Research Article

Crystallization and Melting Behavior of UHMWPE Composites Filled by Different Carbon Materials

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In order to understand the effect of different carbon materials on the crystallization and melting behavior of ultrahigh molecular weight polyethylene (UHMWPE), UHMWPE composites were prepared by different carbon materials through solution mixing in this paper. UHMWPE was oxidized to improve the interfacial interaction between UHMWPE and carbon materials. The UHMWPE composites and oxidized UHMWPE composites were prepared using granular graphite particle (GP), graphite nanoplatelets (GNP), and flaky graphene oxide (GO) as fillers. The effect of the type and the content of carbon materials and the oxidation of UHMWPE on crystallization and melting temperatures, crystallinity, and crystal form of UHMWPE and oxidized UHMWPE composites was investigated by differential scanning calorimetry, X-ray diffraction, scanning electron microscope, X-ray photoelectron spectrum, and Fourier transform infrared spectroscopy. The results indicated that there are coexistence of the heterogeneous nucleation and the hindering effect of crystal growth by carbon materials for UHMWPE crystallization. The different influence of carbon materials on the crystallization and melting behavior of UHMWPE was discussed by the heterogeneous nucleation of carbon materials and the restriction of the macromolecular chain motion of UHMWPE by carbon materials.

1. Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) is widely used in aerospace, military, medical, industrial, and other fields due to its series of superior properties, such as low bulk density and friction coefficient, high chemical stability, impact property, biocompatibility, wear resistance, and good self-lubricating [1–4]. Despite these advantages, the physical and mechanical properties of UHMWPE still need to be improved, such as difficult processing and poor properties, such as hardness, Young’s modulus, creep resistance, coefficient of thermal expansion and heat-deflection temperature, and electrical and thermal conductivity.

In order to improve the properties of UHMWPE, UHMWPE composites filled by carbon fibers (CF) [5–13], carbon nanotube (CNT) [14–32], and graphene oxide (GO) [33–43] were reported. Despite the excellent performance of these nanocomposites, the high cost of these fillers restricted the widely use of the UHMWPE composites. Graphite (GP) with low cost is a possibly more promising filler material relative to the above fillers. Therefore, the preparation and physical and mechanical properties of GP/UHMWPE composites were investigated by many researchers.

Liu et al. [44] prepared GP/UHMWPE nanocomposites and characterized the internal morphology and engineering properties of GP/UHMWPE nanocomposites. It is found good dispersion of GP in the UHMWPE nanocomposites. The yield strength, crystallinity, and pyrolysis temperature of nanocomposites are increased with increasing of GP content. GP/UHMWPE composites prepared by cryomilling followed also showed that crystallinity, hardness, Young’s modulus, and the yield strength of GP/UHMWPE composite are increased with increasing of GP contents [45]. However, Delgado-Rangel et al. [46] found that extruded UHMWPE composite with 0.5 wt% of GP nanoplatelets has a brittle tensile behavior, and bending property and
impact toughness are lower than those of extruded UHMWPE due to the segregation of GP among the powder grains of UHMWPE. Li and Song [47] also found that the addition of GP significantly decreases the tensile strength. The addition of GP with low content can improve the impact strength of UHMWPE.

Lebedev et al. [48] investigated the effect of the type of carbon fillers on the mechanical behavior and electrical conductivity of UHMWPE composites. The mechanical properties of UHMWPE composites are quite similar to those of filler-free UHMWPE. Although the MWCNT composites are attractive because of a low percolation threshold, the GP is possibly more promising filler with the high conductivity and low cost. It is found that increasing of filler content has no significantly decline the tensile strength of composites, allowing its contents in the composites to rise up to a level that provides high electrical conductivity without a noticeable deterioration of tensile property of composites [49].

Although the mechanical properties and electrical conductivity of UHMWPE composites have been investigated, the crystallization and melting behavior of UHMWPE composites filled by different carbon materials, especially graphite, have little been reported. Because the physical and mechanical properties of UHMWPE composites depend on the crystalline morphology and crystallization behavior, the crystallization and melting behavior of UHMWPE composites filled by different carbon materials should be understood. In this paper, three carbon materials, graphite particle (GP), graphite nanoplatelets (GNP), and graphene oxide (GO), were used as fillers. In particular, due to the lack of polar groups on the surface of UHMWPE, the chemical bond between UHMWPE and carbon materials is difficult

**Table 1:** The content ratio of O¹s/C¹s of unoxidized and oxidized UHMWPE.

| Oxidation time (h) | 0         | 0.5       | 1.0       | 2.0       | 4.0       |
|-------------------|-----------|-----------|-----------|-----------|-----------|
| C¹s atomic (%)    | 95.39     | 94.75     | 91.07     | 85.14     | 83.80     |
| O¹s atomic (%)    | 4.61      | 5.05      | 8.20      | 14.20     | 15.40     |
| O¹s/C¹s           | 0.048     | 0.053     | 0.090     | 0.167     | 0.184     |

