

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 oxidization 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

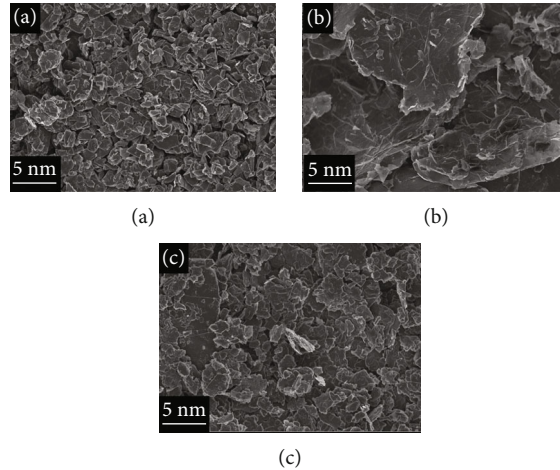


FIGURE 1: SEM images of (a) GP, (b) GNP, and (c) GO at mag. of 2.00 kx.

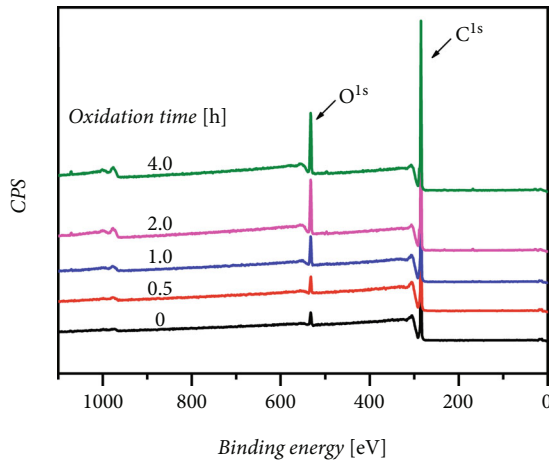


FIGURE 2: The X-ray photoelectron spectrum of unoxidized and oxidized UHMWPE.

TABLE 1: The content ratio of O^{1s}/C^{1s} of unoxidized and oxidized UHMWPE.

Oxidation time (h)	0	0.5	1.0	2.0	4.0
C_{1s} atomic (%)	95.39	94.75	91.07	85.14	83.80
O_{1s} atomic (%)	4.61	5.05	8.20	14.20	15.40
O^{1s}/C^{1s}	0.048	0.053	0.090	0.167	0.184

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

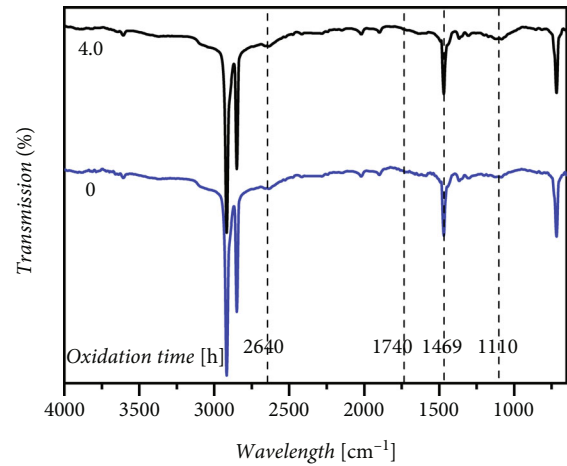


FIGURE 3: FTIR spectrum of unoxidized and oxidized UHMWPE.

