

Influence of the polyethylene structure on the reactivity of the radicals produced by irradiation

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- Irradiation process-

In general, macroradicals are formed during the irradiation process of PE, due to the breaking of the C-H bonds.

In the PE the major radical species is the secondary macro-alkyl radical.

Macro-allyl radicals, polyenyl radicals and tertiary macro-alkyl radicals can also be formed in the PE, due to the presence of double bonds and branching in the polymer chain.



- Irradiation process-

The irradiation process can cause formation or disappearance of double bonds and, in particular, if oxygen is present, can trigger the oxidation process of the material.

The oxidation process leads to the formation of hydroperoxides and ketones as main product¹.



All the reactions involved in the irradiation process regard species fixed on the polymer chain (double bonds) or in very small amount in the amorphous phase (oxygen).

A very high migration rate of the macro-alkyl radicals must be hypothesized to justify the interaction between the radicals and the reactive species².

The aim of this study is to evaluate if the PE morphology affects the evolution of the radiation induced oxidation process.

It has also been attempted to determine in which phase the radicals produced by irradiation remain.

1. L. Costa, I. Carpentieri, P. Bracco "Post electron-beam irradiation oxidation of orthopaedic UHMWPE" *Polymer Degradation and Stability* 2008; 93: 1695-1703.
2. M. Dole "The Radiation Chemistry of Macromolecules", Volume I, Academic Press: New York; 1972.



- Polyethylene -

Virgin Samples

	Trans-vinylene [mol/l]	Vinyl [mol/l]	Vinylene [mol/l]	Methyl [mol/l]	Cristallinity [%]	Melting T [°C]	Lamellae thickness [nm]
VLLDPE	$1.1 * 10^{-2}$	/	$4.6 * 10^{-2}$	6.0	3.7	45	2.6
LLDPE	$4.5 * 10^{-3}$	$3.3 * 10^{-2}$	$4.7 * 10^{-3}$	1.2	38	119	10
LDPE	$2.2 * 10^{-3}$	$1.5 * 10^{-3}$	$2.2 * 10^{-2}$	1.6	34	110	7.6
HDPE	$1.5 * 10^{-3}$	$8.4 * 10^{-3}$	$1.9 * 10^{-3}$	/	63	132	21
UHMWPE	/	$4.8 * 10^{-3}$	/	/	55	135	26

$$L = \frac{2 * \sigma_e * T_m^0}{\Delta H_f * (T_m^0 - T_m) * \rho_c}$$

$$\begin{aligned} T_m^0 &= 418 \text{ K} \\ \rho_c &= 1 \text{ g/cm}^3 \\ \sigma_e &= 93 \text{ mJ/m}^2 \end{aligned}$$



-Methods-

150 microns thick films have been e-beam irradiated at 60 kGy, at RT, in air and in vacuum.

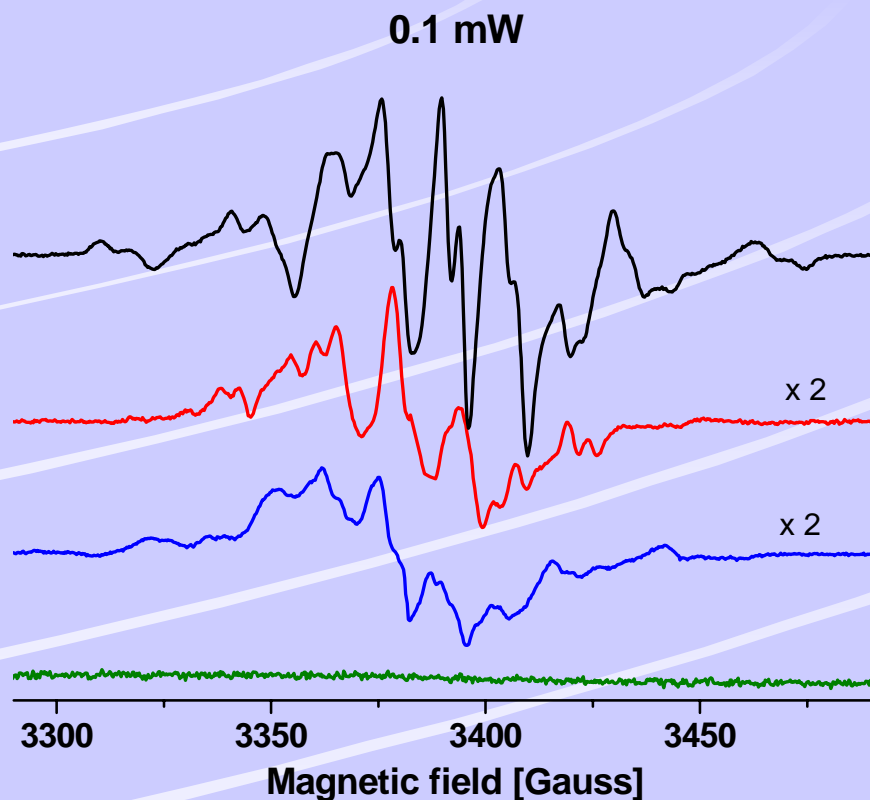
All PE samples have been kept in liquid nitrogen until the measurement began.

