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Effects of clinical X-ray irradiation on UHMWPE films

N. Stojilovic [a,b,*], S.V. Dordevic [c], S. Stojadinovic [d]

[a] Department of Physics and Astronomy, University of Wisconsin Oshkosh, Oshkosh, WI 54901, USA
[b] Department of Chemistry, University of Wisconsin Oshkosh, Oshkosh, WI 54901, USA
[c] Department of Physics, The University of Akron, Akron, OH 44325, USA
[d] Department of Radiation Oncology, University of Texas Southwestern Medical Center, Dallas, TX 75390, USA

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ABSTRACT

Irradiation of biocompatible polymers is generally performed using ^{60}Co gamma sources delivering high doses of radiation, ranging from kGy to MGy levels. This irradiation is typically employed for sterilization and/or crosslinking purposes. However, exposure to gamma rays may generate free radicals responsible for polymer degradation and, therefore, studies of the irradiation effects on these polymers are of great practical interest. In this study, ultra-high molecular weight polyethylene (UHMWPE) films were exposed to high-energy photons to doses comparable to those used in radiotherapy for patients with cancer. Specifically, three dose levels of 30, 60, and 120 Gy were delivered utilizing linear accelerator X-rays (6 MV) and irradiation effects were studied using X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), and Ultraviolet–visible (UV–vis) spectroscopy. It was found that radiation doses up to 120 Gy do not change the polymer crystallinity but affect its optical properties. In particular, the decrease in the optical band gap is observed in irradiated polymers.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is well known for its excellent physical properties (abrasion, wear and impact resistance) and its chemical inertness. In the last several decades this polymer has been used for making artificial joints where it serves as a load-baring material. However, before distribution to clinics and use in total joint (hip or knee) replacement, these polymers are typically sterilized with ^{60}Co gamma radiation (dose range 25–40 kGy) which is now believed to initiate degradation of physical properties of this polymer that could limit the lifetime of the artificial joints [1,2]. Namely, gamma sterilization of UHMWPE might produce microradicals that could react with oxygen present in the air or in the body fluids and cause embattlement and failures [3,4]. Irradiation of UHMWPE can produce chain scission and chain crosslinking (cross-linking doses are generally 50–100 kGy). The chain scission typically occurs via the C—C bond breakage whereas the crosslinking between the neighboring chains is initiated by the free radicals produced by the breakage of the C—H bond. To produce cross-linking that has tribological benefits and, at the same time, to minimize the degradation due to chain breakage the irradiation dose must be optimized. Namely, it is important to find optimal radiation (type of radiation, its energy, and its dose) to prevent detrimental effect on mechanical properties of this polymer.

Although exposure to high-dose gamma radiation (in kGy and MGy) may degrade mechanical properties of UHMWPE and ultimately lead to the polymer failure *in vivo*, irradiation and ion implantation (C, N, O, Ne, Si, and He), on the other hand, can improve polymer surface properties [5–7]. Influence of 1.5 MeV electron beam irradiation (doses ranging from 50 to 500 kGy) on the optical properties of UHMWPE were also investigated and the decrease in the energy band gap with increasing electron dose were reported [8]. Zaki studied the effect of Argon ion bombardment on the optical properties of low-density polyethylene (LDPE) and reported decrease in transmittance attributed to the possible formation of defects and/or carbon clusters accompanied by the decrease in the indirect optical band gap from 3.0 eV for pristine sample to 2.3 eV for polymers irradiated with the fluence of 10^{15} - ions/cm^2 [9]. Khan et al. found that the indirect energy gaps have lower values than direct energy gaps [10]. They found that direct band gap value of UHMWPE changes from 2.85 eV for pristine sample to 2.4 eV for sample irradiated with e-beam to dose of 100 kGy whereas the indirect band gap value decreases from 2.02 eV down to 1.84 eV for the same dose.

* Corresponding author at: Department of Physics and Astronomy, University of Wisconsin Oshkosh, Oshkosh, WI 54901, USA.
E-mail address: stojilovicn@uwosh.edu (N. Stojilovic).

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The effects of low-dose gamma radiation originating from linear accelerator (referred to as clinical X-rays) are not known and they are the subject of this study. Instead of using ^{60}Co gamma radiation we employed clinical linear accelerator X-rays to deliver relatively low dose (30, 60, and 120 Gy) to probe structural and optical properties of medical grade UHMWPE films. The irradiated samples were compared with the pristine UHMWPE films and investigated using X-ray Diffraction (XRD) method, Fourier Transform Infrared (FTIR), Ultraviolet–visible (UV–vis) spectroscopy.

2. Experimental details

Premium grade UHMWPE GUR 1020 (Ticona) films (250 μm thick) with the average molecular weight of 3.5 Mg/mol have been analyzed using XRD, FTIR and UV–vis Spectroscopy. XRD experiments have been performed using Rigaku D/Max – 2000 T powder X-ray diffractometer operating at 40 kV and 40 mA, with Cu Kα radiation (λ = 0.154 nm). Wide-scan step size was set at 0.02^0 whereas narrow scan step size was set at 0.004^0. FTIR measurements (4 cm^{-1} resolution) were performed on a Bruker IFS 66 v/s system whereas UV–vis experiments (1 nm resolution) were conducted using Varian/Cary 300. All measurements were performed at room temperature.

