



## Effects of clinical X-ray irradiation on UHMWPE films



N. Stojilovic<sup>a,b,\*</sup>, S.V. Dordevic<sup>c</sup>, S. Stojadinovic<sup>d</sup>

<sup>a</sup> Department of Physics and Astronomy, University of Wisconsin Oshkosh, Oshkosh, WI 54901, USA

<sup>b</sup> Department of Chemistry, University of Wisconsin Oshkosh, Oshkosh, WI 54901, USA

<sup>c</sup> Department of Physics, The University of Akron, Akron, OH 44325, USA

<sup>d</sup> 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  $^{60}\text{Co}$  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.

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### 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-bearing material. However, before distribution to clinics and use in total joint (hip or knee) replacement, these polymers are typically sterilized with  $^{60}\text{Co}$  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<sup>2</sup> [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: [stojilovici@uwosh.edu](mailto:stojilovici@uwosh.edu) (N. Stojilovic).

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  $^{60}\text{Co}$  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  $\mu\text{m}$  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  $K\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ). Wide-scan step size was set at  $0.02^\circ$  whereas narrow scan step size was set at  $0.004^\circ$ . FTIR measurements ( $4 \text{ cm}^{-1}$  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, Houston, TX). The films were irradiated at a 100 cm source-to-surface distance (SSD) with a  $10 \times 10 \text{ cm}^2$  field size at a depth of maximum percent depth dose of 1.5 cm for 6 MV photons in a  $30 \times 30 \times 22 \text{ cm}^3$  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  $21.6^\circ$  corresponds to (1 1 0) plane, the one at  $24.1^\circ$  to (2 0 0) plane, and the feature that sometimes appear at  $30.0^\circ$  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  $\theta$ , to the full width at half maxima (FWHM),  $W$ , of the most intense peak, in our case (1 1 0), via formula

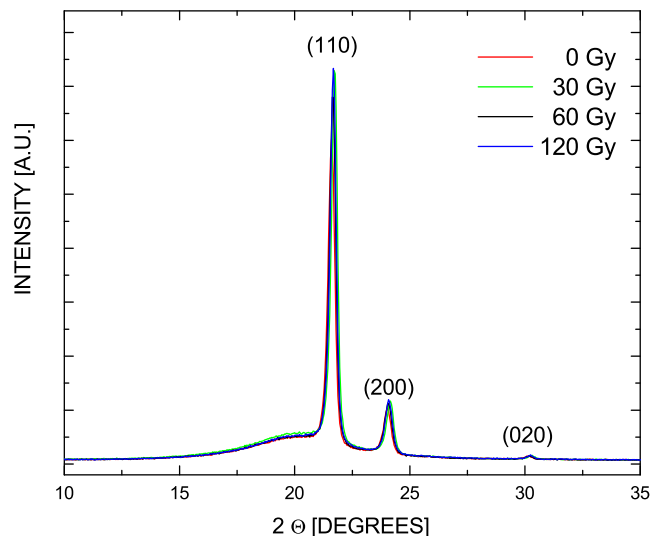


Fig. 1. X-ray diffraction patterns of the pristine and clinical X-ray irradiated UHMWPE films.

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

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  $\lambda$  (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  $S \approx 27 \text{ nm}$ .

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 oxidize 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  $1460 \text{ cm}^{-1}$  due to the methylene group ( $-\text{CH}_2-$ ) vibrations. Oxidation can be monitored by looking at the changes in the carbonyl feature ( $1720 \text{ cm}^{-1}$ ). 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

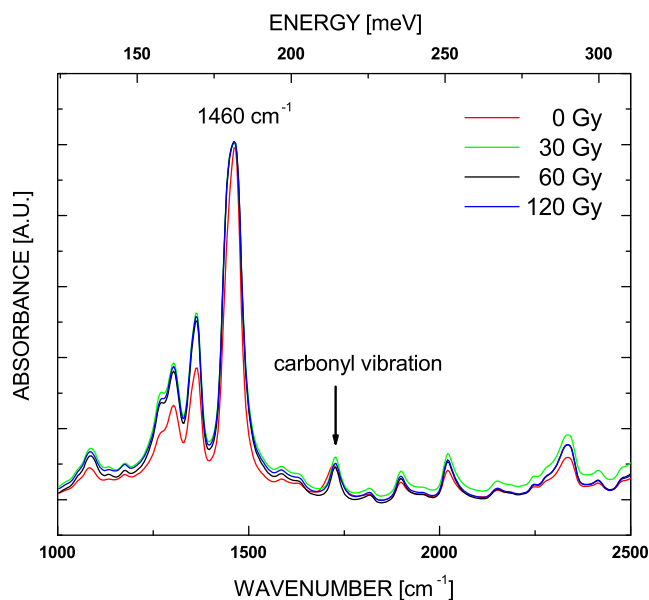


Fig. 2. FTIR Absorbance spectra of pristine and clinical X-ray (6 MV) irradiated UHMWPE films.

