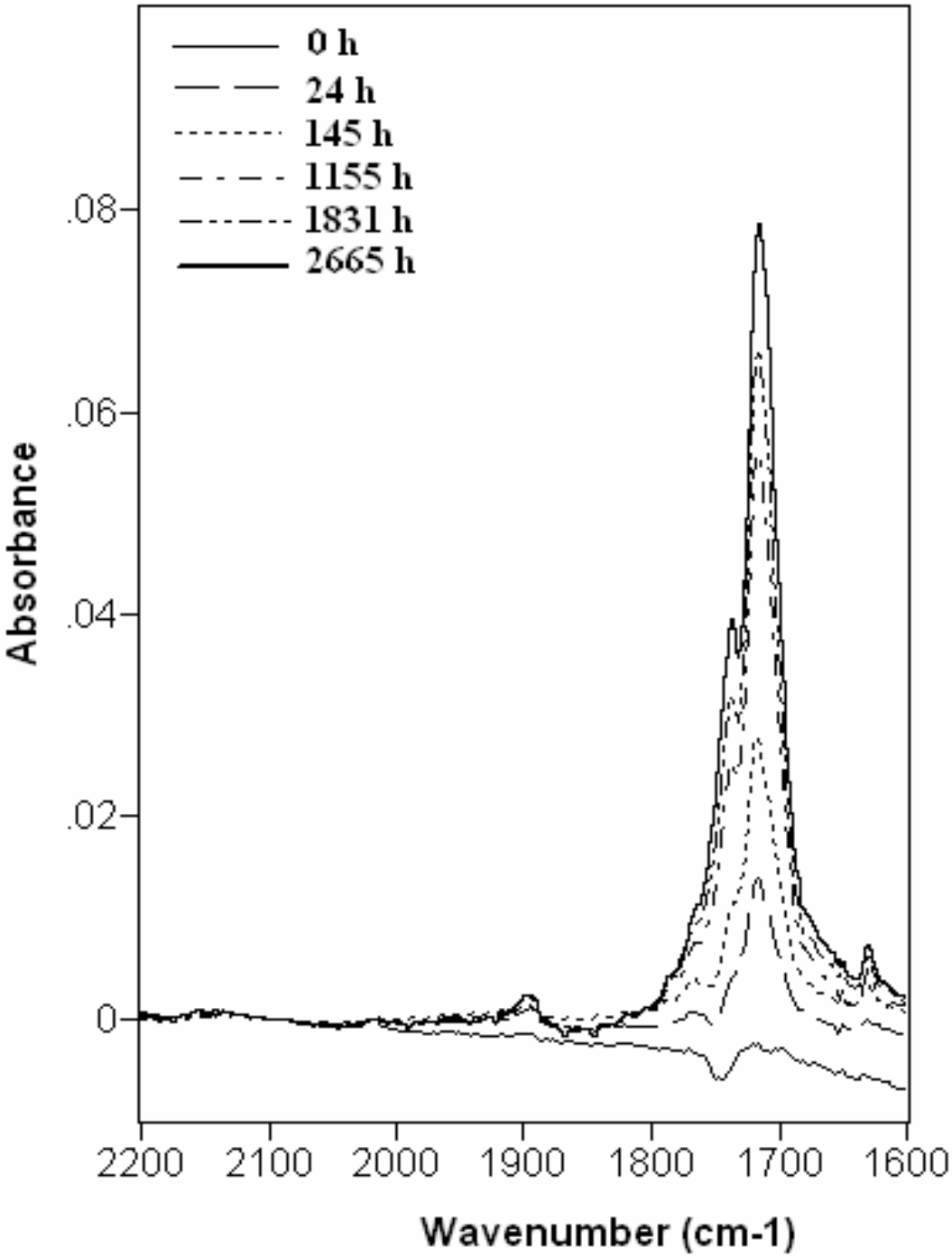


(Curve A: 0h after irradiation; Curve B: 5h after irradiation; Curve C: 360h after irradiation)



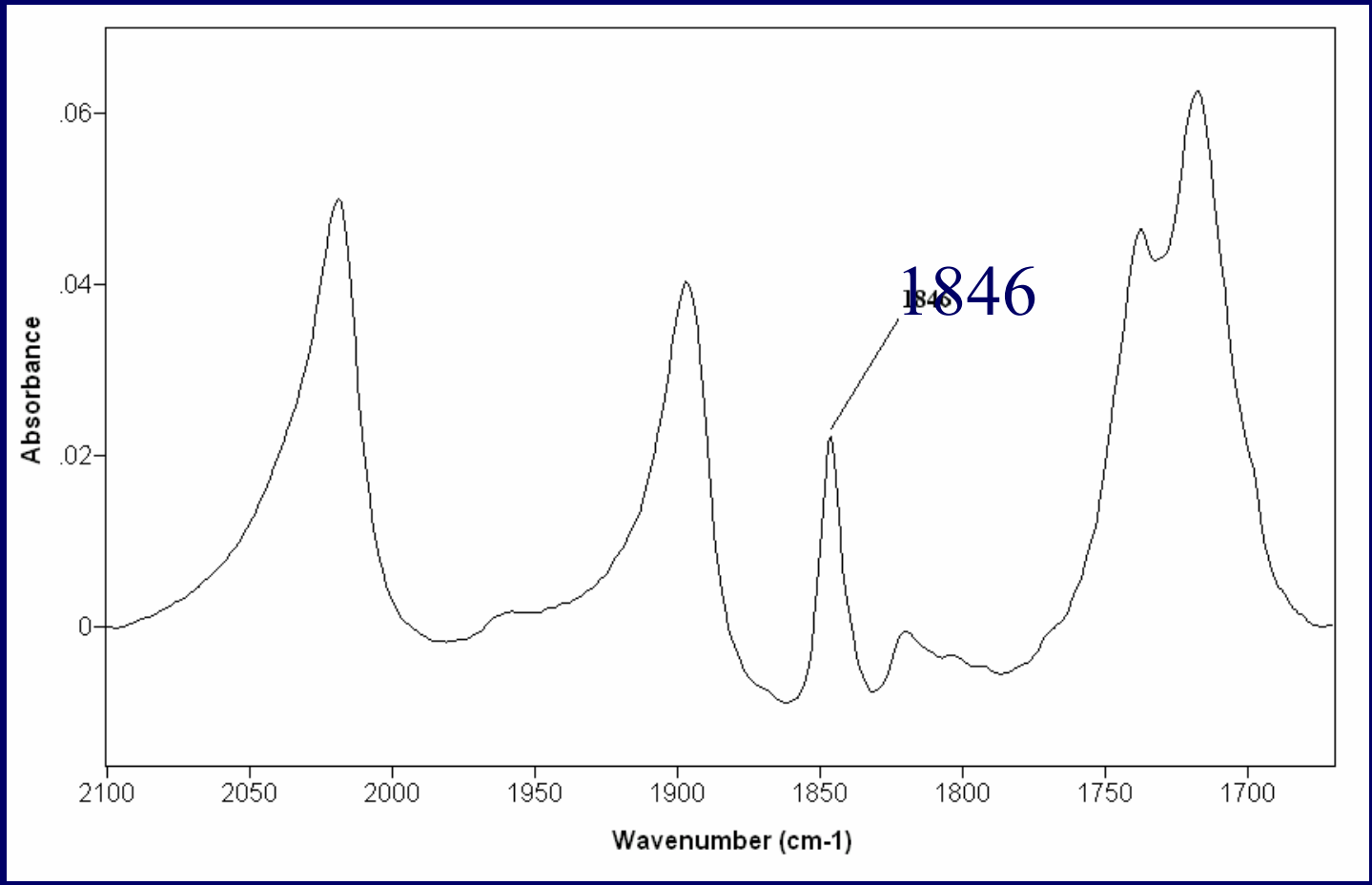
The post-irradiation oxidation at RT films irradiated with e-beam at 60 kGy in vacuum

