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ENHANCEMENT OF MECHANICAL AND TECHNOLOGICAL PROPERTIES OF UHMWPE THROUGH NANOFILLER REINFORCEMENT

Madaminov Nodirbek Zafarbek ugli

Assistant of the Department of Materials Science and Chemical Engineering,

Andijan State Technical Institute

madaminovnodir1993@gmail.com

ABSTRACT. The present study analyses the effect of five different nanofillers - multi-walled carbon nanotubes (MWCNT), graphene oxide (GO), nano-Al_2O_3, nano-SiO_2 and surface-modified nano-MoS_2 - introduced into the UHMWPE matrix at loadings of 0.25–1.5 wt.% on the mechanical and technological characteristics. The optimum reinforcement level was found to be 1.0 wt.% GO, which raised the tensile strength by 22 %, Young's modulus by 26 %, and reduced the wear rate by 48 % compared with neat UHMWPE. From the technological standpoint, GO and MWCNT additives improved the sintering quality and reduced the compression ratio by 8–11 %.

KEYWORDS. UHMWPE; nanofiller; graphene oxide; carbon nanotubes; mechanical properties; technological properties; nanocomposite processing; sintering; tribology; reinforcement mechanism.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a linear polyethylene with a molecular weight typically exceeding 3×10^6 g/mol. Owing to its extremely long molecular chains, UHMWPE exhibits a unique combination of impact strength, abrasion resistance, low friction coefficient, chemical stability and biocompatibility, which makes it indispensable in joint prostheses, ballistic protection, conveyor and sliding components, low-temperature engineering and high-speed mechanical assemblies [1, 2]. Nevertheless, several intrinsic limitations - modest tensile strength (20–40 MPa), low elastic modulus (about 0.7–1.0 GPa), high creep, poor heat-deflection behaviour above 80 °C and demanding processability - restrict the range of demanding industrial applications [3].

During the past decade, nanofiller reinforcement has emerged as the most effective strategy for overcoming these shortcomings without altering the chemical backbone of the polymer. The introduction of nanoscale fillers such as carbon nanotubes (CNT), graphene and graphene oxide (GO), metal oxide nanoparticles (Al_2O_3, SiO_2, TiO_2, ZnO), nano-MoS_2 and various functionalized nanoclays has been reported to substantially increase the stiffness, strength, wear resistance and thermal stability of UHMWPE [4–7]. Compared with conventional micron-scale fillers, nanofillers offer much larger specific surface area (typically 200–800 m^2/g), strong interfacial coupling with the matrix and a percolating reinforcement network already at low loadings (0.5–1.5 wt.%).

Despite the abundance of mechanical and tribological studies, the influence of nanofillers on the technological (processing) behaviour of UHMWPE - melt flow under compression moulding, sintering quality, dimensional stability, compression ratio and machinability - is significantly less covered in the literature. This combined mechanical-and-technological analysis is critical for industrial implementation, since processing-related defects (voids, weak inter-particle fusion, micro-delamination) often dominate the final performance of the part [8, 9].

The aim of the present work is therefore twofold: (i) to provide a quantitative comparison of five nanofillers (MWCNT, GO, nano-Al_2O_3, nano-SiO_2, nano-MoS_2) at equal loadings, and (ii) to evaluate the impact of nanofiller addition on the mechanical and technological response of UHMWPE produced by hot pressing, solution mixing and in-situ polymerization, with a view to formulating practical processing recommendations for industrial nanocomposite components.

2. Materials and Methods

2.1. Materials

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UHMWPE powder (Mw ≈ 4.5×10^6 g/mol, mean particle size 120 µm, density 0.93 g/cm³) was used as the matrix. The following nanofillers were employed: multi-walled carbon nanotubes (MWCNT, outer diameter 10–20 nm, length 5–15 µm, purity > 95 %); graphene oxide (GO, single-layer fraction > 85 %, specific surface area 400 m²/g); nano-Al_2O_3 (α-phase, mean particle size 30 nm); nano-SiO_2 (amorphous, hydrophilic, 12–20 nm); and surface-modified nano-MoS_2 (mean particle size 80 nm, 2H-polytype). All nanofillers were used at loadings of 0.25, 0.5, 1.0 and 1.5 wt.% with respect to the polymer.