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

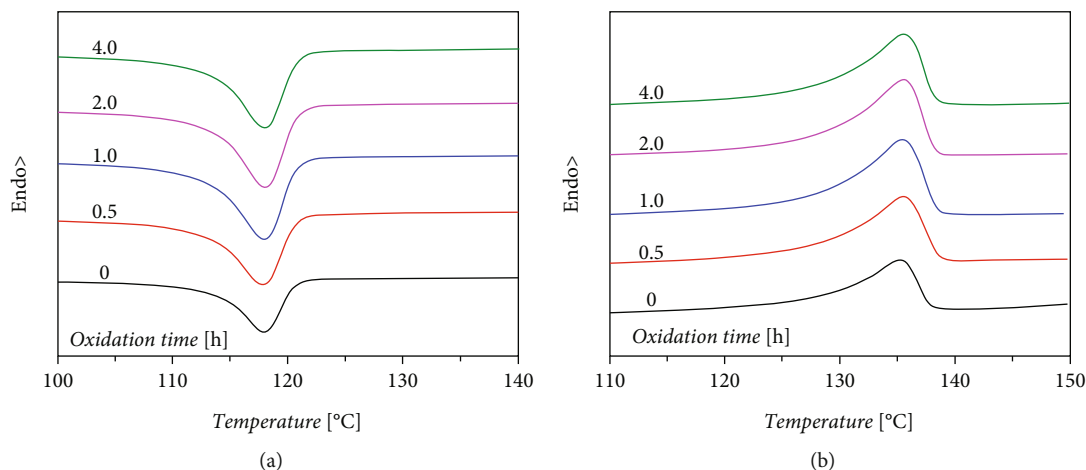


FIGURE 4: The DSC curves of unoxidized and oxidized UHMWPE.

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 ($M_w 3.3 \times 10^6$) was purchased from Mitsui Chemicals, Japan. Graphite powder (GP) with particle size of about $2.6 \mu\text{m}$ was obtained from Aladdin, Shanghai. Graphene nanoplatelets (GNP) with diameter of about $25 \mu\text{m}$ were used from Strem Chemicals, America. Graphene oxide (GO) with diameter of about $10\text{-}50 \mu\text{m}$ 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. And 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 oven at $80^\circ\text{C}/-2.0 \text{MPa}$ 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) ($\text{K}_2\text{Cr}_2\text{O}_7$), sulfuric acid (H_2SO_4), 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 oxidization, 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/Bruker, 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 $10^\circ\text{C}/\text{min}$ and kept this temperature for 3 min to eliminate the thermal history of sample. After that, the sample was cooled at the rate of $10^\circ\text{C}/\text{min}$ from 180°C to 60°C . At last, the sample was reheated up to 180°C at the rate of $10^\circ\text{C}/\text{min}$. The crystallinity of sample (X_{DSC}) is calculated by

$$X_{\text{DSC}}\% = \frac{\Delta H_m}{\Delta H_m^0 \bullet w} \times 100\%, \quad (1)$$

where ΔH_m is the measured melting enthalpy of sample, H_m^0 is the melting enthalpy of 100% crystalline UHMWPE ($291 \text{J} \bullet \text{g}^{-1}$), and w 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 $10^\circ\text{C}/\text{min}$ and kept this temperature for 3 min and then cooled to room temperature at the rate of $10^\circ\text{C}/\text{min}$ in DSC. The treated samples were scanned from 5° to 40° (2θ) at the rate of $10^\circ/\text{min}$ by

