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Evaluation of internal morphology and engineering properties of graphite-filled UHMWPE nanocomposites produced using a novel octa-screw kneading extruder

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Abstract: Ultra-high molecular weight polyethylene (UHMWPE) is a very attractive polymer employed as a high performance material, while filler-reinforced composites have demonstrated its feasibility in various applications. Melt-mixing in an extruder is a key process in the development of polymer nanocomposites. Due to its high melt viscosity, dispersion of fillers is considered as a challenge in UHMWPE nanocomposites preparation process. In this work, we have prepared graphite-filled UHMWPE nanocomposites using a novel octa-screw melt kneading extruder. The engineering properties as well as the morphology of kneaded nanocomposites were characterized using tensile tester, friction and wear tester, scanning electron microscopy, optical profilometer, polarized optical microscope, thermogravimetric analysis, differential scanning calorimetry, etc. The experimental results suggested good dispersion of graphite in the UHMWPE nanocomposites, demonstrating the excellent capability of the octa-screw extruder in compounding the graphite-filled nanocomposites. The yield strengths of the nanocomposites increase by 10% (from 21.6 MPa to 23.8 MPa) with the addition of 2% graphite. When the filler percentage was increased to 20%, the yield strengths improved from 21.6 to 27.4 MPa (an increase of 26.8%) for the graphite-filled composites. Furthermore, the crystallinity of UHMWPE nanocomposites increased with the content of graphite fillers, while the pyrolysis temperature of the composites increased with the content of graphite fillers.

Keywords: composites; graphite; octa-screw extruder; UHMWPE.

1 Introduction

Ultra-high molecular weight polyethylene (UHMWPE) [1] is one of the thermoplastic materials that have attracted the attention of many researchers and has been of great use, especially in artificial bodies, mainly due to its high strength and stiffness, good fatigue resistance, and appropriate wear characteristics. The material also finds itself useful in many other applications including microelectronics, engineering, chemistry and the food industry. Highly cross-linked polyethylene is the material of choice in contemporary use especially for hip arthroplasty. Gamma radiation and electron beam radiation are commonly used to crosslink UHMWPE, and particular treatments need to be performed to avoid material oxidation [2, 3]. Despite these advantages, the material property of UHMWPE still needs to be improved [4]. In order to address this issue, the development of novel materials with improved property, able to extend the life of the implant, has generated great interest. Reinforcing materials-filled UHMWPE composites have been developed as an alternative to the current highly crosslinked UHMWPE produced by high-energy radiation and thermal or antioxidant stabilization. The combination of extraordinary physical properties and the ability to be dispersed in various polymer matrices has resulted in a new class of polymer composites. In particular, the addition of carbon nanostructure to improve the final performance of materials has been a topic of interest over the last few years not only in the orthopedic field but also in other industries, such as the automotive and aerospace industries [5, 6].

Many researchers have dedicated their efforts to the improvement of the UHMWPE properties through the use of nanofiller materials such as carbon nanofibers [7], carbon nanotubes (CNT) [8–10] and graphene fillers [11–16], or via the graphene surface coatings [17–19]. The high aspect dimensional ratio, compared to other nanoparticles, and their carbonaceous nature provide them with exceptional properties. These nanomaterials have demonstrated the ability to improve the wear characteristics and oxidative resistance of UHMWPE without compromising its biocompatibility. Despite the superior performance of CNT and graphene-filled nanocomposites,

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the high cost of these fillers has confounded the overall success of the composites.

In this work, we developed graphite-filled UHMWPE composites [20, 21] and evaluated their engineering properties and internal morphology. A novel octa-screw melt kneading extruder was employed to prepare the nanocomposites. The extruder can provide an enhanced mixing of fillers in the composites, mainly resulting from its advantages including reduction of heat generated from the material in the processing section and improvement in dispersion owing to high-speed screw rotation. Nanocomposite specimens were characterized using tensile tester, friction and wear tester, scanning electron microscopy (SEM), optical profilometer, polarized optical microscope, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), etc. In addition, the internal morphology of the nanocomposites was also inspected.

