Multicomponent Antifriction Composite Based on Extrudable Matrix “UHMWPE - HDPE-g-VTMS - PP” for Additive Manufacturing

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Abstract. Tribomechanical properties of antifriction composites based on the extrudable matrix “UHMWPE + 17 wt. % HDPE-g-VTMS + 12 wt. % PP” with chopped fiberglass formed by three methods: Hot Pressing of Powders (HPP), Hot Pressing of Granules (HPG) and Fused Deposition Modeling (FDM) was studied. It has been found that a composite fabricated by the FDM method possesses the highest strength properties (elastic modulus, yield strength and tensile strength). It is shown that tribological properties (friction coefficient, volumetric wear) of composites fabricated by the three methods are close to each other that is related to impact of the reinforcing filler (fiberglass). The latter takes on compressive and shearing loads during tribo-loading and improves wear resistance of the composite. The studied multicomponent UHMWPE based composite is recommended for use as a feedstock for the manufacturing antifriction products by additive manufacturing.

1. Introduction

Currently, applied studies on the use of 3D printing methods, namely FDM (Fused Deposition Modeling) for manufacturing products with polyolefin matrices (including UHMWPE) using various fillers and plasticizers [1-6] are carried out.

Besides the market available additives traditionally used in industry, some commercially available polymers compatible with UHMWPE can be used as plasticizing fillers. Among them grafted high-density polyethylene HDPE-g-VTMS and HDPE-g-SMA might be mentioned. Loading of such polymeric plasticizers ensures to a blend an acceptable level of melt flow index. This makes it possible to produce extrudable polymer-polymeric composites with UHMWPE matrix with specified strength and wear resistance characteristics for manufacturing products by 3D printing technologies.

According to [7] satisfactory melt flow index of UHMWPE blends can be achieved when the content of plasticizing additives makes at least 20 wt. %. This ensures maintenance of the spherulitic pattern of permolecular structure of the matrix (when material is fabricated by compression sintering).

On the basis of experimentally obtained results an algorithm for determining control parameters (composition) at minimum experimental data available is proposed. The latter gives the required (restrictive) values to the effective properties of polymer-polymeric composites. On the basis of the specified i) composition structure, ii) tribological and iii) mechanical properties of polymer-polymeric UHMWPE composites experimental specimens were fabricated by the FDM (extrusion layer printing) and studied.
It is shown that tribomechanical properties of extrudable polymer-polymeric UHMWPE based composites fabricated by 3D printing surpass the similar properties compared to composites fabricated by compression sintering. The reason of the latter might be associated with the formation of more homogeneous permolecular structure primarily due to the employing a twin-screw compounding technique.

In the present work, some extrudable multicomponent polymer-polymeric UHMWPE composites filled with glass-fibers (200 μm long) have been fabricated. Their tribotechnical properties are studied with a view application in friction units of machines and mechanisms operating under various triboloading conditions.

2. Experimental

Powder of ultra-high molecular weight polyethylene (UHMWPE) by Ticona (GUR-2122) with a molecular weight 5.0 $10^6$ and particle size of 5–10 μm was used as the matrix resin. Grafted high-density polyethylene HDPE-g-VTMS (ground granulate), as well as polypropylene powder grade P21030 (MFR = 3.0 g/10 min) were used as plasticizing agents. Milled glass fibers 200 μm long were used as a filler (supplier "Graphite Pro" LLC, Moscow) at the content of 5 wt. %. Mixing of the matrix powder and fillers for specimen fabrication by Compression Sintering (Hot Pressing) was carried out in a planetary ball mill MP/0.5 (Tekhnocent Ltd., Rybinsk) with preliminary dispersion of the components in an ethanol suspension in an ultrasonic bath PSB-Hals 1335-05 (Gals ltd., Moscow).

In order to efficiently disperse fine UHMWPE particles (units of microns) with coarse particles of the polymer fillers (hundreds of microns) they were compounded in a twin-screw extruder Rondol (10 mm Twin Screw Extruders, Microlab). The temperature at the outlet extrusion nozzle was T=210 °C. Granules (with an average size of 3 – 5 mm) were obtained by subsequent mechanical grinding of the extrudate with the use of a Rondol shredder.

Rectangular shape samples of the polymer composites with the size 65×70×10 mm were fabricated by i) hot pressing of three-component powder mixtures at the specific pressure 10 MPa and the temperature of 200 °C with the use of a laboratory unit based on a hydraulic press "MS-500" (LLC SPC “TechMash” Ltd.) equipped with an split ring furnace; the subsequent cooling rate made 5 °C/min; ii) FDM (Fused Deposition Modeling) from granules of the same polymer blend with the use of a laboratory 3D–printer ArmPrint – 2 (National Research Tomsk Polytechnic University) with a nozzle diameter of 0.4 mm; the temperature of the stage and upper and lower filament (granules) feeding regions was T = 90, 160 and 200 °C, respectively. The layer-by-layer deposition rate and the thickness of the applied layer of the material were 20 mm / s and 0.3 mm, correspondently. Specimens of the required shape and size were cut out from the fabricated tiles with the help of a computer-controlled vertical milling machine.