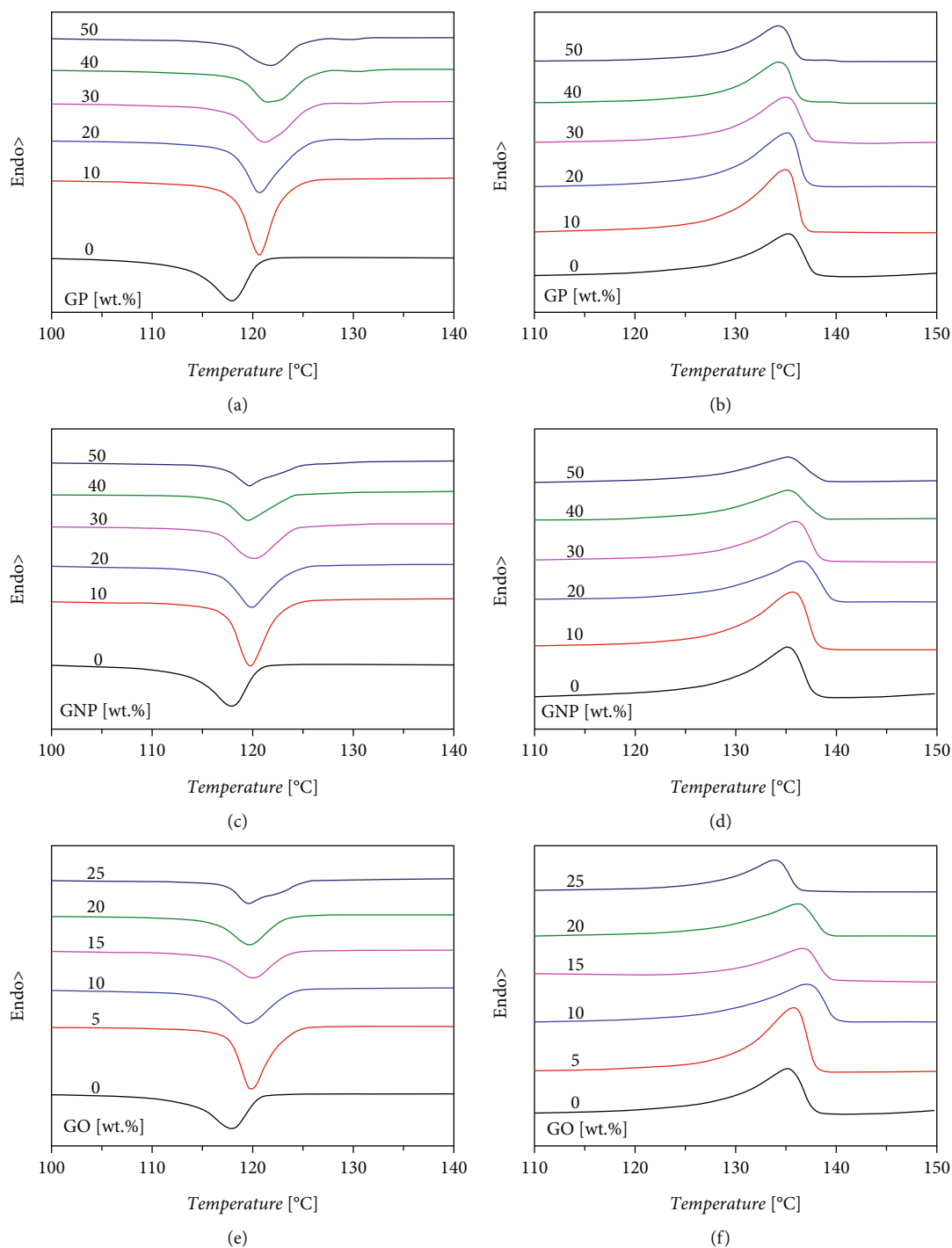


FIGURE 5: The DSC curves of (a and b) GP/UHMWPE, (c and d) GNP/UHMWPE, and (e and f) GO/UHMWPE composites.

D-MAX 2200 VPC (Rigaku, Japan) using Cu-K α ($\lambda = 0.154$ 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 K α 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

TABLE 2: The DSC data of UHMWPE composites.

	wt%	T_m (°C)	ΔH_m (J·g ⁻¹)	X_{DSC} (%)	T_c (°C)	ΔH_c (J·g ⁻¹)	ΔT (°C)
GP	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
	30	133.9	192.0	66.0	121.2	181.4	12.7
	40	133.9	187.2	64.3	121.5	175.2	12.4
	50	134.2	186.0	63.9	121.8	176.6	12.4
GNP	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
	30	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
GO	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
	15	136.7	150.3	51.6	120.0	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

Figure 2 that the peaks of C^{1s} and O^{1s} in the X-ray photoelectron spectrum of unoxidized and oxidized UHMWPE appear at 285 eV and 532 eV, respectively. The content of C^{1s} and O^{1s} on the surface of UHMWPE can be calculated by integrating the peak area of C^{1s} and O^{1s} peaks, and the content ratio of O^{1s}/C^{1s} on the surface of UHMWPE is obtained, listed in Table 1. It can be observed that the oxygen content increased and the carbon content decreased with increasing of oxidation time. At the oxidation time of 4 h, the O^{1s}/C^{1s} ratio of unoxidized and oxidized UHMWPE was 0.048 and 0.184, respectively. It is indicated that the oxidation of UHMWPE significantly increased the oxygen content and the O^{1s}/C^{1s} ratio on the surface of UHMWPE.

The FTIR spectrum of unoxidized and oxidized UHMWPE also proved the presence of oxygen element on the surface of UHMWPE. It can be seen from Figure 3 that unoxidized and oxidized UHMWPE have typical absorption peaks of carbon oxygen groups. The absorption peak intensity at 1110 cm⁻¹ of oxidized UHMWPE is higher than that of unoxidized UHMWPE. The intensity ratio of absorption peak at 1110 cm⁻¹ to the characteristic peak of UHMWPE at 1469 cm⁻¹ is 0.16 for oxidized UHMWPE and 0.09 for unoxidized UHMWPE. It is also shown that the content of carbon oxygen groups of oxidized UHMWPE is higher than that of unoxidized UHMWPE. In accordance with ISO 5834-4:2005, the oxidation index of oxidized UHMWPE is 0.558 and the oxidation index of unoxidized UHMWPE is 0.176, calculated by division of the area A_{ox}/A_{nom} , (A_{ox} represents the total area of the peak absorptions between 1650 and 1850 cm⁻¹ and A_{nom} represents the area of reference peak for polyethylene between 1330 and 1396 cm⁻¹.)

