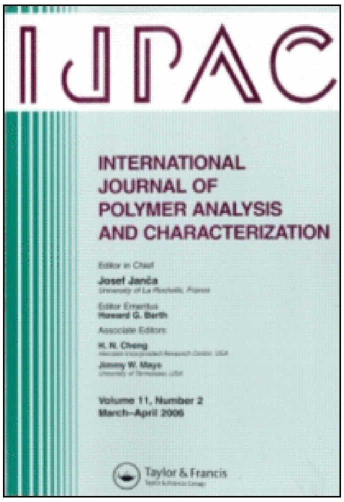

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STUDY OF THE RADICAL SPECIES INDUCED BY ELECTRON-BEAM IRRADIATION IN VACUUM ON BIOMEDICAL UHMWPE

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Ultra high molecular weight polyethylene (UHMWPE) is a component of mobile prostheses. The irradiation performed to sterilize and cross-link the polymer limits its life because of the free radicals originated during this process. In this work, a UHMWPE was electron-beam irradiated under high vacuum and annealed. Mechanical tests were performed on the UHMWPE samples before and after the annealing treatment. The results were compared with a study of radical species type and amount and the crystalline degree changes. Experimental results show that the annealing treatment prevents degrading reactions, favors intermolecular and/or intramolecular chemical rearrangements, and improves wear resistance without compromising the typical elasto-plastic mechanical behavior.

***Keywords*:** EPR; Free radicals; Irradiation; Mechanical properties; Polyethylene (UHMWPE)

INTRODUCTION

Biomedical ultra high molecular weight polyethylene (UHMWPE) is commonly used in antifriction bearings in articulating components of mobile prosthesis. Much research has been done to improve its properties.[1] Despite its biocompatibility and good mechanical performance, which make it suitable for applications in this field, it is known that UHMWPE could be degraded by oxidative reactions, leading in some cases to the need of premature removal of the prosthetic implant.[2] The oxidative degradation of UHMWPE results from the formation of free radical species generated during polymer sterilization treatments and when using high-energy irradiation.[3] In fact, oxygen rapidly reacts with the macro-radicals forming

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peroxides species, which could develop into further chemical species such as alcohols, carboxylic acids, and ketones. In particular, these modifications occur in the amorphous part of the polymer, changing the polymer microstructural organization.[4] In the absence of oxygen, the radical species could interact among them, with formation of double bonds, and resulting in intra- and intermolecular recombination reactions that increase the order degree. These latter processes reflect the macroscopic properties of the polymer, which becomes stiffer and increases its wear resistance[5]

In order to avoid the oxidative degradation of prostheses sterilized with γ-rays in air, the polymeric starting material can be doped by antioxidants, such as α-tocopherol (α-T), which scavenge the free radicals in the material as soon as they form, as reported by some authors.[6] There is also great interest in finding the best conditions to limit polymer degradation phenomena through physical modifications of the polymeric material.[7] In other words, UHMWPE can be irradiated with electron beam followed by a thermal annealing or a remelting process to stabilize the radicals.[8,9] In order to check the radical presence and the effectiveness of the stabilizing process, the electronic paramagnetic resonance (EPR) technique can be successfully employed.

Recently, EPR spectra were found to be very useful in the study of electron beam–irradiated UHMWPE at room temperature in both air and vacuum.[3] In particular, these authors studied the chemical evolution of the radicals and monitored the decay of secondary alkyl macroradicals formed in the amorphous region. Their observations demonstrate that these radicals have a high mobility and ability to react with parts of the polymeric chain due to their prolonged lifetime, which spans from 3 to 10 h, in the polyethylene matrix.

In this work, UHMWPE samples were electron beam irradiated under high vacuum (5×10^{-7} mbar) and high temperature ($T = 110°C$). The UHMWPE was also kept under heating after the electron beam irradiation (annealing at 100°C) for different times (60 or 120 min), in order to avoid oxidative degradation and hence favor cross-linking reactions. We also determined the mechanical performance changes, before and after the annealing, associating them with a spectral EPR analysis of the formed radicals with the specific aim to correlate the changes of material performance to the type of radical rearrangements. To this purpose wear, hardness, and tensile mechanical tests were performed on the UHMWPE samples.