instance, in the study of He-ion bombardment of UHMWPE [17], FTIR showed the ion beam induced formation of carbonyl groups ( $C=O$ ) at  $1720\text{ cm}^{-1}$  on the polymer surface, we see no such effects in our UHMWPE films exposed to clinical X-rays at low-dose. The ion beam, due to its greater stopping power, is more effective in modifying polymer surfaces than clinical X-rays. We see no increase in the intensity of the  $1720\text{ cm}^{-1}$  band with the increase in dose in the 30–120 Gy range and conclude that within this range, an increase in dose does not produce additional oxidation products.

In a related study Zhao et al. observed that the number of carbonyl groups increased with dose for irradiation in air [14]. Their FTIR results provided additional support for the conclusion that the oxidation is limited to the surface layer in the case of irradiation in air. In another related study, Goldman et al. monitored oxidation by looking at the changes in the carbonyl feature in FTIR experiments and observed that oxidation is strongly influenced by sterilization method and aging parameters [18]. Oxygen uptake by UHMWPE was reported to increase as a result of gamma or electron irradiation and during subsequent aging with hydrogen peroxide, resulting in significant oxidation. Sterilization method was proposed to be the most important factor determining whether UHMWPE will oxidize or not. It is noteworthy that exposure of UHMWPE films to dose of 120 Gy utilizing clinical X-rays showed no increase in the carbonyl peak that would signal oxidation of the polymer. This is consistent with XRD results that did not show increase in the crystallinity of UHMWPE films after irradiation which is typically accompanied by sample oxidation.

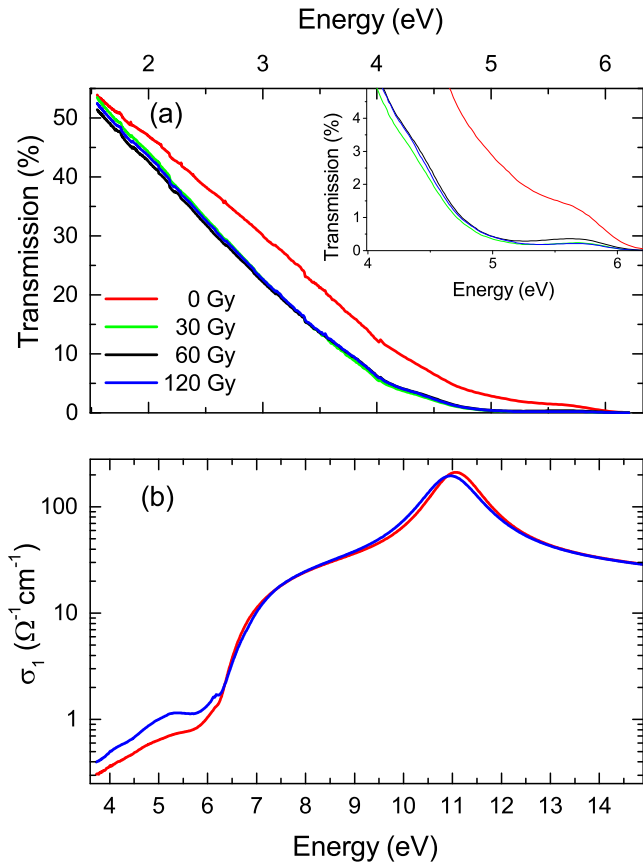
### 3.3. Ultraviolet-visible (UV-vis) spectroscopy