**Figure 1:** SEM images of (a) GP, (b) GNP, and (c) GO at mag. of 2.00 k×.

**Figure 2:** The X-ray photoelectron spectrum of unoxidized and oxidized UHMWPE.

**Figure 3:** FTIR spectrum of unoxidized and oxidized UHMWPE.
to form, resulting in agglomeration and segregation of carbon materials in UHMWPE matrix. UHMWPE was oxidized for different time to improve the interfacial interaction between UHMWPE and carbon materials. UHMWPE composites and oxidized composites were prepared through solution mixing method. The influence of oxidize time of UHMWPE, different carbon materials, and their contents on the crystallization and melting temperatures, crystallinity, and crystal form of UHMWPE composites and oxidized UHMWPE composites was investigated and discussed by the heterogeneous nucleation of carbon materials and the restriction of the macromolecular chain motion of UHMWPE by carbon materials.

2. Experiment

2.1. Materials. UHMWPE (Mw $3.3 \times 10^6$) was purchased from Mitsui Chemicals, Japan. Graphite powder (GP) with particle size of about 2.6 μm was obtained from Aladdin, Shanghai. Graphene nanoplatelets (GNP) with diameter of about 25 μm were used from Strem Chemicals, America. Graphene oxide (GO) with diameter of about 10-50 μm was purchased from Yuanye Bio-Technology, Shanghai. 1,3,5-Trichlorobenzene was obtained from Macklin Shanghai. Tetrahydrofuran (THF) was used from General Reagent.

2.2. Preparation of UHMWPE Composites and Oxidized UHMWPE Composites. The mixtures of UHMWPE powder and 1,3,5-trichlorobenzene were heated to 150°C to completely dissolve the UHMWPE by magnetic stirring. The mass ratio of UHMWPE to solvent was controlled at 1:100. The GP was added and stirred by ultrasound for 30 min to obtain the GP/UHMWPE mixtures. The mixtures cooled to room temperature were dispersed by adding THF and stirred at room temperature for 2 h. The mixtures were filtered to remove the mixed solvent and repeatedly washed with THF until the filtrate was colorless to obtain the GP/UHMWPE composites. All these composites were dried in an oven at 80°C/2.0 MPa for 3 h before testing. The GNP/UHMWPE and GO/UHMWPE composites were also prepared as the same as GP/UHMWPE composites.

The oxidation solution was prepared by mixing potassium dichromate (IV) (K₂Cr₂O₇), sulfuric acid (H₂SO₄), and distilled water in a 7:150:12 mass ratio. The UHMWPE powder was placed in the oxidation solution at room temperature with magnetic stirring and oxidized for 0.5 h, 1 h, 2 h, and 4 h, respectively. After oxidation, the oxidized UHMWPE powder was first washed in distilled water for 2 min and ethanol for 2 min, respectively, and then dried in a vacuum oven at room temperature for 12 h. The GNP/oxidized UHMWPE and GO/oxidized UHMWPE composites were also prepared as the same as GP/UHMWPE composites.

2.3. Characterization. The morphologies of GP, GNP, and GO particles were observed by a field emission scanning electron microscope (SEM, Gemini500, Zeiss/Brucker, Germany) operating at 3 kV. All of the samples were sputtered with gold to avoid electrical charging during examination. The SEM images of GP, GNP, and GO are shown in Figure 1.

The melting and crystallization behavior of UHMWPE and its composites were measured by differential scanning calorimetry at nitrogen atmosphere with the DSC-8500 (PE, America). About 2-3 mg sample sealed in aluminum crucible was firstly heated up to 180°C at the rate of 10°C/min and kept this temperature for 3 min to eliminate the thermal history of sample. After that, the sample was cooled at the rate of 10°C/min from 180°C to 60°C. At last, the sample was reheated up to 180°C at the rate of 10°C/min. The crystallinity of sample ($X_{DSC}$) is calculated by

\[
X_{DSC} \% = \frac{\Delta H_m}{\Delta H_m^0 \cdot \omega} \times 100 \%
\]

where $\Delta H_m$ is the measured melting enthalpy of sample, $H_m^0$ is the melting enthalpy of 100% crystalline UHMWPE (291 J/g), and $\omega$ is the mass content of UHMWPE in the composites.

X-ray diffraction (XRD) was used to investigate the crystal form of UHMWPE and its composites. The samples were firstly heated up to 180°C at the rate of 10°C/min and kept this temperature for 3 min and then cooled to room temperature at the rate of 10°C/min in DSC. The treated samples were scanned from 5° to 40° (2θ) at the rate of 10°/min by

![Figure 4: The DSC curves of unoxidized and oxidized UHMWPE.](image-url)
D-MAX 2200 VPC (Rigaku, Japan) using Cu-Kα (λ = 0.154 nm) as radiation.

Fourier transform infrared spectroscopy (FTIR) measurements were analyzed by a FTIR spectrometer (Nicolet 6700, Thermo Electron Corp., USA) with an ATR device in the wave number range from 4000 to 650 cm⁻¹, with a resolution of 0.2 cm⁻¹.