MATERIALS AND METHODS

Sample Preparation

A Ticona UHMWPE resin GUR 1020 (average molecular weight of 3×10^6 g/mol, density of 0.93 g/cm^3, calcium stearate free) was employed to obtain 120 mm × 120 mm × 1 mm thick sheets. UHMWPE samples were prepared by compression molding using a laboratory press ($T = 200°C$, 15 min, $P = 20$ MPa), according to the conditions used by Suarez and de Biasi.[10]

Some pure UHMWPE sheets were irradiated under high vacuum (pressure of 5×10^{-7} mbar) with accelerated electrons at 5 MeV energy by a 1 kW autofocusing standing wave electron LINAC (linear particle accelerator). The current was

200 mA, the dose 100 kGy, and the dose rate 275 Gy/s. The preconditioning and irradiation temperature was 110°C. The pure UHMWPE is denoted as NT (not treated).

The postirradiation treatment at T = 110°C (annealing) was performed for 60 and 120 min, in the samples denoted as V60 and V120, respectively. The sample denoted as V0 was not annealed. In Table I, all treatments of these samples are summarized.

Electron Paramagnetic Resonance (EPR)

A Bruker Elexsys E500 CW-EPR spectrometer driven by a PC running the XEpr program under Linux and equipped with a Super-X microwave bridge operating at 9.3–9.5 GHz and a SHQE cavity was used throughout this work. All EPR spectra were recorded at room temperature by using quartz tubes of 3 mm internal diameter. In addition, to increase the signal-to-noise ratio of these EPR spectra, several scans were accumulated for each sample. Instrument settings for EPR spectra recording was as follows: number of scans 1–5; microwave frequency 9.770–9.772 GHz; modulation frequency 100 kHz; modulation amplitude 0.2–0.6 mT; time constant 164–327 ms; sweep time 2.8 min; microwave power 1–40 mW; receiver gain $1 \times 10^4 - 2 \times 10^5$.

EPR spectra at different microwave powers (1, 20, 40 mW) of a V0 sample were recorded about 1 min after irradiation and are shown in Figure 1. In order to evaluate the total radical concentration, a double integration was carried out on the EPR spectra obtained at 20 mW.

The experimental spectra were simulated by using the WinSim and Winsim2002 programs[11] and assuming the presence of the following radicals:

$$\text{alkyl } -CH_2-{}^{\bullet}CH-CH_2- \quad (a_H = 22.1\,G,\ a_{4H} = 31.6\,G)$$

$$\text{allyl } -CH_2-{}^{\bullet}CH-CH{=}CH-CH_2-$$
$$(\text{or vinyl},\ a_{2H} = 13.0\,G,\ a_H = 4.0\,G,\ a_{4H} = 13.0\,G)$$

$$\text{dienyl } -CH_2-{}^{\bullet}CH-CH{=}CH-CH{=}CH-CH_2-$$
$$(a_{3H} = 8.9\,G,\ a_{2H} = 1.9\,G,\ a_{4H} = 8.9\,G)$$

Table I. Temperature conditions used before (T_b), during (T_i), and after (T_a) UHMWPE irradiation

	Temperature conditions			
Sample code	Before (T_b) (°C)	During (T_i) (°C)	After (T_a) (°C)	Time[a] (min)
NT	25	25	25	—
V0	110	110	25	—
V60	110	110	110	60
V120	110	110	110	120

[a] Annealing treatment time refers to the time necessary to keep the sample heated after the irradiation.

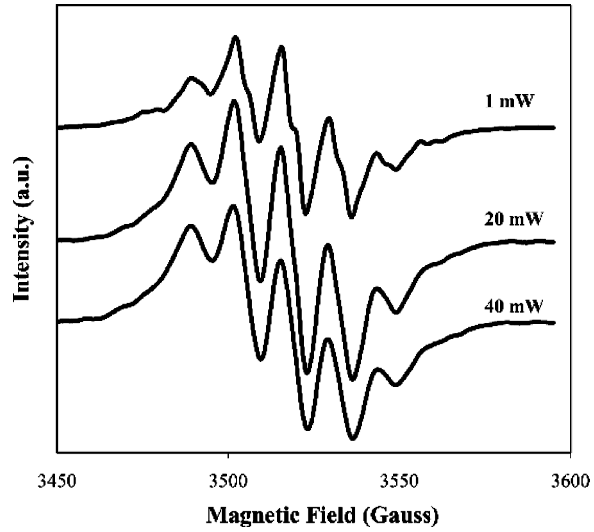

Figure 1. EPR pattern intensities of sample V0 as a function of the applied microwave power.