In a related study on effects of 1 MeV He-ion bombardment on the properties of UHMWPE, the degradation of polymer surface and/or creation of new electronic levels in the energy band-gap was suggested [17]. In this same study a decrease in transmittance with increase in ion fluence was observed and the cleavage of  $C-H$  bonds with release of hydrogen was proposed to follow He-ion bombardment of UHMWPE. Tóth et al. treated the surface of UHMWPE samples by 1 keV N, H and He fast atom bombardment (FAB) to obtain amorphous carbon surface layer and reported

new electronic levels within the forbidden gap in the electronic density of states [15]. In general, a keV particle bombardment of polymers changes their composition and properties due to bond breaking and atom displacement from the polymer chain. Structural modifications occurring in the FAB-treated UHMWPE may introduce new electronic levels into the forbidden gap of its electronic band structure, which are expected to behave either as trap states or as recombination levels. These electronic levels within the energy band gap allow additional optical absorption in a given energy region, not present in the untreated samples. Their UV-vis spectra display a considerable decrease in the transmittance of treated samples, consistent with the formation of new electronic levels within the energy gap. Abdul-Kader [19] also reported that UV-vis absorption experiments revealed increase in optical absorption in ion-bombarded samples, in agreement with the creation of new electronic level in the forbidden energy gap. The bombardment of UHMWPE by energetic ions, when the stopping power is high, will produce active chemical species (radicals, electrons, etc.) that can migrate along the polymer chains. It was reported that the energy band gap decreased with increased ion fluence. The value decreased from 2.86 eV for unexposed sample to 1.83 eV for polymers bombarded with the highest fluence. This was interpreted as a result of creation of carbon enriched clusters due to partial evolution of hydrogen molecules. After hydrogen evolution, the residual carbon can take graphitic form which leads to the decrease in the band gap. The decrease in the band gap may also be result of the formation of defects excited in the band gap.

The optical properties of UHMWPE are very sensitive to gamma radiation [20] but effects of clinical X-rays, to the best of our knowledge, have not been reported in the literature. Raghuvanshi et al. investigated effects of gamma irradiation (500–2000 kGy) on the optical properties of UHMWPE using UV-Visible spectrophotometry [20]. They discussed a decrease in the optical energy band gap with increasing dose of gamma irradiation and reported gamma-induced modifications in the UHMWPE polymer. Based on the absorption curve of the polymer they proposed that it could serve as a dosimeter for the gamma ray irradiation. They observe shift in absorption edge toward longer wavelengths with increasing gamma dose and reported broadening of absorption peak with increasing gamma dose, and interpreted this behavior to be due to the formation of extended systems of conjugate bonds i.e. possible formation of carbon clusters [21].

Fig. 3 displays UV-Vis transmittance spectra of UHMWPE films irradiated by 6 MV clinical X-rays. Irradiated films show reduced transmittance (increased absorption) compared to the pristine sample. The increase in optical absorption in the UV-Vis region in irradiated films compared to the pristine sample suggests the creation of new electronic levels in the energy band gap. Variation of delivered dose in the 30-to-120 Gy range reveals no significant change (within experimental uncertainty) in the transmittance spectra. Panel 3(a) presents the transmission of all studied samples, over the whole measured energy range, from 1.55 eV to 6.20 eV. The transmission of pristine sample reveals characteristic decrease as energy increases, and vanishes above approximately 6 eV. Vanishing transmission is a consequence of inter-band absorption, i.e. excitations across an energy gap. Although transmission spectra of irradiated samples look similar, their curves are suppressed by as much as 10% compared with the pristine sample, which is due to irradiation. Within the error bars of the measurements, all irradiated samples display the same transmission. The increase in the optical absorption due to irradiation can be attributed to the creation of new electronic levels in the energy band gap. The inset of panel 3(a) displays the transmission spectra around the energy gap, on an expanded scale. We see that in this region there are some features that are strongly affected by irradiation.



**Fig. 3.** (a) Transmission spectra of the pristine and clinical X-ray irradiated UHMWPE films. The inset shows the transmission close to the band gap edge. (b) Real part of optical conductivity of UHMWPE films calculated from transmission spectra.

In order to get a better insight into these processes, we fit the transmission spectra using the so-called Lorentz model [22], with several oscillators. Equation for the complex optical conductivity,  $\bar{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ , within this model is given as:

$$\bar{\sigma}(\omega) = \frac{1}{4\pi} \frac{i\omega\omega_p^2}{\omega^2 - \omega_0^2 + i\omega\gamma} \quad (2)$$

