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The assessment of thermal and radiation stability of UHMWPE

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Preirradiated ultrahigh molecular weight polyethylene (UHMWPE) was subjected to other cycle of γ-exposure in order to explain the behavior of this material after radiation processing. The oxygen uptake investigation was selected for the characterization of thermal stability of multisession irradiation. The long life radicals promote crosslinking or oxidative degradation depending on the second irradiation dose and on the environmental conditions. The main kinetic parameters: oxidation period and oxidation rate were evaluated depicting the availability of radiochemical processing of UHMWPE for further long term applications. Irradiation of UHMWPE in salt solution reveals the improvement in the thermal strength for low exposure doses.

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1. Introduction

The high resistance of ultrahigh molecular weight polyethylene (UHMWPE) solves the requirements for production of high performances materials. It means that this material provides a convenient answer to the action of hard service conditions. On this basis, UHMWPE is largely used in the manufacture of prostheses and special medical wear or equipments [1-5].

The quality of materials used for the fabrication of implant articles is stated in ISO 5834-4:2005, where the standard conditions for the oxidation state of materials are imposed. The process of oxidative chain scission starts predominantly in the amorphous phase of materials, which initiates the degradation process in the entire material, either in crystalline or amorphous zones [6].

The oxidation of UHMWPE is in reality a complex sequence of various cascade reactions, which is not fully understood. The main aspect of ageing is related with the maximum oxidation (region of embrittlement) that often occurs 1-2 mm below the surface of UHMWPE components. Perhaps the most convincing explanation for the formation of subsurface maximum in oxidation comes from the work of Yeom et al. [7], who described the cascade of events occurring at various depths within gamma irradiated UHMWPE. At the surface of the UHMWPE the O_2 concentration is highest and most primary alkyl radicals ($-CH_2^{\cdot}$ $^{\cdot}CH_2-$) and secondary alkyl radicals ($-CH_2-CH^{\cdot}-$) produced by gamma irradiation will react to form peroxyl radicals ($-CH-O-O^{\cdot}$ or $>CH-O-O^{\cdot}$, respectively). Other secondary alkyl radicals can combine to form crosslinks. A large concentration of peroxyl radicals exists at the surface and they can combine with O_2 to form ketones, a reaction which does not produce any further free radicals. In the subsurface region, on the other hand, fewer peroxyl radicals form, due to the lower O_2 concentration in this region. Because these peroxyl radicals will be further apart to each other, there will be a lesser tendency to recombine and greater tendency to abstract H atoms from the polyethylene chains, thereby forming hydroperoxides and new free radicals. This initiates a sequence of reactions, where carbonyl groups, chain scission and further free radicals are formed. As oxygen diffuses into the UHMWPE, further reaction with the newly created free radicals can occur, eventually leading to higher levels of oxidation in this inner region relative to material surface. Deeper into the UHMWPE there will be less oxygen available for reaction. Most of the radicals will recombine to produce crosslinks. In fact, the oxidation of this polymer takes place according with the mechanism comprehensively analyzed by Singh [8]. The irradiation of UHMWPE brings about the possibility to test the endurance of material under special conditions.

The radiation crosslinking of UHMWPE exhibits a deep regularity of all σ bonds (Fig. 1), which increases the stability of this polymer.

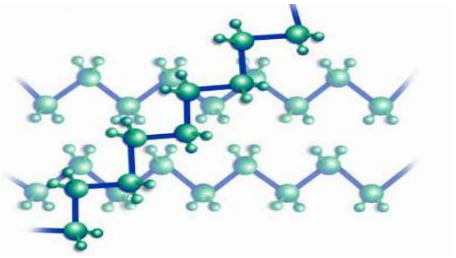

Fig. 1. Spatial structure of radiation crosslinked UHMWPE.

This paper presents the post-irradiation stability of e-beam exposed UHMWPE. These results will be considered for the characterization of life time of prostheses.