X-ray photoelectron spectroscopy (XPS) measurements were made on a Nexsa spectrometer (Thermo Fisher, England) using Al Kα radiation with a cathode voltage of 15 kV, a current intensity of 10 mA, and a pressure of 5 × 10⁻⁹ Torr. The survey scans were recorded from 0 to 1120 eV simultaneously with a step of 100 meV.

3. Results and Discussion

3.1. Effect of Oxidation on UHMWPE. The oxidation of UHMWPE generally increased the oxygen content on the surface of UHMWPE. The oxygen content on the surface of UHMWPE was characterized by XPS. It can be seen from
The effect of oxidation on the crystallization and melting behavior of UHMWPE was characterized by DSC. It can be seen from Figure 4 that the oxidation at room temperature has little influence on the crystallization and melting behavior of UHMWPE. It is indicated that the oxidation at room temperature for 4 h has no obvious influence on the structure of macromolecular chain of UHMWPE.

### 3.2. Crystallization and Melting Behavior of UHMWPE Composites

The DSC curves of UHMWPE composites are shown in Figure 5 and the data are listed in Table 2. For the GP/UHMWPE composites, addition of 10 wt% GP significantly increases the crystallization temperature ($T_c$) of UHMWPE from 117.9°C to 120.6°C. However, the content of GP between 10 wt% and 50 wt% has a slight influence on the $T_c$ of UHMWPE. The $T_c$ of UHMWPE is only increased to 121.8°C at the GP content of 50 wt%. Furthermore, the degree of undercooling ($\Delta T$) is also decreased with increasing of GP content. These results indicated that the addition of GP not only increases the $T_c$ of UHMWPE but also accelerates the crystallization rate of UHMWPE melt. Although the addition of GP increases the $T_c$ of UHMWPE, the melting peak temperature ($T_m$) of UHMWPE is decreased. Addition of 10 wt% GP decreases the $T_m$ of UHMWPE from 135.2°C to 133.9°C. Addition of 10 wt% GP significantly increases the crystallinity ($X_{DSC}$) of UHMWPE from 43.1% to 66.7%. However, the $X_{DSC}$ of GP/UHMWPE composites decreased to 63.9% at the GP content of 50 wt%.

For the GNP/UHMWPE composites, addition of 10 wt% GNP increases the $T_c$ of UHMWPE from 117.9°C to 119.8°C, and the $T_c$ of UHMWPE has little change with increasing of GNP content. The increased $T_c$ of GNP/UHMWPE composites not obvious compared to GP/UHMWPE composites. However, the $T_m$ of GNP/UHMWPE composites is higher than that of UHMWPE and GP/UHMWPE composites. For example, the $T_m$ of GP/UHMWPE and GNP/UHMWPE composites are 134.0°C and 136.5°C at the filler content of 20 wt%, respectively. It is indicated that the crystalline perfection of GNP/UHMWPE composites is higher than that of GP/UHMWPE composites. Addition of 10 wt% GNP increases the $X_{DSC}$ of UHMWPE from 43.1% to 50.9%. Then, the $X_{DSC}$ of UHMWPE composites is gradually decreased with increasing of GNP content. The $X_{DSC}$ of GNP/UHMWPE composites is lower than that of pure UHMWPE at the content of GNP above 20 wt%. However, the $X_{DSC}$ of GP/UHMWPE composites is higher than that of pure UHMWPE and remains above 60% without being affected by the GP contents.

For the GO/UHMWPE composites, addition of 10 wt% GO increases the $T_c$ of UHMWPE from 117.9°C to 119.9°C, and the $T_c$ of GO/UHMWPE composites is not influenced by GO content. Compared with GP/UHMWPE and GNP/UHMWPE composites, the increased $T_c$ in GO/UHMWPE composites is the same as GNP/UHMWPE composites and is lower than GP/UHMWPE composites. However, the $T_m$ of GO/UHMWPE composites are higher than that of GNP/UHMWPE composites. For example, the $T_m$ of GNP/UHMWPE and GO/UHMWPE is 135.6°C and

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**Table 2: The DSC data of UHMWPE composites.**

