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HDPE COMPOSITE WITH HYBRID REINFORCEMENT AS WEAR RESISTANT MATERIAL FOR 3D PRINTING

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This work examines the influence of fused deposition modelling (FDM) and hybrid reinforcement with glassy carbon (GC) and nano alumina (n-Al_2O_3) on the wear behaviour of HDPE composites. The composites containing only n-Al_2O_3 showed the highest wear and unstable friction due to dominant abrasive mechanisms. The GC-filled HDPE exhibited reduced wear, associated with carbon transfer film formation. The hybrid GC/n-Al_2O_3 composite demonstrated a synergistic effect, combining surface hardening with self-lubrication, which markedly reduced wear and stabilized the coefficient of friction. Although the FDM-printed samples had higher wear rates than the compression-moulded ones, their coefficients of friction remained similar. The results highlight that hybrid reinforcement can effectively suppress abrasive wear and improve the tribological stability of FDM-processed HDPE composites.

Keywords: **wear resistance, HDPE, glassy carbon, FDM, 3D printing**

INTRODUCTION

High-density polyethylene (HDPE) is widely recognized as a low-friction and wear-resistant polymer, which makes it a popular choice for low-bearing applications and biomedical components such as acetabular cups or tibial inserts [1–3]. However, the relatively low mechanical strength and hardness of neat HDPE remain limiting factors for its broader engineering use [3]. The most common approach to overcoming these limitations is the reinforcement of HDPE with micro- or nanoscale fillers, which improve its load-bearing capacity and tribological properties [2, 4].

Possible reinforcing agents include ceramic particles such as alumina (Al_2O_3), titanium dioxide (TiO_2), or zirconia (ZrO_2) [5, 6], as well as carbon-based fillers such as carbon nanotubes (CNTs), graphene, graphene oxide, carbon black, or graphite [2, 4, 7, 8]. The addition of these fillers can significantly influence the wear mechanism and the overall tribological behaviour of the composite material. Typically, ceramic reinforcements tend to increase the hardness and stiffness of the matrix but may also promote abrasive wear at higher contact pressures [1, 9, 10]. This phenomena can result in increased wear volume or wear mass [5]. In contrast, carbon fillers often act as solid lubricants, forming a transfer film at the sliding interface, which reduces friction and the wear rate [8, 11–13]. Additionally, the introduction of carbon nanofillers can increase matrix stiffness, which prevents cracking of the polymer matrix and reduces plastic deformation. Hybrid reinforcements (or heterophase reinforcement) combining both ceramic and carbon components have also been explored to achieve a balance between hardness and lubricity, leading to synergistic improvements in tribological performance [2, 11, 12].

Despite extensive research on conventional processing routes (such as injection moulding and compression moulding) studies focusing on HDPE composites tailored for fused deposition modelling (FDM) remain uninvestigated. The use of 3D printing in wear resistance components is an emerging topic in he of HDPE composites. Nevertheless, there is lack of research focused on hybrid reinforcement in such 3D printed composites [3, 7].

This study investigates the effect of 3D printing via fused deposition modelling (FDM) on the tribological behaviour of high-density polyethylene (HDPE) composites. The use of hybrid reinforcement combining glassy carbon (GC) and alumina (Al_2O_3) was evaluated to determine its influence on the wear mechanisms, wear rate and coefficient of friction (CoF).

MATERIALS AND METHODS

To prepare the composite filaments, as the matrix, HDPE HIVOREX 2600J (Lotte Chemical, Seoul, South Korea) was used. The reinforcement particles were micrometric glassy carbon powder (GC) prepared according to previous work [14] and nano alumina (n-Al_2O_3, product number: 544833, Merck KGaA, Darmstadt, Germany) with a declared particle size <50 nm.

