

Effect of γ -Ray Irradiation on Surface Oxidation of Ultra High Molecular Weight Polyethylene/Zirconia Composite Prepared by *in situ* Ziegler-Natta Polymerization

Soonjong Kwak[†]

Polymer Hybrid Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

Dong Il Noh[†] and Heung Jae Chun^{1,*}

Department of Biomedical Sciences, College of Medicine, Catholic University, Seoul 137-701, Korea

¹Institute of Cell and Tissue Engineering, College of Medicine, Catholic University, Seoul 137-701, Korea

Youn-Mook Lim and Young Chang Nho

Division of Radiation Application Research, Korea Atomic Energy Research Institute, Chonbuk 580-195, Korea

Ju Woong Jang and Young Bock Shim

Research Institute of Biomedical Engineering, Korea Bone Bank Co. Ltd., Seoul 153-782, Korea

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Abstract: Novel ultra-high molecular weight polyethylene (UHMWPE)/zirconia composites were previously prepared by the *in situ* polymerization of ethylene using a Ti-based Ziegler-Natta catalyst supported on to the surface of zirconia, as a bearing material for artificial joints. Tribological tests revealed that a uniform dispersion of zirconia in UHMWPE markedly increased the wear resistance. The effects of zirconia content on the oxidation behavior of the γ -ray-treated UHMWPE/zirconia composite surfaces were examined. The oxidation index that estimates the oxidation degree as the content of total carbonyl compounds was monitored using Fourier transform infrared spectroscopy-attenuated total reflectance. The changes in the surface composition due to the oxidation were confirmed by electron spectroscopy for chemical analysis. The extent of oxidation decreased with increasing zirconia content, which was attributed to the increased crystallinity as well as the decreased polymer portion of the UHMWPE/zirconia composites.

Keywords: *in situ* polymerized composites, ultra high molecular weight polyethylene (UHMWPE), zirconia, oxidation, artificial joint.

Introduction

Ultra high molecular weight polyethylene (UHMWPE) has been recognized as being the most suitable bearing material for manufacturing artificial joints, which are mostly implanted into the hips and the knees of the humans.¹⁻⁶ UHMWPE meets material requirements for the artificial joints, such as a low friction coefficient and high wear resistance, as well as excellent chemical resistance, high mechanical strength, and biological inertness.³ For sterilization of the UHMWPE joints, irradiation has been commonly employed, because the irradiation not only remains as the industrial standard, but also improves the wear properties as a result of the cross-linking between PE molecules.^{3,6} How-

ever, irradiation also has the drawback of a later oxidation. The irradiation of UHMWPE induces the chain scission and the formation of free radicals. These free radicals can form cross-linked network through a radical-radical recombination reaction, react with the oxygen, if any present in the vicinity of the formed radicals, or remain trapped in the polymer matrix for a certain period of time after irradiation, which leads to an auto-catalytic oxidative degradation.⁵ This degraded product triggers occasional failures of the implantation within 6-8 years in active or obese patients.⁶ Therefore, extensive investigations have been undertaken on the UHMWPE composite filled with ceramic or metal filler to provide improved wear properties.⁷⁻¹⁰ A previous study noted that the dispersion state of the filler in the UHMWPE matrix is the main factor for determining the wear performance of the composites.¹⁰ In this respect, UHMWPE composite prepared by the *in situ* polymeriza-

[†]These authors contributed equally to this work.

*Corresponding Author. E-mail: chunhj@catholic.ac.kr

tion method displayed superior mechanical and wear properties in comparison to those prepared by the conventional blending method. Previously, UHMWPE/zirconia composites were prepared through the *in situ* polymerization of ethylene using a Ti-based Ziegler-Natta catalyst supported on to the surface of zirconia. The composites showed superior wear resistance to the neat UHMWPE, and the zirconia worked in the composites as excellent wear-resistant filler.¹¹ Although the abrasive wear extensively occurring in the neat UHMWPE was effectively suppressed in the filled composites, the negative behavior against the irradiation still remained as the main issue to overcome before becoming an outstanding substitute for the conventional UHMWPE. Thus, examination of the oxidative properties of the UHMWPE/zirconia composites is of utmost importance. For this purpose, γ -ray irradiation was conducted in air at the generally used sterilization radiation dose of 25 KGy, and the post irradiation behavior on the surface of UHMWPE/zirconia composite was investigated and compared with that of the neat UHMWPE.