trienyl $-CH_2-{}^{\bullet}CH-CH=CH-CH=CH-CH=CH-CH_2-$
$(a_{4H} = 7.7\,G,\ a_{3H} = 0.7\,G,\ a_{4H} = 7.7\,G)$

polyenyl $-{}^{\bullet}CH-(CH=CH-)_n-$ (single large line of about 17 G)

peroxy $-CH_2-CH-(O-O^{\bullet})-CH=CH-CH_2-$ (single line of about 5 G)[12,13]

It is possible to quantify the reaction species originating from the different treatments through the determination of a radical index (R_i) by the following formula:

$$R_i = Q_t/Q_{Ref} \tag{1}$$

in which Q_t is the EPR peak area measured at time *t*, and Q_{Ref} is the EPR peak area of the sample, measured at first survey, which generally occurs after 1 min.

Mechanical Tests

Tensile, wear, and hardness mechanical tests were performed on both the untreated and the electron-irradiated polymer samples. These latter samples were tested 6840 min after the electron beam irradiation.

The sample geometry used for tensile stresses was made according to the ASTM 638 M-3 international protocols (60 mm total length, 10 mm useful length, 2.5 mm minimal width, 1 mm thickness) and was obtained by using a manual DGT System sample cutting press.

Tensile stresses were applied to the UHMWPE samples by a universal testing machine (Lloyd Instruments LR 10 K) with a crosshead speed of 1 mm/min. For each irradiation dose, 10 specimens were tested in order to obtain a mean value of all these quantities. The measurements gave values resulting in the following parameters: the tensile module, E_t (MPa); the tensile yield strength, σ_y(MPa); the ultimate tensile strength, σ_u (MPa); and the elongation at break, ε_u(%). The work to fracture is a parameter that gives an estimate of the material toughness. It was obtained by the integration of the area under the stress-strain curves.

Wear measurements were performed by a "pin on disc" test machine to evaluate the weight loss due to friction material (20 mm × 20 mm × 1 mm thick). The samples were placed on a rotating plate and stainless steel AISI 316 L pin was pressed against the polymer surface, generating a pressure of 10 MPa, without any lubrication liquid. Standard radius of the pin on the disc test machine was 4.25 mm. The simulations were carried out at the speed of 120 rotations per minute (rpm).

The wear rate (Wr) was determined by dividing the weight loss (estimated from the weight difference before and after the wear stress, by using a microbalance) by the number of cycles (expressed in million cycles) based on the following formula:

$$W_r = \frac{P_i - P_f}{\frac{N^\circ cycles}{10^6}} \tag{2}$$

where P_i is the initial weight (g) and P_f is the final weight after the wear stress due to the number of cycles (N° *cycles*). Each sample was polished with ethanol before and after the wear test.

Vickers hardness measurements were performed by applying a load of 0.49 N for 10 s, on samples with 2.5 mm × 10 mm surface dimension (Shimadzu DUH-200 instrument).

RESULTS AND DISCUSSION

Table II shows the results of the tensile, hardness, and wear mechanical tests performed on the samples of polyethylene before (NT) and after electron irradiation under vacuum, on the annealed (V60 and V120) and not annealed (V0) samples. Figure 2 shows the stress/strain curves of these samples.

The mechanical results showed that the electron treatment stiffens the polymer, making it fragile, less hard, and less resistant to fracture and yield. In fact, sample V0 has a higher E_t value (460 MPa) and lower σ_y, σ_u, and ε_u values (22 MPa, 50 MPa, and 540%, respectively) than those of the NT sample ($E_t = 328$ MPa, $\sigma_y = 25$ MPa,

Table II. UHMWPE mechanical characteristics measured before and after irradiation

Sample code	E_T [MPa]	σ_y [MPa]	σ_u [MPa]	ε_u [%]	Work to fracture [MPa]	Vickers hardness [HV]	Wear rate [mg/million of cycles]
NT	328 ± 20	25 ± 1	54 ± 3	769 ± 46	241 ± 11	3.9 ± 0.1	6.0
V0	460 ± 43	22 ± 1	50 ± 3	540 ± 31	170 ± 15	4.5 ± 0.1	5.7
V60	460 ± 26	30 ± 2	65 ± 4	595 ± 32	254 ± 9	4.1 ± 0.1	1.6
V120	512 ± 41	32 ± 2	68 ± 5	560 ± 48	245 ± 13	4.2 ± 0.1	1.2