Both XPS and FTIR results indicated that the oxygen content on the surface of UHMWPE is increased after oxidation.

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 (ΔT) 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 are 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 composite 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

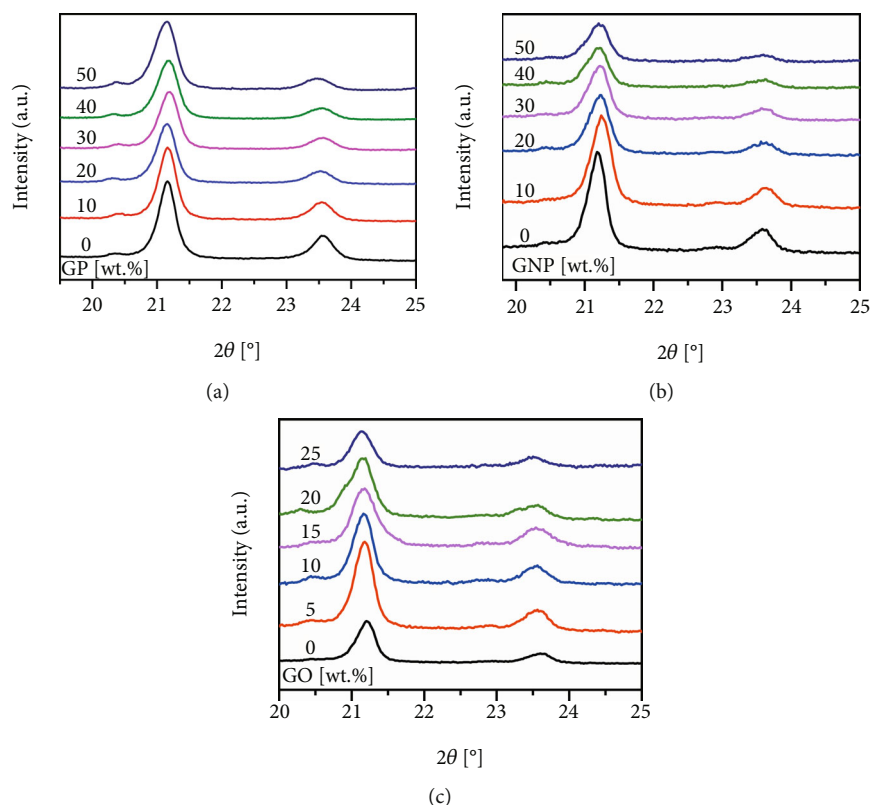


FIGURE 6: The XRD curves of (a) GP/UHMWPE, (b) GNP/UHMWPE, and (c) GO/UHMWPE composites.

137.1°C at the filler content of 10 wt%, respectively. The addition of 10 wt% GO increases the X_{DSC} of UHMWPE from 43.1% to 55.1%. However, the X_{DSC} is gradually decreased with increasing of GO content, but always higher than that of pure UHMWPE. By comparing the X_{DSC} data listed in Table 2, it can be seen that the X_{DSC} of UHMWPE composites from high to low is GP/UHMWPE > GO/UHMWPE > 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 crystallized 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