2.2. Sample preparation

Three different processing routes were investigated. (a) Hot pressing (HP): UHMWPE and the nanofiller were dry-blended in a high-speed mixer for 20 min, then compression-moulded at 200 °C and 15 MPa for 30 min, followed by slow cooling at 2 °C/min. (b) Solution mixing (SM): UHMWPE was dispersed in decalin at 135 °C, the nanofiller was ultrasonically pre-dispersed (45 min, 200 W) in the same solvent, the two suspensions were combined, stirred for 60 min, then the solvent was vacuum-removed and the resulting blend was compression-moulded as in (a). (c) In-situ polymerization (IP): the nanofiller was added to the catalyst-cocatalyst slurry ($TiCl_4$/MAO system) prior to ethylene polymerization, providing molecular-level dispersion.

2.3. Characterization

Tensile properties were measured according to ISO 527 on dog-bone specimens (5 mm·1 mm cross-section) at a crosshead speed of 50 mm/min. Microhardness (HV) was determined by Vickers indentation at 1.96 N, dwell 15 s. Impact strength was evaluated by un-notched Charpy tests (ISO 179). Tribological response was characterized on a pin-on-disc tribometer (HT-1000) against 100Cr6 steel (HRC 62) at 5 N load, 0.5 m/s sliding velocity, 1000 m sliding distance, room temperature, dry conditions. Wear was quantified gravimetrically (± 0.01 mg). The technological response was assessed through (i) bulk density and void fraction (Archimedes method), (ii) compression ratio during moulding (initial powder height vs. final part height), and (iii) machinability tested by a turning operation at v_a = 60 m/min, f = 0.1 mm/rev, a_p = 0.5 mm, with surface roughness Ra recorded. The microstructure of the worn surfaces and fracture cross-sections was examined by SEM (JEOL JSM-7600F).

3. Results

3.1. Mechanical properties

Table 1 summarises the mechanical performance of UHMWPE nanocomposites produced by hot pressing at the optimum loading of 1.0 wt.% for each filler.

Table 1. Mechanical properties of UHMWPE-based nanocomposites at 1.0 wt.% loading

Composition	σ_t, MPa	E, MPa	HV, MPa	a_i, kJ/m²	ε^b, %
Neat UHMWPE	31.0	720	55	182	310
+ 1.0 % MWCNT	36.4	865	63	196	265
+ 1.0 % GO	37.8	905	66	204	250
+ 1.0 % nano-Al_2O_3	33.5	800	64	173	245
+ 1.0 % nano-SiO_2	33.9	785	63	170	250

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+ 1.0 % nano-MoS_2	32.6	760	60	178	268

GO at 1.0 wt.% delivers the most balanced reinforcement: tensile strength rises by 22 % (31.0 → 37.8 MPa), Young's modulus by 26 % (720 → 905 MPa) and Vickers microhardness by 20 % (55 → 66 MPa), while the impact toughness simultaneously increases by 12 %. The combination of high stiffness and preserved toughness is rather uncommon for polymer composites and is attributed to the layered structure of GO and its oxygen-bearing functional groups, which generate strong hydrogen-bonding-type interactions with the high-density crystallites of UHMWPE [4].