2. Experimental

UHMWPE tested in this work was provided by Ultra-Hi Plasticos Industriais Ltda (São Paulo, Brazil) as two sorts: UTEC 3041 (weight average molecular weight 3.10^6 kg/kmol, impact strength: 170 kJ/m^2), and UTEC 6541 (weight average molecular weight 8.10^6 kg/kmol, impact strength: 80 kJ/m^2). The preirradiation (electron beam, maximum energy: 1.5 MeV, dose rate: 22.61 kGy/s) treatment of samples was performed at IPEN, São Paolo, and the second irradiation was carried out in a γ-source (^{137}Cs, dose rate: 0.4 kGy/h) in ICPE CA, Bucharest. During the accelerated electron irradiation of our sampled three different total doses (100, 300 şi 500 kGy) were applied. For γ-irradiation each e-beam irradiated UHMWPE sample was devided into four specimens which received further 0, 10 20 and 50 kGy.

The thermal stability of all kinds of samples was performed by oxygen uptake method [9], which establishes the resistance of material against oxidation by the values of oxidation induction time (the period when the oxidation takes place at the unmeasurable rate), and the oxidation rate – the value of uptaken oxygen on propagation stage of oxidation). The conditions of exidability experiments were: temperature: 200^{0}C, pressure of the oxidation environment (air): 1 atm, sample weight: 20 mg of chips. The oxygen uptake was done as isothermal and isobaric investigations.

The extension of investigation was done on the two types of samples: one kind was native materials (marked with N) and the second kins consisted of recycled UHMWPEs (marked with R). For simulation of human body condition related to the salinity of implant environment, two paralel γ-exposures were accomplised: in air, in distilled water and in salt solution containing NaCl 5 %.

3. Results

The raw materials were qualified by the evaluation of oxidation induction times and oxidation rates in accordance with the nature of samples and the received dose (Table 1).

Table 1. Kinetic parameters of raw and recycled UHMWPEs.

Dose (kGy)	UTEC 3041 N	UTEC 3041 R	UTEC 6541 N	UTEC 6541 R
Oxidation induction time (min)				
0	170	205	138	85
100	84	109	55	46
300	44	42	52	19
500	22	38	30	9
Rate of oxidation (mmol O_2/min)				
0	3.2	2.8	3.9	4.2
100	3.8	3.5	4.5	4.8
300	4.6	4.7	4.8	5.5
500	5.2	5.0	5.1	6.5

The Table 2 presents the kinetic parameters obtained for the irradiated UHMWPE samples in air for the different γ-doses received by all e-beam preirradiated materials. These data concerns the UTEC 3041 N samples, which are representative for all other UHMWPE specimens. Similar results were obtained for the other sorts of ultrahigh molecular weight polyethylene, that demonstrates the similarity in the effect of radiation processing on studied materials.

Table 2. Oxidation parameters for UTEC 3041 N.

Preirradiation dose (kGy)	γ-Irradiation doses (kGy)		
	10	20	50
Oxidation induction time (min)			
0	140	122	191
100	120	130	160
300	140	112	142
500	160	153	123
Rate of oxidation (mmol O_2/min)			
0	3.7	3.9	2.8
100	3.5	3.5	3.4
300	3.4	3.8	3.5
500	3.2	3.6	3.7

The irradiation of UTEC 3041N samples in various environments provided their stability state (table 3).

4. Discussion

The first irradiation of UHMWPE samples with accelerated electrons causes the generation of free radicals, which participate further to other reactions in the function of treatment condition.

The initial materials present a decrease in their thermal stability, which is due to the scission of C-C and C-H bonds. According to the mechanism reported by Bolland and Gee [10], if oxygen is present, peroxyl radical intermediates would be formed and the rate of oxidation increases significantly. From Table 1 it may be remarked that the oxidation induction times decrease sharply for the first 100 kGy. Similar behavior was reported for irradiated other polyolefins [11]. The next doses bring about a lighter alteration in the values of induction periods. However, the modification in the oxidation rate measured on the propagation step does not get large differences between samples, which were irradiated at increasing doses.

