**High Wear Resistance of Ultralow-Wear Polyethylene with Different Molecular Weights Under Different Contact Pressure**

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**Abstract**

Ultralow-wear polyethylene (ULWPE), a type of polyethylene homocomposite with excellent wear resistance, has recently been reported; however, its underlying wear mechanism has yet to be clarified. In the current study, three different molecular weights of ULWPE from 205 to 748 kg/mol were experimentally evaluated on a multidirectional motion pin-on-disk wear tester under a contact pressure from 2 to 4 MPa, compared with conventional UHMWPE. The high wear resistance mechanism of ULWPE was investigated with respect to mechanical, microstructural, and surface properties. Compared with UHMWPE, ULWPE had excellent wear resistance. Structure and mechanical characterization showed that the crystallinity and lamellar thickness of ULWPE were significantly higher than those of UHMWPE, which endowed ULWPE with high hardness and strength. Despite its considerably smaller molecular weight than that of UHMWPE, ULWPE still had high interphase content, leading to its superior toughness. The crystallinity, lamellar thickness, Young’s modulus, yield stress, and elongation at break of ULWPE exhibited a downward trend with the increase of molecular weight. Conversely, the interphase content of ULWPE increased with the molecular weight increase. Among all the ULWPE samples, ULWPE with a molecular weight 748 kg/mol had the least wear, as a result of combined both excellent strength and adequate toughness. With an increase in contact pressure, the wear losses of different polymers tended to increase. The wear losses of the least wear ULWPE were $4.71 \pm 0.04 \, \text{mm}^3/\text{Million Cycles (Mc)}$, $5.11 \pm 0.37 \, \text{mm}^3/\text{Mc}$, and $5.77 \pm 0.62 \, \text{mm}^3/\text{Mc}$ under 2, 3, and 4 MPa. Comprehensive strength and toughness reduced abrasive wear and adhesion wear, endowing ULWPE with excellent wear resistance.

**Keywords** Ultralow-wear polyethylene · Contact pressure · Wear resistance mechanism · Artificial joints

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**1 Introduction**

Ultrahigh-molecular-weight polyethylene (UHMWPE), as a typical bearing material in orthopedic implants, has been widely used for its superior wear resistance, impact resistance, and chemical stability [1, 2]. However, the antiwear properties of UHMWPE are highly dependent on its molecular weight, and the enhanced wear resistance of UHMWPE with an increase in molecular weight is obtained at the expense of its processability [3]. A large amount of wear debris from conventional UHMWPE implants often caused osteolysis and loosening of the prosthesis, which seriously restricts the service life of the joint prosthesis [4]. Highly cross-linked UHMWPE (HXLPE) exhibits better antiwear properties than conventional UHMWPE [5, 6]. However, the cross-linking process involved reduces the fatigue resistance and oxidation resistance of UHMWPE. Adding vitamin
E reduces oxidation but simultaneously decreases the efficiency of cross-linking, increasing the difficulty and cost of production.

A new type of homocomposite polyethylene has recently been developed, referred to as ultralow-wear polyethylene (ULWPE), which exhibits superior strength, impact toughness, and wear resistance [7, 8]. ULWPE is easier to process than the conventional UHMWPE with a molecular weight of more than two million. Moreover, ULWPE can be directly injected into a mold to produce various geometries for implants. In an earlier study using cytotoxicity testing, hemolysis testing, acute/chronic toxicity testing, and muscular implantation testing, ULWPE was found to exhibit excellent biocompatibility and biological safety [8]. Cui et al. [7] experimentally investigated the high wear resistance mechanism of ULWPE, compared with the most widely used artificial joint materials (HDPE, UHMWPE, and HXLPES), during pin-on-disk (POD) wear tests. However, UHMWPE as a mature implant product has been clinically used for decades, whereas ULWPE as a recently introduced type of polyethylene still requires in-depth research and needs to be optimized before expensive full joint simulation tests are conducted [9].

In the present study, we examined the wear resistance of ULWPE with three different molecular weights under different contact pressure levels on a multidirectional motion pin-on-disk (POD) tester. The physical and mechanical properties of ULWPE and UHMWPE were compared with respect to stretching, contact angle, and density. The influence of wear on the structure of polymer surfaces was characterized by Fourier infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), X-ray diffraction, and laser micro-Raman spectroscopy to identify the morphologies of their worn surfaces, degrees of crystallinity, lamellar thicknesses, sizes of their crystalline domains, and their interphase fractions. This study is expected to provide a relevant experimental basis for the future clinical applications of ULWPE.

