Development of Two-Component Polymer-Polymeric Composites Based on UHMWPE-PP Blends for Additive Manufacturing

S V Panin¹², D G Buslovich¹², L A Kornienko¹, V O Alexenko¹², Yu V Dontsov²

¹Institute of Strength Physics and Materials Sciences SB RAS, 634055, Tomsk, Russia
²National Research Tomsk Polytechnic University, 634050, Tomsk, Russia

E-mail: a svp@ispms.tsc.ru

Abstract. In order to develop extrudable polymer composites for additive manufacturing some mechanical and tribological properties of polymer-polymeric mixtures of ultra-high molecular weight polyethylene (UHMWPE) and polypropylene (PP) have been investigated. The problem of selecting rational compositions with the aim of improving the manufacturability (extrudability) of UHMWPE was solved. It is shown that extrudable 3D-printed UHMWPE composites over their tribomechanical properties (wear resistance, friction coefficient, elastic modulus, yield point, tensile strength, and elongation at break) exceed those of the hot pressing fabricated composite. This is related to more uniform ordered permolecular structure formation with increased crystallinity. It is shown that the composite "UHMWPE + 20 wt.% PP" is the most efficient from the standpoint of maintaining high tribomechanical properties and possessing acceptable melt flow rate (MFR) index.

Keywords: ultra-high molecular weight polyethylene, wear resistance, permolecular structure, melt flow index, additive manufacturing

1. Introduction

Ultrahigh-molecular weight polyethylene (UHMWPE) possesses appropriate level mechanical properties (in terms of polymers) as well as a low friction coefficient, high wear and chemical resistance in aggressive media. It is the key reason for its use at manufacturing friction units in mechanical engineering. Besides, it is widely applied in medicine as a component of orthopedic implants [3, 4]. However, due to the high length of the polymer chains UHMWPE has extremely low Melt Flow Rate [1] that significantly hinders its processing by traditional methods for polymers (screw extrusion, injection molding, etc.) [5]. Therefore, the problem of improving extrudability of UHMWPE and its composites is of research and development relevance. This paper is devoted to the study of structure and tribomechanical properties of extrudable polymer-polymeric UHMWPE composites with a different content of PP. The ultimate aim of the study is choosing optimal composition to be used as the feedstocks in additive manufacturing of friction units.

2. Experimental
Ultra-high molecular weight polyethylene (UHMWPE) powder by Ticona (GUR-4120) with a molecular weight $4.5 \times 10^6$ and particle size of 120 $\mu$m was used as the matrix resin. Polypropylene powder grade Р21030 (MFR = 3.0 g/10 min) with particle size of 525 $\mu$m was used as a plasticizing agent (fig. 1). Mixing of the matrix and filler powders for further specimen fabrication by the Compression Sintering (Hot Pressing) was carried out in a planetary ball mill MP/0.5 (Tekhnocentr LLC, Rybinsk) with preliminary dispersion of the components in an ethanol suspension in a ultrasonic bath PSB-Hals 1335-05-(Gals, Moscow).

In order to efficiently combine (disperse) fine UHMWPE particles (about 100 $\mu$m) with large particles of the polymer fillers (hundreds of microns) they were blended in a twin-screw extruder Rondol (10 mm Twin Screw Extruders, Microlab). The temperature at the outlet extrusion head was $T=210 ^\circ C$. 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.

Plates of the polymer composites were fabricated by: a) hot pressing of two-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 pressing machine "MS-500" (LLC SPC "TechMash") equipped with an open ring furnace; b) Fused Deposition Modeling (FDM) from granules of the same polymer blend with the use of a laboratory 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, correspondently. The layer-by-layer deposition rate and the thickness of the applied layer of the material were 20 mm / s and 0.3 mm. Specimens of the required shape and size were cut out from the fabricated tiles of size 65 × 70 × 10 mm with the help of a computer controlled lathe machine.

![Figure 1. SEM-micrographs of as-received polymer powders: UHMWPE$_{4120}$ (a) and PP$_{21030}$ (b).](image)

Mechanical properties were determined under stretching tests with the use of electromechanical testing machine "Instron 5582". Specimens of dog-bone shape were employed.

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 radius of the ball counterface made of bearing steel HRC 60 was 6 mm. Additionally, the wear resistance was evaluated according to the «block-on-ring» scheme using a 2070 SMT-1 friction testing machine (Tochpribor ltd., Ivanovo). The load was equal to $P = 60$ N (contact pressure $P_{max} = 9.7$ MPa), while sliding velocity made $V = 0.3$ m/s. The disk shaped counterface made of bearing steel HRC 60 with a diameter of 35 mm and a width of 11 mm was used. Its temperature was measured with a CEM DT-820 non-contact IR thermometer (Shenzhen Everbest Machinery Industry Co., Ltd., China). The surface roughness of the counterface was 0.2–0.25 $\mu$m.

The observation of the wear tracks surface topography was carried out 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 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 cleavage surface of notched specimens failed after cooling in liquid nitrogen.