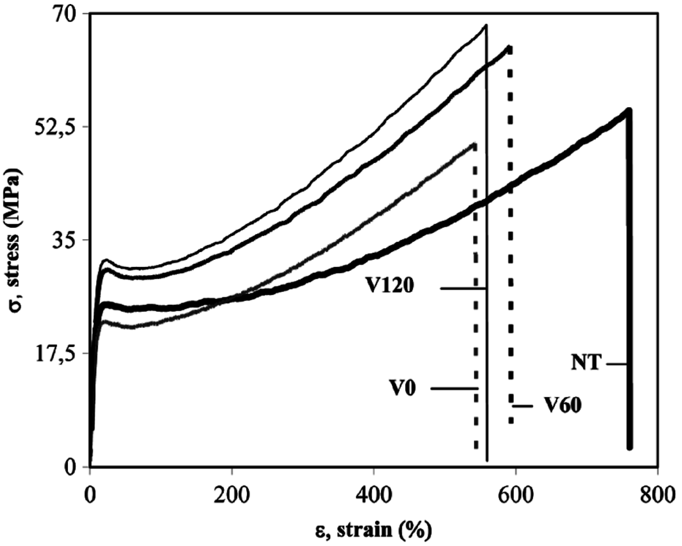

Figure 2. Stress-strain curves of the V0, V60, V120, and NT samples.

$\sigma_u = 54$ MPa, and $\varepsilon_u = 769\%$). As a consequence, the V0 sample is less tough than the NT sample since its work at fracture is lower (170 MPa and 241 MPa, respectively). Instead, the annealed materials (samples V60 and V120) retained an appreciable toughness and hardness and increased their tensile and yield strength, although they were less deformable than the NT sample (see Table II). For example, their work at fracture and hardness values (245–254 MPa and 4.1–4.2 HV, respectively) were higher than that of the NT sample (241 MPa and 3.9 HV) while the ε_u values (595–560%) were lower than that of the NT sample (769%).

Therefore, thermal annealing just after irradiation improves the mechanical properties of UHMWPE, because of reactions of the free radicals produced during irradiation, which highly favor the formation of both intramolecular double bonds and intermolecular cross links, so that the final product is structurally stable, as observed in a previous article.[14]

Another consequence of the cross-link formation produced after annealing is the stiffening of the polymeric chains, which opposes wear stress, according to Medel et al.[8] In fact, V60 and V120 samples show considerable improvement of the wear resistance (73–80%; see Table II) compared to the NT sample, as can be seen from the wear rate that decreases from 6.0 mg/million of cycles to values of 1.6–1.2 mg/million of cycles. The lack of thermal annealing, or an incomplete thermal stabilization process, enhances the chain scission reactions rather than the formation of double bonds and cross-linking. In this case, the presence of a residual amount of free radicals, which generally react with oxygen, gives rise to a polymeric material having poor mechanical properties.[15] The wear test performed on the V0 sample is in agreement with these considerations since the wear resistance (5.7 mg/million of cycles) is nearly the same as that of the NT sample.

In order to test the efficiency of the annealing process in the removal of the free radicals and the subsequent structural transformations induced in the polymer, in

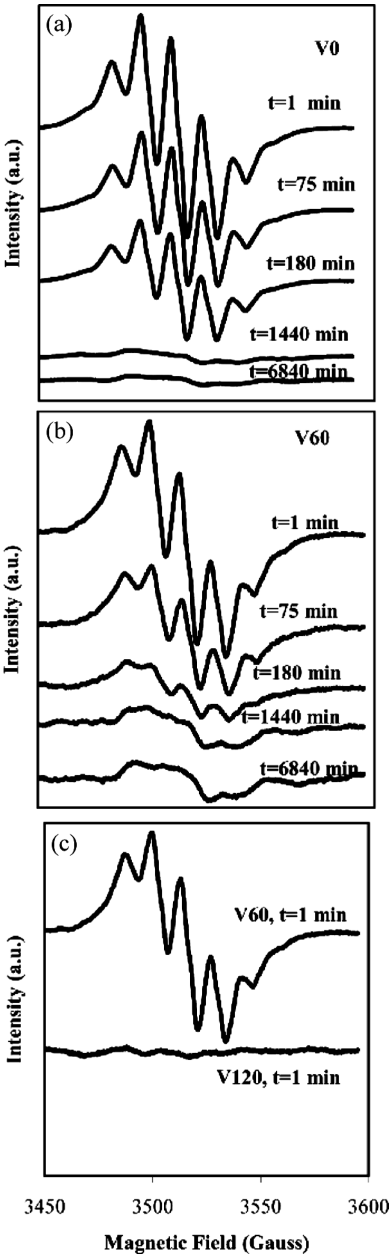

Figure 3. EPR decay spectra of the radical species present in samples V0 (a) and V60 (b) and a comparison of the spectra obtained from samples V60 and V120 at time t = 1 min (c).

