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***EPR study of the relationship between Ultra High Molecular Weight Polyethylene structure and formed radicals during irradiation with high energy sources***

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**Abstract**

Three different samples of ultra high molecular weight polyethylene (UHMWPE) have been irradiated with high energy source (electron beam) and radicals have been generated. Different radical species have been assigned on the basis of their EPR spectra. EPR data have been used also to evaluate the amount of each kind of radicals that have been generated on different starting materials. The structure of the polymer (number of double bonds, or crystallinity) is strictly connected to the response of the sample itself to the irradiation. A rationalization between these different parameters have been performed in order to evaluate the stability of polymer samples towards high energy irradiation processes.

**Keywords:** EPR, Defects, Double bonds, Crystallinity, Irradiation

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## Introduction

Ultra High Molecular Weight Polyethylene (UHMWPE) is one of the most interesting material for the articulating surface in total joint replacements. The necessary sterilisation of UHMWPE prosthetic components is commonly carried out by high energy radiation.<sup>1</sup>

The initial effect produced in solid polymers by the action of high energy radiations is the formation of macro-radicals.<sup>[2-6]</sup> The primary products are involved, after their formation, in complex secondary reactions which result in radiation chemical effects such as crosslinking, gas evolution, unsaturation in chemical bonding.<sup>[7-11]</sup>

A large body of work exists concerning the formation and characterization of radicals in irradiated polyethylene.<sup>[12-17]</sup> Electron Paramagnetic Resonance (EPR) spectroscopy, due to its capability of detecting radical species, is one of the most direct and informative techniques to elicit information relative to radical species. Conventional CW-EPR techniques have been widely applied in the past to study radical intermediates generated by irradiation of polyethylene.<sup>[18-22]</sup> Among the possible radicals that might be produced by irradiation process, the secondary alkyl and the allyl radicals have been detected by electron spin resonance studies.<sup>[16,23-25]</sup>

EPR technique is used not only for the identification of different radicals or defects but also for quantitative evaluations of radicals themselves. Comparing data obtained from different spectroscopic techniques related to the number of double bonds or to the percentage of crystallinity of the sample with EPR results, it is possible to correlate the amount of defect generated during the irradiation with the structure of the starting material.

In this work we used and elaborated EPR results to obtain some new information about the trend of different radicals vs the amount of irradiation dose. Secondly we compared three different polyethylene samples that differ in crystallinity and number of double bonds. We aimed to stabilize a correlation between structural properties of the materials used and their sensitivity towards irradiation to identify the more stable material even after high dose irradiation.

## Experimental

Two different medical grade UHMWPEs were used as resin powders with a molecular mass higher than  $5 \cdot 10^6$  a.m.u: Gur 1050 (Poly Hi Solidur), hereafter Pe-1 and Hifax 1900 (Hercules), hereafter Pe-2.

Moreover, Pe-1 was heated to 180°C in vacuo and dipped soon after that in liquid nitrogen; in this way its crystallinity was modified to a lower value (hereafter Pe-3).

Infrared spectra were performed on a Perkin Elmer 100 FTIR Spectrometer in transmission mode with a  $4\text{ cm}^{-1}$  resolution and 32 scans per spectrum. The amount of vinyl and vinylidene double bonds was calculated from the respective absorption bands using the molar absorptivity proposed by De Kock and Hol.<sup>[26]</sup> Trans vinylidene double bonds were not detectable in our UHMWPEs before irradiation process.

Differential scanning calorimeter (Perkin-Elmer DSC-6) has been used to evaluate the percentage of crystallinity. During DSC analyses the polyethylene samples (4-9 mg) were heated from  $40^{\circ}\text{C}$  to  $180^{\circ}\text{C}$  with a rate of  $10^{\circ}\text{C}/\text{min}$ . The percentage of crystallinity was calculated using a heat of fusion of  $293\text{ J/g}$ .<sup>[27]</sup> Integration limits were set between  $60^{\circ}\text{C}$  and  $160^{\circ}\text{C}$  for all polyethylenes.