Experimental

Preparation of UHMWPE/Zirconia Composite.¹¹ A series of the zirconia-filled UHMWPE polymerized composites (15, 23, and 43 wt%; designated as PC15, PC23, and PC43, respectively) were prepared by the *in situ* polymerization of ethylene using a Ti-based Ziegler-Natta catalyst fixed on the surface of zirconia. Briefly, catalyst fixation on the surface of zirconia and the ethylene polymerization were consecutively performed in a 1-L high pressure glass reactor. Dried zirconia was charged in the reactor and well-dispersed in toluene. The catalyst fixation reaction was initiated by injecting TiCl_4 at 50 °C, and Et_3Al was introduced to activate the TiCl_4 supported on to the zirconia. Subsequently, the ethylene polymerization was initiated by injecting ethylene into the reactor. The polymerization temperature and pressure were fixed at 50 °C and 4 bars, respectively. After a predetermined reaction time, the polymerization was quenched with HCl diluted in methanol. The product was precipitated in methanol, filtered, and dried in a vacuum oven.

The commercial UHMWPE (MipelonTM XM-220, Mitsui chem., Tokyo, Japan) was used as a standard for comparison with the UHMWPE/zirconia composite. For irradiation, UHMWPE and the composites were exposed to ⁶⁰Co γ -rays, accumulating a dosage of 25 kGy at 10 kGy/h (MDS Nordion, CA, IR221n wet storage type C-188) at room temperature.

Fourier Transform Infrared Spectroscopy/Attenuated Total Reflectance (FTIR/ATR). FTIR specimens were microtomed into 200 μm thick slices as described in a previous study.¹² The oxidation profiles were obtained with an FTIR/ATR apparatus (Nicolet Avatar 360, Thermo sci., Waltham, MA, USA) using 64 scans at a resolution of 16 cm^{-1} .

The oxidation index (OI) was calculated as the ratio of the peak area of the ketone (C=O) group absorption band at 1727 cm^{-1} to the area of the methylene group reference band at 1370 cm^{-1} .

Electron Spectroscopy for Chemical Analysis (ESCA).¹³ The surface elemental composition of the sample surfaces were determined by using a Physical Electronic PHI 558 ESCA spectrometer. The source was a 10 KV-30 mA monochromatized X-ray beam from a magnesium anode. Wide scan (0-1,000 eV) and high-resolution scans (10 eV wide) for C1s and O1s were taken, and the areas of the individual peaks were compared in order to examine the total oxidation content of the specimens.

Transmission Electron Microscopy (TEM). The irradiated samples were embedded in Poly/Bed 812[®] (08791-500, Poly sci., Warrington, PA, USA), sectioned into 80 nm thickness, and deposited onto a formvar-coated copper grid. TEM was performed at 60 KV using the JEM1010 microscope (JEM1010, JEOL, Tokyo, Japan).

Differential Scanning Calorimetry (DSC).¹² The crystallinity of the specimens was investigated using (DSC) (DSC-7, Perkin-Elmer, Waltham, MA, USA). The specimens were heated from 40 to 200 °C at 10 °C/min with a continuous nitrogen purge. The melting temperature was determined from the peak of the melting endotherm. The mass fraction of the crystalline regions in the specimens was calculated using the following equation:

$$\text{Crystallinity (\%)} = E/(m_1 - m_2) \cdot \Delta H \times 100$$

where, E is the energy absorbed by the sample in the melting (J), m_1 is the total mass of the specimen, m_2 is the mass of zirconia (mg), and ΔH is the heat of melting of the PE crystals.