addition to the lifetime of radicals, we carried out a qualitative and quantitative study of the radical species formed immediately after the irradiation as well as after the annealing.

Generally, the EPR spectra were recorded one minute after the irradiation (V0 sample) or one minute after the annealing (V60 and V120 samples). Figures 3(a) and 3(b) shows typical examples of EPR spectra of the samples V0 and V60, within the range of 1–6840 min after irradiation.

Sample V0 showed a typical pattern of lines that results from the superposition of several EPR features due to the presence of several radical species generated by irradiation. This pattern persists for a period of 180 min, although its intensity reduces gradually over the time period. Only radical traces have been detected after 1440 min. Conversely, the pattern peak intensities of the V60 sample reduced earlier compared to those of V0, the intensity of the EPR spectrum of the latter recorded after 180 min being roughly the same of that V60 after 75 min. Once again, the comparison of V60 EPR spectra with those of the sample V0 demonstrated that the annealing procedure performed on the sample V60 is an efficient way to decrease the radicals lifetime, by favoring the generated radical chemical reactivity.

The lifetime can be quantified by evaluating a parameter called radical index (R_i), which is calculated as described in the Materials and Methods section. In Table III R_i values of V0, V60, and V120 samples as a function of the irradiation time are gathered. These data show that at the time of 1 min from irradiation, the highest amount of radical species was detected in the sample V0, therefore it has been taken as the reference Q_{ref} value (i.e., $R_i = 1.00$). The annealed sample V60 exhibits a $R_i = 0.11$, clearly indicating that the annealing treatment greatly reduces the total radical amount, by about 90%. In the graph of Figure 4, the R_i values of V0 and V60 samples are plotted as a function of time. The trends of these two curves highlight the strikingly high difference in radical amount between the two samples and how this amount decreases after the annealing treatment. In particular, the R_i value of the V0 sample shows a reduction of 94% after 1440 min ($R_i = 0.06$), which decreases further to 96% after 6840 min ($R_i = 0.04$). On the other hand, the starting R_i value of the annealed V60 sample is already appreciably low ($R_i = 0.11$) and a reduction of 83% is observed after 1440 min, then remaining almost unchanged ($R_i = 0.019$). Moreover, the radical species lifetime changes, depending on the thermal process performed on the polymer: in the unannealed sample, V0, radical species are still present even after 3 h (i.e., 180 min), although the amount is about 50% ($R_i = 0{,}53$) of the initial value, whereas in the annealed V60 sample, radicals are practically quenched ($R_i = 0.028$).

To examine the effect of prolonged annealing on the lifetime of the radical species in irradiated UHMWPE samples, a sample named V120 was annealed for 120 min after the irradiation treatment. The quantitative analysis of the V120 sample

Table III. Radical indexes as a function of time

Time (min)	V0	Sample V60	V120
1	1.00	0.112	0.006
75	0.69	0.061	<0.006
180	0.53	0.028	<0.006
1440	0.06	0.019	<0.006
6840	0.04	0.019	<0.006

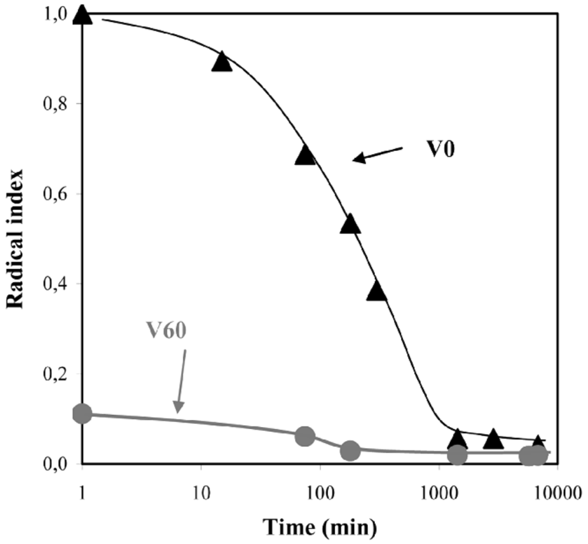

Figure 4. Radical index decay curves as a function of time for V0 and V60 samples.