Samples were irradiated in vacuo with electron beam at different doses, 10, 30, 60 and  $100\text{ kGy}$  in the same way reported elsewhere.<sup>[28]</sup>

Electron beam irradiation was performed with a  $10\text{ MeV}$  accelerator (Bioster, Seriate, Italy), operating at  $25\text{ kW}$  power, with a dose rate of  $6\cdot 10^4\text{ kGy/h}$ , at room temperature.

Samples were kept in liquid nitrogen after irradiation, until the EPR measurements began. The time elapsed between the end of irradiation and the sample freezing was approximately 10 minutes.

The EPR signal was followed for some weeks after the end of irradiation, keeping the powder under vacuum at room temperature. EPR spectra were recorded on a EPR Bruker EMX operating in the X band mode. Experimental settings were as follows: microwave power range from  $0.01$  to  $100\text{ mW}$ , scan width  $30\text{ mTesla}$ , modulation amplitude  $0.201\text{ mTesla}$ . All the obtained EPR signals showed  $g$  values around the  $g$  value for free electron,  $g \approx 2.0023$ . All EPR spectra were reported in magnetic field (B) units of Tesla.

EPR signals were integrated with WINEPR program. The aim was to obtain and compare relative signals intensities between different radical species.

## Results and Discussion

Three different types of high molecular weight polyethylene have been studied and characterized: Pe-1 is a polyethylene with a high crystallinity (about 70%, determined by DSC analysis see Table 1) and with a high number of vinyl groups (determined by infrared spectroscopy, see Table 1), Pe-2 is a polyethylene with a very high crystallinity (about 90%, see Table 1) and with a number of vinyl groups lower than the Pe-1, about one order of magnitude less. Finally the Pe-3 was obtained from the Pe-1 through a thermal treatment at high temperature ( $180^{\circ}\text{C}$ ) and quickly cooled down. This

treatment modified the structural organization of this foil: its percentage of crystallinity is greatly decreased from 70% to 40%. This dramatic structural modification is due to the fact that this type of ultra high molecular weight polyethylene does not behave as a normal polyethylene. Once melted, and then forced to a rapid cooling, the long chains do not have the opportunity to regroup and re-orientate according to the previous structural order. The material therefore presents a low percentage of crystallinity which is limited to 40%. The number of double bonds instead undergoes no variation. The number of these latter, in fact, is not affected by the crystal structure but only by the synthesis process.

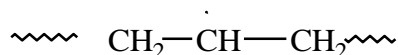
Table 1. Crystallinity percentage and double bonds amount of Pe-1, Pe-2 and Pe-3.

	Vinyl groups /1000C	Crystallinity, % (DSC measurements)
Pe-1	$0.070 \pm 0.001$	70
Pe-2	$0.003 \pm 0.001$	90
Pe-3	$0.070 \pm 0.001$	40

These three materials were irradiated with electron beam at different doses (10 kGy, 30 kGy, 60 kGy and 100kGy). *After irradiation all the samples have been checked to evaluate their stability towards crystallinity and number of vinyl groups; all these data are reported elsewhere<sup>[9]</sup>*. The irradiation generates radicals in all three samples, which is why the electron paramagnetic resonance is the most suitable technique to monitor the formation and the evolution of the radical and paramagnetic species. Figure 1 shows the EPR spectra of the three different polyethylenes recorded at low microwave power (0.1 mW Fig. 1 A) and at high microwave power (100 mW Fig. 1B) respectively. The spectra (a, b, c) in each quadrant are very similar and differ mainly in signals intensity.

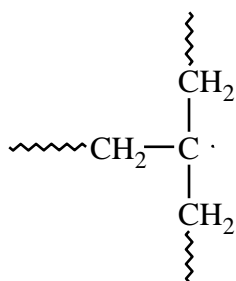
Figure 1

All spectra in the quadrant A show a sextet of lines due to the interaction of an unpaired electron trapped in the p-orbital of the carbon atom inserted in an alkyl chain with coupling constants of approximately 2.3 and 3.1 mT obtained from computer simulations. This radical has already been described extensively in a previous work<sup>[28]</sup> and was unequivocally assigned to a secondary alkyl macroradical.