where  $\omega_0$  is the frequency of the oscillator,  $\gamma$  its width and  $\omega_p$  the oscillator strength. From the fits we generate all other optical functions of interest. The fitting was performed with a share-ware program RefFIT [23]. From the best fits of transmission spectra we generated the complex optical conductivity. The real part of this function quantifies the absorption of energy in solids, whereas the imaginary part quantifies the dispersion of energy [22]. Panel 3(b) displays (on a logarithmic vertical scale) the real part of optical conductivity,  $\sigma_1(\omega)$ , for pristine and sample irradiated to 120 Gy. The spectra are dominated by a strong peak centered around 11 eV. It is due to excitations across a direct gap, which we estimate to be around 9.85 eV in pristine, and 9.57 eV in irradiated sample. In addition we notice sudden increase of  $\sigma_1(\omega)$  around 6.2 eV, which we identify as the indirect gap. The indirect band gap does not change significantly, within the error bars, with irradiation. At even lower energies, inside the band gap,  $\sigma_1(\omega)$  is higher in irradiated samples than in the pristine sample and we interpret it as a clear effect of irradiation. Also, the carbonyl signatures are present in both pristine and irradiated UHMWPE samples and the formation of new electronic levels within the band gap is a direct consequence of irradiation with clinical X-rays, and is not related to the oxidation due to shelf aging.

Raghuvanshi et al. used 1.25 MeV gamma radiation ( $^{60}\text{Co}$  source) in the high vacuum and reported the energy band gap (direct and indirect) values for pristine UHMWPE polymers as  $E_g^{\text{direct}} = 3.21$  eV and  $E_g^{\text{indirect}} = 3.1$  eV [20]. The change in dose from 500 kGy to 2000 kGy resulted in the change in  $E_g^{\text{direct}}$  from 3.10 eV to 2.61 eV and the change in  $E_g^{\text{indirect}}$  from 2.87 eV to 2.06 eV. On the other hand, Abdul-Kader investigated effects of 1.5 MeV electron beam irradiation (doses from 50 to 500 kGy) on the optical properties of UHMWPE and reported the decrease in energy band gap with increasing electron dose, and attributed increase in the optical absorption to the creation of new electron-beam induced electronic levels in the energy bandgap [8], consistent with what we find following irradiation of UHMWPE with clinical X-rays. In his study the pristine UHMWPE sample exhibited a band gap of 3.25 eV whereas UHMWPE irradiated with dose of 500 kGy had a band gap of 2.7 eV. This decrease in the value of energy bandgap, he argued, could be result of the creation of carbon enriched clusters resulting from release of hydrogen via hydrogen molecules and/or the creation of some intermediate electronic energy levels as a consequence of structural rearrangements [24]. Although we observe effects of clinical X-rays on the optical properties of UHMWPE films via the formation of new electronic levels within the forbidden energy gap there is no significant difference between 30 and 120 Gy irradiation.

Structural changes of polymers can be initiated by ion beam bombardment and these can provide new electronic states within the energy band-gap [15]. Radiation effects and degradation mechanisms in UHMWPE were studied in the past [25–27]. Our findings are relevant and novel since they show the evidence that up to 120 Gy dose level using clinical X-rays may also affect optical properties of UHMWPE films by producing new energy level in the optical band gap, without affecting the crystallinity of the polymer and thus without detrimental effects on its mechanical properties.

#### 4. Conclusions

Irradiation of UHMWPE is generally performed using gamma radiation with doses ranging from kGy to MGy and using  $^{60}\text{Co}$  as a gamma radiation source. In this study, however, medical grade UHMWPE films were irradiated to 30, 60, and 120 Gy using clinical X-rays (6 MV) and irradiation effects were studied using XRD, FTIR, and UV–vis spectroscopy. Although XRD reveals no significant changes in the crystallinity due to irradiation, the increase in the optical absorption due to irradiation can be attributed to the creation of new electronic levels in the energy band gap. This decrease in the band gap may be due to formation of defects excited in the band gap but warrants further studies. Within the error bars of our measurements, all irradiated polymers had identical transmittance following exposure to 30–120 Gy. From the fit of the transmittance we extracted the real part of optical conductivity,  $\sigma_1$  that we then used to estimate the values of the optical band-gap. The optical conductivity data reveal that the direct band gap ( $\sim 9.57$  eV) of irradiated polymers decreases compared to the value of the pristine sample ( $\sim 9.85$  eV). Sudden increase of  $\sigma_1(\omega)$  around 6.2 eV we identify as the indirect gap and it showed no significant change after irradiation. It was known that structural changes of UHMWPE induced by ion beam bombardment can provide new electronic states within the energy band-gap [15]. Our study shows that a low-dose irradiation using clinical X-rays causes no significant change in the structure of UHMWPE, but may introduce new electronic levels within the energy band-gap and the reduction of the optical band-gap.



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