(Table III) shows a very low R_i value of 0.006, from the earliest time after irradiation, suggesting the absence of any radical species. The effect of the annealing treatment is also clearly shown by comparing the EPR spectra of the V60 and V120 samples at the initial time of monitoring (t = 1 min), as can be seen at a glance in Figure 3(c). This confirms the quite total absence of free radical species in the V120 sample, while a noticeable amount is still present in the V60 specimen. So this result confirms the necessity to increase the annealing time, from 60 to 120 min, in order to completely eliminate radicals in the irradiated sample by allowing their quenching reactions.

In order to get a deep insight about the nature of the radical species formed after the irradiation of the UHMWPE samples, a simulation of some spectra belonging to different specimens was undertaken. Besides revealing the nature of the radical species involved, each simulation allowed us to assess the proportional contribution of each species to the whole simulated spectrum. The deconvolution of the EPR pattern of V0 and V60 samples evidenced the presence of at least five radical species, i.e., allyl, dienyl, trienyl, polyenyl, and peroxide radicals (see Table IV). In particular, allyl radicals are present in the highest amount among all the radical species in both the V0 and V60 samples. Moreover, in the V0 sample peroxide radicals are also

Table IV. Radical species percentages detected on UHMWPE samples just after irradiation or annealing (t = 1 min)

Sample	Allyl (%)	Dienyl (%)	Trienyl (%)	Polyenyl (%)	Peroxy (%)
V0	80.20	0.70	1.65	0.23	17.2
V60	43.80	5.20	14.00	37.00	0.0
V120	0.00	0.00	0.00	0.00	0.0

present in an appreciable percentage (17%), while in the V60 sample the major percentage is represented by polyenyl radicals (37%). Finally, smaller amounts of the other radical species are also present.

Figure 5 shows the intensity changes of the three main radical species (allyl, polyenyl, and peroxide) on both V0 and V60 samples over 1440 min. The graphs show that the decay rates of allyl and polyenyl radicals are generally faster than those of peroxy radicals, which might possess a sufficient stability in the UHMWPE matrix. A closer inspection of the allyl and polyenyl radical trends makes apparent a nearly complete quenching of the radicals after about 1440 min because they evolve by means of rearrangements towards either new radicals or nonradical species (which unfortunately are EPR silent). These results support a mechanism by which the allyl and polyenyl radicals react, forming chemical species not containing the peroxy moiety. In fact, peroxy radicals are nearly missing in the V60 sample, confirming that double bond formation or other chemical rearrangements are generally favored in the annealed samples. A support to this hypothesis came from results for the V60 sample, which revealed the presence of a high amount of allyl and polyenyl radicals due to the one-hour annealing process under vacuum. This treatment gives rise to the possibility of new chemical rearrangements for the allyl radicals towards the formation of polyenyl species rather than the peroxy radicals. In contrast, the high amount of peroxy radicals in the V0 sample is a direct consequence of the irradiation in the presence of air.

In the reaction scheme (Figure 6) the probable radicals formed after the electron beam irradiation of the polymeric chains in vacuum are indicated. In particular, one or more radicals can be formed along the chains or near their endings (Figure 6(a)). If the radicals originated on vicinal (adjacent) carbon atoms, they can stabilize themselves, by forming a double bond (Figure 6(b)). The presence of double bonds along a polymeric chain (intramolecular bonds) is supported by the presence of the EPR feature of the allyl radical species. In particular, we can consider the following resonant radical form:

$$-CH_2-CH^{\bullet}-CH{=}CH-CH_2- \leftrightarrow -CH_2-CH{=}CH-CH^{\bullet}-CH_2-$$

as the most common chemical recombination of the macro-radicals occurring in vacuum-irradiated polyethylene.