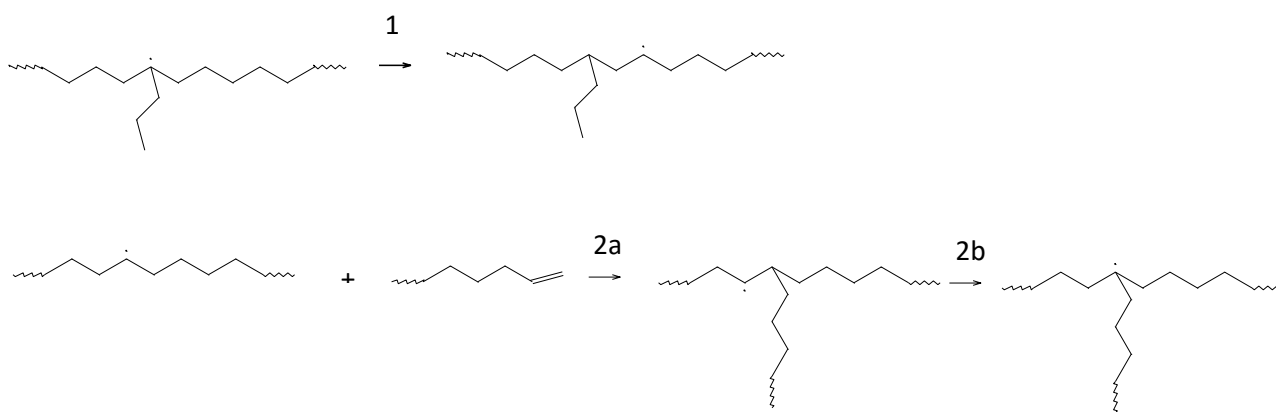
The structure of the EPR signal is very well observable in the sample Pe-2, in which the sextet spectrum stands out well in all its components. In samples Pe-1 and Pe-3 spectral components are less clear and also the intensities are smaller. In particular, the spectrum of the sample Pe-3 is the less intense because the material shows a very low crystallinity (only 40%) because of the thermal treatment led to the formation of agglomerates of particles larger than the single particle. During irradiation radicals are formed in the whole structure of polyethylene in both amorphous and crystalline zones. The radicals formed in the amorphous regions, however, are not observable because of a rapid recombination due to their mobility along the chain and/or through the chains.<sup>29</sup> Only the radicals formed in the crystalline phase have greater life spans and therefore can be observed. In the crystalline phase of these polyethylenes with high molecular weight, in fact, the mobility of radicals is drastically reduced<sup>30</sup>.

Figure 1B shows the spectra of the same samples recorded at 100 mW of microwave power, as already explained elsewhere, the signal of the secondary alkyl macroradical is almost completely saturated and a new species appears. This species has been assigned<sup>[28]</sup> to a tertiary alkyl-macroradical according to the following scheme:



In this case, we can see well distinct spectral components for both Pe-1 and Pe-2. The sample Pe-3, because of the agglomerates of particles generated during heating and then rapid cooled down, shows spectral lines less clear. Moreover, Pe-1, rich in vinyl double bonds, shows the more intense EPR spectrum than Pe-2 and Pe-3. This is due to the fact that this radical can be formed through a reaction between a secondary alkyl radical and a terminal double bond. The formation of this radical is therefore closely linked to the presence of double bonds and/or ramifications in the polymer chain.

The reactions for the formation of a tertiary radical can be summarized in the following scheme:



*In reaction 1 the formation of a tertiary alkyl macroradical is strictly connected with the presence of branches, that are not so evaluable in UHMWPE because of their very low concentration.*

*Reaction 1 is an intramolecular migration of the unpaired centre to form a more stable radical.*

*On the other hand, pattern 2 shows a different tertiary alkyl macroradical formation. In fact, secondary alkyl macroradical react with a vinyl double bond to obtain a Y-shaped crosslinking (2a),<sup>[31]</sup>. When reaction 2a has occurred, reaction 2b is likely to occur because of the higher stability of a tertiary alkyl macroradical. This process takes place in the amorphous phase or at least in the “all-trans phase”<sup>32</sup>, the region between the crystalline and the amorphous zone where vinyl double bonds are present. The reaction involved thus lead to the formation of a secondary radical macroalkyl in the amorphous phase.*