Results and Discussion

FTIR/ATR Study. Figure 1 shows the FTIR/ATR spectra of the γ -ray-irradiated UHMWPE composites with different zirconia contents. The main differences in the spectra of the neat and irradiated samples were found in the 3695-3300 and the 1775-1670 cm^{-1} regions. The weak and narrow absorption peaks around 3695 cm^{-1} were attributed to the non-hydrogen-bonded alcohols and hydroperoxides. The broad absorption band around 3300 cm^{-1} was assigned to the hydrogen-bonded hydroxyl groups, including alcohols, hydroperoxides, and carboxylic acids.¹⁴ The multi-functional absorption bands in the range of 1775-1670 cm^{-1} could be correlated to various carbonyl species, ketones, aldehydes, and lactones, formed during the oxidation.¹⁴ The radicals detected after the irradiation could extract the H atom from a second UHMWPE molecule, thereby forming a secondary macro alkyl radicals and a new chain end group, CH_3 . As a consequence, the molecular weight of the polymer decreased, allowing the new radicals to be injected into the system. The

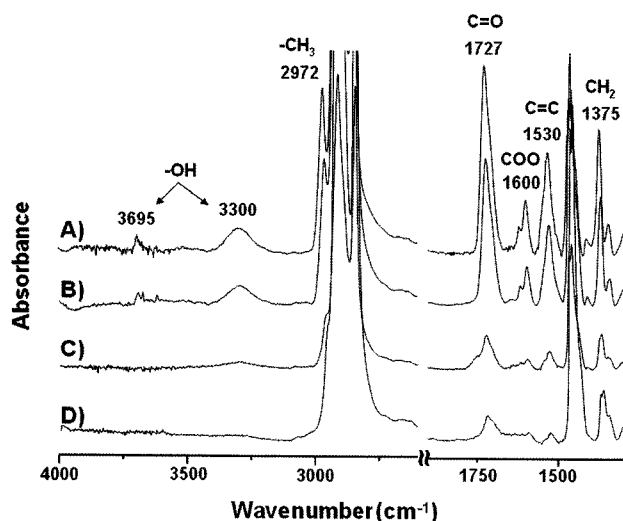


Figure 1. FTIR/ATR spectra of γ -ray irradiated neat UHMWPE and polymerized composites (PC): (A) neat UHMWPE^a, (B) PC15, (C) PC23, (D) PC43. Filler content for each filled composite is listed in Table I. ^aNeat UHMWPE was prepared with commercially available Mipelon™.

sharp peak at 2972 cm⁻¹ was assigned to CH₃.¹ So far, several indices using FTIR have been proposed to characterize the oxidation profiles of UHMWPE. Generally, peak heights or areas, as the content of a single- or multiple-oxidized species, have been used to estimate the degree of oxidation.¹⁴ In the present study, however, the A_{3400}/A_{1300} (calculated peak area ratio between the 3420-3150 and 1395-1330 cm⁻¹, the latter being the CH₂ bending, the internal standard region) and the A_{ox}/A_{1300} (between the carbonyl 1775-1670 and 1395-1330 cm⁻¹ regions) were used to compare the relative extent of the hydroxyl and the carbonyl oxidations present in the samples (Table I) in a manner similar to ISO 5834-4:2005, because the quantitative determination of the individual functional groups based on the FTIR spectra is relatively difficult due to the complex shape of the absorption bands.¹⁵

ESCA Study. Though FTIR/ATR is recognized as a potent method for identifying the changes in the chemical compositions of the polymer surface, the quantitative and the qualitative analyses of the surface oxidation cannot depend solely on FTIR.¹³ Therefore, ESCA was employed to achieve a

Table I. Relative Extent of Hydroxyl and Carbonyl Content in the γ -Ray Irradiated Neat UHMWPE and Polymerized Composites (PC) Obtained from the FTIR/ATR

	Neat UHMWPE	PC15	PC23	PC43
Filler Content (wt%)	0	15	23	43
Polymer Content (wt%)	100	85	77	57
A_{3300}/A_{1300}	0.97	0.76	0.54	0.21
A_{ox}/A_{1300}	2.96	2.36	1.53	0.60

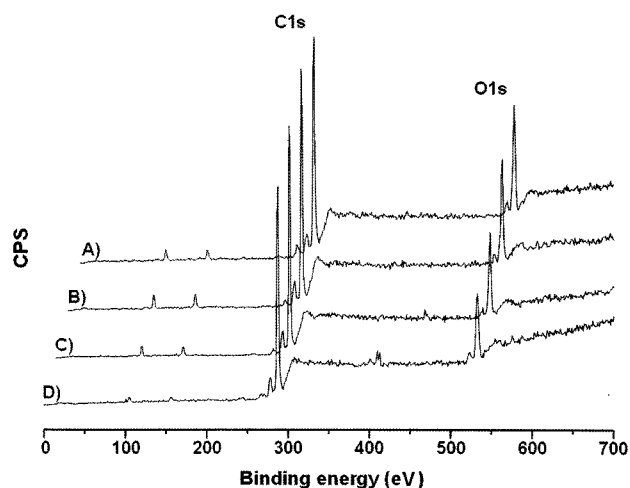


Figure 2. ESCA survey spectra of γ -ray irradiated neat UHMWPE and polymerized composites (PC): (A) neat UHMWPE, (B) PC15, (C) PC23, and (D) PC43.