| wt% | $T_m$ (°C) | $\Delta H_m$ (J·g$^{-1}$) | $X_{DSC}$ (%) | $T_c$ (°C) | $\Delta H_c$ (J·g$^{-1}$) | $\Delta T$ (°C) |
|-----|------------|-----------------|---------------|------------|-----------------|----------------|
| 0   | 135.2      | 125.4           | 43.1          | 117.9      | 109.7           | 15.3           |
| 10  | 133.9      | 194.1           | 66.7          | 120.6      | 180.7           | 13.3           |
| 20  | 134.0      | 192.4           | 66.1          | 120.7      | 180.4           | 13.3           |
| GP  | 133.9      | 192.0           | 66.0          | 121.2      | 181.4           | 12.7           |
| 30  | 133.9      | 187.2           | 64.3          | 121.5      | 175.2           | 12.4           |
| 40  | 134.2      | 186.0           | 63.9          | 121.8      | 176.6           | 12.4           |
| 50  | 135.1      | 198.8           | 41.2          | 129.7      | 194.1           | 15.4           |
| 10  | 135.6      | 148.2           | 50.9          | 119.8      | 150.1           | 15.8           |
| 20  | 136.5      | 126.3           | 43.4          | 119.9      | 132.8           | 16.6           |
| GNP | 135.9      | 124.9           | 42.9          | 120.1      | 129.7           | 15.8           |
| 40  | 135.3      | 121.3           | 41.7          | 119.6      | 122.5           | 15.7           |
| 50  | 135.1      | 119.8           | 41.2          | 119.7      | 129.4           | 15.4           |
| 5   | 135.7      | 160.3           | 55.1          | 119.9      | 185.8           | 15.8           |
| 10  | 137.1      | 151.6           | 52.1          | 119.7      | 177.0           | 17.6           |
| GO  | 136.7      | 150.3           | 51.6          | 119.8      | 161.9           | 16.7           |
| 20  | 136.2      | 148.5           | 51.0          | 119.7      | 156.3           | 16.5           |
| 25  | 133.9      | 147.8           | 50.8          | 119.6      | 150.7           | 14.3           |
137.1°C at the filler content of 10 wt%, respectively. The addition of 10 wt% GO increases the $X_{\text{DSC}}$ of UHMWPE from 43.1% to 55.1%. However, the $X_{\text{DSC}}$ is gradually decreased with increasing of GO content, but always higher than that of pure UHMWPE. By comparing the $X_{\text{DSC}}$ data listed in Table 2, it can be seen that the $X_{\text{DSC}}$ of UHMWPE composites from high to low is $\text{GP/UHMWPE} > \text{GO/UHMWPE} > \text{GNP/UHMWPE}$. However, addition of GP, GNP, and GO has no influence on crystal type of UHMWPE, shown in Figure 6.

A lot of investigation indicated that the addition of filler increases the crystallization temperature of polymers, attributed to the heterogeneous nucleation of filler [13, 14, 42, 43]. The interfacial interaction between filler and polymer makes nucleation easier, therefore polymer crystalized at a higher temperature. The above results indicated that GNP, GO, and GP have different effects on crystallization and melting behavior of UHMWPE. GP/UHMWPE composites have high crystallization temperature and crystallinity. The addition of GNP and GO is not as obvious as GP in increased crystallization temperature and crystallinity of UHMWPE. A lot of investigation proved that addition of fillers increases the crystallinity of UHMWPE [8, 18, 50–53] and the crystallinity of UHMWPE is decreased at a high amount of filler [8, 54]. It is suggested that there are coexistence of the heterogeneous nucleation and the hindering effect of crystal growth by carbon materials for UHMWPE crystallization. The different influence of carbon materials on the crystallization and melting behavior of UHMWPE is attributed to the synergistic effect both the heterogeneous nucleation and the restriction of the macromolecular chain motion of UHMWPE by carbon materials.

The higher crystallization temperature of UHMWPE composites than UHMWPE is attributed to the heterogeneous nucleation of GP, GNP, and GO. The heterogeneous nucleation of GP is higher than that of GNP and GO, attributed to the higher specific surface area of granular GP than that of flaky GNP and GO, which results in the higher crystallization temperature and nucleation density. However, the flaky GNP and GO has a stronger restriction of the macromolecular chain motion of UHMWPE than granular GP to hinder the crystal growth of UHMWPE, resulting in decreased crystallinity in GNP/UHMWPE and GO/UHMWPE composites. With increasing of filler contents, the decreased crystallinity in UHMWPE composites is also attributed to the restriction of the macromolecular chain motion of UHMWPE by the fillers.

### 3.3. Crystallization and Melting Behavior of Oxidized UHMWPE Composites

#### 3.3.1. Crystallization and Melting Behavior of GNP/Oxidized UHMWPE Composites

The DSC curves and data of oxidized UHMWPE composites filled by 10 wt% GNP are shown in Figure 7 and Table 3. It can be seen that the $T_c$ of GNP/oxidized UHMWPE composites is not significantly affected by oxidation time. However, the $T_c$ of GNP/oxidized UHMWPE composites is about 2°C higher than that of oxidized UHMWPE. The results showed that the heterogeneous nucleation of GNP can also increase the $T_c$ of
oxidized UHMWPE as the same as the GNP/UHMWPE composites. Introduction of oxygen-containing groups into the surface of UHMWPE during the oxidation has no influence on the $T_c$ of GNP/oxidized UHMWPE composites. However, the oxidation of UHMWPE has a great influence on the crystallinity of GNP/UHMWPE composites. The crystallinity of GNP/oxidized UHMWPE composites is higher than that of GNP/UHMWPE composites. The crystallinity of GNP/oxidized UHMWPE composites is first increased and then slightly decreased with the extension of oxidation time. The crystallinity of GNP/oxidized UHMWPE composites is increased from 50.9% to 61.6% at the oxidation time of 0.5 h, and the crystallinity is decreased to 56.3% at the oxidation time of 4 h, still higher than the crystallinity of GNP/UHMWPE composites. On the one hand, the heterogeneous nucleation of GNP increased the nucleation density of oxidized UHMWPE, which is beneficial to the increased crystallinity. On the other hand, the surface of oxidized UHMWPE has more oxygen-containing polar groups, which is conducive to the interaction with GNP and further promoting the nucleation, thus leading to the increased crystallinity of GNP/oxidized UHMWPE composites. However, the increased oxygen-containing groups reduced the regularity of UHMWPE molecular chain and hindered the crystal growth of UHMWPE, resulting in the decreased crystallinity of GNP/oxidized UHMWPE composites with increasing of oxidation time.