### 2 Materials and Methods

#### 2.1 Sample Preparation

Four polymers were used in this study, including three kinds of ULWPE samples with different molecular weights (China National Petroleum Corporation) and UHMWPE (Chirulen®, GUR 1050). ULWPE was obtained based on the weight-average molecular weight (Mw) and determined by gel permeation chromatography (Table 1). The three kinds of ULWPE samples—namely, ULWPE-200, ULWPE-300, and ULWPE-700—had weight-average molecular weights of 205, 282, and 748 kg/mol, respectively. All ULWPE appeared as homogeneous fine white granules. Table 1 lists the number-average molecular weight (Mn), weight-average molecular weights (Mw), and polydispersity index (PDI) of the three ULWPE samples.

The ULWPE samples were compression-molded using a manual hydraulic unit model (#3925, Carver Inc., United States) in accordance with ASTM D4020-18. The UHMWPE samples were cut from a polymer sheet (Beijing Chunlizhengda Medical Instruments Co., Ltd.). All the pin samples were finished by machining. Cobalt–chromium (CoCr) alloy disks used in the tribological testing were the same as the alloy used clinically (Beijing Chunlizhengda Medical Instruments Co., Ltd.).

#### 2.2 Tribological Testing

Tribological tests were performed using four kinds of polymer pins and CoCr alloy disks. The pin specimens (20 mm × Φ 8 mm) were tailored from compression-molded sheets. The test surface of each polymer sample was machined to Ra < 2 μm. The CoCr alloy disks were processed into disks with a height of 10 mm and a diameter of 40 mm. All disk samples were polished to Ra < 0.01 μm. All pin samples were soaked with deionized water at least 35 days before the test to ensure that the material reached water absorption saturation.

The multidirectional motion POD wear tester (Biotribopod-M732, Shanghai University, China) (Hua et al., [10]) in the current study consisted of 12 wear stations, similar to our previous study [10]. Wear tests were performed for 1,000,000 cycles (1 Mc), with normal loads of 100, 150, and 200 N (corresponding to 2, 3, and 4 MPa). Bovine calf serum (Gibco, United States), which was used as the base lubricant, was diluted with deionized water to a target total protein concentration of 30 g/L for POD wear testing in accordance with ASTM F732-00 standards.

The degrees of wear of the four polymers were determined gravimetrically after each test interval (0.33 Mc) by using an electronic analytical balance with high precision (Sartorius MSA225S-ICE-DU, Germany). After wear testing, the surface morphology of the pin samples was observed using an optical microscope (Leica DM-2500M, Germany). A white light interferometer (SuperView W1, Zhongtu, China) was used to measure the surface roughness of the pin and disk samples. The wear rate of the
polymer was calculated as the wear volume loss per million cycles. The wear factor was determined using the formula \( k = \Delta V/(F \cdot L) \) per ASTM G99-05, where \( \Delta V \) is the volume loss converted from mass loss and density, \( F \) is the compressive load, and \( L \) is the sliding distance. The wear factor \( k \) was calculated as the wear volume per unit compressive load and per unit sliding distance [11].

### 2.3 Characterization of Mechanical Properties

Tensile tests were conducted on a universal material testing instrument (5567, Instron Corp., United States), with the strain rate set to 50 mm/min in accordance with ISO 527-2: 2012. Tensile specimens were punched out to dog-bone shapes (Type 1BB of ISO 527-2). All mechanical properties were tested under an ambient temperature of 25 °C. At least five specimens were measured for each group to ensure repeatability.

The densities of the compression-molded samples were calculated from the measured mass and volume. The volume was measured using a gas pycnometer (AccuPyc II 1340, Micromeritics, United States), and the mass was determined using a high-precision electronic analytical balance (Sartorius MSA225S-ICE-DU, Germany).

The static contact angles of the samples were measured with a contact angle instrument (DSA100, KRUS, Germany) under distilled water. The examination points were selected randomly, and the procedure was repeated ten times for each sample; the average value obtained was then considered as the contact angle.

### 2.4 Structural Characterization

The crystalline behavior of the compression-molded samples was characterized by differential scanning calorimetry (DSC 3500 Sirius, Netzsch, Germany). DSC exhibiting different heat responses toward various crystalline structures as temperature varies. The DSC instrument was calibrated with indium under a high-purity nitrogen atmosphere. Samples of about 7–10 mg were sealed in aluminum pans for DSC characterization with a fixed cooling or heating rate (10 °C/min). The thermal history was erased by heating the samples to 200 °C and holding them for 10 min, followed by cooling the sample to 40 °C. After being stabilized for 2 min, the sample reheating/cooling circle data were used for the melting and crystallization temperature counts. All processes were conducted under the N₂ atmosphere.