The granulates for extrusion were prepared by introducing powder reinforcement onto the surface of the HDPE granules. First, the mixture of polymer and powder additives was mixed with ethyl alcohol 96% (Warchem, Warszawa, Poland). Later, the mixture was treated with ultrasonic waves for 15 minutes in an ultrasonic bath. In next step, the mixture was poured into a polypropylene container and left to dry at 50°C until the excess of alcohol evaporated. After approximately 2 hours, the mixture was mechanically mixed for 1 minute, followed by further drying for approximately 12 hours. The composite filaments were extruded utilising a ZAMAK DTR EHP-2x16S twin screw extruder (Zamak Mercator Sp. z o.o., Skawina, Poland). The nozzle temperature during extrusion was 180°C and the obtained filaments were ~1.6 mm in diameter. The composition of the obtained filament is presented in Table 1. The amount of powder reinforcement needed to obtain the desired GC content was investigated in another work [14]. The amount of nano alumina was fixed to reflect the content of GC, which is presented in Table 1.

TABLE 1. **Composite composition**

	Volume content [%]		
	HDPE	μGC	n-Al_2O_3
HDPE	100.0	-	-
μGC	99.0	1.0	-
n-Al_2O_3	99.0	-	1.0
μGC/n-Al_2O_3	99.0	0.5	0.5

The prepared filaments were used to prepare samples via 3D printing with the FDM method and hot pressing. Hot pressing was performed in a steel mould at 150°C under 30 MPa pressure. The diameter of the samples was 30.0 mm. The 3D printing process was performed at Original Prusa Mini (Prusa Research a.s., Prague, Czech Republic) with a BondTech dual gear extruder upgrade (BondTech AB, Värnamo, Sweden). The printing parameters are presented in Table 2.

TABLE 2. **3D printing parameters**

Parameter	Value
Nozzle diameter	0.4 mm
Nozzle temperature	200.0˚C
Bed temperature	85.0˚C
Bed surface	PE tape
Print speed	30.0 mm/s
Feed rate	1.1 – 1.5
Layer height	0.1 mm
Extrusion width	0.45
Cooling rate (Cooling fan speed)	15.0% (40 RPM)
Retraction distance	0.0 mm
Infill ratio	100%
Perimeter count	2.0

The tribological tests to ascertain the coefficient of friction (COF) and mass wear of the materials were conducted in ambient conditions under technically dry friction conditions using a pin-on-block tribotester set up (Fig. 1). The samples were cylindrical in shape, 20.0 mm in diameter and height of 2.0 mm for the 3D printed samples and 7.0 mm for the hot-pressed samples. The printed paths were 45° to the sliding movement. This angle was chosen as the best performing in accordance with other studies [15]. In the test, the normal force of 10.0 N was used and the sliding speed was 0.1 m/s. The test was conducted over a sliding distance of 1000.0 meters. The counterpart material was a 6 mm alumina ball. During the tribological tests, the friction load was measured continuously by means of a strain gauge connected with an analogue-digital converter and recorder. The obtained data was employed to calculate the coefficient of friction. The samples were weighed before and after the test. The mass wear rate was calculated with Eq. 1. The wear track of the investigated composites was analysed utilising a Hitachi S-3400N scanning electron microscope (SEM).

$$W = \frac{m_0 - m_1}{m_0} * 100 \quad (1)$$

where:
W – mass wear rate [%], m_0 – sample mass before test [g], m_1 – sample mass after test [g]