2 Materials and methods

2.1 Materials

The polymeric material used in this study was UHMWPE (630M, Mitsui Chemicals, Inc., Japan) with a molecular weight of 3.4×10^6 Da. The graphite utilized included Model CGB-20 powders (Gr①), Model UP-5N powders (Gr②) and Model UP-20 spherical powder (Gr③), all purchased from Nippon Graphite Industries, Japan. Figure 1 shows the images of these graphites, observed under a JSM-6510 scanning electron microscope (JEOL Ltd., Japan). The microscopic results suggested that Gr① graphite shows an ellipsoid shape and has a particle size of approximately 10 μm . Gr② graphite displays a tiny laminate shape and possesses a size of 5 μm , while graphite in Gr③ exhibits laminate geometry and has a size of about 20 μm .

2.2 Preparation of graphite-filled nanocomposites

While a twin-screw extruder has considerable performance compared with a single-screw extruder, certain limits are still associated with the twin-screw extruder when additional performance is needed. In this current study, we employed a novel intermeshing co-rotating parallel octa-screw kneading extruder (WDR 150T-45MG-NH, Technovel Co., Ltd., Japan) to prepare the graphite-filled

nanocomposites. Figure 2 shows photographically the extruder used to compound the nanocomposites. The seven temperature settings, including six on the extruder and one at the die, were all maintained at 240°C. The kneading time and the screw rotational speed were 150 s and 400 rpm, respectively. The extrusion rate is 1.70 kg/h.

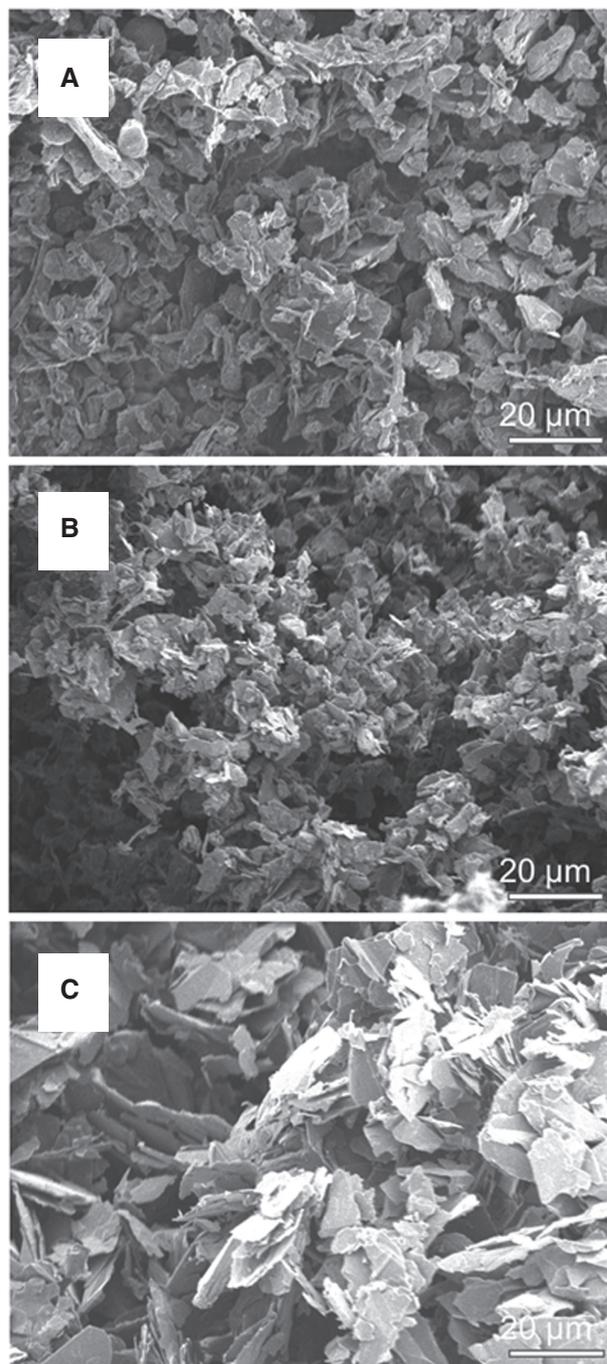


Figure 1: SEM photos of filling graphite. (A) Model CGB-20 powders in Gr①, (B) model UP-5N powders in Gr②, and (C) model UP-20 spherical powder in Gr③.

