FTIR Investigation of UHMWPE Oxidation Submitted to Accelerated Aging Procedure

*Magda F. Rocha, Alexandra A. P. Mansur, Herman S. Mansur**

Summary: In the present study, an accelerated ageing by oxidative degradation of UHMWPE in hydrogen peroxide solution was performed and the inhibition with ascorbic acid (vitamin C) was analyzed. Both systems were extensively characterized by Fourier Transformed Infrared Spectroscopy (FTIR). Different chemical groups of UHMWPE associated with the degradation reaction were monitored for over 120 days in order to evaluate the possible oxidation mechanisms involved and the inhibitory behavior of vitamin C. The results have provided strong evidence that the oxidation mechanism is rather complex, and 2 stages with their own particular first-order kinetics reaction patterns have been clearly identified. Furthermore, the vitamin C has proven to be an efficient antioxidant for UHMWPE under the evaluated conditions.

Keywords: accelerated aging; polymer degradation; polymer oxidation; UHMWPE

Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a biomaterial widely used as part of prostheses that require articulating surfaces for its excellent mechanical qualities. Prosthesis-wear and delamination are two major problems that limit the life of UHMWPE implants, with both phenomena being mainly the result of chemical oxidation of polymer.[1–5] The process of natural oxidative degradation of UHMWPE usually takes years and it is not possible to wait that long for data to be available when testing biomaterials. Hence, the oxidation of polymer is frequently conducted at highly stressing conditions, such as chemical, temperature and pressure. Accelerated aging has been studied extensively with a combination of elevated temperatures, radiation dose, oxygen partial pressure but using hydrogen peroxide has scarcely been reported.[6] Only in the last years some *in vitro* studies have addressed the chemical oxidation of UHMWPE focused to the knee prosthesis however its mechanism still remains unclear. Despite of a large number of works in the last 2–3 decades indicating a relative satisfactory behavior of UHMWPE for bearing application, further research needs to be carried out in order to properly predict lifetime of these prostheses when implanted.[5–11] The oxidation of UHMWPE is a very complex sequence of various cascading reactions which is not fully understood. More recently, α-Tocopherol (vitamin E) has been used in order to minimize the oxidation and degradation of UHMWPE in biomedical applications, which has recently been approved by ASTM standards. Vitamin C or ascorbic acid is a natural and powerful reducing agent and its effectiveness as antioxidant has been broadly known. Thus, it has been considered as a promising alternative for inhibiting the oxidation of UHMWPE.[12]

Hence, the aim of this research was to investigate and characterize the accelerated degradation of UHMWPE under exposure to an aggressive hydrogen peroxide medium as well as to assess the antioxidant potential of vitamin C for this polymer.

Department of Metallurgical and Materials Engineering, Laboratory of Biomaterials and Tissue Engineering, Federal University of Minas Gerais, Av. Antônio Carlos 6627, 31270-901, Belo Horizonte, Brazil
E-mail: hmansur@demet.ufmg.br

Both mechanisms oxidation and inhibition were evaluated by FTIR spectroscopy.

Materials and Methods

The polyethylene used in this work was ram-extruded UHMWPE (not sterilized) bar stock GUR 1020, of commercial grade and approved for surgical implants (ISO 5834–2/2005), and was kindly donated by Ticona Engineering Polymer (USA). The bar stock was sectioned with a steel blade into 50 mm × 50 mm × 50 mm cubic blocks and samples were sliced with thickness ranging from 150 to 250 μm. All samples were cleaned in an ethanol (P.A., Sigma) and distilled water ultrasound bath, air dried, and submitted to experimental analysis. The experiments were divided into two groups: The group-1, where non-oxidized slices triplicates ($n = 3$) of UHMWPE ("reference control group") were immersed in 30 mL of hydrogen peroxide 30 v/v% and incubated at 37°C. In the group-2, non-oxidized slices ($n = 3$) of UHMWPE were immersed in 30mL of hydrogen peroxide and vitamin C solution at 0.3 e 1.0 w/v% and incubated at 37°C. The degradation oxidative solution was prepared using 30v/v% hydrogen peroxide (analytical grade, H_2O_2, > 30% v/v, ~ 8.8 mol.L^{-1}), which was replaced every five days to maintain the activity of the solution. This solution replacement was based on the estimated half-life of H_2O_2 of approximately seven days at 37°C. The experimental aging times were monitored at 0 (initial state, reference), 7, 14, 21, 28, 60, and 120 days, and such oxidized samples were referred as UHMWPE-Ox.