precise analysis on the compositional changes of the samples. ESCA is a relatively benign technique with generally minimal radiation damages to the sample. The information obtained is inherently quantitative; all elements except hydrogen are analyzed, and the core-level chemical spectra provide a reasonable degree of structural information on the polymer surface.¹⁶ Figure 2 shows the ESCA survey scan spectra of γ -ray irradiated UHMWPE samples with different zirconia contents. In all samples, oxidation of the materials generated similar patterns of O1s spectra at 532 eV, whose intensities decreased with the increase in the content of zirconia. In addition to the oxidation, the presence of zirconia could be the other factor that created the O1s spectra on the surface of the composites, because the O1s spectrum of zirconia (ZrO₂) around 530 eV is one of the important representatives of the ESCA photoelectron peaks for the stoichiometric analysis of zirconia.¹⁷ In this respect, the result that the intensities of O1s spectra decreased with the increase in the content of zirconia may raise a question. This could be explained by the restricted sampling depth of ESCA. A previous study revealed that the zirconia composite used in the present study had a grown size of 0.5-1.0 μ m, and each zirconia particle was evenly covered with the polyethylene layer (molecular weight, 1.22×10^6 g mol⁻¹) grown on the surface of zirconia.¹¹ Though the incident X-ray is able to penetrate the polymer sample up to 1 μ m, only the photoelectrons within 3λ (<10 nm) of the surface can escape from the sample.¹⁸ The fact that the characteristic peaks of Zr:Zr3d (183 eV), Zr3p (330 eV), among others, cannot be found in Figure 2 is the strong evidence for the above. Figure 3 shows the C1s core spectra of the γ -ray-irradiated UHMWPE polymerized composite. The strong peak at 285.0 eV was due to the C1s electrons from the C-C and C-H bonds of UHMWPE Figure 3(A). The presence of

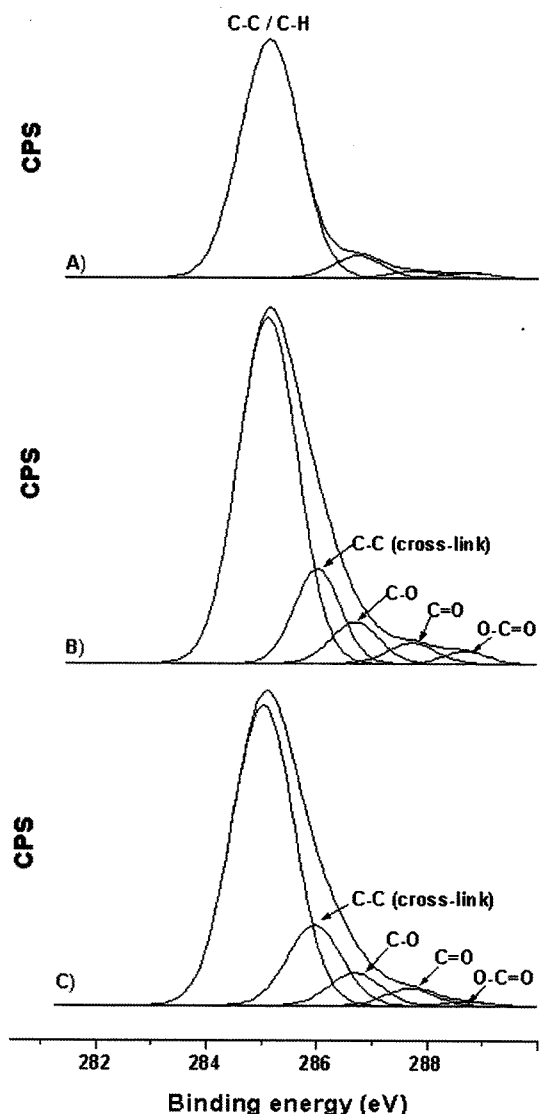


Figure 3. C1s spectra of neat UHMWPE and polymerized composite: (A) untreated neat UHMWPE, (B) γ -ray irradiated neat UHMWPE, and (C) γ -ray irradiated polymerized composite. The filler content for the polymerized composites was 43 wt%.