The degree of crystallinity of polyethylene was calculated using \( X_c = \Delta H/\Delta H_0 \), where \( X_c \) (%) is the crystallinity of polyethylene, \( \Delta H \) (J/g) is the measured melting enthalpy on the DSC melting curve, and \( \Delta H_0 \) (J/g) is the theoretical melting enthalpy of polyethylene with 100% crystallinity, with \( \Delta H_0 = 289.3 \text{ J/g} \) [12].

The lamellar thickness was measured using the Thomson-Gibbs equation [13] \( L = 2 \pi T_m^0/\Delta H(\Delta H_0 - T_m) \), where \( L \) (nm) is the lamellar thickness of the material and \( \Delta H \) (J/cm²) is the surface free energy of the polyethylene sheet, which is \( 9.0 \times 10^{-6} \text{ J/cm²} \). \( T_m^0 \) is the equilibrium melting point of polyethylene (418.7 K) and \( T_m \) (K) is the actual melting temperature of the polymer.

X-ray diffraction (D8 Advance, Bruker AXS, Germany) was performed using Cu–Kα radiation with a wavelength (\( \lambda \)) of 0.154 nm. The specimens were scanned from 10° to 60° at the rate of 8°/min.

FTIR was conducted on an infrared spectrometer (Nicolet iS50, ThermoFisher Scientific, United States) which generated transmission absorption spectra over the 4000–400 cm⁻¹ range at a resolution of 4 cm⁻¹ by attenuated total reflectance to measure the surface oxidation of polyethylene samples. The oxidation index (OI) of polyethylene was calculated per ASTM F2102-17, where OI is the ratio of the area of the carbonyl absorption peak(s) centered at 1720 cm⁻¹ (＞C=O absorption) to that centered at 1370 cm⁻¹ (CH absorption).

Laser micro-Raman spectroscopy (LabRAM HR Evolution, Horiba, Japan) was conducted to evaluate the interphase fractions of molded polymer samples. Raman spectra were recorded using a laser light source with a wavelength of 532 nm under the following conditions: laser power, 10 mW; slit width, 300 μm; and accumulation time, 80 s (collected five times).

The relative contents of the three phases can be calculated using Strobl’s process [14]:

\[
I_T = I_{1293} + I_{1305}
\]

\[
X_a = I_{1305}/I_T
\]

\[
X_c = I_{1415}/(0.46I_T)
\]

\[
X_i = 1 - X_a - X_c
\]

where \( I_T \) as the internal intensity standard measured from the Raman spectral signal data in the range 1350–1250 cm⁻¹, which can be decomposed into two halves, with peaks at 1293 cm⁻¹ (\( I_{1293} \) for the crystalline and trans phases) and 1305 cm⁻¹ (\( I_{1305} \) for the amorphous phase). The CH₂-bending vibration (\( \delta_{CH_2} \)) signal region in the 1510–1390 cm⁻¹ range could be decomposed into three parts, with peaks at 1413 cm⁻¹ (\( I_{1415} \) for the crystalline phase), 1437 cm⁻¹ (for the amorphous and trans phases), and 1459 cm⁻¹ (for the amorphous phase). \( X_c, X_a, X_i \) denote the contents of the crystalline phase, amorphous phase, and interphase of polyethylene. All decomposition results were obtained using the Lorentzian curve-fitting procedure.
2.5 Statistical Analysis

In this study, all data of parallel groups were presented as averaged value ± one standard deviation (SD). The statistical difference of the data was determined by the non-paired Student’s t test. A P value of less than 0.05 was considered a significant difference (**).

3 Results

3.1 Tribological Behavior

3.1.1 Wear Volume and Wear Factor

Figure 1 depicts the wear volume (bar chart) and wear factor (line chart) of four types of polyethylene samples sliding against the CoCr disks at applied loads of 2, 3, and 4 MPa under calf serum lubricated conditions after 1,000,000 cycles (1 Mc) on a multidirectional motion wear tester. From the perspective of wear volume, wear loss increased with an increase in contact pressure. Among the ULWPE samples, ULWPE-700 showed the best antiwear properties under all loading conditions, which was 4.71 ± 0.04, 5.11 ± 0.37, and 5.77 ± 0.62 mm³/Mc, respectively. No significant difference was found between ULWPE and UHMWPE (P > 0.05, ANOVA) under contact pressure levels of 2 and 3 MPa; by contrast, significant differences were determined between ULWPE-300/700 and UHMWPE (P < 0.05, ANOVA) under 4 MPa. The wear tests indicated that the wear resistance of ULWPE with relatively low molecular weight was not inferior to that of UHMWPE.