- **EPR spectroscopy** explores the nature of the radicals produced upon irradiation and assesses their decay as a function of time. Experimental settings: microwave power range from 0.01 to 100 mW, scan width 300 G and modulation amplitude 2.01 G.
- **FTIR spectroscopy** estimates the presence and the amount of double bonds and oxidation products. All spectra were run on thin sections in the transmission mode with a 4 cm⁻¹ resolution and 16 scans per spectrum. Use of spectral subtraction!



-EPR results-

All the samples were irradiated and stored in vacuum.



- EPR spectrum obtained immediately after irradiation for UHMWPE and HDPE (secondary macro-alkyl radical).
- EPR spectrum of UHMWPE and HDPE recorded 24h after irradiation (macro-allyl radical)³.
- In LDPE and LLDPE the signal of the macro-allyl radicals was recorded immediately after irradiation.
- No radicals have been detected after irradiation of VLLDPE, nearly completely amorphous.

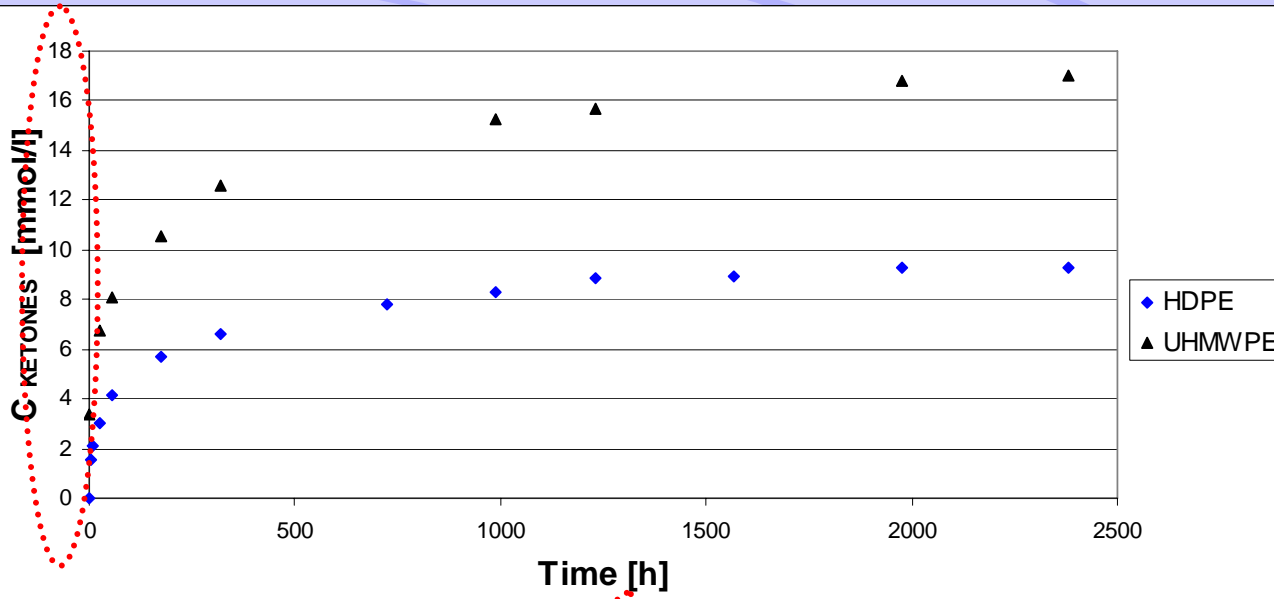
The radicals formed in the amorphous phase decayed in very short time and cannot be detected in the timescale of our experiment.