the small peaks at 286–289 eV in the C1s indicated the formation of the surface photo-oxidation products caused by the exposure to the air. Compared to Figure 3(A), the irradiated samples (Figure 3(B) and (C)) created peaks ascribed to five different types of the carbon atoms. The peak at 285.95 was attributed to the -C-C- cross-linking caused by irradiation. The peaks of C1s bands appearing at 286.65, 287.7 and 288.7, were assigned to the -C-O-, -C(=O)-, and -C(=O)-O- groups, respectively.^{19–23} The O1s core spectra (Figure 4) were obtained by incorporating the sample surfaces of the -C-O-, -C(=O)-, and -C(=O)-O- groups. The changes in the surface composition due to oxidation were also characterized by the separation of the peaks of O1s

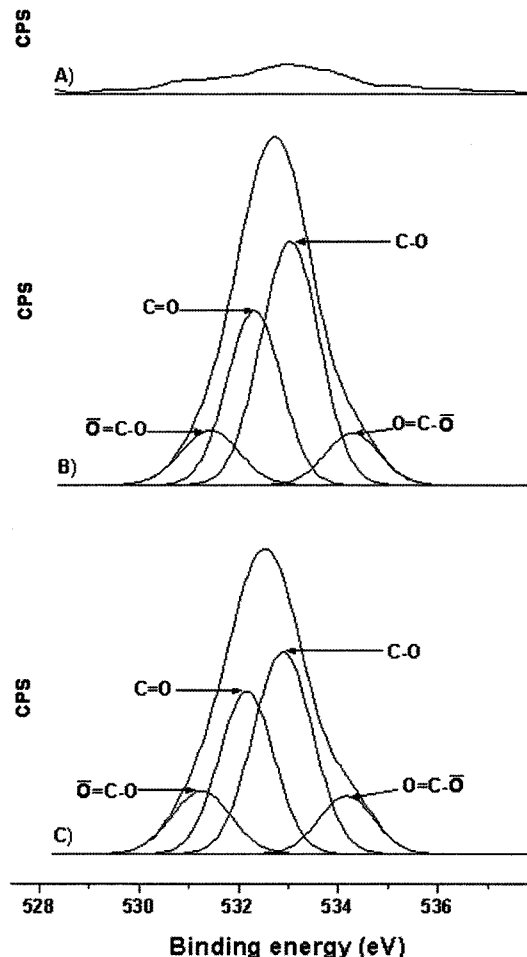


Figure 4. O1s spectra of neat UHMWPE and polymerized composite (PC): (A) untreated neat UHMWPE, (B) γ -ray irradiated neat UHMWPE, and (C) γ -ray irradiated polymerized composite. The filler content for the polymerized composites was 43 wt%.

bands appearing at 532.88, 532.15, 531.25, and 534.16, which were assigned to the -C-O-, -C(=O)- and -C(=O)-O- groups. In the case of -C(=O)-O- group, the O1s spectrum split into two bands at 531.25 and 534.16, respectively attributed to -C(=O)-O- and -C(=O)-O- groups.^{21–23} In contrast to FTIR, ESCA spectra provide quantitative information on the contents of the various types of the carbon and the oxygen atoms present in the UHMWPE composites, because the percent of peak area and FWHM of ESCA spectra reflect the binding energy values and thus are commonly used in the polymer analysis. It is generally known that the γ -ray-sterilized PEs are likely to contain alkyl and peroxy radicals,²⁴ which form the photo-labile hydroperoxides through the hydrogen atom extraction. The decomposition of hydroperoxide, in turn, gives alcohols, acids, esters, and ketones.²⁵ In the present study, the ESCA spectra (Figures 3 and 4) also showed the characteristic peaks corresponding to the alcohols together with carbonyls for acids

Table II. Extent of Oxidation within γ -Ray Irradiated Neat UHMWPE and Polymerized Composites (PC) Obtained from the ESCA

	Neat UHMWPE	PC15	PC23	PC43
O1s Area	2867.06	2723.64	2703.10	2295.35
C1s Area	10104.21	9748.41	9830.38	8828.25
O/C (%)	28.37	27.94	27.50	25.52

and ketones. In addition, the changing trends in the proportion and the magnitude of the individual species presented in C1s core spectra were very similar to those observed in the O1s core spectra.