As already reported the secondary alkyl macroradical, which form a sextet, is well observed at low microwave power and its EPR spectrum shows an amplitude of about 17.5 mT. On the contrary the tertiary macroradical, which form a septet of rows, is observed clearly at high microwave power and its spectrum has a width of about 10.0 mT, both radicals are centered at a  $g = 2.002$ . Therefore, the spectra of the two radicals overlap only in the central part. It is reasonable to assume that the lateral parts of the spectrum with a greater amplitude correspond only to the secondary alkyl macroradical species without interference or overlapping with tertiary macroradical species. To better highlight the saturation trend only of the secondary alkyl macroradicals towards the microwave power has been considered for all the irradiation doses (10, 30, 60 and 100 kGy). . In fact, evaluating the integrated intensity of the lateral wings (that is a partial integration of EPR spectra), it is possible to follow the secondary alkyl macroradical amount modification as a function of the square roots of the microwave power. Figure 2 shows the performance obtained only for the sample Pe-2, in which due to the high crystallinity the lateral wings of secondary alkyl macroradical are well visible, better than in the case of Pe-1 and Pe-3 samples.



## Figure 2

Figure 2 shows that, increasing microwave power, EPR signal grows up to about 1 mW for all irradiation doses while at higher microwave power the signal intensity decreases (a part for the sample irradiated at 10 kGy that is constant). This is typical of radicals which signals follow a saturation trend.

It is possible to compare Pe-1 and Pe-2 intensities trend respect to the secondary alkyl macroradical considering low microwave power spectra (0.1 mW) vs the integrated lateral wings signals for all the irradiation doses. In figure 3 this trend is reported .

## Figure 3

As irradiation dose increases the secondary alkyl macroradical amount increases.

This amount for all the irradiation doses is greater for Pe-2 sample respect to Pe-1, in effect, Pe-2 is the sample with the highest crystallinity and consequently with the highest number of secondary alkyl macroradical that survives after the end of irradiation.

In figure 4, on the other hand, the total integrated intensities for Pe-1 and Pe-2 spectra at 1 mW are reported as a function of irradiation dose. Unfortunately for Pe-3 it was not possible to integrate signals for all irradiation doses because of the EPR spectra low intensity.

## Figure 4

The integrated intensity of the spectra is proportional to the number of all radicals present and in absence of saturation phenomena (see fig. 2). At this microwave power (1mW) the signal due to the tertiary alkyl macroradical is already present, even if with low intensity. From the figure 4 it is clear that for both samples the radical amount increases with the dose of radiation but this increase is not perfectly directly proportional.

At this microwave power all radicals are detected and so this graph can be considered as a sum of two different behavior:

- a) secondary alkyl macroradicals amount increase with the irradiation dose
- b) tertiary alkyl macroradicals increase but not directly proportional with the dose. The double bond amount plays an important role in the formation of these radicals and consequently in the total intensities of the EPR spectra.

For Pe-2 the secondary alkyl macroradical contribution is higher than the tertiary alkyl macroradical one and the total integral value increases with a quasi linear trend with the dose.

For Pe-1 with a lower secondary alkyl macroradicals amount the tertiary alkyl macroradical contribution is not negligible. It is possible to observe a quasi linear increase up to 30 kGy, then the amount of double bonds is not enough to further produce new tertiary alkyl macroradicals, so a lesser increase is visible between 30 and 60 kGy), then the subsequent increase is again related to the further formation of the secondary alkyl macroradical.

Moreover, Pe-2 for all irradiation doses shows a bigger amount of radicals respect to Pe-1, but at low doses the difference is less evident. This behavior is due to the different crystallinity percentage in the two samples. At low irradiation doses higher crystallinity can compensate the lower amount of double bonds and the result is a very similar amount of radicals generated in the two samples.