The $T_m$ of GNP/oxidized UHMWPE composites is lower than that of GNP/UHMWPE composites. The oxidation of UHMWPE for 0.5 h decreased the $T_m$ of GNP/UHMWPE composites from 135.6°C to 131.4°C. The decreased $T_m$ of GNP/oxidized UHMWPE composites is attributed to the formation of a large number of crystals by the heterogeneous nucleation of GNP, resulting in rapid crystal growth and reduction of crystalline perfection. The increased oxygen-containing groups in the oxidized UHMWPE reduce the regularity of UHMWPE molecular chain, thus forming crystals with low crystalline perfection. However, oxidation of UHMWPE has no influence on crystal type of UHMWPE, shown in Figure 8.

### 3.3.2. Crystallization and Melting Behavior of GO/Oxidized UHMWPE Composites

The DSC curves and data of GO/oxidized UHMWPE composites are shown in Figure 9 and Table 4. The $T_c$ of GO/oxidized UHMWPE composites is also higher than that of oxidized UHMWPE. Addition of GO content at 5% increased the $T_c$ of oxidized UHMWPE from 118.0°C to 119.8°C and is slightly increased with increasing of GO content. At the GO content at 20%, the

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**Table 3: The DSC data of GNP/oxidized UHMWPE composites.**

| Oxidation time (h) | $T_m$ (°C) | $\Delta H_m$ (J·g⁻¹) | $X_{DSC}$ (%) | $T_c$ (°C) | $\Delta H_c$ (J·g⁻¹) | $\Delta T$ (°C) |
|-------------------|------------|----------------------|---------------|------------|----------------------|--------------|
| 0                 | 135.6      | 148.2                | 50.9          | 119.8      | 150.1                | 15.8         |
| 0.5               | 131.4      | 179.4                | 61.6          | 120.2      | 170.5                | 11.2         |
| 1.0               | 131.6      | 168.5                | 57.9          | 119.6      | 159.4                | 12.0         |
| 2.0               | 131.8      | 165.5                | 56.9          | 119.3      | 158.0                | 12.5         |
| 4.0               | 132.3      | 163.7                | 56.3          | 119.0      | 153.7                | 13.3         |
$T_c$ of GO/oxidized UHMWPE composites reaches 122.6°C, while the $T_c$ of GO/UHMWPE composites is 119.7°C. However, the $T_m$ of GO/oxidized UHMWPE composites is slightly decreased with increasing of GO content. For example, the $T_m$ of oxidized UHMWPE is decreased from 135.5°C to 132.5°C at GO content of 20%. By comparing the of $T_m$ GO/UHMWPE and GO/oxidized UHMWPE composites, it is found that the $T_m$ of GO/UHMWPE composite is higher than that of GO/oxidized UHMWPE composites.

It can be seen from Tables 2 and 4 that the crystallinity of GO/oxidized UHMWPE composites is higher than that of GO/UHMWPE composites. The crystallinity of GO/oxidized UHMWPE composites is first increased and then decreased with increasing of GO content. But it is always higher than the crystallinity of oxidized UHMWPE matrix. It is believed that the heterogeneous nucleation of GO in the oxidized UHMWPE crystallization is more significant than that of GO in the UHMWPE, resulting in the increased $T_c$ and nucleation density of oxidized UHMWPE, which are conducive to the increased crystallinity. The introduction of oxygen-containing groups into the UHMWPE by oxidation is conducive to the interaction between UHMWPE and GO to further promote the heterogeneous nucleation, leading to the increased crystallinity of GO/oxidized UHMWPE composites.

### 4. Conclusions

Ultrahigh molecular weight polyethylene (UHMWPE) and oxidized UHMWPE composites were prepared by using three carbon materials, graphite particle (GP), graphite nanoplatelet (GNP), and graphene oxide (GO), as fillers through solution mixing.

The oxidation of UHMWPE at room temperature significantly increased the oxygen content on the surface of UHMWPE. But it is no obvious influence on the crystallization and melting behavior of UHMWPE.

The GNP, GO, and GP have different effect on crystallization and melting behavior of UHMWPE. GP/UHMWPE composites have high crystallization temperature ($T_c$) and crystallinity. Addition of GNP and GO is not as obvious as GP in increased $T_c$ and crystallinity of UHMWPE.