In accordance with the calculation formula of the wear factor k, the k values of the four polymers under different compressive loads are presented as a line chart above the wear volume bar chart. With an increase in contact pressure, the k values of ULWPE-200, ULWPE-700, and UHMWPE first decreased and then tended to remain the same, and ULWPE-300 gradually decreased. The value of k showed no significant difference (P > 0.05, ANOVA) under 3 and 4 MPa, except that of ULWPE-300. The average wear factors of UHMWPE under 2, 3, and 4 MPa were $2.36 \times 10^{-6}$ mm³/N·m, $1.33 \times 10^{-6}$ mm³/N·m, and $1.59 \times 10^{-6}$ mm³/N·m, which were within a reasonable range, consistent with previous studies [15].

3.1.2 Surface Wear Morphology

Figure 2 presents the surface morphology of the polymer pin as determined by optical microscopy under 2, 3, and 4 MPa and scanning electron microscopy under 4 MPa after 1 Mc. As viewed through optical photos, both ULWPE and UHMWPE had scratches and pits on the surface. Among the samples, ULWPE-700 exhibited excellent antiwear performance, revealing slight wear scars on the surface. The wear mechanism of the four types of polyethylene mainly consisted of abrasive wear and adhesive wear. Notably, fibrous polyethylene was observed on the worn surfaces of ULWPE-200 and ULWPE-300. Long and thin fibrous polyethylene appeared on the worn area of ULWPE-200, whereas short and thick ones appeared on the worn area of ULWPE-300. However, ULWPE-700 and UHMWPE only showed some wear particles on the wear morphologies and no fibers on the worn surface. With an increase in the molecular weight, the number of scratches was significantly reduced; moreover, no pits were observed, indicating that ULWPE with larger molecular weights had better wear resistance. The wear morphology results reflected on the worn surface tended to be similar to the tensile and wear test results; ULWPE-200 and ULWPE-200 300 showed excellent toughness, and UHMWPE exhibited higher strength, whereas ULWPE-700 exhibited both plastic toughness and strength.

3.2 Physical and Mechanical Properties

3.2.1 Tensile Tests

Figure 3A presents the uniaxial stress–strain curves. The tensile curves of ULWPE-200 and ULWPE-300 varied from those of ULWPE-700 and UHMWPE. Those of ULWPE-200 and ULWPE-300 showed a plateau after yielding. ULWPE-700 and UHMWPE, which had relatively large molecular weights, had no platform stage, and stress increased with an increase in strain. UHMWPE had no significant yield point. Figure 3B presents significant decreases in the Young’s modulus and yield strength as the molecular weights of the four types of polyethylene increase. The polymer with a wide plateau stage showed a large elongation at break, which was 2–3 times that of ULWPE-700 and UHMWPE. Notably,
Fig. 2 Surface morphology of the polymer pin on the optical microscope and scanning electron microscope after 1 Mc. A: ULWPE-200, B: ULWPE-300, C: ULWPE-700 and D: UHMWPE. I-Edge surface morphology of polyethylene pins under 2 MPa after 1 Mc for 100 times magnification, II-Edge surface morphology of polyethylene pins under 3 MPa after 1 Mc for 100 times magnification, III-Edge surface morphology of polyethylene pins under 4 MPa after 1 Mc for 100 times magnification, IV-Central surface morphology of polyethylene pins under 4 MPa after 1 Mc for 100 times magnification, V-Scanning electron microscope images of central surface morphology of polyethylene pins under 4 MPa after 1 Mc for 100 times magnification.
the ultimate tensile strength of ULWPE was greater than that of UHMWPE. The molecular weight of ULWPE-300, which held the highest breaking strength, was less than 1/10th of the molecular weight of UHMWPE.

### 3.2.2 Density

Table 2 lists the density of the four polyethylene samples. ULWPE-200, ULWPE-300, ULWPE-700, and UHMWPE have densities equal to 0.967 ± 3.14E−04, 0.962 ± 2.01E−04, 0.950 ± 3.74E−04, and 0.935 ± 6.57E−04 g/cm³, respectively. As shown, the densities decrease with an increase in the molecular weight. A significant difference was found between ULWPE and UHMWPE ($P < 0.05$, ANOVA).