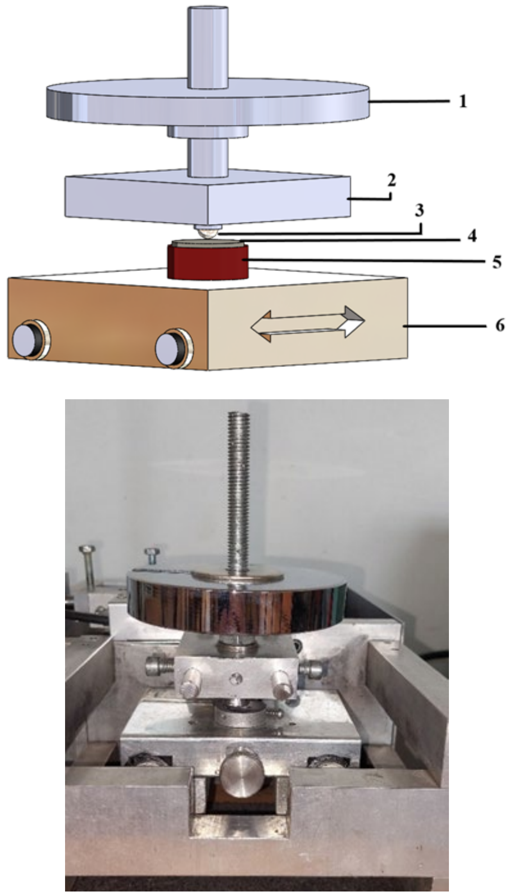

Fig. 1. Diagram of tribotester set up (left), 1 – load, 2 – strain gauge holder, 3 – counterpart (ball), 4 – sample, 5 – sample holder, 6 – moveable plate, and actual set up photo (right)

RESULTS

The samples after the tribological tests are shown in Figure 2. The composites containing only nano alumina (n-Al_2O_3) particles exhibit the most pronounced volumetric wear, regardless of the manufacturing technique, which suggests an abrasive wear mechanism. The hybrid composite (GC/n-Al_2O_3) shows visibly less wear than the composite with nano alumina. Nonetheless, the 3D printed sample displays a wear track with rough edges. These observations point to a synergistic effect between the reinforcements that reduces the overall wear rate, and also indicate that the FDM processing of HDPE can affect wear resistance. This trend is supported by the results presented in Table 3.

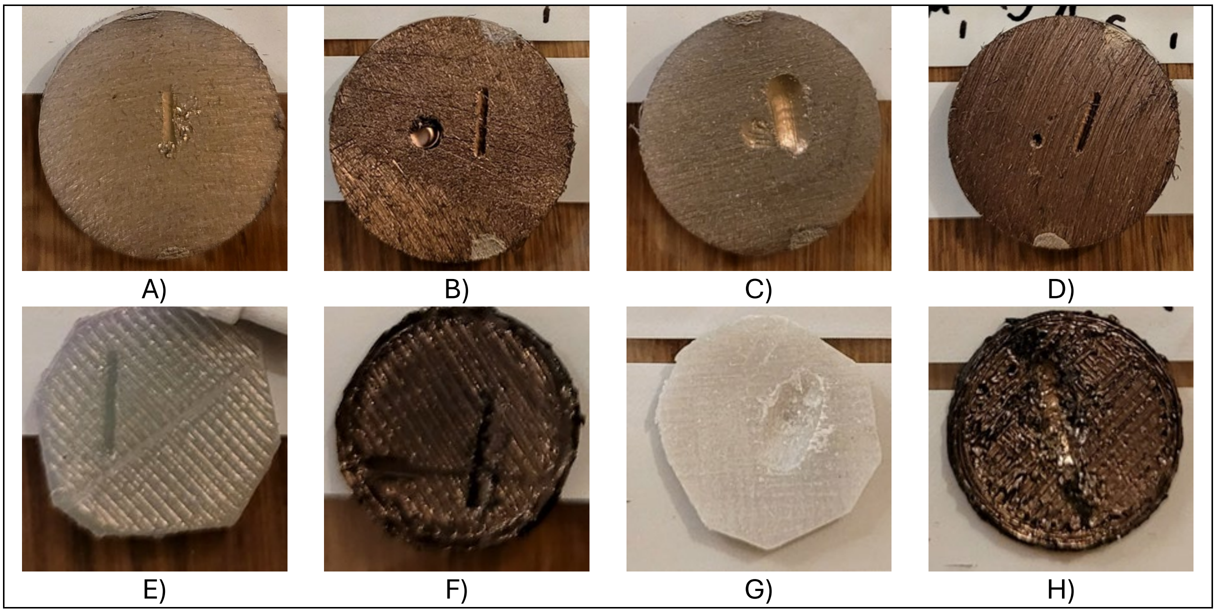

Fig. 2. Samples after tribology tests. A - D compression moulded composites, E - H 3D printed : A) and E) HDPE, B) and F) μGC, C) and G) n-Al_2O_3, D) and H) μGC/n-Al_2O_3