Fourier Transformed Infrared Spectroscopy (FTIR) spectra were collected in Transmission mode with wavenumber ranging from 4,000 to 400cm^{-1} during 64 scans, with 2cm^{-1} resolution (Paragon 1000, Perkin-Elmer, USA). The FTIR spectra were normalized and major vibration bands were identified and associated with the main chemical groups. The total level of oxidation (Iox) was determined by FTIR according to ISO 5834–2[7] as shown in Eq. 1.

$$I_{ox} = A_O / A_R, \tag{1}$$

where A_O = Integrated area from 1650 cm^{-1} to 1850 cm^{-1} and A_R = Integrated area from 1330 cm^{-1} to 1396 cm^{-1}. The areas were calculated using the software Origin Program®, version 7.0.

Regarding to the evaluation of oxidation some international standards are used, for instance the ISO 5834, that is similar to ASTM Standard F648 (Part 4) and ASTM F2102.

Results and Discussion

Initially, the FTIR spectra presented in Figure 1 were obtained from UHMWPE samples after 28, 60, 120 days of accelerated aging in hydrogen peroxide and compared to non-oxidized reference. The main changes in the FTIR spectrum upon oxidation of polyethylene samples involved the formation of typical products such as isolated hydroperoxides (3,550 cm^{-1}), hydrogen bonded hydroxyls including hydroperoxides (3,410 cm^{-1}), lactones (1,860 cm^{-1}), esters (1,740 cm^{-1}), acids and ketones (1,710 – 1,720 cm^{-1}).[6–11,13–18] In addition, an increase in the absorbance in the 1,400 – 1,180 cm^{-1} region associated with –C-O-C vibrations and in the region from 800 – 1,100 cm^{-1} mostly related to unsaturated C = C groups was noted. In Figure 1, the detail (top, right) emphasizes the main peak in the FTIR spectra corresponding to the strong signal of carbonyl (C = O) groups, in the 1,700 – 1,750 cm^{-1} region, which is rather dependent of specimen degradation. A significant absorbance increase was observed in the test period from 28 to 120 days. The carbonyl functional group is common to several chemical species, for instance ketones, esters and carboxylic acids, usually associated with oxidative degradation of UHMWPE used in prosthesis. In Figure 2 is shown a schematic representation of oxidative degradation of UHMWPE produ-

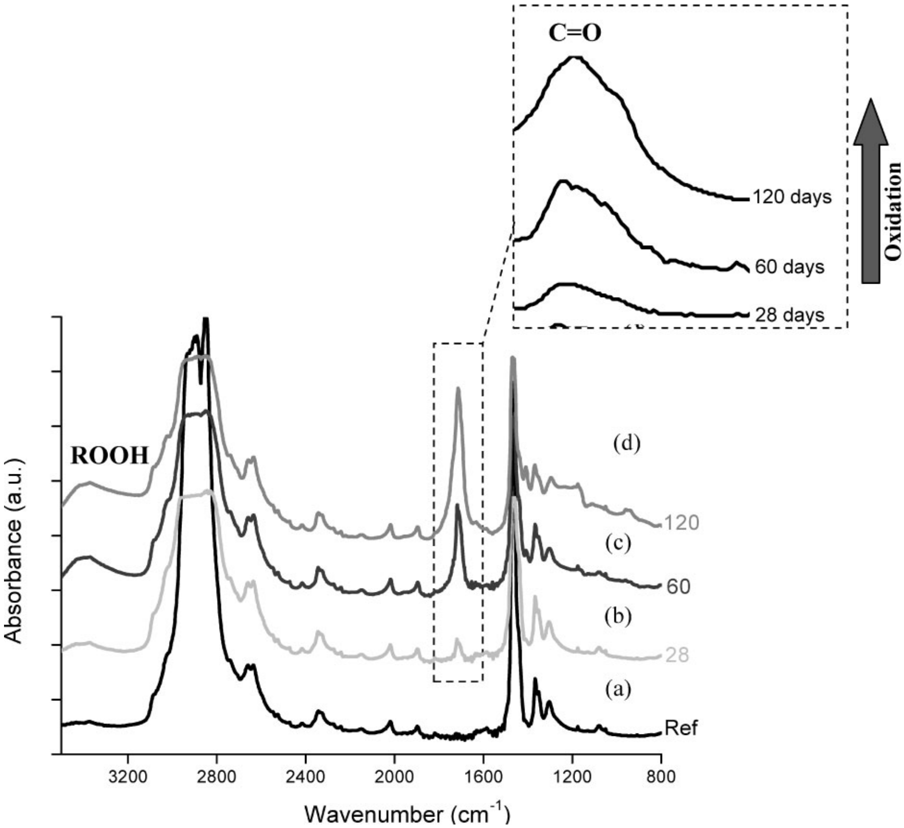

Figure 1.
FTIR spectra of reference UHMWPE (a) and UHMWPE oxidized for (b) 28 days, (c) 60 days and (d) 120 days; **Detail:** carbonyl group evolution with time.