3. Ohnishi SI. ESR Study of the radiation chemical process in Polyethylene. *J Polymer Science* 1962; 35(2): 254-259.

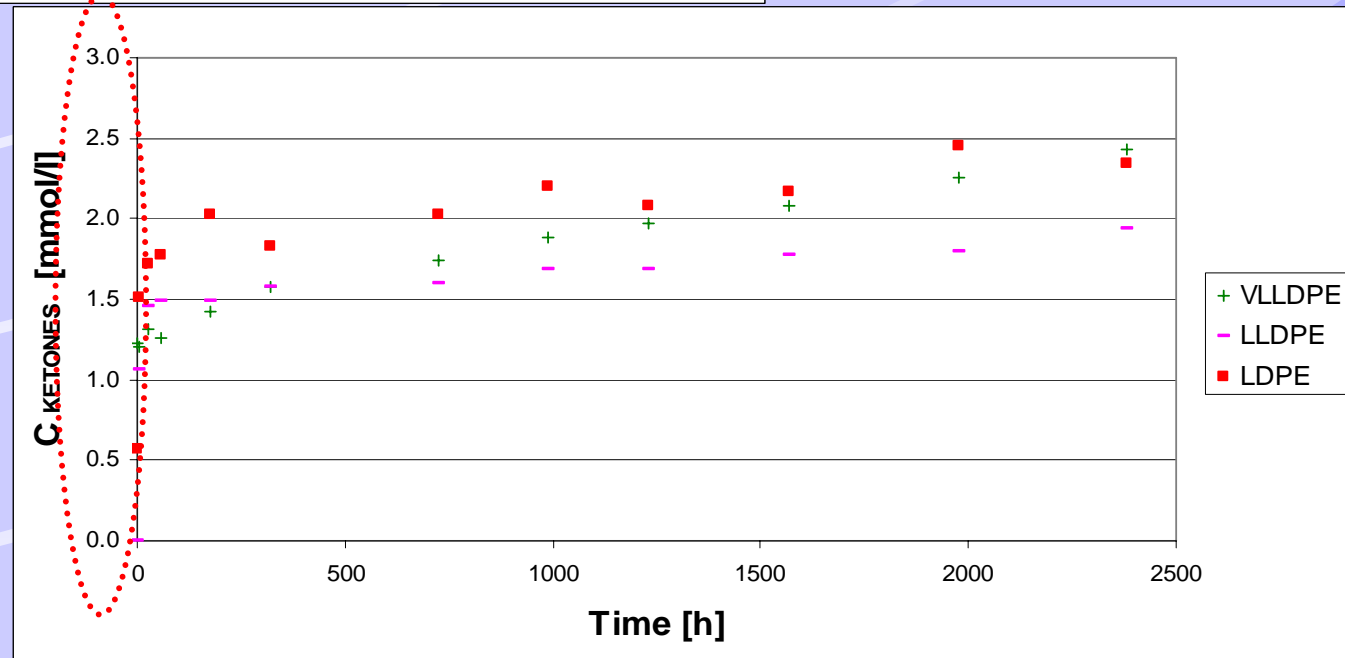


-FTIR results-

Ketone amount was estimated considering the IR absorption (1718 cm^{-1}) in the spectral subtraction. Only ketones are reported because they are easily detectable, unlike hydroperoxides.