Spectral subtraction of UHMWPE irradiated in vacuum 60 kGy and stored in air at RT minus reference GUR 1050

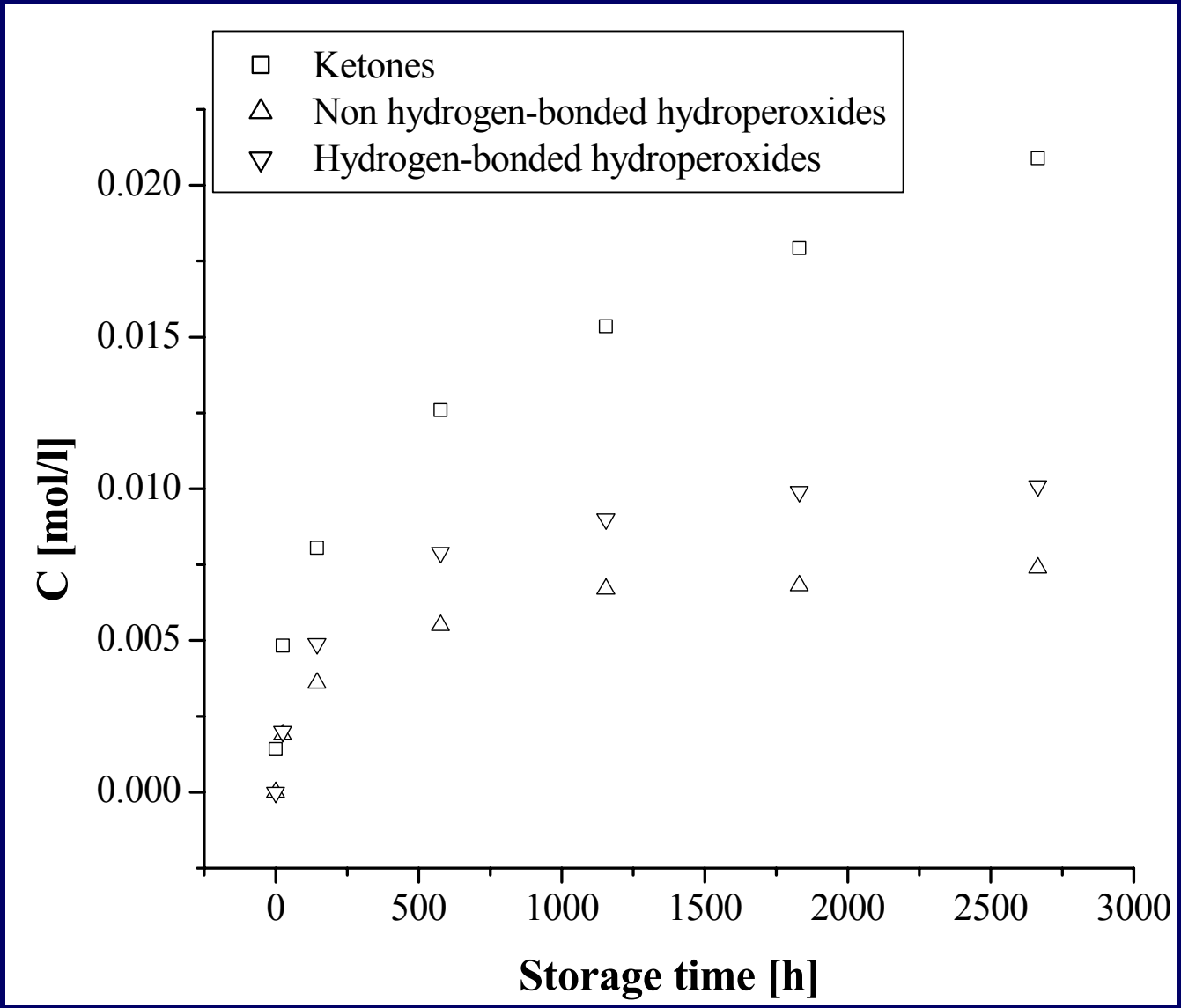


The post-irradiation oxidation at RT films irradiated with e-beam at 60 kGy in vacuum

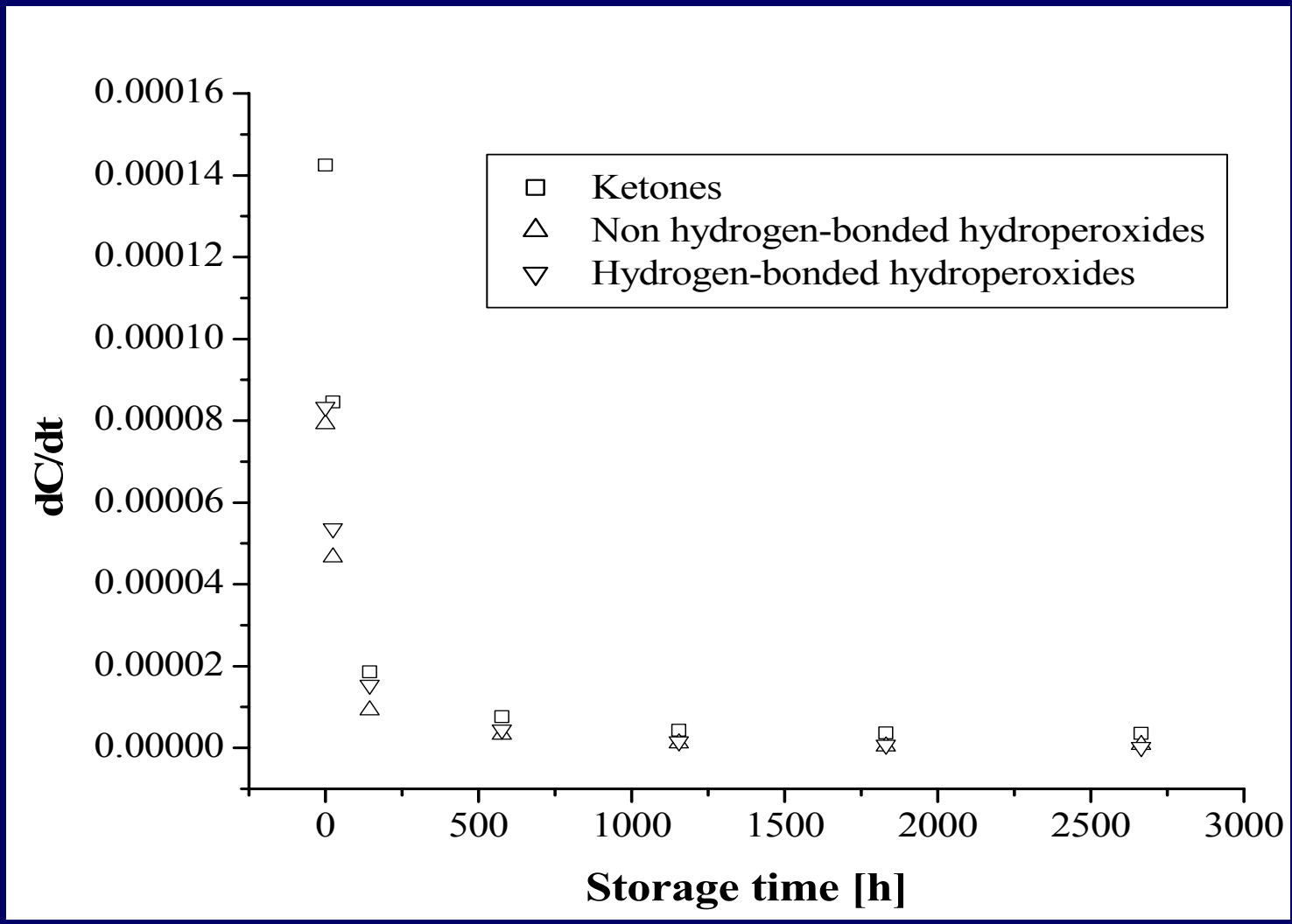
Formation of acids



Spectra of UHMWPE after SF_4 treatment with : film irradiated 60 kGy in vacuum and stored in air at RT for about 2500 h