In order *to have an idea* of the contribution of the tertiary macroradical, which exhibits a narrower spectrum and completely overlapped in the central part to the spectrum of the secondary alkyl radical, *we decided to* subtract the intensity of the integrated secondary alkyl radical spectrum (at low microwave power) from the integrated intensity spectrum of the high power microwave radical. *Even if, as shown in fig. 3, the intensity of alkyl radicals at high microwave power and for higher irradiation doses is not negligible, subtracting the integrated intensity of the low power signal to the high power signal, the tertiary radical intensity trend can be roughly evaluated (Figure 5).*

Figure 5

Increasing the dose of irradiation also the EPR integrated intensity spectra of the two polyethylenes gradually increases, in particular however, there is a greater intensity for the Pe-1 with an opposite trend with respect to Figure 4. This behavior can be explained considering that the tertiary radical is formed by the interaction of an alkyl radical with a double bond. In the Pe-1 the amount of double bonds is an order of magnitude greater than the Pe-2 (see Table 1).

Finally it was rated the decay of the radicals generated after irradiation in the three polyethylenes versus time. First of all, we shall consider that, according to a statement from Dole <sup>[16]</sup> if the irradiation is performed at room temperature, 96% of the radicals formed have time to recombine. For this reason, when the first EPR spectra were recorded only a small fraction of the generated radicals survived. As noted previously the Pe-2, sample with the greater crystallinity, presents a higher number of radicals, followed by the Pe-1 and Pe-3 by exactly according to the percentage of crystallinity present in each sample (respectively 90, 70, 40% ).

In figure 6 total integrated intensity at time t divided by value at time 0 is reported as a function of time for the three polyethylenes.

## Figure 6

In Figure 6B (magnification) the performance of the Pe-3 is stressed. It shows a slower decay compared to the Pe-1 and Pe-2 that behave in a similar way. This is due to the fact that in the first 24 hours, the decay is primarily due to the disappearance of secondary alkyl macroradicals. In the sample Pe-3 the number of residual generated radicals is lesser than the amount of radicals in the Pe-1 and Pe-2. The radicals generated in the Pe-1 and Pe-2 fell drastically in the first 1500 minutes and then reach a plateau. The radical species that survives longer in time is due to tertiary macroradical. After about 3500 minutes the samples Pe-1 and Pe-3 with a similar amount of tertiary radicals show a reduction of total radicals of about 35%, the Pe-2, which on the contrary has a lower number of tertiary radicals due to a smaller amount of vinyl double bonds, has a residual amount of radicals of about 50%.

## Figure 7

In Figure 7 a comparison between the EPR spectra of the sample Pe-1 recorded soon after irradiation and 7 days after is reported. After 7 days from the irradiation, in the sample Pe-1 some radicals are still present. A further comparison between the intensities of the different radicals in the spectra recorded at different microwave power is shown.

The EPR spectrum at 0.1 mW has been modified, in fact secondary alkyl radicals are no longer present in the samples after 24 hours<sup>[28]</sup>. The EPR signal is a septet and it has been attributed to a more stable allyl radical, which remains in the sample for a longer time after irradiation. The allyl radical is in part already present immediately after the irradiation but covered by the stronger and wider signal than the secondary alkyl radical and in part is formed by intramolecular migration of the unpaired electron of the secondary alkyl radical.<sup>[33]</sup>

The EPR spectra recorded at 100 mW and related to the tertiary alkyl macroradical do not change in time, neither in shape nor in intensity. In effect tertiary radicals are much more stable than the secondary alkyl macroradicals.<sup>34</sup>

## Conclusions

The polymer synthesis process determines its structure, termination reactions are responsible for the different amounts of double bonds and consequently of the percentage of crystallinity.

These two factors are the fundamental results in the stabilization and in the reactivity of the radicals generated on the same materials by a high energy radiation such as electron beam.

The irradiation always generates radicals both in the amorphous and in the crystalline phase, but in the amorphous phase a rapid recombination of the radicals themselves is possible through electrons mobility in the material. In the crystalline phase, mobility is reduced and radicals occur more stable. Although the various types of radicals (secondary and tertiary alkyl or allyl) are influenced by the chemical structure of the system, materials with a large number of double bonds form more tertiary alkyl macroradicals, which are quite stable over time. On the contrary polymers with a low number of double bonds will form a lower number of radicals and tertiary alkyl radicals will form more secondary, whose stability is certainly lower in time (about 24 hours).

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