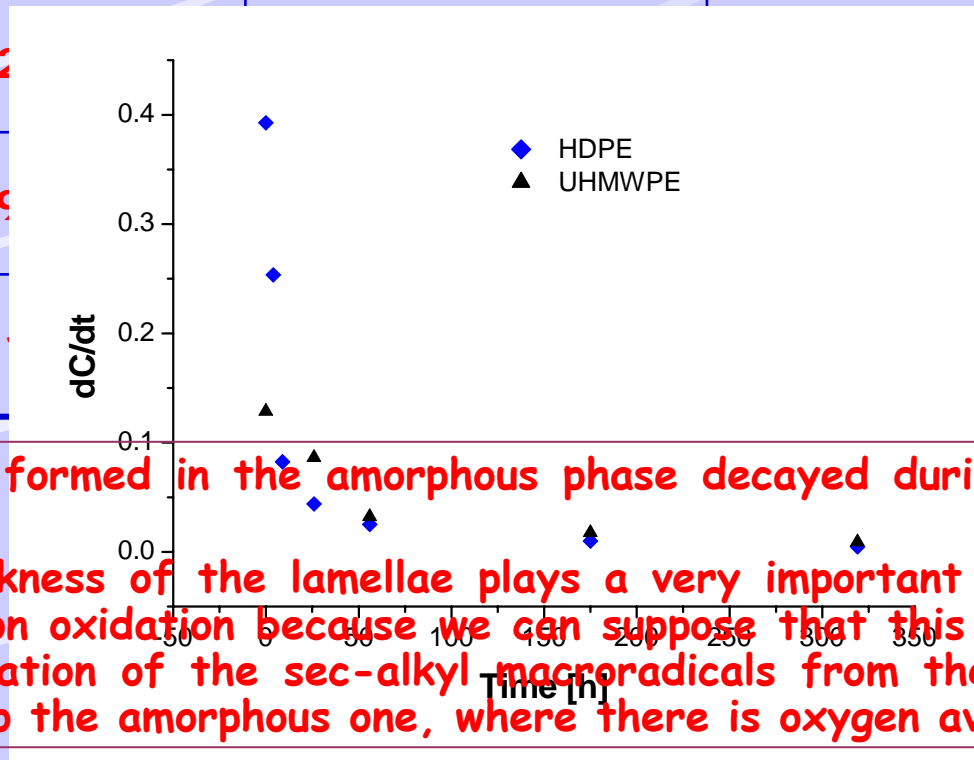


The maximum oxidation level in the post-irradiation time is reached in few hours for VLLDPE, LLDPE and LDPE, while it takes longer for UHMWPE and HDPE.



-Results-

	Ketone amount at the plateau [mmol/l]	Time to reach the plateau [h]	EPR signal immediately after irradiation	Lamellae thickness [nm]
VLLDPE	2.4	Immediately after irradiation	No rad.	2.6
LLDPE	2.0	About 20	Allyl	10
LDPE	2.0	10	Allyl	7.6
HDPE	0.9	10	Allyl	21
UHMWPE	0.7	10	Allyl	26



- Radicals formed in the amorphous phase decayed during the irradiation time.
- The thickness of the lamellae plays a very important role in the post-irradiation oxidation because we can suppose that this process is due to the migration of the sec-alkyl macroradicals from the crystalline/inter phases to the amorphous one, where there is oxygen available.



-Results-

The secondary macro-alkyl radicals are responsible of post-irradiation oxidation.

The VLLDPE is an almost completely amorphous polymer; the secondary macro-alkyl radicals in the amorphous phase disappear very fast then the oxidation level is very low and it is reached during the irradiation time.

Lamellae thickness till 10 nm
(LLDPE, LDPE)



Time of migration of the secondary macro-alkyl radicals from the crystalline/inter phases to the amorphous one is very short (sec-alkyl macroradicals not detectable!).



Post-irradiation oxidation level very low and reached in very short time.

Lamellae thickness more than 10 nm
(HDPE, UHMWPE)



Long time of migration of the sec-alkyl macroradicals from the crystalline/inter phases to the amorphous one.



Post-irradiation oxidation level high and reached in a long time.



-Conclusion-

- The macroradicals detected after the irradiation process at RT are those in the crystalline/inter phases.
- The migration rate of the secondary macro-alkyl radicals from the crystalline/inter phases to the amorphous one defines the oxidation level and the time to reach the maximum of oxidation during the post-irradiation period.



Thank you!

