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Journal Name

ARTICLE

Various surface functionalization of ultra-high-molecular-weight polyethylene based on fluorine-activation behavior

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ultra-high-molecular-weight-polyethylene (UHMWPE) is an excellent biological material, but covalently introducing a variety of functional groups on its surface is very difficult owing to its inherent inert structure. In this study, the surface functionalization of UHMWPE based on fluorine-activation and subsequent derivatization reactions was reported, which offered a simple and convenient pathway to the incorporation of useful functional groups and patterned surface functionality. A large number of carboxyl groups, -C-Fx and C=C bonds are covalently bonded to the macromolecular chain structure through fluorine-activated process in the presence of oxygen, greatly increasing the surface polarity and wettability. Its surface energy is increased from 34.5 mN m⁻¹ to 57.5 mN m⁻¹, and the polar component arises from 4.0 to 23.8 mN m⁻¹. In contrast, there is only stable C-F forming when treated with only fluorine (no oxygen), producing hydrophobic Teflon-like surface structure and poor wettability. Moreover, the UHMWPE with carboxyl groups and double bonds, used as precursor, were further covalent functionalized through subsequent derivatization reactions with fluorine, bromine and amine-terminated molecules, by which the carbon-bromine bond and amino groups are successfully grafted onto UHMWPE surface. The results demonstrate that the fluorine-activated strategy developed in this work is an effective means to improve the surface hydrophilicity and derivatization reaction capacity of UHMWPE.

1. Introduction

Due its nontoxicity, high mechanical strength and impact strength as well as excellent resistance to corrosion and abrasion, ultra-high-molecular-weight polyethylene (UHMWPE) is one of the commonest polymeric materials used for medical applications such as the replacement of damaged cartilage in total joint arthroplasty, or the surgical reconstruction of a disease joint.¹⁻³ However, as is already established, the applications of UHMWPE as biomaterials and reinforcing materials for composite remain limited due to its chemical inertness that causes the difficulty to obtain wettability/biocompatibility with fluids/tissues and strong interfacial adhesion with other polymeric materials.⁴⁻⁶ Therefore, covalent surface functionalization of UHMWPE is of fundamental importance to adjust surface and interface performances, creating an active surface layer to improve its biocompatibility and interfacial adhesion.^{7,8} The various conventional surface modification treatments are difficult to achieve high-effective activation and high-density

functional group aggregation without damaging the surface structure.⁹⁻¹² Direct fluorination has been currently recognized as an effective method to modify and control physicochemical properties of chemically inert polymers without any assisted initiation, irradiation, or catalysts due to high reactive capability of fluorine gas. The surface nature of activated layer can be controlled by direct fluorination forming high hydrophobic Teflon-like structure or by oxy-fluorination introducing hydrophilic oxygen-containing groups regardless of whether polymers are hydrophobic or hydrophilic.¹³ In the previous direct fluorination and oxy-fluorination modification research, high ratio fluorine in mixtures was used, and most of groups introduced on the macromolecular chain were the stable -C-F bonds.

In this study, the high-reactive fluorine gas was employed as an initiator under substantial oxygen atmosphere, thus many -C(=O)F groups were introduced. The active -C(=O)F can be easily transformed into -COOH groups by hydrolysis in the presence of atmospheric moisture or water during storage. It is generally considered that the C-F bond is very strong just like that of Teflon structure, which is widely used as a chemically inert and thermally stable non-adhesive surface. However, in the case of oxy-fluorination with substantial oxygen, the partial decarboxylation behavior may occur from polymeric backbone when adjacent to the C-F bond with strong attracting electron effect, resulting in the formation of CH=CH structure. That is similar to the transformation of unstable end-groups in perfluorinated copolymers such as

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tetrafluoroethylene/hexafluoropropene copolymer. The unstable $-C(=O)OH$ group can be transformed into $-CF=CF_2$.¹⁴
¹⁵ That behavior cannot occur before the hydrolysis of $-C(=O)F$.
^{16, 17}