There are coexistence of the heterogeneous nucleation and the hindering effect of crystal growth by carbon materials in the UHMWPE composites. The different influence of carbon materials on the crystallization and melting behavior of UHMWPE is attributed to the synergistic effect both the heterogeneous nucleation and the restriction of the macromolecular chain motion of UHMWPE by carbon materials. The heterogeneous nucleation of GP is higher than that of GNP and GO, attributed to the higher specific surface area of granular GP than that of flaky GNP and GO. However, the flaky GNP and GO have a stronger restriction of the macromolecular chain motion of UHMWPE than granular GP to hinder the crystal growth of UHMWPE. With increasing of filler contents, the decreased crystallinity in UHMWPE composites is attributed to the restriction of the macromolecular chain motion of UHMWPE by the fillers.

The $T_c$ of GNP/oxidized UHMWPE composites is about 2°C higher than the $T_c$ of oxidized UHMWPE and GNP/UHMWPE composites. The crystallinity of GNP/oxidized UHMWPE composites is also higher than that of oxidized UHMWPE and GNP/UHMWPE composites. On the one hand, the heterogeneous nucleation of GNP increased the $T_c$ and nucleation density of oxidized UHMWPE, which is beneficial to the increased crystallinity. On the other hand, the surface of oxidized UHMWPE has more oxygen-containing polar groups, which is conducive to the interaction with GNP and further promoting the nucleation, thus leading to the increased crystallinity of GNP/oxidized UHMWPE composites.

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**Table 4:** The DSC data of oxidized UHMWPE composites.

| GO (wt%) | $T_m$ (°C) | $\Delta H_m$ (J·g$^{-1}$) | $X_{DSC}$ (%) | $T_c$ (°C) | $\Delta H_c$ (J·g$^{-1}$) | $\Delta T$ (°C) |
|---------|-----------|---------------------|------------|------------|-------------------|--------------|
| 0       | 135.5     | 129.1               | 44.4       | 118.0      | 128.6             | 15.5         |
| 5       | 135.2     | 168.0               | 57.7       | 119.8      | 214.9             | 15.4         |
| 10      | 134.0     | 182.3               | 62.3       | 120.8      | 244.1             | 13.2         |
| 15      | 133.3     | 165.4               | 56.8       | 121.2      | 236.2             | 12.1         |
| 20      | 132.5     | 162.1               | 55.7       | 122.6      | 233.5             | 10.1         |

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**Figure 9:** The DSC curves of GO/oxidized UHMWPE composites.
The $T_c$ and crystallinity of GO/oxidized UHMWPE composites is higher than that of oxidized UHMWPE and GO/UHMWPE composites. However, the $T_m$ of GO/oxidized UHMWPE composites is higher than that of GO/oxidized UHMWPE composites. The heterogeneous nucleation of GO in the oxidized UHMWPE composites is more significant than that of GO in the UHMWPE composites. The introduction of oxygen-containing groups into the UHMWPE is conducive to the interaction between GO and GO to further promote the heterogeneous nucleation.

Addition of GP, GNP, and GO and the oxidation of UHMWPE at room temperature have no influence on crystalline type of UHMWPE.

Nomenclature

\[ \Delta H_c: \text{ Crystallization enthalpy (°C)} \]
\[ \Delta H_m: \text{ Melting enthalpy (°C)} \]
\[ T_c: \text{ Crystallization temperature (°C)} \]
\[ T_m: \text{ Peak melting temperature (°C)} \]
\[ \Delta T: \text{ Crystallization undercooling (°C)} \]
\[ X_{DSC}: \text{ Crystallinity of composites determined by DSC method (%)} \]

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest.

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References

[1] S. Gürgen, "Wear behavior of UHMWPE composites under oxidative effect," *Polymer Degradation and Stability*, vol. 199, p. 109912, 2022.

[2] S. Gürgen, "Wear performance of UHMWPE based composites including nano-sized fumed silica," *Composites Part B: Engineering*, vol. 173, p. 106967, 2019.

[3] X. Dangsheng, "Friction and wear properties of UHMWPE composites reinforced with carbon fiber," *Materials Letters*, vol. 59, no. 2-3, pp. 175–179, 2005.

[4] S. Gürgen, A. Sert, and M. C. Kuşhan, "An investigation on wear behavior of UHMWPE/carbide composites at elevated temperatures," *Journal of Applied Polymer Science*, vol. 138, no. 16, p. 50245, 2021.

[5] S. Y. Li and D. G. Li, "Carbon fiber reinforced highly filled charcoal powder/ultra high molecular weight polyethylene composites," *Materials Letters*, vol. 134, pp. 99–102, 2014.

[6] A. A. Stepashkin, D. I. Chukov, M. V. Gorshenkov, V. V. Tcherdyntsev, and S. D. Kaloshkin, "Electron microscopy investigation of interface between carbon fiber and ultra high molecular weight polyethylene," *Journal of Alloys and Compounds*, vol. 586, pp. S168–S172, 2014.