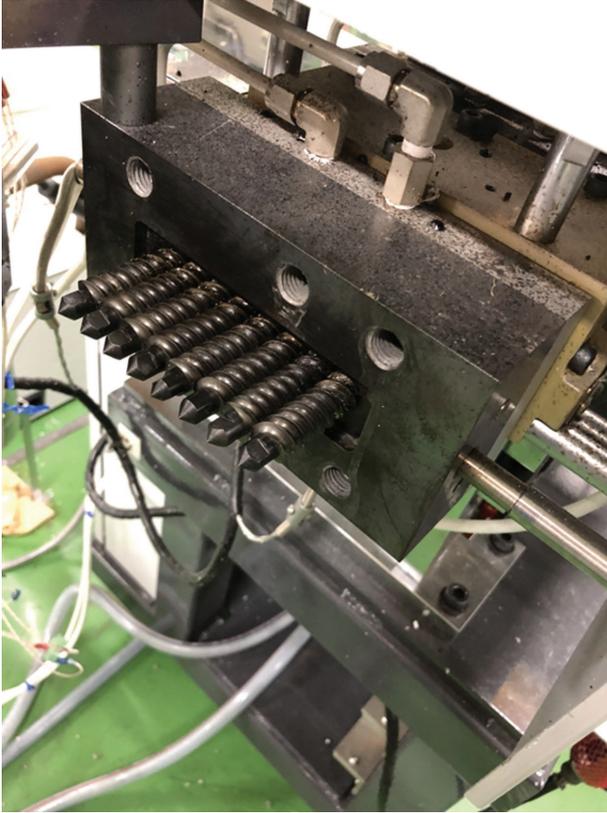


Figure 2: Photograph of the octa-screw extruder.

2.3 Characterization of composite specimens

2.3.1 Tensile test

Tensile tests were completed on a Stograph VGS1E (Toyo Seiki Seisaku-sho, Ltd., Japan) tensiometer equipped with a 50 N load cell, in a manner consistent with the ASTM D638 standard. To prepare the test specimens, graphite-filled nanocomposites were first compressed molded into a thin sheet with a thickness of 0.35 mm using a vacuum hot press (Imoto machinery Co., Ltd., Japan) at a temperature of 300°C and a pressure of 40 MPa. A dumbbell-shaped tensile bar was then cut from the molded sheet and held between two clamps that were separated by 2 cm. During measurement, the test bar was pulled by the top clamp at a rate of 50 mm/min. The force and elongation before the bar was broken were recorded.

2.3.2 Friction and wear test

The specimen for the test was prepared using a hand-extrusion type injection molding machine (Hand Truder

M-1, Toyo Seiki Seisaku-sho Ltd., Japan), and has a dimension of 1 cm by 1 cm and a thickness of 1 mm. Friction and wear test was conducted on a Frictoron EFM-III-F tester (Orientec Corporation, Japan). The surface contact pressure was 16 MPa, and the rotational speed was 30 rpm. The test time was 10 min.