It is found that various functional groups, C-Fx, COOH and especially for C=C bonds, are covalently bonded into the polymeric surface structure through fluorine-activated process. An active surface layer produced greatly improves the wettability and expands the application of UHMWPE as reinforcing materials in composites.¹⁸ Moreover, UHMWPE with a large number of carboxyl groups and double bonds can serve as an intermediate to the subsequent derivatization reactions for further covalent functionalization of UHMWPE with bromine and amine-terminated molecules, thereby greatly simplifying the chemistry. Herein, not only the direct fluorination is a high-effective activation method, but also subsequent derivatization reactions based on this activation can be available, which develops a simple and convenient way to introduce high-density various functional groups in variety on the inert material.

2. Experimental

2.1 Materials

Ultra-high-molecular-weight polyethylene (UHMWPE) particle (GUR4150-3, 0.94gcm⁻³, Intrinsic viscosity 3150 cm³/g, Ticona, American) with average diameter 65.9 μ m 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. UHMWPE sheet samples were fabricated by hot pressing at 170°C. The F₂/N₂ (10 vol% for F₂) mixture and O₂ with purity up to 99.99% were obtained from Chendu Kemeite Fluorine Industry Plastic Co., Ltd. N, N'-dimethylformamide (DMF), obtained from Chengdu Kelong Chemical Reagent Co., was distilled over P₂O₅ under reduced pressure. All other chemical reagents were commercially analytical grade and used without further purification.

2.2 Fluorine-activated reaction process

Fluorine-activated reaction of UHMWPE particles and sheet samples was carried out in closed stainless steel (SUS316) chamber equipped with a vacuum line. About 15 g of UHMWPE particles were scattered on a Teflon tray of 25 cm length by 15 cm width, which ensured 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. A piece of compression-molded UHMWPE sheet sample was treated together with UHMWPE particles in order to control the same treatment condition with the particles.

The air in the closed chamber was removed and replaced by nitrogen gas for three cycles to remove residual oxygen and moisture in the chamber. Then O₂ (0.4 bar) and different content F₂/N₂ (10 vol% for F₂) mixture gas were introduced into the chamber before the chamber was attached to the vacuum for reaction at temperature of 80°C for 1h. The concentration of fluorine was controlled as 4.0% and 5.5% by

volume, denoted as OF-4.0% and OF-5.5% respectively. To further obtain uniform and sufficient fluorination treatment of UHMWPE particles, a small amount of N₂ was passed into the chamber for stirring mixture gases during the fluorination process. After the completion of reaction, the gas in the chamber was pumped out, then N₂ gas (99.99% purity) was carefully introduced into the chamber until atmospheric pressure was reached, at which point the sample could be extracted.

In order to consider the influence of gas components, another two samples were treated with the same fluorine concentration (4.0% and 5.5%) at the condition without O₂. Other operations were the same as the above, denoted as F-4.0% and F-5.5%. The fact that samples taken at various locations on the Teflon tray show similar spectra confirms the homogeneity of direct fluorination treatment.

2.3 Derivatization reaction-amidation

UHMWPE particles (OF-4.0%, 2 g) were stirred in 30 ml of a 20:1 mixture of thionyl chloride (SOCl₂) and DMF at 70 °C for 24 h. After the acyl chlorination, SOCl₂ and DMF were removed through vacuum distillation. After that, ethylene diamine (20 ml) was immediately added to react with acyl-chlorinated UHMWPE particles at 100°C for 24h until no HCl gas existed. After cooling to room temperature, the UHMWPE particles, collected on a filter, were washed with anhydrous ethanol to remove the rest ethylene diamine. Then the particles were further washed repeatedly in Soxhlet extractor with anhydrous ethanol and dried in a vacuum oven.

2.4 Characterization

2.4.1 Contact angle and Surface energy

To measure the surface energy (total surface energy and its polar components), static contact angle measurements were carried out using the conventional Owens-Wendt method on the Germany Krüss 100 type surface tension meter with deionized water and diiodomethane at room temperature. The surface energy of UHMWPE can be estimated through measuring the surface energy of compression-molded UHMWPE sheet sample. The UHMWPE samples for contact angles measurements, which were produced by the compression molding of UHMWPE particles at 170°C, were modified together with UHMWPE particles. All contact angles represent the average value of successful measurements performed on five different locations on the sample surface.