Concurrently, other recombination reactions are also possible between the $-CH-$ radicals belonging to different chains. In other words, intermolecular recombination reactions are favored when the polyenyl radicals are embedded in long $-(CH_2)_n-$ chains, which disfavor or even greatly hinder an intramolecular reaction. These chemical rearrangements give rise to the formation of branched and/or cross-linked species from different polymeric chains so that the formation of new intermolecular bonds is preferred (Figure 6(c)). This bond formation is accomplished by the allyl and the polyenyl decay, which show an evolution toward new chemical species.

Furthermore, the alkyl radical was not observed in any of the EPR spectra, although it normally forms as a primary radical after irradiation. This evidence can be explained on the basis of a very short lifetime of the alkyl radical under our experimental conditions. In other words, this fast decay compared with other

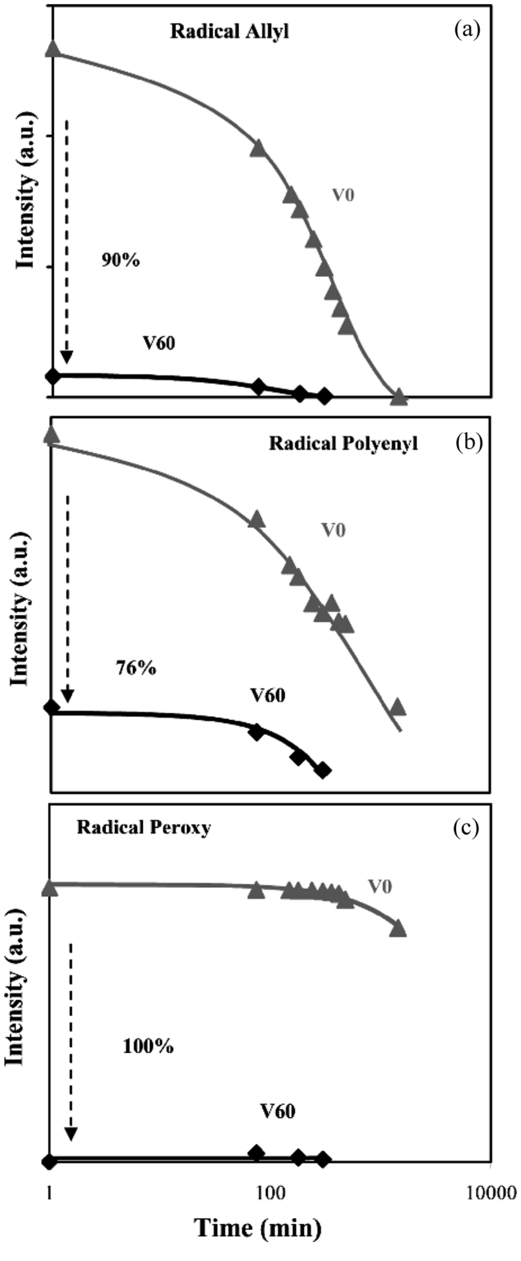

Figure 5. Allyl (a), polyenyl (b), and peroxy (c) radicals species decay curves as a function of time.

radicals also present in the inert atmosphere makes the alkyl radical undetectable on our EPR experiment time scale.[12,13]

Finally, the presence of peroxy radicals indicated that a reaction with oxygen occurred and caused chain scissions, as previously discussed. The macroscopic

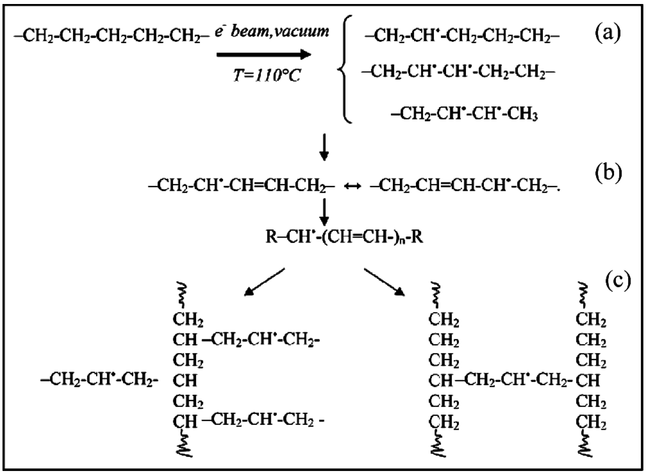

Figure 6. Scheme depicting a possible formation pathway of radical species highlighting the (a) intramolecular and (b) intermolecular processes and (c) rearrangement reactions.

consequence is a loosening of mechanical features in terms of both wear resistance and material toughness. The EPR results are in line with the mechanical studies, in fact, the peroxy radical presence was revealed in the V0 sample, the tensile and wear resistance of which are decreased.