### 3.2.3 Contact Angle

The static contact angle measurements of the different pin samples before and after wear at 2 MPa under distilled water are shown in Fig. 4. The original contact angle of UHMWPE was the lowest ($82.97° ± 15.02°$). A significant difference was found between ULWPE-700 and the other three polymers ($P < 0.05$, ANOVA). The static contact angle decreased after the wear process for ULWPE and increased for UHMWPE. The static contact angle of ULWPE was smaller than that of UHMWPE because of the wear process, but no significant difference between ULWPE and UHMWPE ($P > 0.05$, ANOVA).

### 3.3 Microstructures and Oxidation Index

#### 3.3.1 Differential Scanning Calorimetry and X-ray Diffraction: Crystallinity and Crystallite Size

Polyethylene is typically a partially crystalline polymer, with a molecular chain arrangement ordered in the crystalline region. Crystalline phase analysis was extensively performed by differential scanning calorimetry and X-ray polycrystalline diffraction. Figure 5 presents the DSC thermographs of
the four kinds of polyethylene. The heat and cool absorption peak area, melting point, crystallization point, and crystallinity were measured. The crystallinity of the polymer was proportional to the melting enthalpy of the material at the time of crystallization. The melting enthalpy of the material is expressed as the area of the endothermic peak on the DSC curve. The corresponding data are listed in Table 3.

The crystallization peak temperature ($T_c$) and melting start temperature ($T_{onset}$) of the different samples slightly varied from one another, but the crystallization peak of UHMWPE was wider. The melting peak temperature ($T_m$) of UHMWPE was slightly lower than that of ULWPE. Meanwhile, a significant difference in melting enthalpy was observed between ULWPE and UHMWPE. The melting enthalpies of ULWPE were markedly higher than that of UHMWPE, and a significant difference was determined ($P < 0.05$, ANOVA). This result indicated that the molecular weight of ULWPE was not as high as that of UHMWPE, which was similar to high-density polyethylene (HDPE) and easy to crystallize [16]. The crystallinity of the polyethylene samples decreased with increasing molecular weight.

The lamellar thickness relations were as follows: ULWPE-200 (24.73 ± 0.76 nm) > ULWPE-300 (23.54 ± 0.49 nm) and ULWPE-700 (23.50 ± 0.42 nm) > UHMWPE (20.11 ± 0.22 nm), with a significant difference. The great lamellar thickness of ULWPE was also a factor influencing the mechanical properties and wear resistance of the material.

Figure 6 presents the XRD curves of the surface of the initial granule, molded samples (before wear tests), and worn samples (experienced 1 Mc at 2 MPa) of the four polyethylene samples. Figure 6 presents the XRD curves of the surface of the initial granule, molded samples (before wear tests), and worn samples (experienced 1 Mc at 2 MPa) of the four polyethylene samples in a wide-angle zone (10°–50°). Three intensive peaks appeared at 21.8°, 24.2°, and 29.9° corresponding to the (110), (200), and (210) crystal planes of the orthorhombic phase. The degrees of crystallinity could also be determined from the XRD curves, which were area fractions calculated using the fitting curves of the orthorhombic crystalline peaks [(110), (200), (210)] and the amorphous sections. Figure 7 showed the changes in the crystallinity (Fig. 7A) and average crystallite size (Fig. 7B) of the initial granule, molded samples (before wear tests), and worn samples (after 1 Mc at 2 MPa) of the four polyethylene samples. In Fig. 7A, the crystallinity of polyethylene increases after the molding process and decreases after the wear process. Although the degrees of

| Material     | $T_c$ (K) | $T_{onset}$ (K) | $T_m$ (K) | $\Delta T$ | $\Delta H$ (J/g) | Crystallinity (%) | $L$ (nm) |
|--------------|-----------|-----------------|-----------|------------|------------------|-------------------|----------|
| ULWPE-200    | 390.01    | 398.53 ± 0.29   | 408.11 ± 0.32 | 9.58 ± 0.03 | 202.35 ± 2.98   | 68.38 ± 0.97      | 24.73 ± 0.76 |
| ULWPE-300    | 391.01    | 398.99 ± 0.20   | 407.58 ± 0.23 | 9.47 ± 0.18 | 197.35 ± 4.77   | 66.85 ± 1.39      | 23.54 ± 0.49 |
| ULWPE-700    | 390.96    | 397.53 ± 0.07   | 407.56 ± 0.20 | 10.03 ± 0.30 | 182.22 ± 1.23   | 61.23 ± 0.58      | 23.50 ± 0.42 |
| UHMWPE       | 391.58    | 397.09 ± 0.21   | 405.69 ± 0.14 | 8.60 ± 0.33 | 153.45 ± 1.23   | 51.65 ± 0.17      | 20.11 ± 0.22 |
crystallinity measured using two different methods were different in value, the variations with an increase in the molecular weight were similar, with each exhibiting a descending trend. Figure 7B shows the average crystallite sizes of the orthorhombic phase of the different polyethylene samples. With similar trends of crystallinity, the average crystallite size increased from the initial granule to the molded plate and decreased after the wear process. The degrees of crystallinity and average crystallite size increased from the initial granule to the molded plate. The average crystallite size of ULWPE decreased after wear; specifically, ULWPE-300 and ULWPE-700 changed significantly. However, no change in the crystallite size of UHMWPE was observed after the wear process.