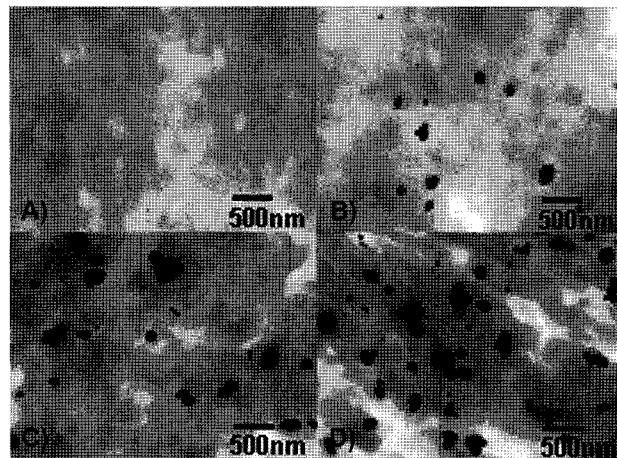
The quantification of oxidation was carried out by calculating the ratio of the oxygen and carbon atoms, the extent of oxidation (O/C), expressed in %. Table II shows the values of O/C decreased with the increase in the content of zirconia. In order to explain the results obtained, the proportion of zirconia in the volume of the composite has to be considered. The composites prepared by the *in situ* polymerization contained up to 43% zirconia in total weight. Even though the density of zirconia was six folds higher than that of UHMWPE, its volume accounted for as much as 11% of that of the composites. Therefore, the decreased proportion of UHMWPE in the composites due to the inclusion of zirconia may lead to the diminution of the total oxidation against the γ -ray irradiation. The other plausible explanation of the findings of the present study follows from the assumption that crystallinity of the samples increases with increasing content of zirconia.

DSC Measurement. Table III shows the DSC results of the neat and the polymerized composites. Although decreased heat absorptions were found in the polymerized composite samples, the crystallinity of the samples gradually increased with the increase in the contents of zirconia. The carbon-hydrogen and carbon-carbon bonds, either in the amorphous or in the crystalline phase, are known to absorb the energy of the sterilizing radiation. However, in the crystalline phase, the oxygen diffusion is negligible compared to that in the amorphous phase.²⁵

Morphology. Figure 5 shows the TEM pictures of the neat and the polymerized composites; the zirconia particles were uniformly dispersed throughout the whole matrix.

Table III. DSC Results of Neat UHMWPE and Polymerized Composites (PC)

	Neat UHMWPE	PC15	PC23	PC43
Heat Absorb (E, J)	776.25	732.78	757.35	546.24
Total Mass (mg)	4.5	4.6	5.1	4.8
ZrO ₂ Mass (mg)	-	0.69	1.17	2.06
Crystallinity (%)	59.28	64.40	66.27	68.81

**Figure 5.** TEM images of neat UHMWPE and polymerized composites (PC): (A) neat UHMWPE, (B) PC15, (C) PC23, and (D) PC43.

This uniform dispersion of zirconia was attributed to the fact that zirconia is used as the nucleation site for the *in situ* polymerization. The zirconia particles were surrounded by a dark zone, which could be presumed as crystallines.²⁶ In addition, the dark area increased with the increase in the content of zirconia. Together with the DSC results, TEM examinations strongly support the postulation of the present study that crystallinity increases in proportion with the zirconia content, which, in turn, reduces the oxidative property of the composites.

Conclusions

We have investigated the effects of zirconia content on the oxidation behavior of the γ -ray-treated UHMWPE/zirconia composite surfaces. The oxidation indices of the samples decreased with the increase in the zirconia contents. The DSC results indicated that the crystallinity of the samples gradually increased with the increase in the contents of zirconia. In addition, the TEM pictures showed that the zirconia particles were uniformly dispersed throughout the whole matrix up to 43 wt% of filler contents. Therefore, it is concluded that the decreased oxidative behavior is attributed to the increased crystallinity as well as the decreased polymer portion of the UHMWPE/zirconia composites.

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