Consequently, it may be assumed that the long life radicals that remains in the e-beam irradiated UHMWPE remained as trapped entities. The low rate diffusion of oxygen into these materials does not react with free radicals, and they can survive in the exposed specimens.

The second irradiation (γ-exposure) had allowed radicals to react with each other or with oxygen that is dissolved or diffused into processed samples. The most important results were obtained on the samples that they were not previously subjected to electron beam. They emphasize the availability of radicals to recombine. They rebuild the 3D structure by crosslinking. The kinetic parameters, oxidation induction time and oxidation rate, attend very promising values, which demonstrate the possibility of the delay of significant degradation, if two

steps irradiation processing are included in the processing of bone prostheses.

Table 3. Kinetic parameters of irradiation of UTEC 3041 N in various irradiation environments.

Dose (kGy)	Distilled water	5 % NaCl aqueous solution
10 kGy of γ-dose		
Oxidation induction time (min)		
0	233	464
100	193	189
300	171	112
500	62	74
Rate of oxidation (mmol O_2/min)		
0	2.4	1.9
100	2.8	2.8
300	3.0	3.3
500	3.7	4.1
20 kGy of γ-dose		
Oxidation induction time (min)		
0	399	350
100	170	295
300	68	138
500	14	27
Rate of oxidation (mmol O_2/min)		
0	2.2	2.1
100	2.9	2.8
300	3.6	3.6
500	4.5	4.6
50 kGy of γ-dose		
Oxidation induction time (min)		
0	236	499
100	133	219
300	168	60
500	82	36
Rate of oxidation (mmol O_2/min)		
0	2.8	2.0
100	3.4	3.1
300	3.3	3.8
500	3.0	4.5

These second irradiated samples present higher thermal resistance after irradiation in aqueous salt solution. It means that the contribution of environment would favor the recombination of radicals. This process was depicted as charge transfer process, which involves chloride ions from the interface between polymer and solution. It was also reported in the case of the irradiation of ethylene-propylene copolymers [12]. The difference between the oxidation parameters for the irradiation of UHMWPE in water and aqueous salt solution demonstrates the possibility of enhance in the thermal strength of polyolefins by their radiation treatment at low doses in the presence of salts. The diffusion of oxygen is hindered by the existence of a water layer behind the contact surface of polymer sample. This kind of "protection" is a physical way on which neither additive, nor radical scavengers would offer.

The recycled UHMWPE and UTEC 3041R exhibit higher thermal resistance in comparison with the native corresponding material. This aspect would be explained by the presence of a stabilizer, which retards the radiation oxidation of processed samples. The lack of stabilizer in the formulation of UHMWPE, UTEC 6541R, causes the faster degradation of samples in comparison with the native sort of polyethylene.

These results are in a good agreement with other papers which are concerned with the thermal degradation of various sorts of polyethylene [13 – 15]. The durability of radiation conditioning materials depends strictly on the sequence of applied operations that involve the reactions of free radicals: crosslinking and oxidation [16 – 18].

5. Conclusions

The post irradiation treatment by γ-exposure brings about an improvement in the thermal resistance of the investigated UHMWPE materials. The presence of salt (NaCl) in a low concentration allows decreasing the weariness of materials during the retention in human body.

The modification in the kinetic parameters of degrading UHMWPE depicts the availability of free radicals formed in the first step of irradiation for the recombination with each other.

The testing conditions influenced the level of results. It means that a sequence of the two types of irradiations, accelerated electrons treatment followed by electromagnetic radiation exposure is more favorable for the increase in the thermal stability of UHMWPE. This order involves the formation of high amount of long life radicals, which can react further under the energetic action of γ-radiation.

For medical purposes, the radiation treatment of UHMWPE brings about not only an advanced crosslinking state, but also a sterilization of prostheses and medical wear.

This study confirms the large potential of oxygen uptake method in the characterization of engineering polymer materials.

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