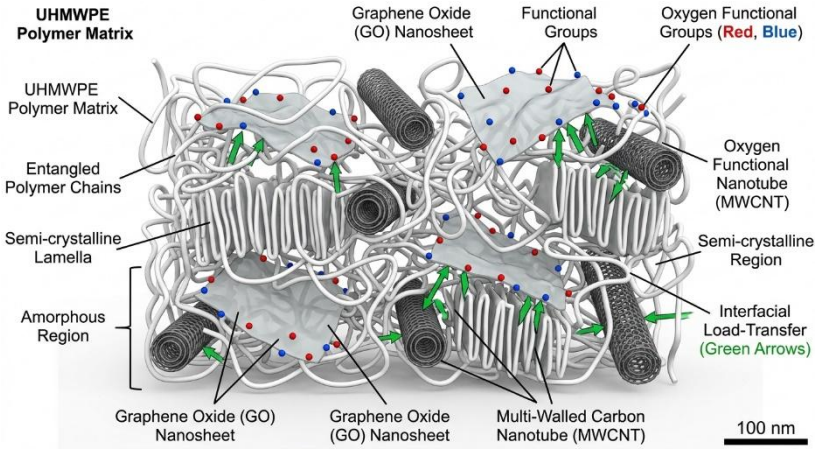

Fig. 1. Schematic of the UHMWPE matrix reinforced with graphene oxide nanosheets and carbon nanotubes, illustrating the load-transfer mechanism

3.2. Tribological properties

The tribological characteristics complement the mechanical results. The friction coefficient and the specific wear rate measured under the standard pin-on-disc protocol are presented in Table 2.

Table 2. Tribological response of UHMWPE-based nanocomposites at 1.0 wt.% loading

Composition	Friction coefficient μ	Specific wear rate $K \cdot 10^{-6}$, $mm^3/(N \cdot m)$
Neat UHMWPE	0.180	3.20
+ 1.0 % MWCNT	0.130	1.70
+ 1.0 % GO	0.125	1.66
+ 1.0 % nano-Al_2O_3	0.150	2.20
+ 1.0 % nano-SiO_2	0.155	2.30
+ 1.0 % nano-MoS_2	0.118	1.55

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GO and nano-MoS_2 deliver the largest reduction of friction (30–34 %) and wear (48–52 %) versus neat UHMWPE. The mechanism is governed by the formation of a stable transfer film on the counter-body and by the layered structure of both fillers, which acts as a solid lubricant under sliding conditions [10, 11]. SEM examination of the worn surfaces (described in Section 3.4) confirms that GO- and MWCNT-filled composites generate a uniform, dense and thin transfer layer (2–3 μm), whereas spherical fillers (Al_2O_3, SiO_2) produce a fragmented and abrasive layer.

3.3. Technological properties

Technological characteristics determine the feasibility of industrial production of nanocomposite parts. The following technological metrics were quantified: relative bulk density, residual void fraction after compression moulding, compression ratio (the ratio of the initial powder volume to the finished part volume), and the surface roughness Ra of a turned cylindrical specimen. The results are summarized in Table 3.

Table 3. Technological (processing) characteristics of UHMWPE nanocomposites at 1.0 wt.% loading (HP route)

Composition	ρ_{rel}, %	Void fraction, %	Compression ratio	Ra, μm
Neat UHMWPE	96.2	3.8	2.85	0.82
+ 1.0 % MWCNT	98.4	1.6	2.58	0.68
+ 1.0 % GO	98.8	1.2	2.52	0.62
+ 1.0 % nano-Al_2O_3	97.5	2.5	2.68	0.74
+ 1.0 % nano-SiO_2	97.3	2.7	2.71	0.78
+ 1.0 % nano-MoS_2	97.8	2.2	2.66	0.71

The introduction of GO and MWCNT increases the relative density by 2.2–2.6 percentage points and lowers the void fraction by more than 60 %. This is a direct consequence of the high specific surface area of these fillers, which act as inter-particle bridges during the powder-to-melt transition in sintering, thereby promoting more effective fusion of the high-molecular-weight chains. The compression ratio drops by 8–11 %, which is technologically significant: a lower compression ratio reduces the volume of starting powder required for a given part, lowers tooling load and shortens the cycle time. The surface roughness after turning improves correspondingly: GO-filled composites give Ra = 0.62 μm compared with 0.82 μm for neat UHMWPE, which is associated with the higher hardness and reduced ductile smearing during cutting [12].