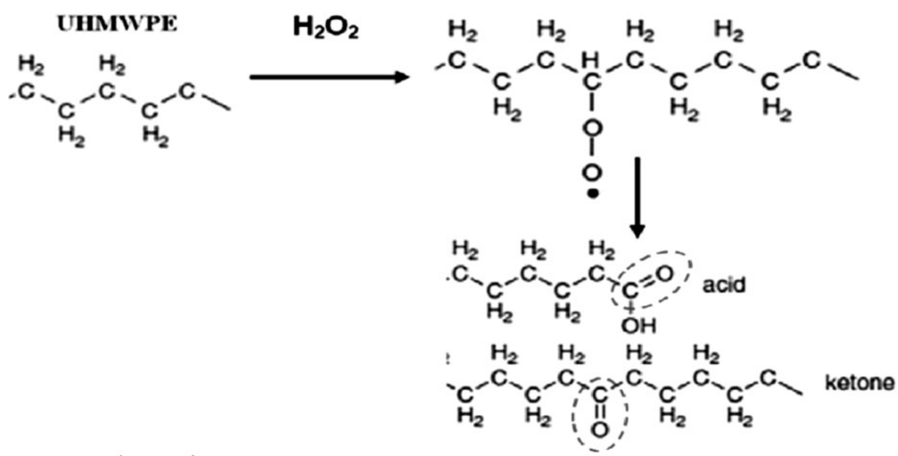

Figure 2.
Schematic representation of oxidative degradation of UHMWPE by H_2O_2 producing chemical species with carbonyl groups.

cing chemical species with carbonyl groups. Thus, such results provide strong evidence that UHMWPE oxidation has taken place via chemical reactions of the polyethylene chain with hydrogen peroxide from the aging solution.

The level of oxidation with data from 7, 14, 28, 45, 60 and 120 days test periods for oxidation degradation of UHMWPE without any antioxidant (group-1) are shown in Figure 3. The curve obtained, based on the overall reaction (I_{ox}), clearly indicated that oxidation of the UHMWPE has taken place, with a slow evolution up to approximately 28 days. Then, a steep rise could be observed up to 120 days of evaluation.

The oxidative degradation of UHMWPE that usually occurs under *in vivo* conditions is compared to the obtained results from the aging procedure in H_2O_2 solution (Figure 4). It can be observed that the prosthesis I_{ox} value is approximately 6.0, corresponding to the samples assayed for 60 days. In other words, one may use the developed test in this study to estimate the future performance of UHMWPE knee prosthesis as far as the chemical degradation is concerned. That could be a very useful tool on evaluating materials prior to the actual surgical implanting procedure.

Figure 5 shows that UHMWPE degradation in H_2O_2 has followed a first-order kinetics reaction for the entire evaluated curve, which was interpreted as two-stage pattern. At Stage-I the kinetics mechanism is mostly controlled by surface reaction and at Stage-II mainly determined by ‘‘bulk’’ (volume) reaction, as supported by $k_1 > k_2$ and $Ea_1 < Ea_2$ (Arrhenius Equation).[6]

In Figure 6, it is shown the accelerated oxidation of UHMWPE under 3 different conditions, i.e., without vitamin C (Figure 6a), with addition of 0.3% (Figure 6b) and 1.0% (Figure 6c). The results have indicated a significant reduction on the oxidation index (I_{ox}) of UHMWPE which is attributed to the effective antioxidant vitamin C behavior. Moreover, it can also be noted that vitamin C has shifted the curve to a longer time at the first stage of oxidation compared to the previous not inhibited H_2O_2 system. That is likely to be associated with the capturing of free radicals by vitamin C, relatively reducing the concentration of oxidative species (.OH) in solution for the degradation of polyethylene chain (competing reaction). An analogy can be drawn to these results as in living organisms, vitamin C seems play a crucial role as an inhibitor of harmful free radicals. Thus, a similar

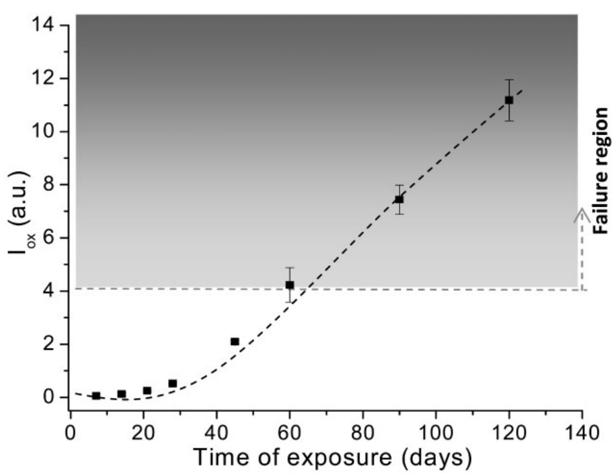

Figure 3.
Evolution of UHMWPE degradation in H_2O_2 evaluated by FTIR using the Oxidation Index (I_{ox}) at different aging times.

