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A composite with excellent tribological performance derived from oxy-fluorinated UHMWPE particle/polyurethane

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Supporting Information

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Experimental section

1.1 Direct fluorination

Prior to direct fluorination, UHMWPE particle was placed in acetone with aid of ultrasonication to remove impurities on the surface and then dried in a vacuum oven at 60°C for 12 h.

Direct fluorination of UHMWPE particle was carried out in closed stainless steel (SUS316) chamber (10 L) equipped with vacuum line. First, About 15 g of UHWMPE particle was scattered on a Teflon tray of 25 cm length by 15 cm width, which ensure that the particles could be adequately in contact with the reactive gas. The thickness of the particle deposition was less than 1 mm in order to favor the diffusion of fluorine gas in the whole volume. After that, UHMWPE particle was placed into the chamber. The air in the closed chamber was removed and replaced by nitrogen gas for three cycles to removed residual oxygen and moisture in the chamber. Then F_2/N_2 (10 vol% for F_2) mixture and O_2 gas were introduced into the chamber before the chamber was attached to the vacuum chamber for reaction at temperature of 75ºC for 1h, and the gas partial pressures of gases above were controlled at 60 kPa and 10kPa, respectively. To further obtain uniform and sufficient fluorination treatment of UHMWPE particles, 5 kPa N_2 was passed into the chamber at interval of 15 min for stirring mixture gases during the process of direct fluorination. After the completion of reaction, the gas in the chamber was pumped out, then N_2 gas (99.99% purity) was carefully introduced into the chamber until atmospheric pressure was reached, at which point the sample could be extracted. The non-fluorinated and fluorinated samples were denoted as U-UHMWPE and FO-UHMWPE, respectively.

1.2 Preparation of the blended composites

The manufacture process of the composite was as follows: TPU pellets were dissolved in

N,N’-dimethylacetamide (DMAc) solvent by mechanical stirring with the aid of heating at 100°C. The UHMWPE particles were placed in DMAc solvent and ultrasonicated for 30 min to obtain uniform dispersion. Then the dispersed UHMWPE solution was added into TPU solution by mechanical stirring and ultrasonication to obtain homogeneous blended solutions. The solid content of the blended solutions is controlled at 47-50%. The degased solutions were first cast onto clean and dry glass plates by a doctor’s blade. The samples were heated at 40°C for 1 h, 60°C for 1 h, 80°C for 1 h, 100°C for 1 h, and 120°C for 1 h in a vacuum oven to remove DMAc solvent to obtain blended composites with the thickness of 250-270 μm, denoted as TPU/U-UHMWPE, TPU/FO-UHMWPE. Then the obtained composites were further dried in a baking oven to remove residual solvent.

1.3 Characterization

1.3.1 Abrasion resistance tests

The abrasion resistance tests were conducted on an HY-766 DIN rotating drum abrasion tester (Guangdong, China) according to GB/T (China) 9867-2006 (DIN 53516) standards. A test specimen with the diameter of 16±0.2 mm and thickness of 6-8mm, produced by the compression molding of composite, was gripped in a specimen holder in such a manner that it projected 2±0.2 mm beyond the face on the grip. The cylinder was rotated at 40 rpm. The test specimen was tested under constant contact pressure (10 N) and at a constant speed through a defined abrasion distance (40m) across an abrasive cloth attached to the surface of a rotating cylinder. The samples were cleaned with the brush and accurately weighed to the nearest 0.1 mg using an electronic balance before and after the wear testing. The loss in mass of specimen was converted to volume from its calculated density. Net wear volume losses were adopted to evaluate wear-resistance properties.

1.3.2 Friction coefficient test

The friction coefficient was the ratio of the maximum static friction force to the vertical gravity force, which was measured according to GB/T (China) 5870-2006. A surface chromium plated stainless steel block was used as the slide block. The surfaces of the steel block and composites were cleaned with ethanol prior to every measurement.

1.3.3 SEM

The blends were cryo-fractured in liquid nitrogen to obtain the fracture surface. Both fracture surface and wear surface were coated with gold for examination of morphology by scanning electron microscope FEI Inspect F (FEI company, EU/USA) at 20.0 kV accelerating volt.

1.3.4 ATR-FTIR

Attenuated total reflection infrared spectroscopy (ATR-FTIR) was operated on the Nicolet 560 infrared spectrometer employing attenuated total reflection mode in the range 4000-400 cm^{-1} for observing the chemical changes on the samples.

1.3.5 XPS analysis

To assess the elemental composition of the treated samples and their chemical states, X-ray photoelectron spectroscopy (XPS) measurement was performed on a Kratos ASAM 800 spectrometer (Kratos Analytical Ltd., U.K.) with nonmonochromatic Al Kα (1486.6 eV) X-ray source (a voltage of 15 kV, a wattage of 250 W) radiation. The vacuum chamber pressure was controlled at a range of 10^{-6}-10^{-7} Pa. The elemental compositions were estimated from the areas of each of the peaks in the resulting XPS spectra, using a sensitivity factor associated with the apparatus.