[7] J. H. Wang, H. Gao, L. L. Gao, Y. Cui, and Z. Y. Song, "Ratcheting behavior of UHMWPE reinforced by carbon nanofibers (CNF) and hydroxyapatite (HA): experiment and simulation," *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 88, pp. 176–184, 2018.

[8] G. Sui, W. H. Zhong, X. Ren, X. Q. Wang, and X. P. Yang, "Structure, mechanical properties and friction behavior of UHMWPE/HDPE/carbon nanofibers," *Materials Chemistry and Physics*, vol. 115, no. 1, pp. 404–412, 2009.

[9] D. I. Chukov, A. A. Stepashkin, M. V. Gorshenkov, V. V. Tcherdyntsev, and S. D. Kaloshkin, "Surface modification of carbon fibers and its effect on the fiber-matrix interaction of UHMWPE based composites," *Journal of Alloys and Compounds*, vol. 586, pp. S459–S463, 2014.

[10] D. I. Chukov, A. A. Stepashkin, A. V. Maksimkin et al., "Investigation of structure, mechanical and tribological properties of short carbon fiber reinforced UHMWPE-matrix composites," *Composites Part B: Engineering*, vol. 76, pp. 79–88, 2015.

[11] C. Z. Peng, "Improved interfacial properties of carbon fiber/ UHMWPE composites through surface coating on carbon fiber surface," *Surface and Interface Analysis*, vol. 50, no. 5, pp. 558–563, 2018.

[12] Q. J. Liao, F. He, M. Yang, and D. Yang, "The addition of acid treated carbon nanotube on the interfacial adhesion of carbon fiber reinforced UHMWPE composite," *Surface and Interface Analysis*, vol. 49, no. 8, pp. 717–720, 2017.

[13] Y. S. Pan, J. H. Mao, and J. Ding, "Effect of carbon fiber surface modification on the mechanical properties of carbon-fiber-reinforced ultrahigh-molecular-weight polyethylene composite," *Journal of Materials Engineering and Performance*, vol. 28, no. 4, pp. 1995–2005, 2019.

[14] S. R. Bakshi, J. E. Tercero, and A. Agarwal, "Synthesis and characterization of multiwalled carbon nanotube reinforced ultra high molecular weight polyethylene composite by electrostatic spraying technique," *Composites Part A: Applied Science and Manufacturing*, vol. 38, no. 12, pp. 2493–2499, 2007.

[15] K. R. Manoj, S. K. Sharma, K. B. V. Manoj, and D. Lahiri, "Effects of carbon nanotube aspect ratio on strengthening and tribological behavior of ultra high molecular weight polyethylene composite," *Composites Part A: Applied Science and Manufacturing*, vol. 76, pp. 62–72, 2015.

[16] A. V. Maksimkin, S. D. Kaloshkin, M. S. Kaloshkina et al., "Ultra-high molecular weight polyethylene reinforced with multi-walled carbon nanotubes: fabrication method and properties," *Journal of Alloys and Compounds*, vol. 536, pp. S538–S540, 2012.

[17] S. S. Khasraghi and M. Rezaei, "Preparation and characterization of UHMWPE/HDPE/MWCNT melt-blended nanocomposites," *Journal of Thermoplastic Composite Materials*, vol. 28, no. 3, pp. 305–326, 2015.

[18] T. Deplancke, O. Lame, S. Barrau, K. Ravi, and F. Dalmas, "Impact of carbon nanotube prelocalization on the ultra-low electrical percolation threshold and on the mechanical behavior of sintered UHMWPE-based nanocomposites," *Polymer*, vol. 111, pp. 204–213, 2017.

[19] J. C. Baena and Z. X. Peng, "Dispersion state of multi-walled carbon nanotubes in the UHMWPE matrix: effects on the
tribological and mechanical response,” *Polymer Testing*, vol. 71, pp. 125–136, 2018.

[20] J. X. Wang, C. L. Cao, D. S. Yu, and X. D. Chen, “Deformation and stress response of carbon nanotubes/UHMWPE composites under extensional-shear coupling flow,” *Applied Composite Materials*, vol. 25, no. 1, pp. 35–43, 2018.

[21] N. Camacho, E. A. Franco-Urquiola, and S. W. Stafford, “Wear performance of multilayered carbon nanotube-reinforced ultra-high molecular weight polyethylene composite,” *Advances in Polymer Technology*, vol. 37, no. 6, pp. 2261–2269, 2018.

[22] W. Chen, H. T. Duan, K. L. Gu, Y. L. Xiang, H. F. Shang, and J. Li, “Tribological properties of MWNTs reinforced UHMWPE composites,” *Polymeric Materials Science and Engineering*, vol. 31, pp. 62–67, 2015.

[23] J. Shariati, A. R. Saadatabadi, and F. Khorasheh, “Thermal degradation behavior and kinetic analysis of ultra high molecular weight polyethylene based multi-walled carbon nanotube nanocomposites prepared via in-situ polymerization,” *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, vol. 49, no. 9, pp. 749–757, 2012.