The highest CoF and the greatest mass wear rate were recorded for the n-Al_2O_3 composites. In addition, the 3D-printed samples show higher wear rates than their compression-moulded counterparts, which may be attributed to weak interlayer bonding in the printed parts. Poor interlayer strength of FDM parts is a known issue [16], and especially in abrasive type of wear, fragments of layers might delaminate during friction. However, in this case the manufacturing technique does not impact the CoF of the composites. Also, the usage of hybrid reinforcement not only reduces wear in comparison to the pure n-Al_2O_3 composite, but also stabilizes the coefficient of friction. This effect is confirmed by the CoF curves presented in Figure 3. The neat HDPE samples, regardless of processing, show a stable run over the whole distance. The composites with GC have higher values, but also tend to exhibit slight instability over 500 meters. This might be to heat accumulation during friction or most probably to the formation of carbon film and further self-lubrication. The composites with n-Al_2O_3 have a highly unstable CoF as a consequence of constant abrasive wear. Nevertheless, this effect is not observed in the composite with hybrid reinforcement. This suggests a mixed type of wear mechanism, which leads to a more stable friction curve than the pure composites. It was observed that the coefficient of friction and wear rate of the hybrid composite are at a similar level as the neat HDPE sample. On the other hand, in previous works was it was found that the addition of GC improves the mechanical properties of HDPE because of the increase in polymer crystallinity, reduction of crystallite size and their internal stress [17]. A similar effect should be expected from hybrid composites, especially since a positive effect on both the modulus of elasticity and compressive strength was observed in the work of Nabhan et al. [12].

TABLE 3. **Coefficient of friction and mass wear rate of composite samples**

Sample name	CoF	Wear rate
HDPE	0.11±0.03	0.00%
GC	0.17±0.05	0.00%
Al2O3	0.35±0.13	0.30%
GC/Al2O3	0.14±0.04	0.00%
PrintHDPE	0.12±0.04	0.10%
PrintGC	0.20±0.07	0.50%
PrintAl2O3	0.34±0.12	2.10%
PrintGC/Al2O3	0.16±0.05	0.10%

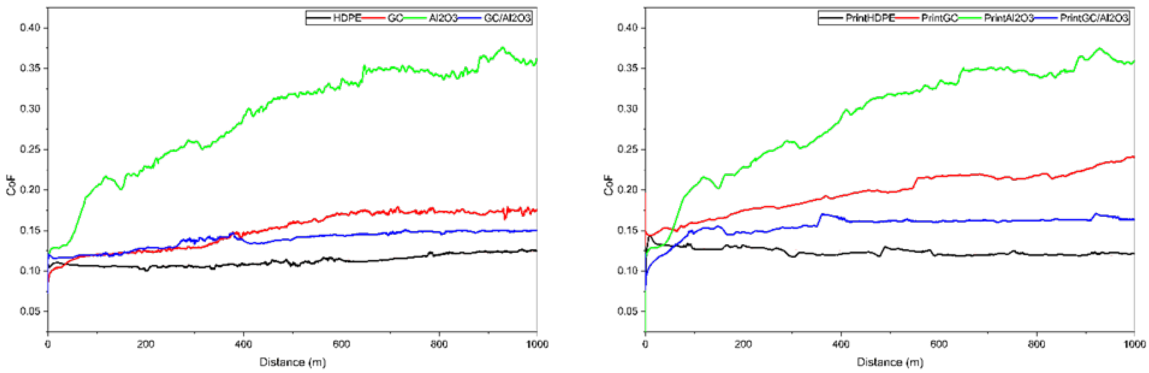

Fig. 3. Coefficient of friction curves: left - compression moulded samples, right - 3D printed samples