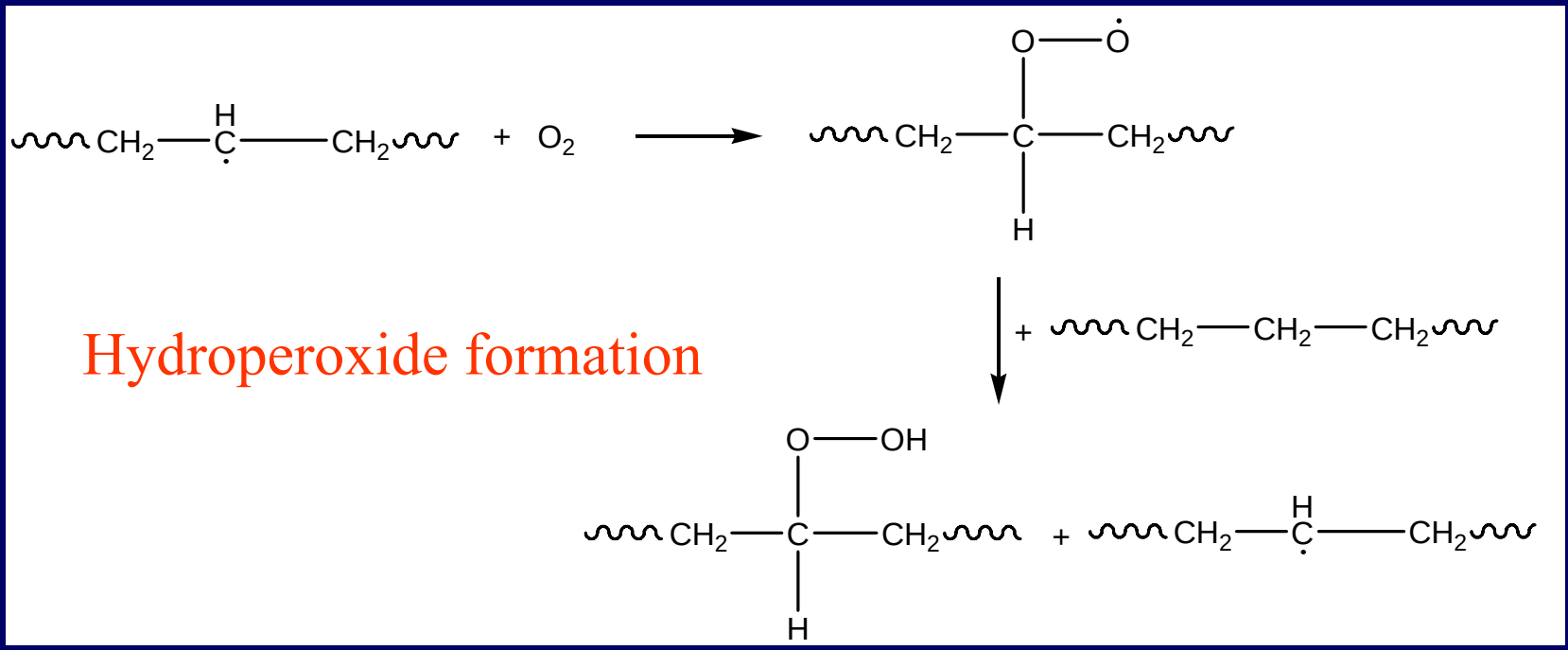


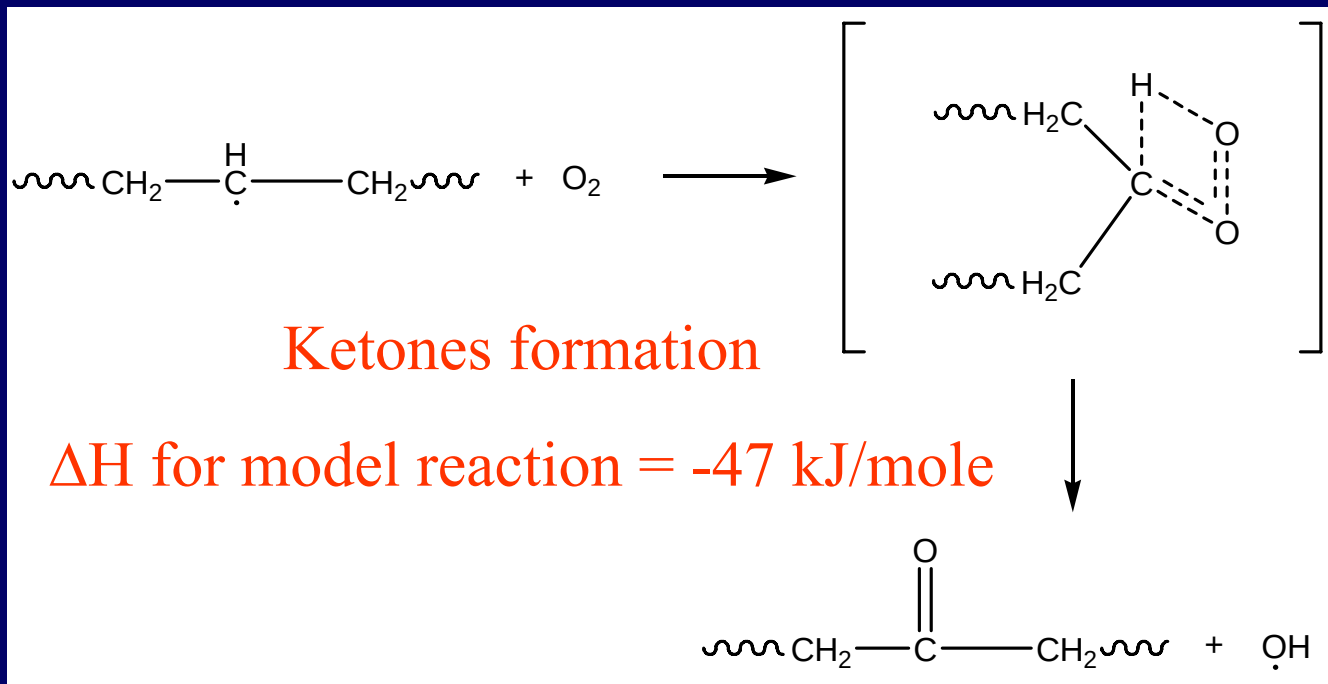
Oxidation products in function of the storage time in a film of UHMWPE irradiated in vacuum 60 kGy and ageing in air at RT;