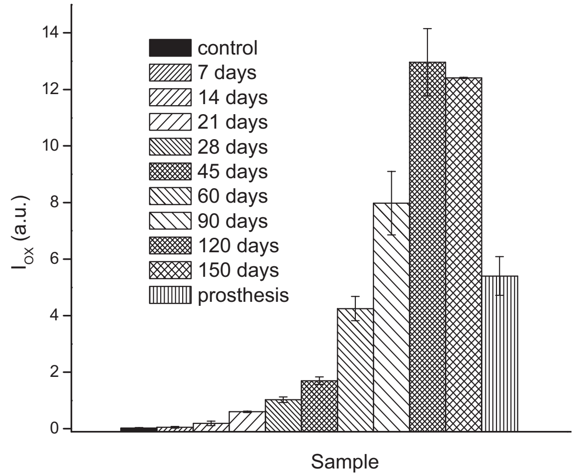

Figure 4.
UHMWPE degradation in H_2O_2 evaluated by FTIR compared to (I_{ox}) value measured in retrieved failure knee prosthesis.

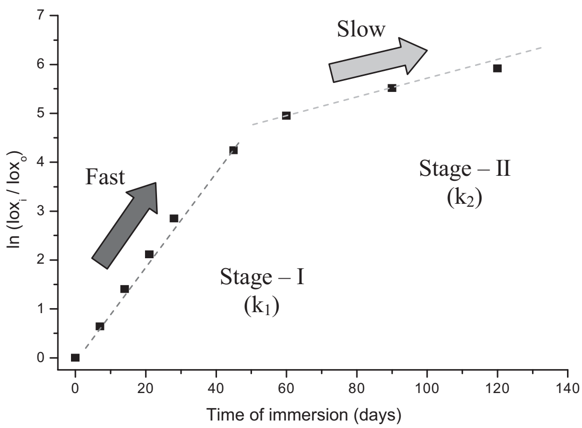

Figure 5.
Kinetics study of the oxidation of UHMWPE aged in H_2O_2.

mechanism associated with donation of H^+ ions or interacting with hydrogen peroxide to capture OH radicals, limiting the UHMWPE oxidation.

Conclusion

In the present study it was presented an accelerated aging procedure based on hydrogen peroxide in order to investigate the chemical stability of UHMWPE. Relevant and novel information concerning to the oxidation of UHMWPE was shown, and two degradation stages were clearly indentified. Moreover, ascorbic acid (vitamin C) has proven to be a rather effective on reducing the oxidation of UHMWPE and modifying the kinetics of the first stage to slower reaction rate. Both mechanisms of oxidation and its inhibition by natural antioxidants are still largely unknown and need to be more in-depth investigated in order to minimize or ideally prevent

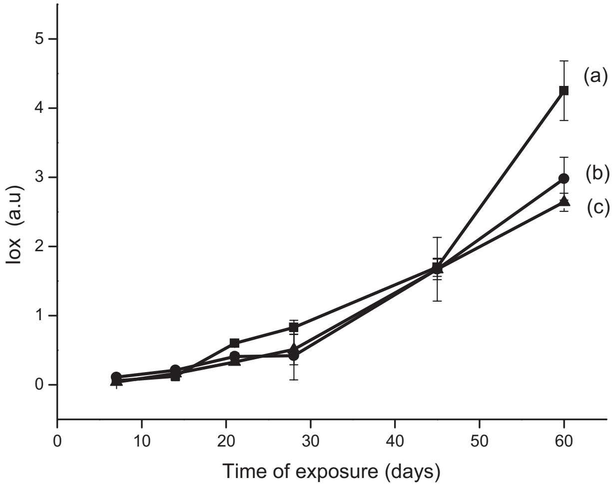

Figure 6.
Effect of the addition of vitamin C as antioxidant at the degradation of UHMWPE at different aging times: (a) no antioxidant (no vitamin C), (b) 0.3% vitamin C and (c) vitamin C 1.0%.

degradation from occurring under clinical usage in orthopedic implants.

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