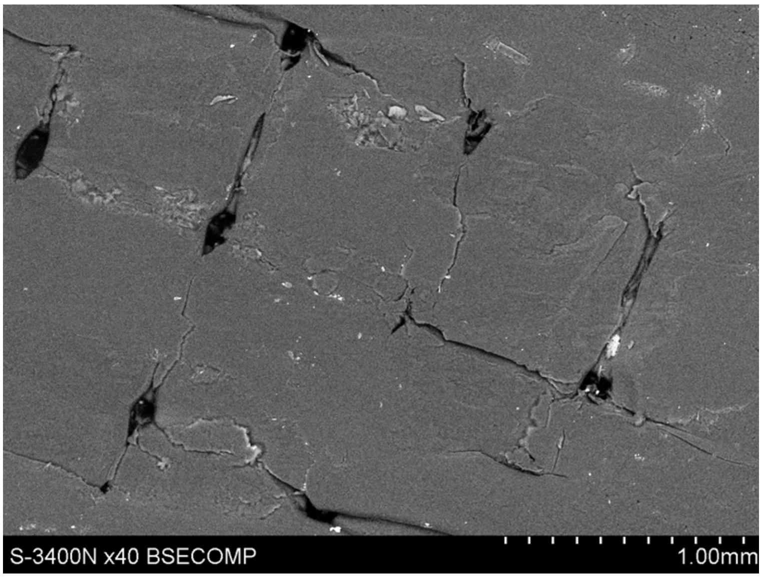

Fig. 4. Wear track of 3D printed HDPE sample

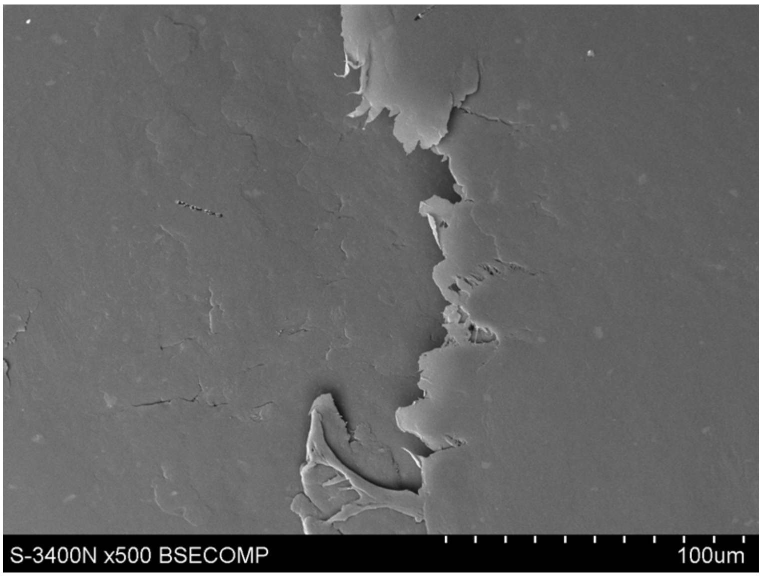

Fig. 5. Wear track of 3D printed GC composite sample

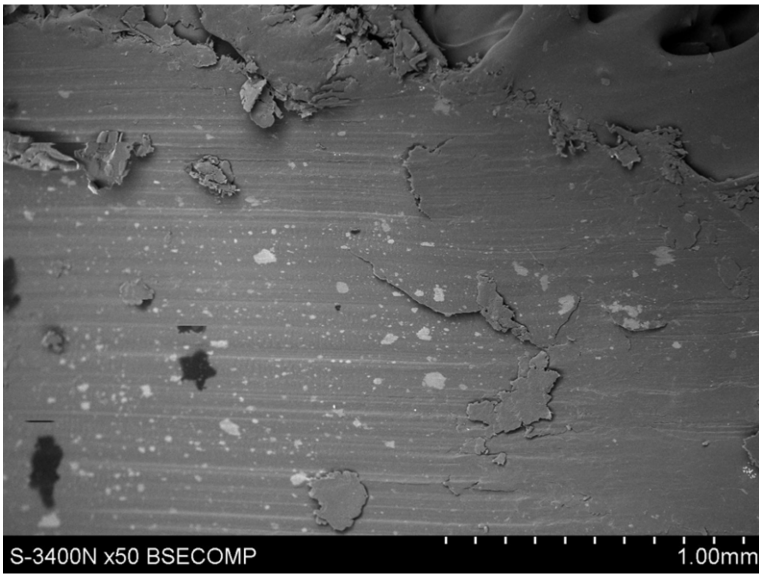

Fig. 6. Wear track of 3D printed n – Al2O3 composite sample

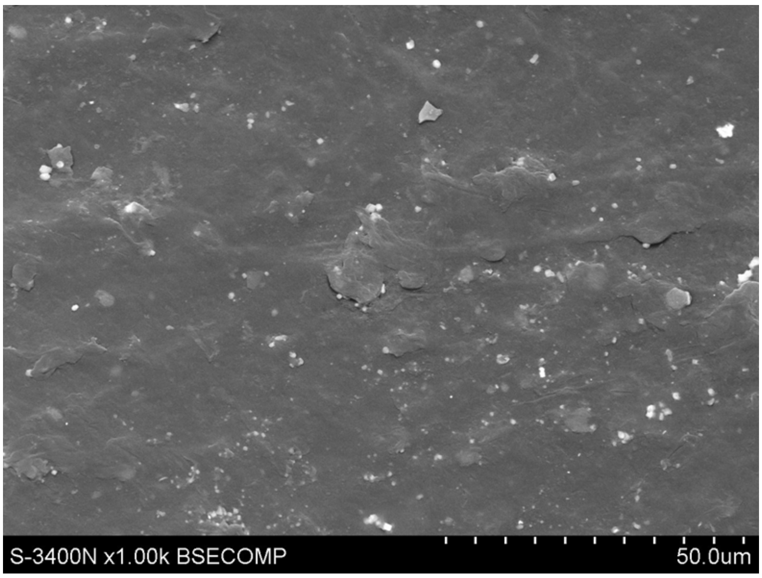

Fig. 7. Wear track of 3D printed GC/n – Al2O3 composite sample

Figures 4–7 present the wear tracks of the 3D printed samples. In the neat HDPE sample, the wear mechanism involves plastic deformation, the accumulation of wear debris and cracking. The cracks frequently originate at layer interfaces and along the print path. For the GC-only composite, plastic deformation predominates and only faint traces of carbon reinforcement along with deformed matrix particles are observed on the surface, suggesting that the initial wear follows a mechanism similar to neat HDPE before the onset of self-lubrication. During sliding, the GC particles were either pulled out together with the matrix debris or fragmented and smeared across the contact surface, becoming incorporated into the forming tribofilm. In the n-Al_2O_3 composite, a strong abrasive wear mechanism is evident, together with the agglomeration of ceramic particles. This suggests that the ceramic particles are pulled-out from the matrix during friction and act as microcutting agents until they agglomerate. At times, the nano alumina particles may be re-embedded into the matrix. This behaviour was not observed in the hybrid composite. Its wear track shows plastic deformation, matrix debris, and surface agglomerates of both the alumina and GC particles. Thus, as expected, the surface was hardened by ceramic particles that had previously been pulled from the matrix owing to abrasion, while concurrently, the GC particles were smeared over the surface to form a carbon tribofilm that mitigates further abrasion. This combination leads to stabilization of the CoF and minimizes or even prevents further material loss.

CONCLUSIONS

From the conducted research, following conclusions were formulated:

- The usage of hybrid reinforcement leads to more a stable CoF during wear than the composite with only glassy carbon or nano alumina particles.
- The wear mechanism of the hybrid reinforcement involves initial abrasive wear of the reinforcement particles, the agglomeration of ceramic particles, which hardened the surface, and the formation of a carbon tribofilm that prevents further abrasive wear.
- The 3D printing process can lead to significantly higher wear values due to poor interlayer strength.

Further research should focus on correlation between layer strength and wear resistance of 3D printed composites. The impact of the printing parameters or other practices to improve layer adhesion should be considered in the future. Also, optimization of the composite composition will be performed to find the best ratio of GC and n–Al_2O_3, that ensures a positive wear mechanism but also improves the stiffness and mechanical strength of the composite.

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