Irradiation was performed using 6 MV photons generated by a medical linear accelerator (2100EX, Varian Medical Systems, Inc., Palo Alto, CA). The accelerator was calibrated in accordance with the Task Group 51 recommendations of the American Association of Physicists in Medicine (AAPM) [11]. The ionization chamber used for calibration has an absorbed-dose-to-water calibration factor traceable to national primary standards. An independent output verification of the linear accelerator was done using lithium fluoride thermoluminescent dosimeters (TLDs) provided by the Radiation Dosimetry Services (MD Anderson Cancer Center, Huston, TX). The films were irradiated at a 100 cm source-to-surface distance (SSD) with a 10 × 10 cm^2 filed size at a depth of maximum percent depth dose of 1.5 cm for 6 MV photons in a 30 × 30 × 22 cm^3 Solid Water phantom.

3. Results and discussion

3.1. X-ray Diffraction

In spite of the beneficial effects of irradiating UHMWPE with gamma rays, this polymer can undergo oxidative degradation accompanied by the increase in the density of crystallinity, making it more brittle, and affecting its mechanical properties [12,13]. UHMWPE is a linear homopolymer whose chain folds display local order in the form of crystalline lamella within amorphous matrix. The orientation of crystalline lamella and the degree of crystallization primarily depend on molecular weight and processing conditions. XRD experiments, displayed in Fig. 1, were performed on films directly mounted on a sample holder. The peak at 21.6^0 corresponds to (1 1 0) plane, the one at 24.1^0 to (2 0 0) plane, and the feature that sometimes appear at 30.0^0 is (0 2 0) plane of the orthorhombic unit cell. There is no significant shift of the Bragg (1 1 0) peak that would indicate the change in the interplanar spacing after irradiation of UHMWPE films. Consistent with what we observe, Zhao et al. reported that the crystalline structure and size did not change after 180 kGy irradiation in vacuum or in air [14]. However, structural changes of these polymers can be initiated by ion beam bombardment [15].

The average crystallite size was estimated using the Scherrer equation which relates the angle of incidence θ, to the full width at half maxima (FWHM), W, of the most intense peak, in our case (1 1 0), via formula

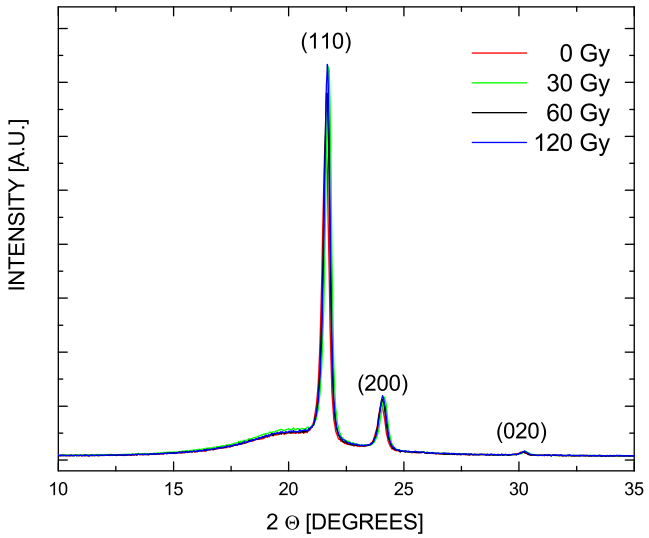

Fig. 1. X-ray diffraction patterns of the pristine and clinical X-ray irradiated UHMWPE films.

$$S = c\lambda / W \cos\theta \quad (1)$$

where S is the crystallite size, c is the Scherrer constant whose value depends on the shape of the particles and takes values between 0.9 and 1.2, and λ (0.154 nm) is the wavelength of the incident monochromatic X-rays. In our estimates the spherical shape was assumed (c = 1) and the average crystallite size was found to be S ≈ 27 nm.

Gamma rays can generate free radicals via bond cleavage. If these free radicals are produced in the crystalline regions of UHMWPE they can diffuse into amorphous regions of the polymer and participate in chemical reactions. This free–radical reaction mechanism is the main concern for radiation-induced degradation of polymers in the presence of oxygen. Chain scission results in shorter chain segments which can then fold more efficiently into crystalline regions which results in greater crystallinity. It was reported that the more crystalline the irradiated polymer was, the higher the free radical concentration and extent of oxidation [16]. Free radicals created by irradiation are much less mobile in the crystalline regions than in the amorphous regions of the polymer. The more mobile radicals in the amorphous region can recombine or lead to crosslinking before absorbing oxygen and reacting to become peroxy radicals. Materials that are less crystalline have more free radicals produced in the amorphous region. Oxygen uptake is less likely to occur in materials with reduced crystallinity whereas more crystalline materials oxidize more. Since our irradiated samples show no signs of increased crystallinity in our XRD data we conclude that exposure of UHMWPE to X-ray dose up to 120 Gy will not further oxide the polymer nor degrade its mechanical properties.

3.2. FTIR

Fig. 2 displays FTIR absorbance versus wavenumber spectra of UHMWPE films. Films exposed to 6 MV clinical X-rays with dose levels of 30, 60, and 120 Gy are compared to the spectra of unexposed film. All spectra display a strong feature at 1460 cm^{-1} due to the methylene group (—CH_2—) vibrations. Oxidation can be monitored by looking at the changes in the carbonyl feature (1720 cm^{-1}). Signatures of oxidation present in all of our samples are attributed to sample aging and do not depend on dose in the 30–120 Gy range. Moreover, there are no significant changes in the entire mid-IR spectra with the change in dose. Although, for