Therefore, it is important that all radicals must be quenched before extracting the sample from vacuum, since their reaction with oxygen lead to the formation of peroxy species. In addition, allowing the radicals to form both double bonds and cross links results in an improvement of the mechanical features of the polymeric material, especially in terms of wear resistance and maintenance of elasto-plastic behavior.

The optimal tensile and wear performance of the V120 sample is in agreement with the EPR results since this sample was annealed for a longer time (120 min), so no free radicals were detected after the treatment.

Finally, in Figure 7 the crystalline degree (χ_c) values of the NT, V0, V60, and V120 samples versus annealing time are plotted. The χ_c values of the three irradiated samples (68.8%, 81.1%, and 83.8%) are all higher than that of the untreated sample (NT, 52.7%). Interestingly, this plot shows that the crystalline degree proportionally increases as a function of the annealing time. These experimental data are supported by the results found in a previous work, which outlined the proportionality of the crystalline degree to the formation of cross links and, hence, to the wear resistance of the polymer.[14] In addition, these data are in agreement with our EPR results and wear mechanical tests, as shown in the V120 sample, which was annealed for the longest time, and, as a direct consequence, exhibited the highest mechanical performance, especially in terms of wear resistance, together with complete absence of free radicals.

All the result reported here clearly suggest the necessity of performing polymer irradiation under high vacuum in order to exclude any UHMWPE contact with oxygen before the annealing treatment has gone to completeness. This method of

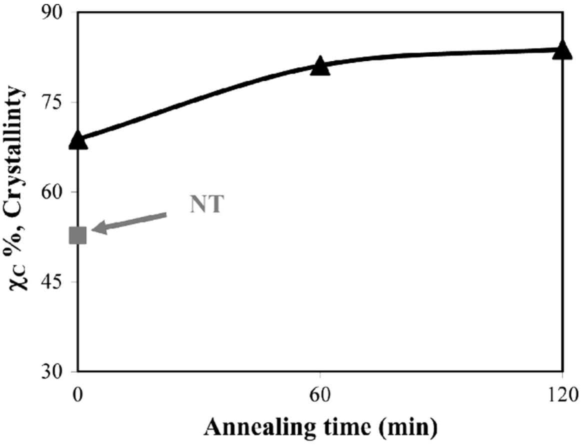

Figure 7. Crystalline degree changes of NT, V0, V60, and V120 samples as a function of annealing time.

treating the polymer ensures not only that all of the formed radicals quench and peroxy species cannot form, but also that its mechanical properties are improved due to the formation of both double bonds and cross links.

CONCLUSIONS

In this work, the biomedical polyethylene UHMWPE was irradiated with electron beams at an energy of 5 MeV under high vacuum followed by an annealing treatment. In particular, polymer samples have been studied before and after the annealing procedure by means of physical and mechanical characterizations.

The experimental results showed that:

1. Free radicals are formed during the electron beam irradiation;
2. In the absence of oxygen and if the macromolecular chains have enough mobility, radicals decay, preferentially forming double bonds and cross links;
3. Annealing treatment for a time of 120 min allows the radical species to react nearly to completeness so that they are reduced to less than 10% of their initial amount.

Allyl, polyenyl, and peroxy radicals are the main species present in an appreciable amount in unannealed samples. The radical species lifetime in the samples annealed for 60 min is very low since they are almost completely eliminated after 3 h. Notably, a 120 min annealing treatment completely eliminates all the radicals.

Free radicals are highly reactive species that lead to the formation of oxidized species, especially in the presence of oxygen. Oxidized species, even in a small amount, decrease the mechanical performance of the polymer. In fact, the results of mechanical tests indicate a weakening of properties for unannealed polyethylene. Strikingly, the mechanical properties of annealed samples are significantly improved, since the polymer becomes harder and stiffer and more crystalline, as well as gaining higher wear resistance, although it is less deformable than the pure material.

In conclusion, electron beam irradiation can be considered not only a mere sterilization process, but also an effective way to induce intermolecular and/or intramolecular new bonds in the polymer. The results shown in this study encourage the use of electron beam irradiation (under high vacuum and heat, followed by an annealing treatment) as a procedure to improve the mechanical wear resistance of the polymer and a means to minimize its degradation during its lifetime as prostheses.

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