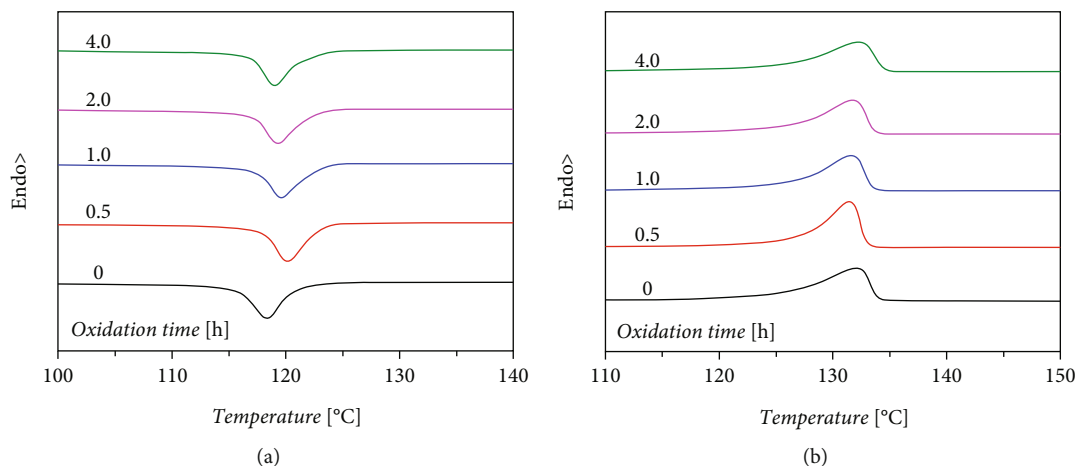


FIGURE 7: The DSC curves of GNP/oxidized UHMWPE composites.

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

Oxidation time (h)	T_m (°C)	ΔH_m (J·g ⁻¹)	X_{DSC} (%)	T_c (°C)	ΔH_c (J·g ⁻¹)	ΔT (°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

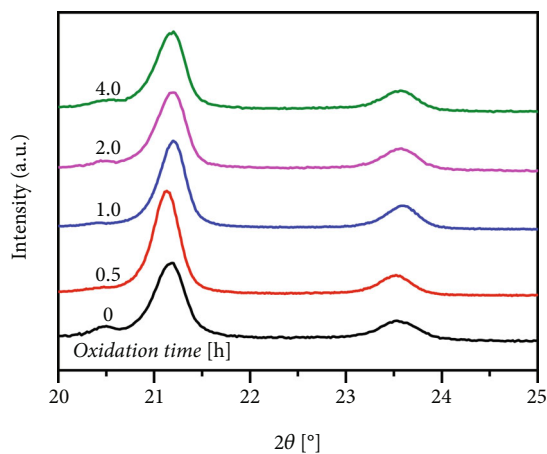


FIGURE 8: The XRD curves of GNP/oxidized UHMWPE composite.

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

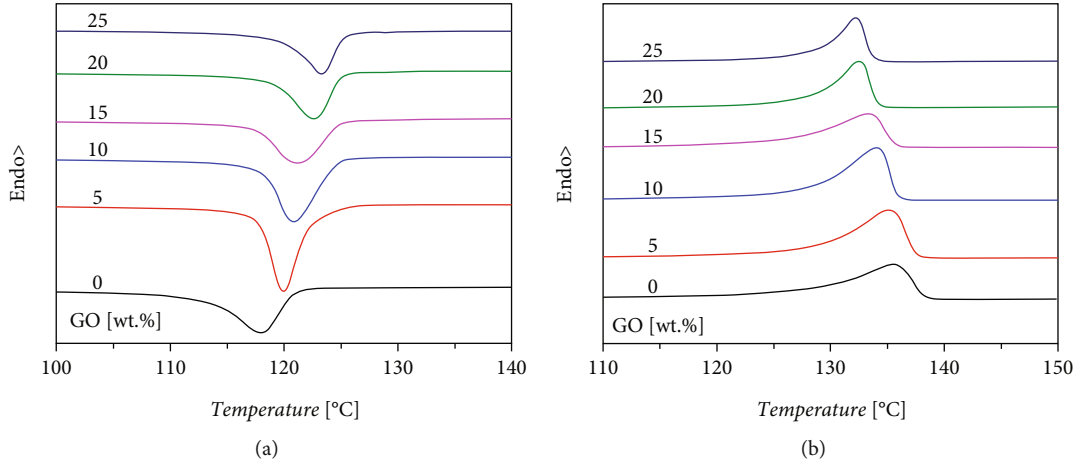


FIGURE 9: The DSC curves of GO/oxidized UHMWPE composites.

TABLE 4: The DSC data of oxidized UHMWPE composites.

GO (wt%)	T_m (°C)	ΔH_m (J·g ⁻¹)	X_{DSC} (%)	T_c (°C)	ΔH_c (J·g ⁻¹)	ΔT (°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

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.

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/UHMWPE composite 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 UHMWPE 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 crystal type of UHMWPE.

Nomenclature

- ΔH_c : Crystallization enthalpy ($^{\circ}\text{C}$)
 ΔH_m : Melting enthalpy ($^{\circ}\text{C}$)
 T_{cl} : Crystallization temperature ($^{\circ}\text{C}$)
 T_m : Peak melting temperature ($^{\circ}\text{C}$)
 ΔT : Crystallization undercooling ($^{\circ}\text{C}$)
 X_{DSC} : 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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