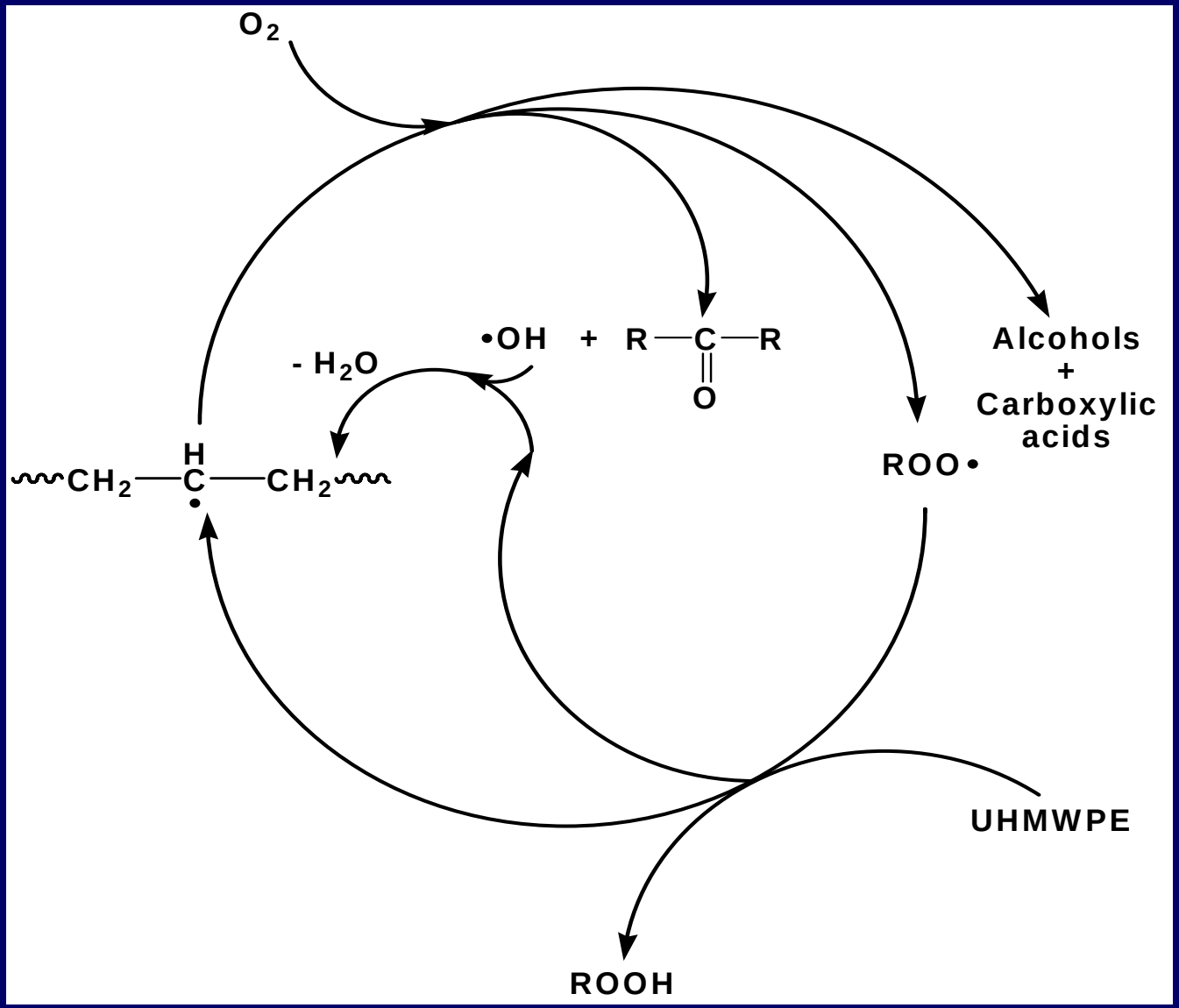
Rate of formation of oxidation products in function of the storage time in a film of UHMWPE irradiated in vacuum 60 kGy and ageing in air at RT

1. **The ketones and ROOH are accumulated during the post-irradiation process**
2. **The rate of ketones formation is high when the concentration of ROOH is minimum**
3. **The ketones and ROOH formation rate are very similar.**
4. **Ketones and ROOH could form with same mechanism: direct reaction between macroalkyl radicals and oxygen**
5. **The first part of oxidation is due to the reaction of O_2 and the alkyl macroradicals produced by e-beam in amorphous phase. In the same time the macroradicals can decay.**
6. **The second part of oxidation could be due to the alkyl macroradicals present in crystalline phase that move to amorphous phase or O_2 move to crystalline-amorphous interphase.**


Hydroperoxide formation


Ketones formation
ΔH for model reaction = -47 kJ/mole

The Bolland cycle



The UHMWPE stabilisation against oxidation and post-irradiation oxidation.

UHMWPE- Ultra High Molecular Weight Polyethylene

for prosthetic utilisation

UHMWPE is controlled by ASTM F648-06 or ISO 5834

ASTM Designation F 648-06 "Standard specification for UHMWPE powder and fabricated form for surgical implant"

The standards states the minimum mechanical characteristics of the original UHMWPE powder and the absence of any stabiliser

5.1.1 "No stabilizers or processing aids are to be added to the virgin polymer powder during manufacture of a fabricated form."

ČESKOSLOVENSKÁ SOCIALISTICKÁ REPUBLIKA (19)

POPIS VYNÁLEZU K AUTORSKÉMU OSVĚDČENÍ

221405 (11) (B1)

(22) Přihlášeno 23 12 81
(21) (PV 9738-81)

(51) Int. Cl.³ [illegible]

(40) Zveřejněno [illegible]

(45) Vydáno [illegible]

ÚŘAD PRO VYNÁLEZY A OBJEVY

(75) Autor vynálezu: ADAMÍROVÁ LUDMILA ing., DOLEŽEL BŘETISLAV ing. CSc., [illegible] ZDENĚK ing., PRAHA

The way of medically acceptable stabilization of polyolefins

(54) Způsob zdravotně nezávadné stabilizace polyolefinů proti degradaci ionizujícím zářením

against degradation by ionizing radiation

1

[illegible]

MINISTERO DELL'INDUSTRIA DEL COMMERCIO E DELL'ARTIGIANATO

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001085	94	TORINO	28 12 1994	A61F

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TITOLO IMPIANTO PROTESICO COMPRENDENTE UN COMPONENTE DI MATERIALE PLASTICO

INVENTORE
BRACH DEL PREVER ELENA MARIA
CAMINO GIOVANNI
COSTA LUIGI
DALLERA ALESSANDRO
GALLINARO PAOLO
LUDA DI CORTEMIGLIA MARIA PAOLA
CROVA MAURIZIO