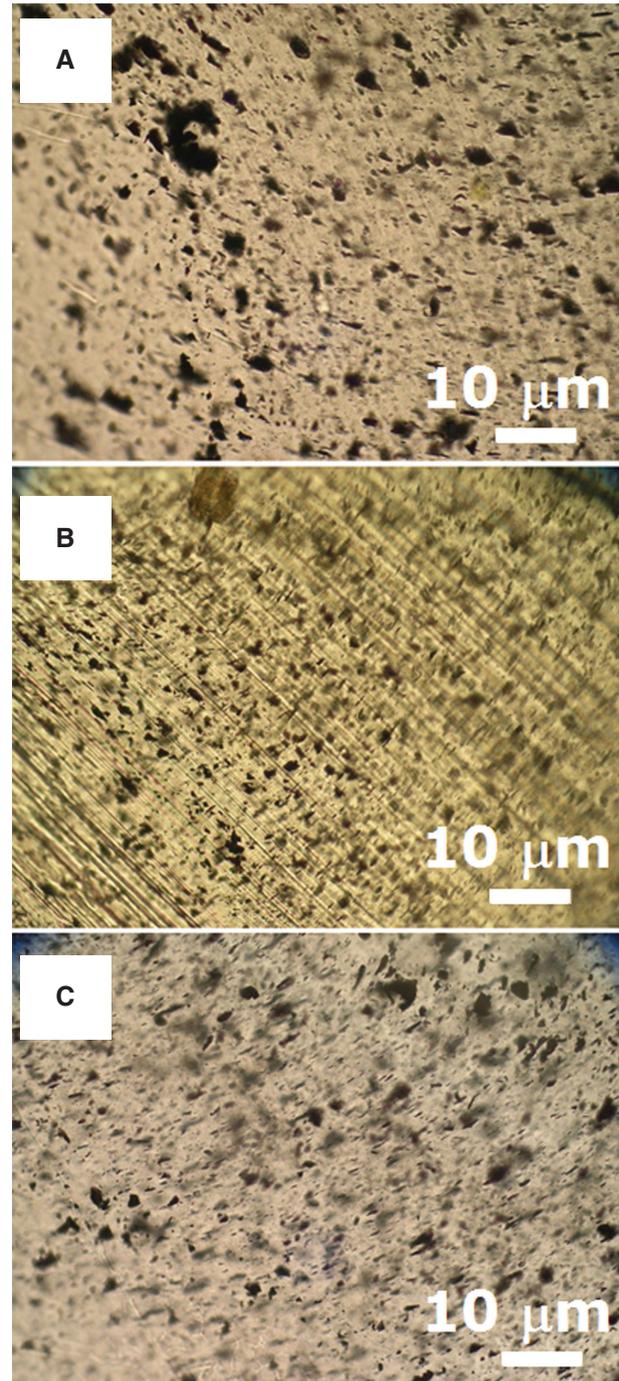


Figure 3: Dispersion of graphite in UHMWPE nanocomposites observed under the polarized optical microscope. (A) CGB-20, (B) UP-5N, and (C) UP-20.

2.3.3 TGA

TGA analysis was carried out on a thermogravimetric analyzer (TA Instruments QA-50, USA). The temperature of the furnace was programmed to rise at constant heating rate of 5°C/min from 40 to 600°C. The tests were performed under an air flow of 60 ml/min. The amount of nanocomposite material used for the tests was weighed with a balance of ± 0.1 mg of accuracy and was ranging 9–11 mg.

2.3.4 SEM

The specimens were prepared by cryostat sectioning, and the internal morphology was observed at low vacuum condition under a scanning electron microscope (JSM-6510, JEOL Ltd., Japan) after Pd-Pt vapor deposition.

2.3.5 Optical profilometer

The surface profile of graphite-filled nanocomposites was observed using an optical profilometer (Zygo 3D Optical Surface Profilers, Japan). Specimens were examined before and after the wear test.

2.3.6 Polarized optical microscopy

The cross sections of virgin UHMWPE and graphite-filled UHMWPE nanocomposites were observed under a polarized optical microscope (OLYMPUS BX51, Japan). Specimens for observation were prepared by cryostat sectioning.

2.3.7 DSC

A TA-Q200C differential scanning calorimeter was used to characterize the thermal properties of the nanocomposites. The range of temperature for analysis was 30–400°C, and the heating rate was 3°C/min.

3 Results and discussion

3.1 Internal morphology

An important property of composites is the possibility of purposely planned structure to obtain desired