Mechanical properties were determined under tensile tests with the use of electromechanical testing machine "Instron 5582". Dog-bone shape specimens were prepared for testing with the number of each type not less than 4.

The volumetric wear of specimens under the dry sliding friction was determined by the "pin-on-disk" scheme with the use of CSEM CH2000 tribometer (CSEM, Switzerland) at the load of P = 5 N (calculated contact pressure $P_{max} = 31.8$ MPa) and sliding velocity $V = 0.3$ m/s. The diameter of the bearing GCr15 steel ball counterface (HRC 60) was 6 mm.

The observation of the wear tracks surface topography was carried with the use of Neophot 2 optical microscope (Carl Zeiss Jena, Germany) equipped with a digital photo camera Canon EOS 550D (Canon Inc., Japan) as well as a stylus profilometer Alpha-Step IQ (KLA-Tencor). Structural studies were performed with the help of scanning electron microscope LEO EVO 50 (Carl Zeiss, Germany) at the accelerating voltage of 20 kV on the rupture surface of notched specimens failed after preliminary exposure in liquid nitrogen. The crystallinity was measured with the use of a combined analyzer SDT Q600 (TA Instruments, USA).

3. Results and discussion
Mechanical properties of neat UHMWPE, multicomponent mixture "UHMWPE + 17 wt. % HDPE-g-VTMS +12 wt. % PP" and their composite fabricated by all three methods are shown in table 1. It is seen that mechanical properties (elastic modulus, yield strength, tensile strength) of the composite fabricated by 3D-printing exceeds those of the composite prepared by powder hot pressing (HPP) by 10%.

SEM micrographs of permolecular structure of the thermoplastic three-component mixtures "UHMWPE + 17 wt. % HDPE-g-VTMS +12 wt. % PP" and composites based on this matrix fabricated by granulate sintering (HPG) and the FDM are presented in Figure 1. It is seen from the figure that loading of the fiberglass at granules hot pressing (HPG) ensures more uniform permolecular structure. The latter is formed first of all due to twin-screw compounding (Figure 1, c and d). This provides an increase of key mechanical properties (Table 1).

Table 1. Mechanical properties of UHMWPE and its composites with loading 30 wt. % of polymer plasticizers (total) as well as additionally filled with GF.

| Filler content, wt. % | Density, g/cm³ | Shore D hardness | Elastic modulus E, MPa | Yield point σ₀.₂, MPa | Ultimate strength σᵤ, MPa | Elong. at break ε, % |
|----------------------|---------------|------------------|------------------------|-----------------------|--------------------------|---------------------|
| UHMWPE               | 0.934         | 57.7±0.6         | 711±40                | 21.6±0.6              | 42.9±3.1                | 485±28              |
| "UHMWPE + 17 wt. % HDPE-g-VTMS +12 wt. % PP" (powder blend, HPP) | 0.933 | 57.8±0.3 | 876±71 | 25.1±0.3 | 19.1±1.3 | 149±38 |
| - Granulate, HPG     | 0.939 | 59.1±0.2 | 907±75 | 26.8±0.6 | 34.3±2.7 | 414±69 |
| - Granulate, FDM "UHMWPE +17 wt. % HDPE-g-VTMS +12 wt.% PP + 5 wt.% GF" (powder blend, HPP) | 0.947 | 59.9±0.6 | 1303±99 | 24.1±1.9 | 20.9±0.5 | 49±11 |
| - Granulate, HPG     | 0.945 | 60.4±0.6 | 1093±83 | 26.5±0.9 | 25.3±3.2 | 228±68 |
| - Granulate, FDM     | 0.929 | 61.5±1.2 | 1376±71 | 29.3±0.3 | 29.9±2.1 | 306±19 |

Figure 1. SEM- micrographs of permolecular structure of UHMWPE (a) and its composites "UHMWPE+17 wt. % HDPE-g-VTMS +12 wt. % PP + 5 wt. % GF" (b- powder blend, HPP; c - Granulate, HPG; d- Granulate, FDM).

Further, the tribological properties of the composites, including ones filled with the fiberglass were studied under dry sliding friction. The results are shown in table 2.

Table 2. Data on friction coefficient and volumetric wear of UHMWPE based composites loaded with 5 wt. % of fiberglass ("pin-on-disk" scheme).

| №  | Filler content, wt. % | Wear rate, mm³/h | Friction coeff., f |
|----|-----------------------|------------------|-------------------|
|    |                       |                  |                   |
It is seen in the table 2 that loading of fiber glasses up to 5 wt. % into thermoplastic matrix «UHMWPE + 17 wt. % HDPE-g-VTMS +12 wt. % PP» gives rise to decreasing volumetric wear and friction coefficient of composites formed by all three methods (HPP, HPG and FDM). Moreover, their values are close to each other regardless of the method of composites’ fabrication. This is clearly seen in Figure 2, a, b as well.