3. Results and discussion

As noted in [6, 7], an acceptable melt flow rate of polymer-polymeric UHMWPE blends at maintaining tribomechanical properties at the level of the neat polymer is ensured at loading at least 10 wt. % plasticizing polymer fillers which depends on their rheological properties. However, to enable uniform layer-by-layer FDM printing it is necessary to add at least 20 wt. % of the above industrially produced plasticizing polyolefin component [7]. Data on mechanical properties of polymer-polymeric composites with the PP content from 20 % to 40 % fabricated by the FDM and CS methods are presented in Table 1. It is seen in the table that the density and Shore D hardness of the 3D–printed composites is lower than that of neat UHMWPE as well as the ones formed by hot pressing. The modulus of elasticity, yield strength, tensile strength, elongation at break of the FDM specimens, on average exceeds the corresponding properties of the CS composites by 14–16 %.

Table 1. Mechanical properties of UHMWPE and its composites with PP various (hot pressing and 3D-printing).

| Filler content, wt. % | Density, g/cm³ | Shore D hardness | Elastic modulus E, MPa | Yield point σ₀₂, MPa | Ultimate strength σ_U, MPa | Elong. at break ε, % |
|-----------------------|----------------|------------------|------------------------|----------------------|--------------------------|-------------------|
| UHMWPE                | 0.924          | 55.9±0.6         | 624±61                 | 20.2±0.8             | 33.7±4.1                 | 420±33            |
| UHMWPE+20 PP (CS)     | 0.931          | 57.9±0.6         | 705±50                 | 20.9±0.5             | 18.2±0.3                 | 139±16            |
| UHMWPE+20 PP (3D-printing) | 0.853      | 57.7±0.8         | 819±24                 | 23.9±0.6             | 20.9±1.9                 | 124±35            |
| UHMWPE+30 PP (CS)     | 0.931          | 61.9±0.5         | 863±76                 | 17.9±1.8             | 17.9±1.8                 | 4.63±0.6          |
| UHMWPE+30 PP (3D-printing) | 0.841      | 57.9±0.9         | 931±71                 | 25.9±0.5             | 21.5±0.9                 | 49±18             |
| UHMWPE+40 PP (CS)     | 0.929          | 62.8±0.8         | 907±59                 | 21.6±0.9             | 21.2±0.8                 | 12.58±2.43        |
| UHMWPE+40 PP (3D-printing) | 0.835      | 57.2±1.5         | 1003±63                | 24.4±3.63            | 23.6±2.1                 | 12.1±3.49         |

Loading diagrams (Fig. 2) clearly demonstrate the difference in mechanical properties of the UHMWPE composites fabricated by two methods (hot pressing and FDM).
Figure 2. Loading diagrams of UHMWPE and its composites containing n wt. % polypropylene; hot pressing (a, c) and FDM (b, d).

The permolecular structure of UHMWPE composites fabricated by the CS and FDM methods was than investigated. Fig. 3 and 4 testify for the heterogeneity of permolecular structure of polymer-polymeric hot pressed composites (Fig. 4, b, d, f) while a uniform mixing of the polypropylene in the UHMWPE matrix is characteristic feature for the FDM (Fig. 4, c, e, g).

Figure 3. Optical images of failed under stretching specimens of UHMWPE (a) and its composites: “UHMWPE + 20 wt.% PP” (b, c), “UHMWPE + 30 wt.% PP” (d, e), “UHMWPE + 40 wt.% PP” (f, g); Hot pressing (a, b, d, f), FDM (c, e, g).
Figure 4. SEM-micrographs of permolecular structure of UHMWPE (a) and its composites: "UHMWPE + 20 вес.% PP" (b, c), "UHMWPE + 30 wt.% PP" (d, e), "UHMWPE + 40 wt.% PP" (f, g); hot pressing (a, b, d f), FDM (c, e, g).

Studies of tribotechnical properties of polymer-polymeric UHMWPE composites fabricated by two employed methods are presented in Table 2 and fig. 5.

Table 2. Tribotechnical properties of UHMWPE and its composites with various PP content ("pin-on-disk" scheme; P=5 N, V=0,3 m/s.

| Filler content, wt. % | Wear rate, mm$^{3}$/h | Friction coeff., $f$ |
|-----------------------|------------------------|----------------------|
| UHMWPE               | 0.163±0.015            | 0.095±0.005          |
| UHMWPE+20 wt. PP (CS)| 0.131±0.013            | 0.098±0.012          |
| UHMWPE+30 wt. PP (CS)| 0.108±0.019            | 0.100±0.006          |
| UHMWPE+40 wt. PP (CS)| 0.096±0.006            | 0.073±0.003          |
| UHMWPE+20 wt. PP (3D-printing) | 0.107±0.013   | 0.082±0.004          |
| UHMWPE+30 wt. PP (3D-printing) | 0.124±0.013   | 0.066±0.003          |
| UHMWPE+40 wt. PP (3D-printing) | 0.133±0.032   | 0.071±0.002          |
It is seen from the table 2 and fig. 6 that, firstly, the content of 20 wt. % PP is high enough in order to attain high wear resistance of the FDM composite as well as required melt flowability (volume wear is equal to 0.107 mm$^3$ and friction coefficient - 0.082). Secondly, the friction coefficient possesses a stable value throughout the whole tribotesting time (as opposed to the compression sintering). The topography of wear track surfaces of polymer-polymeric composites fabricated by two methods is shown in Fig. 6, and fully correlates with the data in fig. 5.
Figure 6. Optical images of wear track surface topography of the polymer specimens (a, b) and bearing steel counterface (c, d): 1) UHMWPE, 2) “UHMWPE + 20 wt. % PP”, 3) “UHMWPE + 30 wt. % PP”, 4) “UHMWPE + 40 wt. % PP”; “pin-on-disk” scheme (CSEM CH2000 tribometer); hot pressing (a, c), FDM (b, d).