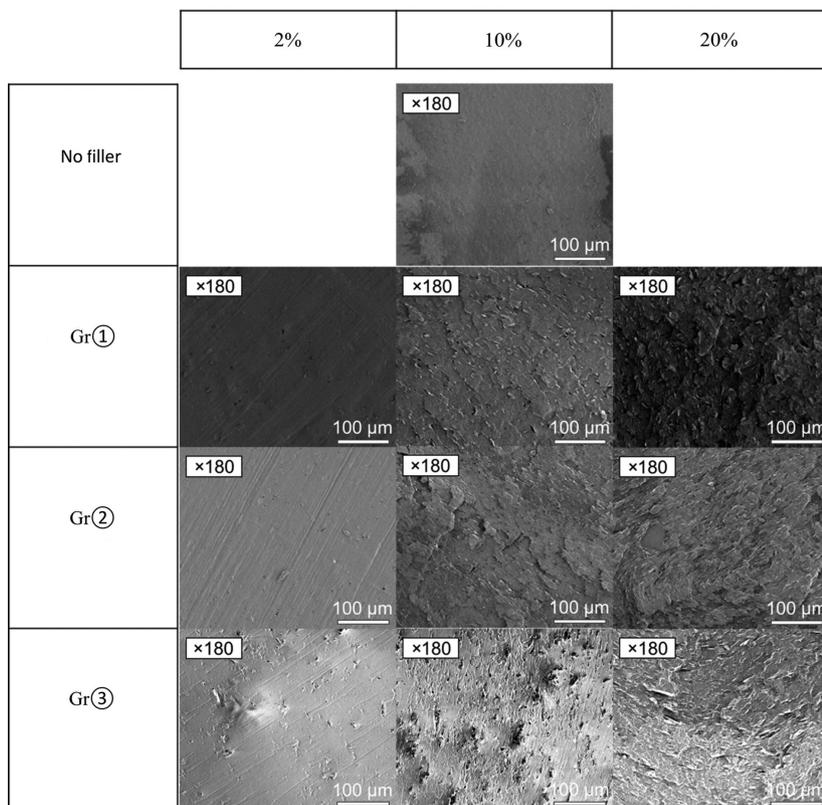


Figure 4: Cross-sectional morphology of virgin UHMWPE and graphite-filled nanocomposites.

characteristics. Good filler dispersion in a polymer matrix is crucial for achieving the desired performance. The cross sections of the graphite-filled composites were observed under a polarized optical microscope. The images in Figure 3 showed good dispersion of graphite in the UHMWPE nanocomposites, demonstrating the excellent capability of the octa-screw extruder in compounding the graphite-filled composites.

SEM was also employed to characterize the cross-sectional morphology of the materials. The images in Figure 4 suggest that the pure UHMWPE exhibited a smooth cross-sectional surface. At 2% graphite filling, both Gr①- and Gr②-filled nanocomposites displayed relative smooth cross-sectional surface, while Gr③-filled composites showed rough and some irregular surface. As the percentage of graphite was increased to 10%, all composites displayed rough cross-sectional surfaces. Gr③-filled composites demonstrated the roughest surface, followed by those filled by Gr② and Gr①. At 20% graphite filling, all composited material showed even rougher cross-sectional surfaces. Due to the laminate geometry of Gr② and Gr③, delamination could be found in the nanocomposites filled by these graphites. Again, laminate graphite (Gr②- and Gr③)-filled composites exhibited rougher surface than ellipsoid graphite (Gr①).

3.2 Engineering properties

The tensile properties of graphite-filled nanocomposites were measured. The experimental results in Figure 5 suggested that the yield strengths of the nanocomposites increase by 10% (from 21.6 MPa to 23.8 MPa in Table 1) with the addition of 2% Gr① graphite. The geometries of the graphite fillers demonstrated their influence on the tensile properties of UHMWPE nanocomposites. Ellipsoid-shaped Gr① (CGB group)-filled composites showed a greater yield strength than the tiny laminate-shaped Gr② graphite, while the big laminate-shaped graphite Gr③ exhibited the lowest strength. The yield strengths of the filled composites increased with the content of the graphite, while the elongation at break decreased with the addition of the graphite fillers. When the filler percentage was increased to 20%, the yield strengths improved from 21.6 to 27.4 MPa (an increase of 26.8%) for the Gr① graphite-filled nanocomposites. However, the elongation at break at 20% graphite filling is quite limited.