1.3.6 Mechanical properties test

Tensile testing was performed on rectangular-shaped specimens cut from composites at room temperature using an Instron (4301) tensile tester at 25ºC with a crosshead speed of 200 mm·min^{-1} according to ASTM D412-98. For tearing experiments, trouser specimens with 100 mm in length, 15 mm in width and a longitudinal slit of 40 mm were used. During testing, the force was applied normally to the plane, operating at a crosshead speed of 100 mm·min^{-1} following the rubber and thermoplastic elastomers tear strength test standard GB/T 529-2008 (China) (ISO34-1: 2004).

1.3.7 Wide angle X-ray diffraction (WXRD)

Wide angle X-ray diffraction (WXRD) of UHMWPE particles was carried out on a Philips X'Pert PRO-MPD instrument. Scans were taken from 5º to 45º with a step size of 0.06º.

1.3.8 Surface energy

Contact angles analysis were carried out on the Germany Krüss 100 type surface tension meter with deionized water and diiodomethane at room temperature, then surface energy was calculated according to a conventional method.[1] The UHMWPE samples for contact angles measurements, which were modified by direct fluorination together with UHMWPE particles, were produced by the compression molding of UHMWPE particles at 170°C.

Additional Figures and Tables

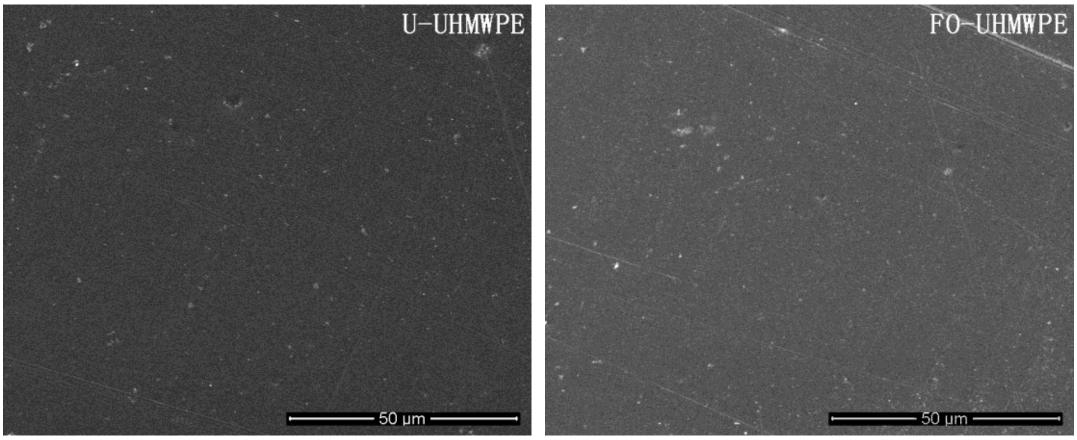

Fig. S1 the surface morphology of UHMWPE compression-molded sample before (left) and after (right) fluorination

Table S1 Surface energy of UHMWPE before and after fluorination

Samples	**Static contact angle(°)**		**Surface energy (mN/m)**		
	water contact angle	diiodo-methane contact angle	disperse	polar	total
U-UHMWPE	95.7±3.2	55.7±2.6	30.52	3.96	34.48
FO-UHMWPE	64.5±2.7	35.3±1.8	39.17	15.30	54.47

Contact angles depend on the surface roughness and surface chemical composition.[2,3] The SEM surface morphology of the UHMWPE compression-molded sample shown in **Fig. 1S** indicates that their surfaces are relatively smooth before and after fluorination. Therefore, the surface roughness has a little influence on the measured contact angles. The surface energy depends primarily on surface chemical composition. Each contact angle value was the average of more than five successful measurements on different locations. The errors for contact angles measurement is provided in **Table S1**.

The surface energy of UHMWPE compression-molded sample, which is made by the compression molding of UHMWPE particles and modified by direct fluorination together with UHMWPE particles, is significantly improved by direct fluorination, which is enhanced from 34.48 mN/m to 54.47 mN/m, about 57.9% improvement. Polar component (γ_s^P) of F-UHMWPE is increased from 3.96 to 15.30 mN/m, about 286.3% improvement compared with that of the U-UHMWPE sheets shown in **Table S1**, indicating that the direct fluorination modification can indeed increase the polarity of UHMWPE surface. The significant increase in surface energy is mainly attributed to large number of polar groups on the surface introduced by direct fluorination, which facilitate the excellent compatibility between UHMWPE particles and TPU matrix. The results are consistent with the FT-IR and XPS characterization.