![Figure 2](image_url)

**Figure 2.** Volumetric wear (a) and coefficient of friction (b) for UHMWPE (1) and its composites: "UHMWPE + 17 wt. % HDPE-g-VTMS +12 wt. % PP" formed by the HPP (2), HPG (3), FDM (4) "UHMWPE + 17 wt. % HDPE-g- VTMS +12 wt. % PP + 5 wt. % GF" formed by the HPP (5), HPG (6), FDM (7).

In other words, micron-sized glass fibers in a multicomponent composite with the extrudable UHMWPE matrix effectively take on compressive and shear loads during triboloading and protect the matrix from wear. This is supported by the observed topography micrographs of wear track surfaces of fiberglass-reinforced composites fabricated by all three methods (HPP, HPG and FDM) (Figure 3).
Figure 3. Optical images of wear track surface topography of polymer composites (1, 2) and bearing steel counterface (3): UHMWPE (a, b, c) and polymer composites "UHMWPE + 17 wt. % HDPE-g-VTMS + 12 wt. % PP" fabricated by HPP (d, e, f), HPG (g, h, i), FDM (j, k, l); "UHMWPE + 17 wt. % HDPE-g-SMA + 12 wt. % PP + 5 wt. % GF" obtained by HPP (m, n, o), HPG (h, g, r), FDM (s, t, u).

Dry sliding friction; V=0.3 m/s and P= 5 N ("pin-on-disk"; CSEM CH2000 tribometer).
Data of figures 2 and 3 that under moderate tribolading conditions (V = 0.3 m/s and P = 5 N) a multicomponent extrudable UHMWPE based composite with the GF content of 5 wt. % possess quite high wear resistance. It means that this composite can be processed both at standard manufacturing methods (screw extrusion, injection moulding, etc.), as well as for FDM-printing for fabricating complex shape products for friction units in mechanical engineering.

4. Conclusion

Tribomechanical properties of antifriction composites based on the extrudable matrix "UHMWPE + 17 wt. % HDPE-g-VTMS + 12 wt. % PP" loaded with milled fiberglass formed in three ways: hot pressing of powders (HPP), hot pressing of granules (HPG) and layer-by-layer extrusion printing of granules (FDM) have been investigated. It has been shown that the highest strength properties (elastic modulus, yield strength and tensile strength) are possessed by a composite fabricated by the FDM method. The tribological properties (friction coefficient, volumetric wear) of composites fabricated in three ways are close to each other that is related to the reinforcing filler (fiberglass) which takes on compressive and shear loads during tribo-loading and protects the matrix from wear. The reason might be also related to use tribotesting scheme “pin-on-disk” when a highly localized loading of ductile elastic polymer is not accompanied with high wear rate.

The studied multicomponent composite based on UHMWPE is recommended as a feedstock to manufacturing anti-friction products by FDM printing.

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References

[1] Kurtz S 2016 High Pressure Crystallized UHMWPEs in UHMWPE Biomaterials Handbook: 3rd Edition ed. S Kurtz (Norwich, NY,William Andrew Publishing) pp. 434-448.
[2] Borges R A, Choudhury D, Zou M 2018 3D printed PCU/UHMWPE polymeric blend for artificial knee meniscus Tribol. Int. 122 pp 1–7
[3] Bala A S, Wahab M S, Ahmad M, Soon C F, and Ramli M S 2016 Processability and Thermal Properties of Ultrahigh Molecular Weight Polyethylene/Polypropylene Blends ARPN Jour. of Engin. and Appl. Sci. 11 (8) pp 5481–86.
[4] Ramli M S, Wahab M S, Ahmad M, Bala A S 2016 FDM preparation of bio-compatible UHMWPE polymer for artificial implant Int. J. Adv. Manuf. Technol. 11 (8) pp 5473-5480
[5] Changhui S, Aibing H, Yongqiang Y et al. 2016 Customized UHMWPE tibial insert directly fabricated by selective laser sintering Int. J. Adv. Manuf. Technol. 85 pp 1217–1226
[6] Gongde Liu, Huilin Li 2003 Extrusion of ultrahigh molecular weight polyethylene under ultrasonic vibration field J. Appl. Polym. Sci. 89 (10) pp 2628–2632
[7] Panin S V, Buslovich D G, Kornienko L A, Alexenko V O, Dontsov Yu V, S.V. Shil’ko 2019 Structure, as well as the Tribological and Mechanical Properties, of Extrudable Polymer-Polymeric UHMWPE Composites for 3D Printing J. Frict. Wear 40 pp 107–115