Figure 6 shows the wear depth versus friction coefficient of the nanocomposites. The results of the wear test showed that the friction coefficient and wear depth of UHMWPE nanocomposites increase as the

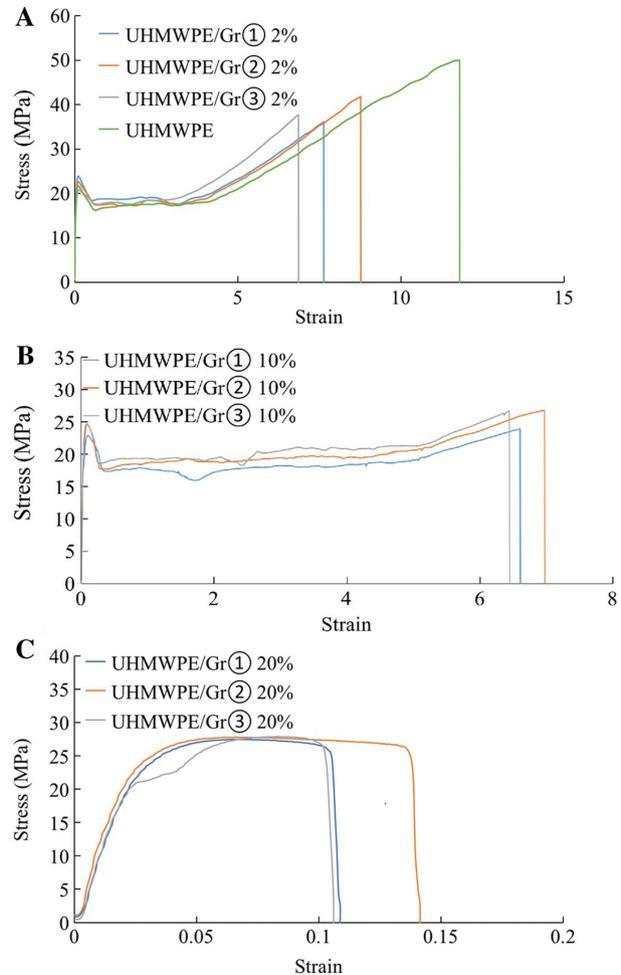


Figure 5: Tensile properties of (A) 2%, (B) 10%, and (C) 20% graphite-filled UHMWPE.

Table 1: Yield strengths of graphite-filled composites.

Graphite (%)	2% (MPa)	10% (MPa)	20% (MPa)
Gr①	23.8	22.6	27.4
Gr②	22.6	24.7	27
Gr③	21.8	24.5	27.6

graphite content increases. At 2% concentrations, all filled UHMWPE nanocomposites showed comparable wears to virgin UHMWPE. The wear resistance decreased as the filler percentage was increased, mainly due to a rougher surface caused by the fillers (see Figure 4). The wear increased significantly as the filler concentrations exceeded 10%. As the fillers are increased, the fillers may not be completely encapsulated by the matrix. Delamination may thus increase and in turn lead to higher wear of the composites. Gr②- and Gr③-filled composites exhibited a little higher wear than the Gr①-filled composites. At 20% filling percentage, composites

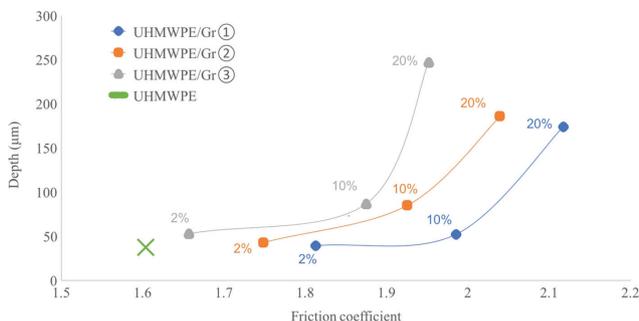


Figure 6: Wear depths of graphite-filled nanocomposites.

filled with Gr③ demonstrated a greater wear than the other groups, mainly due to the fact that Gr③-filled composites showed rough and some irregular surface. UHMWPE/Gr① exhibited the best wear resistance properties and highest friction coefficient, while UHMWPE/Gr③ showed the opposite. Ellipsoid graphite-filled composites showed higher wear resistance than laminate graphite-filled composites. This might be due to the fact that compared to ellipsoid graphite, the laminate graphite may not be completely encapsulated by the surrounding matrix and is easier to be released from the matrix. The released graphite particulates from the UHMWPE nanocomposites may act as wear aid and accelerate the wearing of the composites. In addition, laminate fillers of greater size led to lower friction coefficient. The 20 µm sized laminate graphite may be easier to be broken and released than 5 µm sized graphite from the matrix. UHMWPE/Gr③ nanocomposites thus exhibited smaller wear resistance than the UHMWPE/Gr② composites. The experimental results also suggest that there exists a critical filler percentage, which is approximately 10% for the nanocomposites developed in this study, after which the wear increases significantly.