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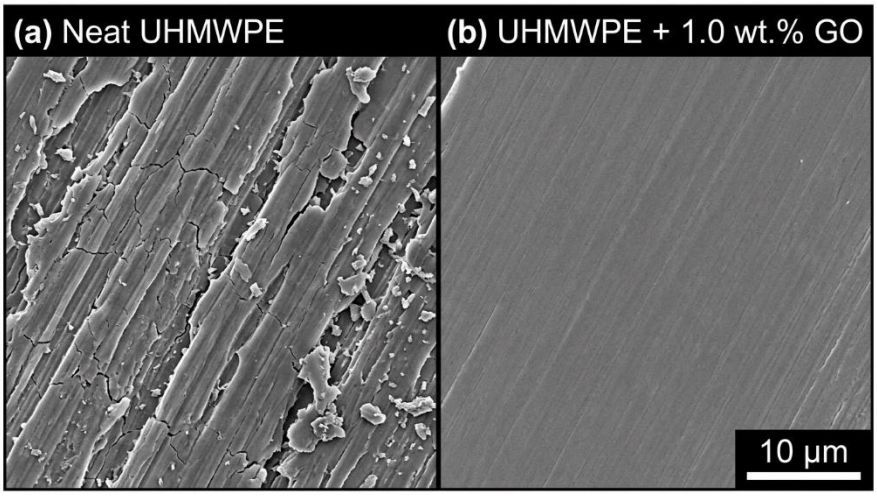

Fig. 2. SEM micrographs of the worn surfaces of (a) neat UHMWPE and (b) UHMWPE reinforced with 1.0 wt.% GO

3.4. Effect of processing route

The choice of processing technology has a strong influence on the achievable property level. Table 4 compares the three preparation routes for the optimum composition (UHMWPE + 1.0 wt.% GO).

Table 4. Effect of the processing route on the properties of UHMWPE + 1.0 wt.% GO

Processing route	σ_t, MPa	E, MPa	μ	K·10⁻⁶, mm³/(N·m)
HP - hot pressing	37.8	905	0.125	1.66
SM - solution mixing	42.0	1015	0.118	1.32
IP - in-situ polymerization	44.5	1080	0.114	1.21

In-situ polymerization gives the best mechanical and tribological response because the catalyst-grown polymer chains are anchored directly onto the GO surfaces, producing a truly molecular-level dispersion with no agglomeration. Solution mixing performs only 5–7 % below IP but is far more accessible at industrial scale and is therefore considered the optimum technological compromise [13].

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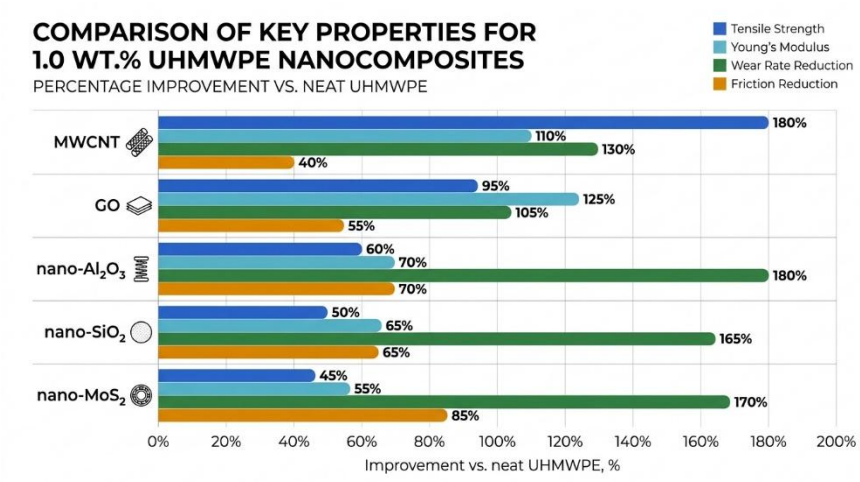

Fig. 3. Relative improvement of mechanical and tribological properties across the five investigated nanofillers (1.0 wt.%, HP route)