3.3.2 FTIR Spectra and Raman Spectra: Branch Chain, Oxidation Index, and Interphase

The molecular configuration, bond, and OI of ULWPE and UHMWPE were evaluated by FTIR spectroscopy (Fig. 8A). The original wear surface of the polymers was drawn with dotted lines, and the surface after wear (2 MPa, 1 Mc) was presented with solid lines. The main characteristic peaks of ULWPE were similar to those of UHMWPE with no

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Fig. 7 Changes in the crystallinity (A) and average crystallite size (B) of the initial granule, molded samples (before wear tests), and worn samples (after 1 Mc at 2 MPa) of the four polyethylene samples.

Fig. 8 FTIR spectra (A) and oxidation index (OI) (B) of the original and worn surfaces (under 2 MPa after 1 Mc) of the four polyethylene samples.
apparent deviation. The main absorption bands of the four materials in the spectrum appeared within the ranges 3000–2843 cm⁻¹, 1490–1350 cm⁻¹, and 1010–650 cm⁻¹, which were ascribed to the CH stretching vibration peak (ν_CM), CH shear vibration peak (δ_CM), and CH bending and rolling vibration peak (ρ_CM). Oxidation leads to the peak formation of carbonyls, which include ketones, esters, and ethers, with principal absorption peaks between 1650 and 1850 cm⁻¹ [17]. The FTIR curves showed that no acromion was present at 1378 cm⁻¹, indicating that the CH₃ group at the branch chain was undetected. Thus, both ULWPE and UHMWPE were smooth (CH₂) main-chain structures and almost had no side branch.

The OI of the polymers is shown in Fig. 8B. The surface OI before the wear process of the four types polyethylene samples nearly slightly increased with increasing molecular weight. ULWPE and UHMWPE showed no significant difference. Compared with that of UHMWPE, the surface oxidation index of ULWPE increased after wear. The larger the molecular weight of ULWPE, the greater the severity of surface oxidation after wear; meanwhile, that of UHMWPE slightly increased. However, UHMWPE had experienced decades of modification treatment in clinical applications, including the addition of vitamin E to reduce oxidation. With this consideration, ULWPE can also be further optimized in oxidation resistance. Notably, both ULWPE-200 and ULWPE 300 showed no significant change from UHMWPE.

In the past two decades, experiments and theories had proved that an interphase region between the crystalline and amorphous regions of partially crystalline polymers exists [18–21]. The use of the “three-phase model” instead of the classic “two-phase model” to describe the structure of polymers had been confirmed theoretically by Flory [22] and verified experimentally using small angle X-ray scattering (SAXS) [23], nuclear magnetic resonance (NMR), and Raman spectroscopy [14]. Among these characterization techniques, Raman spectroscopy is particularly sensitive to the vibration behavior induced by chain conformations.

Figure 9A shows the Raman spectrum curves of four polyethylene surfaces before and after wear (2 MPa, 1 Mc), with the original surface of polymers drawn using dotted lines, and the worn surface is presented with solid lines. The characteristic signals of the polyethylene samples were the C–C stretching vibration (1128 cm⁻¹ for asymmetric stretching, 1060 cm⁻¹ for symmetric stretching; ν(CC), CH₂-rocking vibration (1167 cm⁻¹; ν(CH₂), CH₂-twisting vibration (1293 cm⁻¹; τ(CH₂), CH₂-wagging vibration (1368 cm⁻¹; ω(CH₂), and CH₂-bending vibration (1459 cm⁻¹ for the antiphase, 1413 cm⁻¹ for in-phase; δ(CH₂)). The main characteristic peaks of ULWPE showed no apparent deviation from those of UHMWPE.