Figure 7 shows the DSC measurement results. The crystallinity of UHMWPE nanocomposites increased with the content of graphite fillers. As expected, the crystallinity decreased with the content of the filling graphite. In addition, Gr③-filled UHMWPE nanocomposites showed the highest crystallinity, while Gr①-filled composites exhibited the lowest crystallinity. Due to the nucleating effect of the graphite fillers, the polymeric materials crystallized at a higher speed and thus resulted in a higher crystallinity of the composites.

Finally, the thermal gravimetric properties of graphite-filled UHMWPE nanocomposites were characterized. Figure 8 shows the pyrolysis temperatures of the graphite-filled nanocomposites. Obviously, the pyrolysis temperature of the materials increased with the addition of graphite

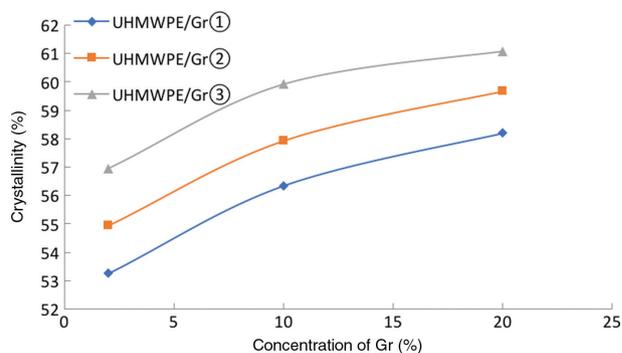


Figure 7: Crystallinity of UHMWPE with different concentrations of filled graphite.

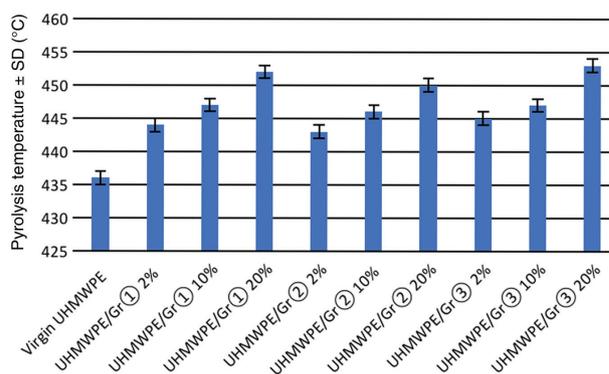


Figure 8: Pyrolysis temperature of graphite-filled nanocomposites.

Table 2: Graphite contents of graphite-filled nanocomposites.

Samples	Actual graphite (%)
Virgin UHMWPE	0
UHMWPE/Gr① 2%	1.952
UHMWPE/Gr① 10%	8.945
UHMWPE/Gr① 20%	16.76
UHMWPE/Gr② 2%	1.927
UHMWPE/Gr② 10%	9.007
UHMWPE/Gr② 20%	16.163
UHMWPE/Gr③ 2%	1.958
UHMWPE/Gr③ 10%	9.059
UHMWPE/Gr③ 20%	16.636

fillers. The temperatures also increased with the content of graphite (listed in Table 2) in the nanocomposites. This can be explained by the fact that graphite can act as barriers for heat transfer during the pyrolysis process. Pyrolysis temperatures thus increased with the addition of graphite fillers. In addition, the increased degradation temperature is also possibly a consequence of the superior thermal stability of the dispersed graphite, which also acted as barrier to mass transfer during thermal scanning [22].