Roma, 4 GIUGNO 1997

IL DIRETTORE DELLA DIV. V
F.to GIOVANNA MORELLI

06 OTT. 1997

PER COPIA CONFORME DELL'ORIGINALE

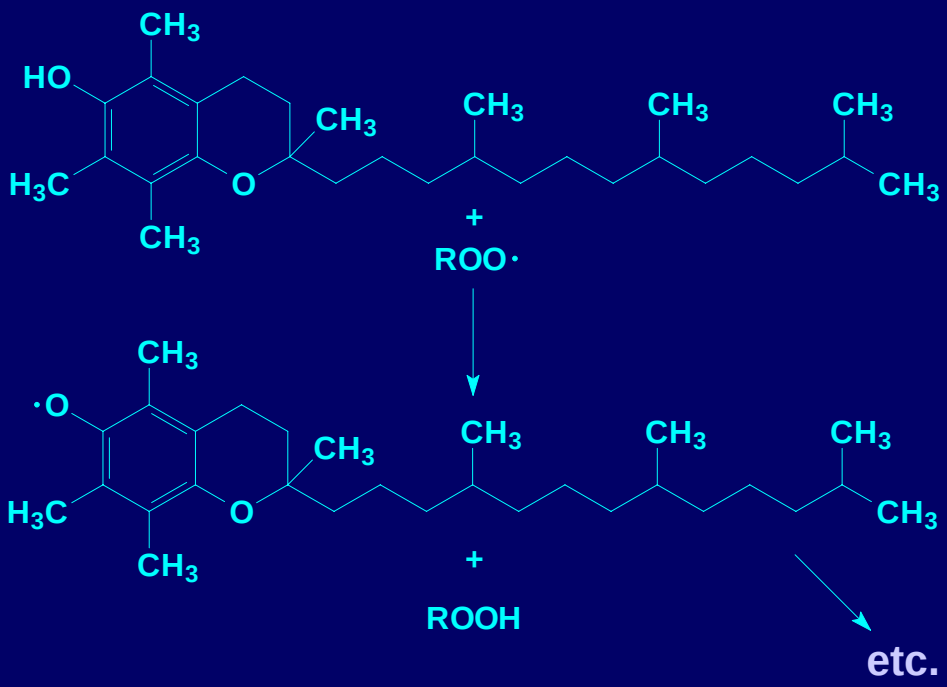
Consegnato il

Il Direttore UPICA

SEGUE

VITAMIN E (α-tocopherol):

- Biocompatible
- Approved for food-packaging and orthopedic applications



CHAIN-BREAKING DONOR

Al-Malaika et al. 1994, 1999;

Designation: F XXX–00

ENGLISH

Item 1

Work Item Number: WK14943

Date: June 7, 2007

To: Members of ASTM F04.11 - Polymeric Materials

From: Jon Moseley

Subject: WK14943 *Standard Specification for Ultra-High Molecular Weight Polyethylene Powder Blended With Alpha-Tocopherol (Vitamin E) and Fabricated Forms for Surgical Implant Applications*

Sec alkyl macroradicals can react with:

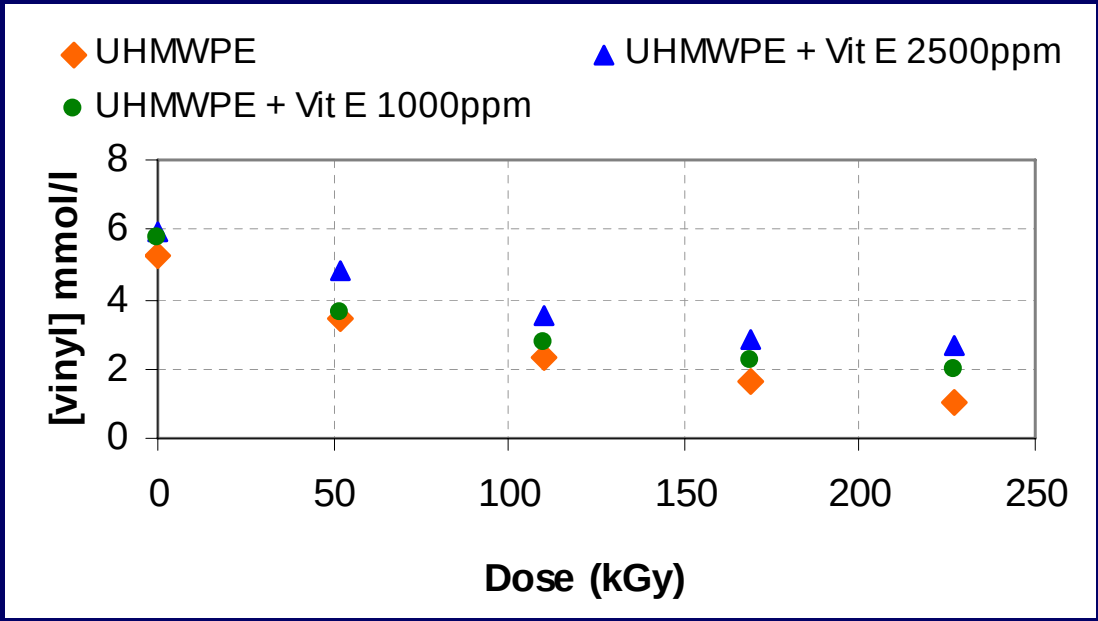
1. Vinyl double bond to form crosslink
2. Residue of catalyst and macroradicals may be decay
3. Oxygen to form ROO° and ROOH, ketones and acids
4. **Additive (H donator) to form PH and Additive° (stable radical; does not react with UHMWPE)**