Figure 9B shows the crystalline phase (χ_c), interphase (χ_i), and amorphous phase (χ_a) of the original and wear surfaces of ULWPE and UHMWPE. The crystallinity exhibited a monotonically decreasing trend with increasing molecular weight, which was consistent with the DSC and XRD data. The number χ_c for each sample remained steady throughout the wear process. The interphase ratio varied in the different polymers. The calculation results for the interphase contents revealed that ULWPE-200 contained the lowest ratio, whereas UHMWPE exhibited the highest one. However, ULWPE-300 and ULWPE-700 with no high molecular weight still showed a high mass fraction of the interphase.

Fig. 9 Raman spectroscopy (A) and phase compositions (B) for the original and worn surfaces (under 2 MPa after 1 Mc) of the four kinds polyethylene samples. χ_c crystalline phase, χ_i interphase, χ_a amorphous phase
4 Discussion

ULWPE is a new type of high-density polyethylene synthesized by metallocene catalysts, which can potentially be applied in artificial joint replacements. Previously, the mechanism underlying the high wear resistance of ULWPE was investigated in the aspects of microstructure, crystallization properties, mechanical, physical, and chemical properties. However, its tribological characteristics and surface structure variations under the wear process have to be clarified. In this study, by comparing with UHMWPE, ULWPE with different molecular weights was experimentally evaluated, including wear behavior, mechanical/physical properties (tensile, contact angle, and density), and its surface structure change during the wear process.

Compared with UHMWPE, ULWPE had excellent wear resistance. All the ULWPE samples had lower wear loss than UHMWPE under 2 MPa. Even the ULWPE-200 which had the worst wear behavior had no significant differences with UHMWPE under all contact pressure conditions. It has been commonly assumed that the wear rate is strongly affected by the ultimate tensile strength and the breaking elongation of the material [24]. In the tensile test, the ultimate tensile strength of ULWPE was greater than that of UHMWPE, and the fracture strain energy was also higher. The molecular weight of ULWPE-300 with the highest breaking strength was less than 1/10th that of UHMWPE. Basically, ULWPE exhibited superior fracture toughness and strength, even higher than those of UHMWPE, which has a larger molecular weight.

The wear resistance and mechanical properties of polymer are closely related to its structure. A relatively high values of Mn may not prone to pulling out through crystals or entanglement loci during wear, thus improving its wear resistance. Tervoort et al. [25] considered that the wear coefficient should correlate with $\phi$Mn, and not simply with Mn, in which the parameter of $\phi$ was the volume fraction “effective” polymer, which was related to the structure parameters (such as entanglements and crystallites). Both ULWPE and UHMWPE are homopolymerized semicrystalline polyethylene. The crystallinity of polymers was affected by their molecular chains. Both ULWPE and UHMWPE were smooth CH$_2$ main-chain structures and almost had no side branch. But DSC tests indicated that the crystallinity and lamellar thickness of ULWPE were larger than those of UHMWPE, owing to its relatively low molecular weight. This is also confirmed by the crystallinity observed by XRD and Raman tests. During sliding wear tests, the specimens would bear compressive stresses at the microscopic level. Some mechanisms of plastic deformation like shearing and fracture of the lamellae occur. The great lamellae thickness will improve the resistance to deformation [26] and reduce abrasive wear. On the other hand, the microhardness value of polymers was mainly determined by the crystallinity of the material and the hardness of the crystalline region. There was a positive correlation between the hardness value $H_c$ of the crystalline region of polyethylene and the lamellar thickness of the material. Therefore, the high crystallinity and larger lamellar thickness endowed ULWPE with high hardness and strength. According to Ratner–Lancaster correlation [27, 28], the wear rate of the polymer was positively related to the material hardness $H$, and tensile fracture stress $\sigma_u$, and tensile fracture strain $\varepsilon_u$. So the larger lamellar thickness will have positive influences to its antiwear properties.

The noncrystalline domain itself can be viewed as a two-component region [29, 30]: a compliant core (amorphous phase) sandwiched between two more rigid layers (interphase). The transition layers were more rigid than the central region that connect them [19]. The molecular connections between the crystallites of the semicrystalline polymer affected its mechanical properties. If those molecular connections composed of covalent bonds did not exist, the crystallites would be held together just by weak van der Waals or hydrogen interactions, and they would slip easily past one another or split away from one another under stress; this would result in macroscopic brittleness of the material [18]. High-molecular-weight samples had more entanglements, which promoted more interphases. Despite its considerably smaller molecular weight than that of UHMWPE, ULWPE (especially ULWPE-700) still had high interphase content, which led to its superior toughness.