[24] P. Q. Wang, H. L. Wang, Y. X. Wang, and F. Y. Yan, “Synergistic effect of BN and MWCNT hybrid fillers on thermal conductivity and thermal stability of ultra-high-molecular-weight polyethylene composites with a segregated structure,” *Journal of Polymer Research*, vol. 23, no. 2, pp. 1–11, 2016.

[25] G. Y. Xu and Q. R. Zhu, “Studies on crystallization and melting behaviors of UHMWPE/MWNTs nanocomposites with reduced chain entanglements,” *Polymers*–*Polymer Composites*, vol. 25, no. 6, pp. 495–506, 2017.

[26] P. G. Ren, S. Y. Hou, F. Ren, Z. P. Zhang, Z. F. Sun, and L. Xu, “The influence of compression molding techniques on thermal conductivity of UHMWPE/BN and UHMWPE/(BN + MWCNT) hybrid composites with segregated structure,” *Composites Part A: Applied Science and Manufacturing*, vol. 90, pp. 13–21, 2016.

[27] B. Li, T. Z. Ji, J. Li, and W. L. Liu, “Electrical properties of MWNTs/UHMWPE composites,” *Polymeric Materials Science and Engineering*, vol. 28, no. 2, pp. 45–48, 2012.

[28] E. Enqvist, D. Ramanenka, P. A. P. Marques, J. Gracio, and N. Emami, “The effect of ball milling time and rotational speed on ultra high molecular weight polyethylene reinforced with multiwalled carbon nanotubes,” *Polymer Composites*, vol. 37, no. 4, pp. 1128–1136, 2016.

[29] A. Q. Li, Z. X. Wu, Z. S. Zhang, and K. Mai, “Preparation and characterization of ultrahigh molecular weight polyethylene composites with high content of multiwall carbon nanotubes,” *Polymer Composites*, vol. 41, no. 5, pp. 1972–1978, 2020.

[30] Y. Y. Guo, C. L. Cao, F. B. Luo et al., “Largely enhanced thermal conductivity and thermal stability of ultra high molecular weight polyethylene composites via BN/CNT synergy,” *RSC Advances*, vol. 9, no. 70, pp. 40800–40809, 2019.

[31] A. Vinoth and S. Datta, “Design of the ultrahigh molecular weight polyethylene composites with multiple nanoparticles: an artificial intelligence approach,” *Journal of Composite Materials*, vol. 54, no. 2, pp. 179–192, 2020.

[32] R. Wang, Y. Y. Zheng, L. H. Chen, S. Y. Chen, D. X. Zhuo, and L. X. Wu, “Fabrication of high mechanical performance UHMWPE nanocomposites with high-loading multiwalled carbon nanotubes,” *Journal of Applied Polymer Science*, vol. 137, article 48667, 2020.
[47] J. Z. Li and H. N. Song, “Study on the properties of UHMW-PE modified by graphite,” Chemistry and Adhesion, vol. 35, no. 4, pp. 21–23, 2013.

[48] O. V. Lebedev, A. N. Ozerin, A. S. Kechekyan et al., “A study of oriented conductive composites with segregated network structure obtained via solid-state processing of UHMWPE reactor powder and carbon nanofillers,” Polymer Composites, vol. 40, no. S1, pp. E146–E155, 2019.

[49] O. V. Lebedev, A. N. Ozerin, A. S. Kechekyan et al., “Strengthened electrically conductive composite materials based on ultra-high-molecular-weight polyethylene reactor powder and nanosized carbon fillers,” Nanotechnologies in Russia, vol. 10, no. 1-2, pp. 42–52, 2015.

[50] E. G. Celebi, C. Bindal, and A. H. Ucisik, “Characterization of UHWPE-TiO2 composites produced by gelation/crystallization method,” Acta Physica Polonica A, vol. 132, no. 3, pp. 767–769, 2017.

[51] X. Q. Zhang, Y. B. Tan, Y. H. Li, and G. Z. Zhang, “Effect of OMMT on microstructure, crystallisation and rheological behaviour of UHMWPE/PP nanocomposites under elongation flow,” Plastics Rubber and Composites, vol. 47, no. 7, pp. 315–323, 2018.

[52] J. T. Yeh, C. K. Wang, A. Yeh et al., “Preparation and characterization of novel ultra-high molecular weight polyethylene composite fibers filled with nanosilica particles,” Polymer International, vol. 62, no. 4, pp. 591–600, 2013.

[53] X. C. Yin, S. Li, G. J. He, Y. H. Feng, and J. S. Wen, “Preparation and characterization of CNTs/UHMWPE nanocomposites via a novel mixer under synergy of ultrasonic wave and extensional deformation,” Ultrasonics Sonochemistry, vol. 43, pp. 15–22, 2018.

[54] Z. X. Wu, Z. S. Zhang, and K. Mai, “Non-isothermal crystallization kinetics of UHMWPE composites filled by oligomer-modified CaCO3,” Journal of Thermal Analysis and Calorimetry, vol. 139, no. 2, pp. 1111–1120, 2020.