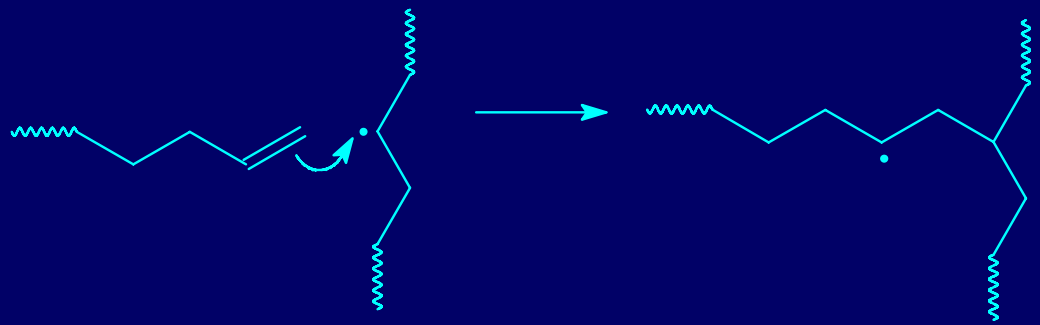
0.05 % of Vit. E = 1.2 mmoli/l

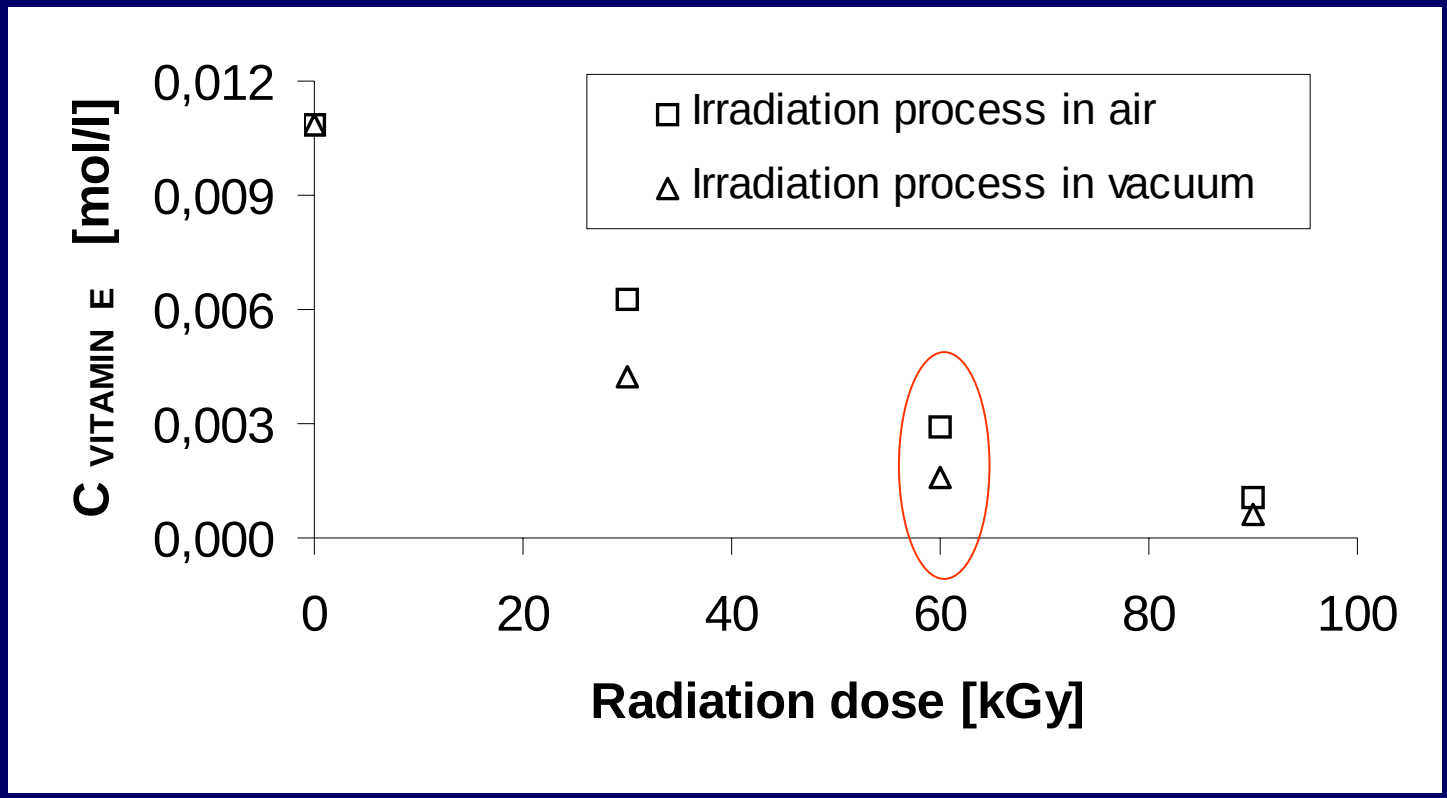
0.1% of Vit. E = 2.4 mmoli/l

0.5% of Vit. E= 12 mmoli

Vinyl consumption:

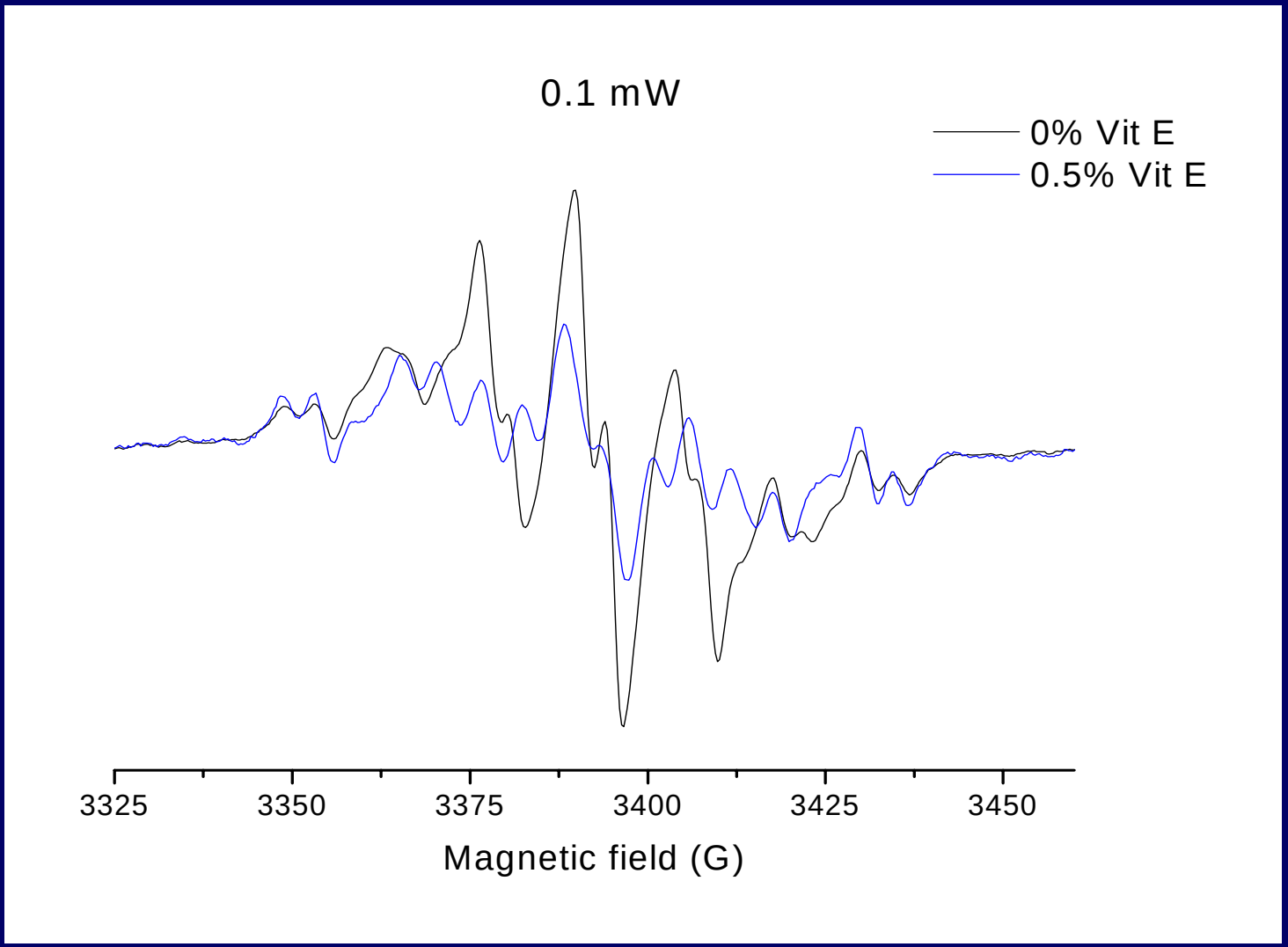




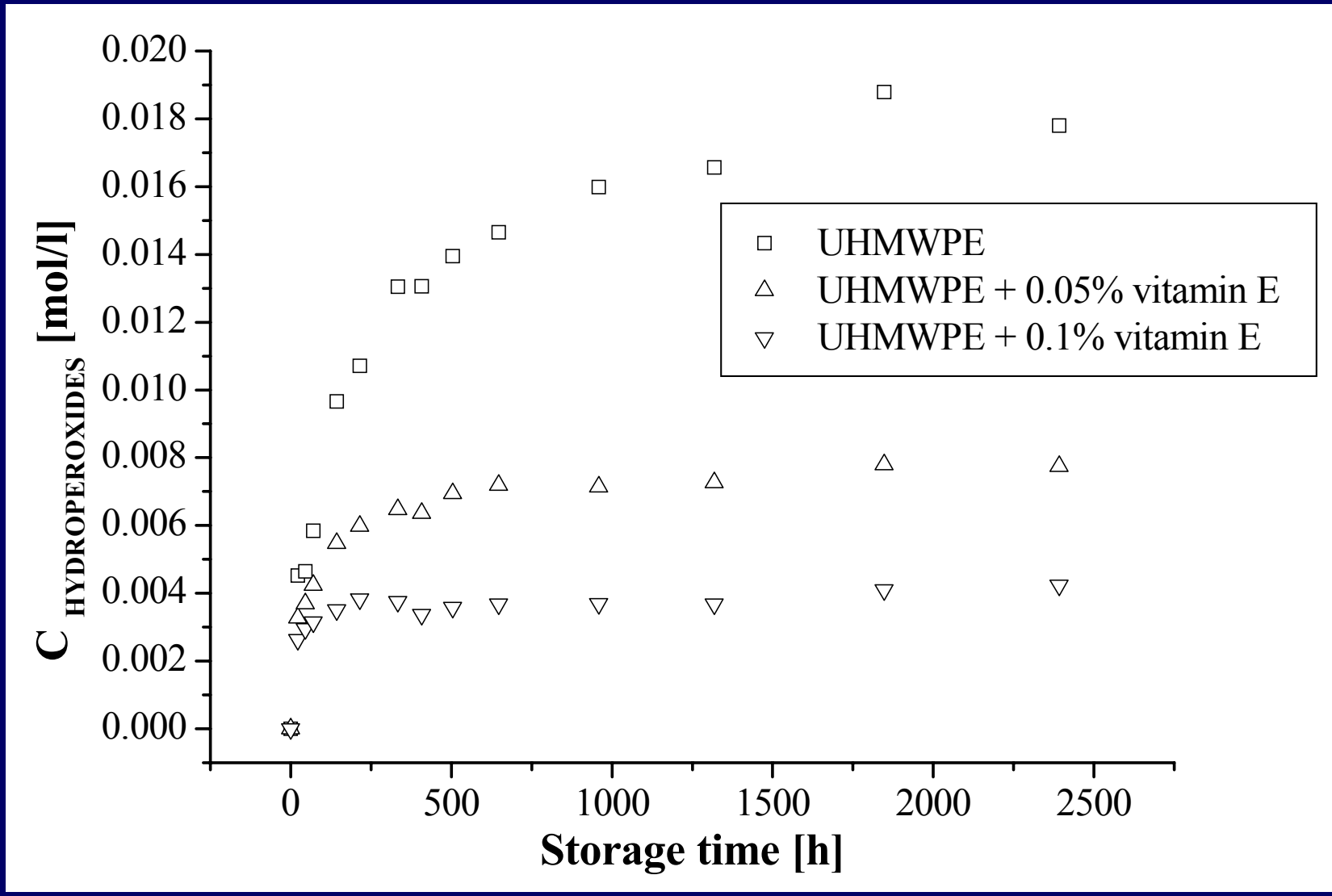


Film of UHMWPE + 0.5% vitamin E: vitamin E consumption of OH species as a function of radiation dose.