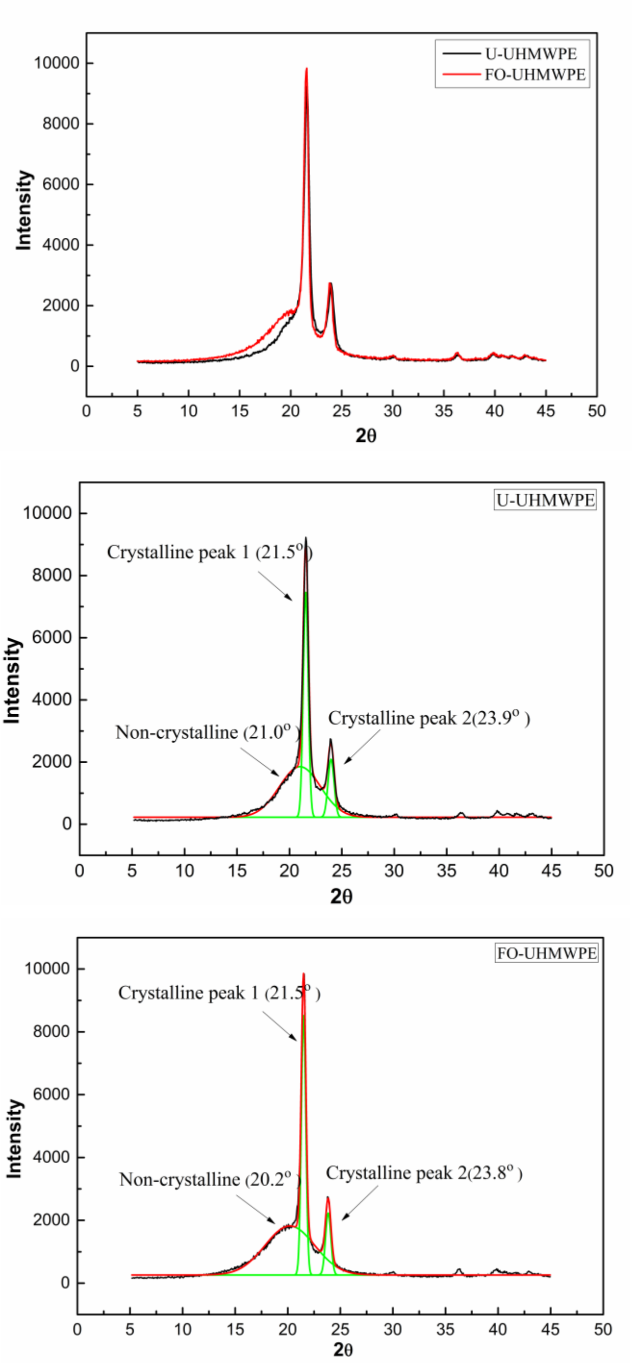

Fig. S2 the XRD spectra of U-UHMWPE and FO-UHMWPE particles

Table S2 the area of each crystallization and non-crystallization peak and the degree of crystallization of UHMWPE particles

Samples	Crystalline peak area 1	Crystalline peak area 2	Non-crystalline peak area	Non-crystalline peak width	Degree of crystallization
U-UHMWPE	4335.04	1331.20	7968.99	3.91	41.6%
FO-UHMWPE	4448.31	1270.21	9205.89	4.70	38.3%

Fig. S2 and **Table S2** show the XRD spectra and analysis results of non-fluorinated and oxy-fluorinated UHMWPE particles. The non-crystalline peak center for FO-UHMWPE shifts to lower and has a larger peak width than that of U-UHMWPE. Non-crystalline peak area shows a slight increase owing to that the surface oxy-fluorinated UHMWPE molecule chain is difficult to enter the crystal lattice.[4] The sub-peaks in XRD curves have been obtained by origin pro 9.0 software using Gaussian function. The degree of crystallization (X_c) is obtained by the ratio of crystalline peak area (A_c) to the total peak area (A_c+A_a).

$$X_c(\%)=A_c/(A_c+A_a) \tag{1}$$

Where A_c is the crystalline peak area, and A_a is the amorphous peak area.

Compared with that of non-fluorinated UHMWPE particles (41.6%), the degree of crystallization of oxy-fluorinated UHMWPE particles shows a slightly decrease. It can be concluded that the direct fluorination surface modification results in the formation of a very thin fluorinated surface layer. While the surface properties of UHMWPE particles are changed dramatically, the bulk properties remain unchanged. The related literatures indicates for majority of polymers only upper surface layer is modified (0.01-10μm in thickness depending on application area), but the bulk properties remain unchanged.[5, 6]

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