For ULWPE, Young’s modulus and yield strength decreased with an increase in the molecular weight, which was governed by the crystalline structure. The crystallinity and lamellar thickness decreased with an increase in molecular weight. The polymer with a wide plateau stage showed a large elongation at break, the value for ULWPE-200 and ULWPE-300 was 2–3 times for ULWPE-700. The results of crystalline structure and mechanical properties tests were consistent with the phenomenon of the worn surface morphology in the ULWPE pin samples. Under the action of cyclic compressive stress and shear stress, the asperities of ULWPE were continuously elongated until they exceeded the elongation limit of the material. Pulled-out fibrils of ULWPE-200 and ULWPE-300 can be observed in the SEM images (Fig. 2A-V/B-V). Although ULWPE-200 and ULWPE-300 had higher crystallinity, the contribution was mainly reflected in the crystal region. The noncrystalline phase with soft and compliant made the crystal grains of ULWPE easy slip with each other. At the ULWPE-700 worn surface (Fig. 2C-V), only some wear particles and slight scratches were observed. High mass fraction of the interphase in which tie-molecules might exist, greatly improving the toughness of ULWPE-700. The comprehensive
strength, hardness, and toughness of ULWPE reduced the abrasive wear and adhesive wear damage and endowed the materials with superior wear resistance. However, the surface oxidation index of ULWPE increased after wear. The larger the molecular weight, the more noticeable the increase, which was not an advantage for ULWPE. The crystallinity decreased with an increase in the molecular weight of ULWPE. Correspondingly, the amorphous phases and interphases were higher. Compared with the crystalline phases which were densely arranged, the amorphous phases and interphases were more susceptible to oxidation by free radicals.

A multidirectional motion wear tester was adopted to evaluate the wear volume and wear factor of the four types of polyethylene samples under three different contact pressure levels. The overall wear loss increases with increasing contact pressure. Among all the ULWPE samples, ULWPE-700 had the best wear resistance under all loading conditions. However, several anomalies were found. For instance, the wear loss of ULWPE-300 under 4 MPa was less than that under 3 MPa. The reason was considered a test artifact caused by the creep of the material surface under excessive pressure [31]. Increasing the nominal contact stress to 4 MPa from 2 MPa increases the real contact area between the polymer pin and the metal disk. Consequently, resulting in more adhesion points and a more apparent “cold welding” phenomenon. An increase in load also increases the tensile, compressive, and bending interactive force on the adhesion points. Several protuberances were observed at the center and the edges of ULWPE and UHMWPE surfaces when the pressure exceeded 3 MPa (Fig. 2-II/III/IV). The generation of these protuberances prompted the material that should have been removed re-covering the surface, causing the measured amount of wear to deviate from the true value. As a conventional implant material, UHMWPE had been studied on the influence of contact pressure under multidirectional sliding wear conditions [32]. The wear mechanisms and wear factors were consistent with the clinical findings when the pressure was set to 2 MPa; when pressure was in the critical range of 2–3.5 MPa, the results started to vary from clinical ones. The discrepancy then became apparent when pressure exceeded 3.5 MPa. The dependence of ULWPE and UHMWPE on contact pressure seemed the same. The 2 MPa pressure should not be exceeded in POD wear tests to perform wear properties assessments accurately [32].

5 Limitation

This study focused on the contact pressure dependence of ULWPE with different molecular weights on contact pressure. The high toughness of ULWPE can be attributed to its high interphase content. However, the mechanism of the microstructure that confers high toughness on ULWPE has yet to be explored. The number and role of effective molecular entanglement in ULWPE should be clarified. Further studies should also focus on the clinical applications in terms of implant testing, sterilization, oxidation, etc.

6 Conclusion

The wear resistance of ULWPE with different molecular weights under different contact pressure was studied on a multidirectional motion pin-on-disk tester to reveal the mechanisms underlying its ultrahigh wear resistance. The main conclusions are as follows:

- Particularity at crystallinity, lamella thickness, elongation at break, and interphase provided the superior wear resistance of ULWPE. Owing to the optimal relationship of strength and toughness, ULWPE with a relatively low molecular weight had excellent wear resistance compared with UHMWPE.

- With the increase of molecular weight, the crystallinity, Young’s modulus, and yield stress decreased. The interphase content increased, conversely. ULWPE-200 and ULWPE-300 showed a high crystallinity and break elongation, leading to combined excellent strength and toughness. The higher crystallinity of ULWPE-700 maintained the basic strength; meanwhile, the high content of interphase reduced the slip of crystalline domains, significantly improved the wear resistance.

- The wear losses of different polymers tended to increase with an increase in contact pressure. ULWPE-700 had the best wear resistance under all loading conditions.

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Declarations

Conflict of interest The authors declare no possible conflict of interests.
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