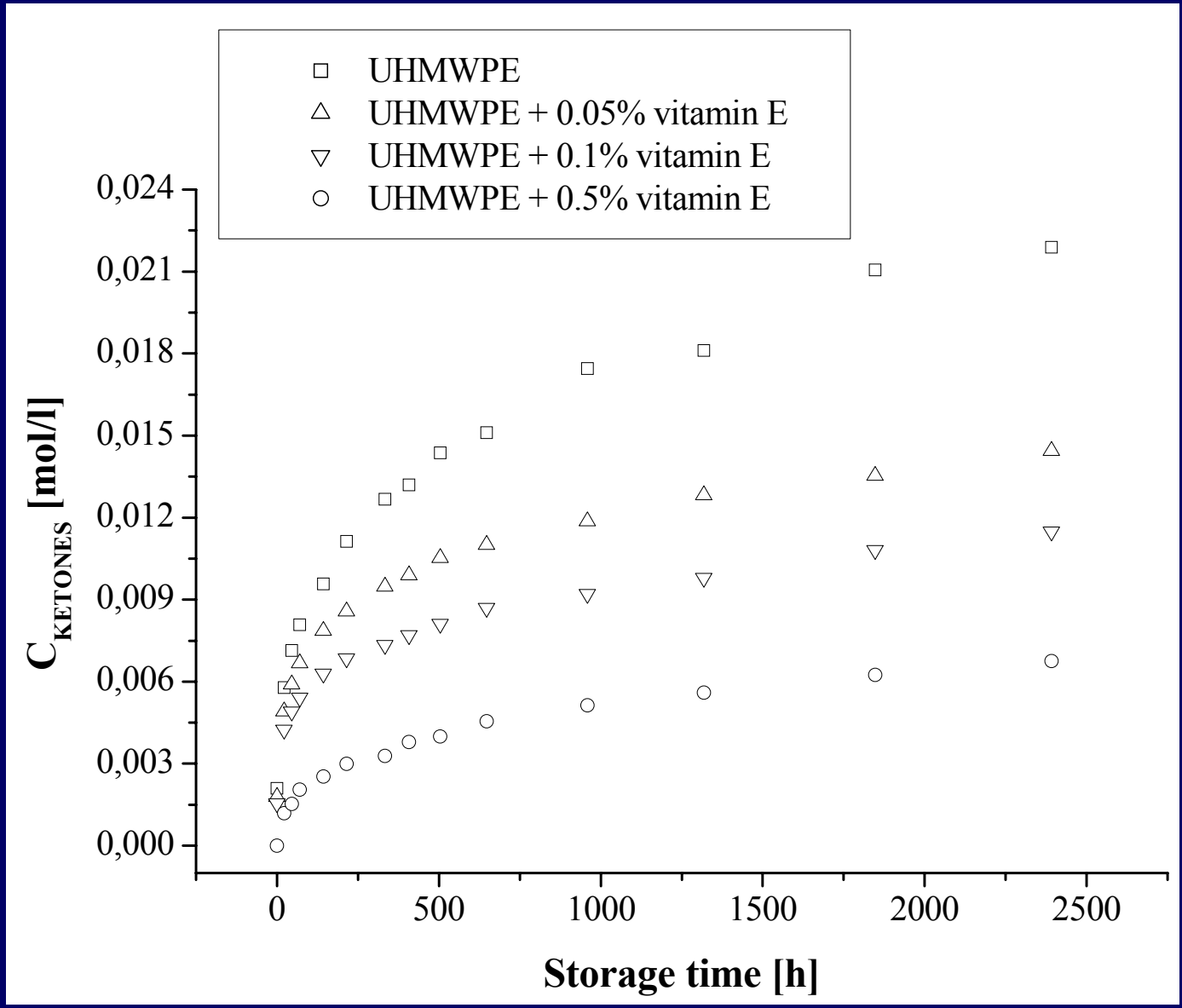
Radicals evolution



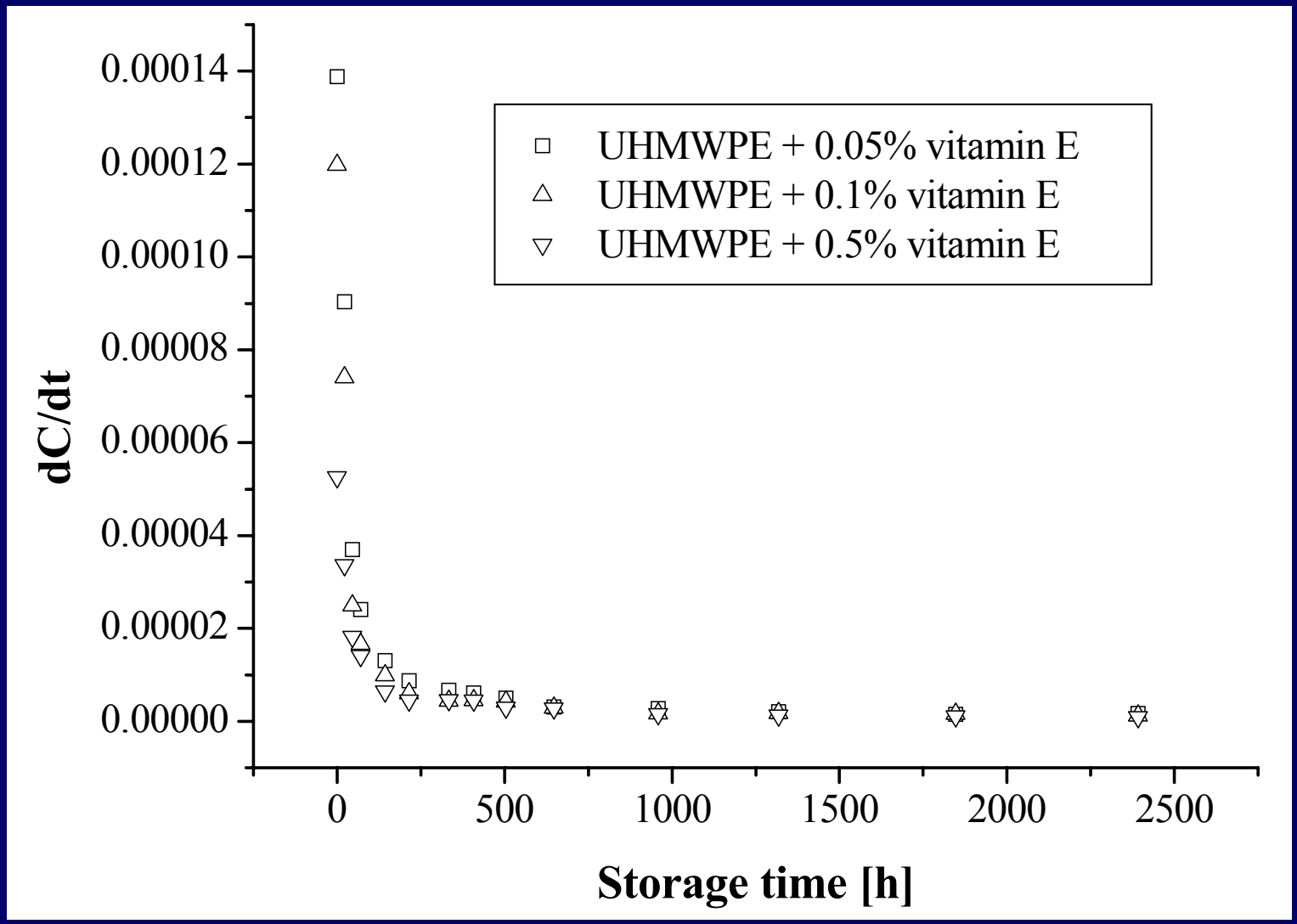
EPR spectra of UHMWPE + Vit° irradiated at 60 kGy



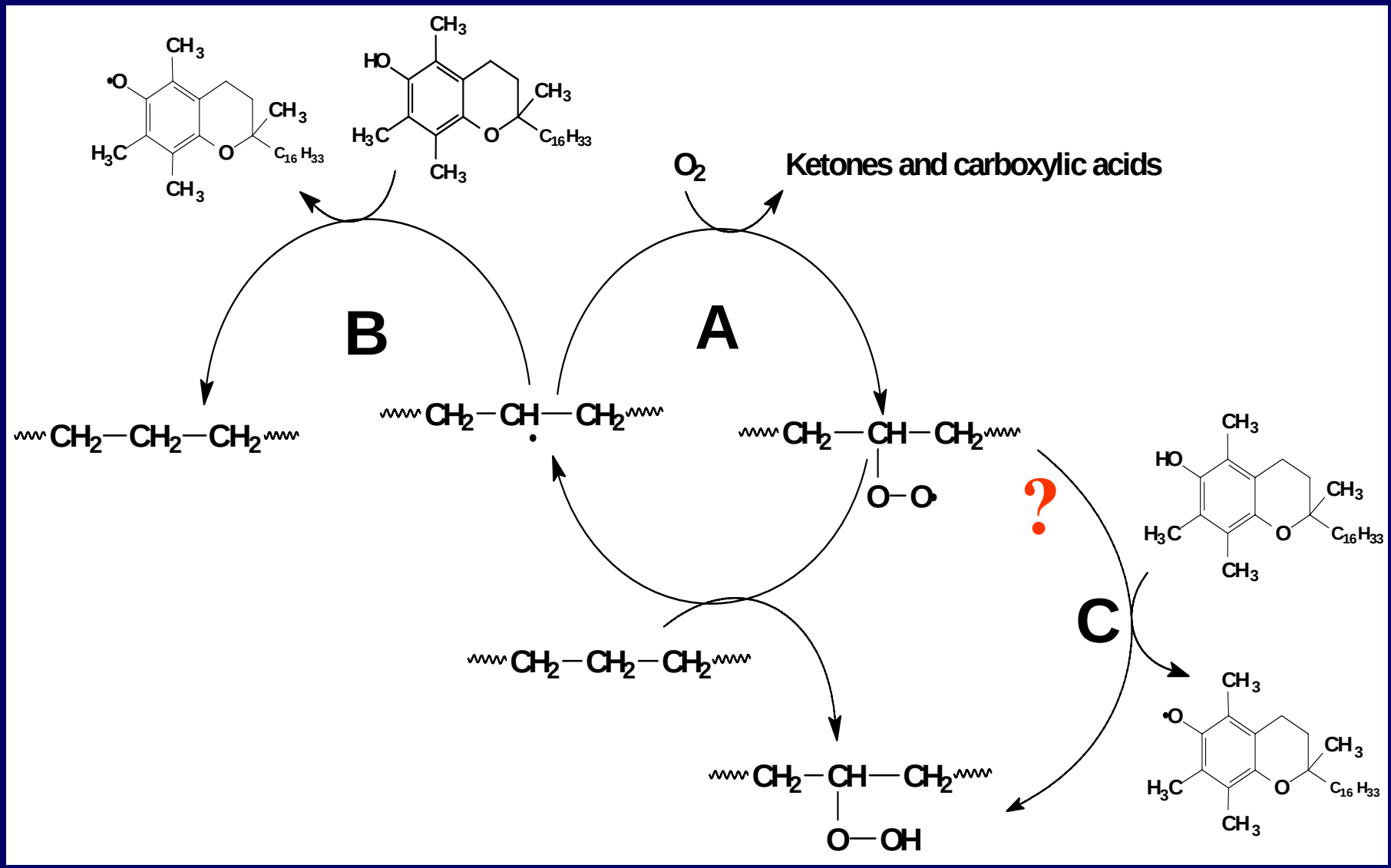
Hydroperoxides concentration as a function of amount of vitamin E and of storage time in air at RT. The samples are irradiated to 60 kGy in air.



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.



Rate of formation of ketones as a function of amount of vitamin E and of storage time in air at RT.


O2
Ketones and carboxylic acids
B
A
C
?

Acknowledgements

to the students
S. Cordero, A. Pistone, S. Possamai, F. Savognian, R. Vallero
M. Montechian, E. Carena, A. Romagnolo, Battaglio F. , S. Chiaberge, F. Peditto, F. Fasano, L. Sidoti, E. Demartino, M. Ponchione

To orthopaedic surgery colleagues : Prof. P. Gallinaro and Prof. ssa Brach del Prever

To my coworkers Prof. M.P. Luda, Dr. P. Bracco, V. Brunella, M. Zanetti, I. Carpentieri,

To the industry

Bioster for E-beam treatment,

Lima , Zimmer for the financial support

Thank you