The complete melting of polypropylene particles with their uniform mixing and distribution in the UHMWPE matrix during extrusion combining (in the framework of FDM method) provides a low friction coefficient and high wear resistance of “UHMWPE + PP” composites fabricated by this method. There is only a small amount of wear debris found at the counterface surface (Fig. 6, d). Thus, according to the data of tribotechnical testing the polymer mixture “UHMWPE + 20 wt.% PP” looks to be most efficient.

To determine a proper application range of the developed polymer-polymeric composites “UHMWPE + PP” under various operating conditions their tribological properties were studied by the “block-on-ring” scheme (P = 60 N and V = 0.3 m/s). The data on their wear rate, counterface surface temperature, and elastic recovery (mm$^3$ and %) after triboloading for 24 hours are shown in table 3 and fig. 7.

It is seen at fig. 7 that wear resistance of polymer-polymeric composites under these triboloading conditions is equivalent to that at testing by “pin-on-disk” scheme (Table 2).

Table 3. Tribotechnical properties of UHMWPE and its composites with various PP content (“block-on-ring” scheme; P=60 N, V=0.3 m/s)

| Filler content, wt. % | Wear, mm$^3$ | Elastic recovery, mm$^3$ | Elastic recovery, % | Temperature, °C |
|-----------------------|--------------|------------------------|-------------------|-----------------|
| UHMWPE                | 0.08±0.024   | 0.043±0.013            | 46.5              | 28±2            |
| UHMWPE + 20 wt. % PP (CS) | 0.079±0.021 | 0.043±0.019            | 45.6              | 26.6±2          |
| UHMWPE + 30 wt. % PP (CS) | 0.098±0.006 | 0.067±0.012            | 31.6              | 26.9±2          |
| UHMWPE + 40 wt. % PP (CS) | 0.156±0.011 | 0.121±0.004            | 22.4              | 27.1±2          |
| UHMWPE + 20 wt. % PP (3D) | 0.078±0.021 | 0.048±0.005            | 38.5              | 26.1±2          |
| UHMWPE + 30 wt. % PP (3D) | 0.135±0.041 | 0.084±0.013            | 37.8              | 26.1±2          |
| UHMWPE + 40 wt. % PP (3D) | 0.177±0.039 | 0.130±0.026            | 26.6              | 26.4±2          |

Elastic recovery as a parameter being characteristic of the rheological properties (first of all of the permolecular structure formed in the composite [8]) is of the same order for the composites fabricated by both the CS and the FDM methods. This evidences for the fact that tribotechnical properties of the
studied polymer-polymeric mixtures are defined by the PP distribution in the UHMWPE matrix. This is supported by the stability of the temperature of the counterbody surface as well as topography of the wear track surfaces of the composites fabricated by two employed methods (Fig. 8).

**Figure 7.** Volumetric wear (mm$^3$) of UHMWPE and its composites “UHMWPE + n wt. % PP” under dry sliding friction at velocity of 0.3 m/s and the load 60 N (“block-on-ring” scheme; friction testing machine 2070 SMT-1); hot pressing (a), FDM (b)
Figure 8. Wear track surface topography of: 1) UHMWPE, 2) “UHMWPE + 20 wt. % PP”, 3) “UHMWPE + 30 wt. % PP”, 4) “UHMWPE + 40 wt. % PP”; friction machine 2070 SMT-1; “block-on-ring” scheme; hot pressing – (a); FDM-method – (b)

4. Conclusion
The mechanical and tribological properties of polymer-polymeric UHMWPE – PP composites were studied in order to develop extrudable UHMWPE-based feed stocks for additive manufacturing of the parts for tribounits in mechanical engineering.

It is shown that extrudable UHMWPE composites fabricated by 3D printing over their tribomechanical properties (wear resistance, coefficient of friction, elastic modulus, yield strength, tensile strength, elongation at break) exceed those obtained by hot pressing due to the formation of more uniform distribution of polypropylene in UHMWPE matrix. It is shown that the composite “UHMWPE + 20 wt.% PP” is the most efficient from the standpoint of maintaining tribomechanical properties and possessing acceptable melt flow rate (MFR) index.

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