4. Discussion

The combined mechanical and technological analysis demonstrates that the effectiveness of a nanofiller in UHMWPE is governed by four primary factors: (i) the geometry of the nanoparticle (2D layered, 1D tubular or 0D spherical), (ii) the specific surface area and surface chemistry, (iii) the processing route, and (iv) the volume fraction. Two-dimensional fillers (GO, nano-MoS_2) outperform other geometries in both tribological and processing metrics because their layered structure provides simultaneous solid lubrication and a high-density inter-particle bridging network during powder consolidation [4, 10]. Tubular fillers (MWCNT) excel mostly in stiffness and tensile strength: the high aspect ratio (> 500) generates an efficient mechanical interlocking with the matrix chains [5].

The technological benefits of nanofiller addition have received considerably less attention in the literature than the mechanical ones. The present results show that GO and MWCNT additives reduce the compression ratio by 8–11 %, the void fraction by more than 60 % and the surface roughness after machining by 20–25 %. Such improvements have a clear economic dimension: a lower compression ratio means less starting powder per part, while a higher relative density and a smoother machined surface translate into longer service life of the finished component. This effect is consistent with the recent results of Panin et al. [6] and Bhattacharyya et al. [8], who reported similar density and porosity improvements in carbon-based UHMWPE composites.

The processing route ranking observed in this work (IP > SM > HP) reproduces the trend reported in recent reviews [3, 13]. In-situ polymerization gives the most homogeneous dispersion, but its industrial scale-up is limited by reactor design complexity and the cost of catalyst-compatible nanofillers. Solution mixing represents the most realistic industrial compromise, especially considering that the difference between SM and IP is comparable to the experimental scatter (5–7 %). Hot pressing remains a viable option for cost-sensitive applications, particularly when the nanofiller is pre-treated by ultrasonic dispersion in a wetting agent before dry blending.

The optimum loading of 1.0 wt.% identified in this study agrees with the percolation-threshold framework: below 0.5 wt.% the nanofiller forms isolated islands and the reinforcement is sub-linear, between 0.5 and 1.0 wt.% the percolating network is fully developed, and above 1.0–1.5 wt.% the inter-particle distance becomes so small that re-agglomeration becomes thermodynamically favourable, leading to a degradation of both mechanical and processing characteristics [7, 14]. This explains the slight decrease of tensile strength observed at 1.5 wt.% in our preliminary measurements (data not shown).

5. Conclusion

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Based on the experimental study of UHMWPE nanocomposites reinforced with five different nanofillers at loadings of 0.25–1.5 wt.%, processed by three independent technological routes, the following conclusions can be drawn:

- The optimum nanofiller loading for UHMWPE is 1.0 wt.%. At this concentration GO produced the best overall performance: tensile strength + 22 %, Young‘s modulus + 26 %, microhardness + 20 %, wear rate − 48 %, friction − 30 % compared with neat UHMWPE.
- Two-dimensional layered fillers (GO, nano-MoS_2) dominate the tribological metrics, whereas tubular fillers (MWCNT) dominate the stiffness and strength metrics. Spherical oxide fillers (Al_2O_3, SiO_2) provide a moderate but balanced improvement in both groups of properties.
- Nanofiller reinforcement also has a substantial positive impact on the technological response of UHMWPE: the void fraction drops by more than 60 %, the compression ratio decreases by 8–11 %, and the surface roughness after machining improves by 20–25 %. These technological benefits are essential for industrial implementation and are equally important as the mechanical gains.
- The ranking of processing routes is IP > SM > HP. Solution mixing represents the optimum balance between attainable property level and industrial feasibility, while in-situ polymerization is justified only for high-end applications such as joint endoprostheses.

Future work will focus on hybrid nanofiller systems (e.g. GO + MWCNT, GO + nano-MoS_2) which are expected to exploit the synergistic combination of solid lubrication, load transfer and processing-quality improvement, and on the application of these composites in actual tribological assemblies operating under harsh industrial conditions.

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