4 Conclusions

The following conclusions can be drawn based on the experimental results:

1. The SEM photos showed good dispersion of graphite in the UHMWPE composites, demonstrating the excellent capability of the octa-screw extruder in compounding the graphite-filled composites.
2. The yield strengths of the composites increased by 10% (from 21.6 MPa to 23.8 MPa) with the addition of 2% Gr^① graphite. When the filler percentage was increased to 20%, the yield strengths improved from 21.6 to 27.4 MPa (an increase of 26.8%) for the Gr^① graphite-filled composites.
3. The crystallinity of UHMWPE composites increased with the content of graphite fillers. Gr^③-filled UHMWPE composites showed the highest crystallinity, while Gr^①-filled composites exhibited the lowest crystallinity.
4. Pyrolysis temperature of the composites increased with the content of graphite fillers.
5. Gr^③-filled composites demonstrated the most rough surface, followed by those filled by Gr^② and Gr^①. This matches well with the experimental results of wear resistance test, namely, that Gr^③-filled composites possessed the highest wear, followed by those of Gr^② and Gr^①.

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References

- [1] Bracco P, Bellare A, Bistolfi A, Affatato S. *Materials* 2017, 10, 791–722.
- [2] Tripathi SN, Srinivasa Rao GS, Mathur AB, Jasra R. *RSC Adv.* 2017, 7, 23615–23632.
- [3] Huang G, Ni Z, Chen G, Zhao Y. *Int. J. Polym. Sci.* 2016, 2016, 1–9.
- [4] Xiong L, Xiong D, Jin J. *J. Bionic Eng.* 2009, 6, 7–13.
- [5] Peng Y, Wang Z, Zou K. *Langmuir* 2015, 31, 7782–7791.
- [6] Aly AA, Zeidan EB, Alshennawy AA, El-Masry AA, Wasel WA. *World J. Nano Sci. Eng.* 2012, 2, 32–39.
- [7] Wood WJ, Maguire RG, Zhong WH. *Compos. Part B-Eng.* 2011, 42, 584–591.
- [8] Gupta A, Triphahi G, Lahiri D, Balani K. *J. Mater. Sci. Technol.* 2013, 29, 514–522.
- [9] Puertolas JA, Kurtz SM. *J. Mech. Behav. Biomed. Mater.* 2014, 39, 129–145.
- [10] Visco A, Yousef S, Galtieri G, Nocita D, Pistone A, Njuguna J. *JOM* 2016, 68, 1078–1089.
- [11] Bahrami SAH, Ramazani A, Shafiee M, Kheradmand A. *Polym. Adv. Technol.* 2016, 27, 1172–1178.
- [12] Kheradmand A, Bahrami SAH, Khorasheh F, Baghalha M, Bahrami H. *Polym. Adv. Technol.* 2015, 26, 315–321.
- [13] Xu L, Zheng Y, Yan Z, Zhang W, Shi J, Zhou F, Zhang X, Wang J, Zhang J, Liu B. *Appl. Surf. Sci.* 2016, 370, 201–208.
- [14] Choi B, Lee J, Lee S, Ko J-H, Lee K-S, Oh J, Han J, Kim Y-H, Choi IS, Park S. *Macromol. Rapid Commun.* 2013, 34, 533–538.
- [15] Bhattacharyya A, Chen S, Zhu M. *Express Polym. Lett.* 2014, 8, 74–84.
- [16] Suner S, Joffe R, Emami N. *Compos. Part B-Eng.* 2015, 78, 185–191.
- [17] Shen B, Chen S, Chen Y, Sun F. *Surf. Coat. Tech.* 2017, 311, 35–45.
- [18] Chen S, Shen B, Chen Y, Sun F. *Diam. Relat. Mater.* 2017, 73, 25–32.
- [19] Chen S, Shen B, Sun F. *Diam. Relat. Mater.* 2017, 76, 50–57.
- [20] Liu T, Li B, Lively B, Eyster A, Zhong WH. *Wear* 2014, 309, 43–51.
- [21] Gu J, Li N, Tian L, Lv Z, Zhang Q. *RSC Adv.* 2015, 5, 36334–36339.
- [22] Chiu FC, Chen YJ. *Compos. Part A-Appl. S.* 2015, 68, 62–71.