2.4.2 XPS and ATR-FTIR analysis

The elemental composition and their chemical states in the near surface of UHMWPE samples were analyzed by X-ray photoelectron spectroscopy (XPS) on a Kratos ASAM 800 spectrometer (Kratos Analytical Ltd., U.K.) with nonmonochromatic Al K α (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. All the binding energies were referenced to the C 1s peak at 284.8 eV originating from the surface carbon contamination. The treatment of core peaks was carried out using a nonlinear Shirley-type background.¹⁹ The quantification of surface

composition was based on the areas of each of the peaks in the resulting XPS spectra using Scofield’s relative sensitivity factors.

Nicolet 560 FTIR spectrometer (Thermo Electron) using Attenuated Total Reflection (ATR) mode was used to measure the changes in various functional groups on UHMWPE surface. The spectra were measured in a wavenumber range of 4000–600 cm^{-1} at a resolution of 4 cm^{-1} .

2.4.3 Energy-dispersive X-ray cartography (EDX)

To measure the distribution of various elements across the polymer surface, the elemental mapping was performed with energy dispersive X-ray spectroscopy (EDX) analyzer (Inca Pneta FET×3, Oxford instruments).

3. Results and discussion

3.1 Wettability, Contact angles and Surface energy



Figure 1. Photograph of dispersibility of UHMWPE particles in deionized water.

Figure 1 shows the dispersion of surface modified UHMWPE particles with different reactive gas components in deionized water. As can be seen from these photographs, the UHMWPE particles treated only with fluorine gas clustered immediately above water just like the virgin sample when contacting with water shown in Figure 1 (F-4.0% and F-5.5%). Obviously, hydrophobic structure must be produced or maintained in the only fluorine/nitrogen case. The introduction of oxygen in mixtures makes UHMWPE particles well disperse in deionized water, and a uniform dispersion of UHMWPE particles in water

is obtained. Color in particles turns slight yellow for OF-4.0% and OF-5.5% samples. There may exist some conjugated structures on their surface that determine the UHMWPE particles are yellow. The above results shows that the surface nature of activated layer can be controlled by direct fluorination forming high hydrophobic structure or by oxy-fluorination introducing hydrophilic groups.

Table 1 Surface free energy and water contact angle of UHMWPE sheets

Samples	Static contact angle		Surface energy (mN m^{-1})		
	water contact angle	diiodo-methane contact angle	disperse	polar	Total
Virgin	95.7	55.7	30.5	4.0	34.5
F-4.0%	100.3	61.7	27.0	0.6	27.6
F-5.5%	101.6	64.0	25.7	0.6	26.3
OF-4.0%	53.1	44.7	35.3	22.6	57.9
OF-5.5%	51.8	47.6	33.7	23.8	57.5

Contact angle measurements were performed to reveal the wettability of UHMWPE by fluorine-activated modification. High water contact angle and low surface energy indicates the highly hydrophobic nature of the F-4.0% and F-5.5% samples in Table 1. Introduction of oxygen in mixtures gives a significant reduction in the apparent water contact angle and a great increase in surface energy of UHMWPE. It is evident that the total surface energy and its polar components highly depend on the reactive gas components. The water contact angle reduces from 95.7° to 53.1° (Figure 2 b, inset). The lower contact angle of water is caused by a decrease in the free surface energy of the solid/liquid interface. The total surface energy is markedly increased (from 34.5 up to 57.9 mN/m). The increase of polar component is more pronounced, ranging from 4.0 mN/m to 22.6 mN/m , about six-fold improvement compared with that of virgin UHMWPE. A three-dimensional digital microscope VHX-1000C instrument (Keyence, Japan) with 3D profile measurement mode was used to characterize surface roughness, showing that the surface roughness is less than 1 μm in all samples shown in Figure 2 and Figure 1s (see Supporting Information file).The contact angle and surface energy analyses mentioned above demonstrate that the well

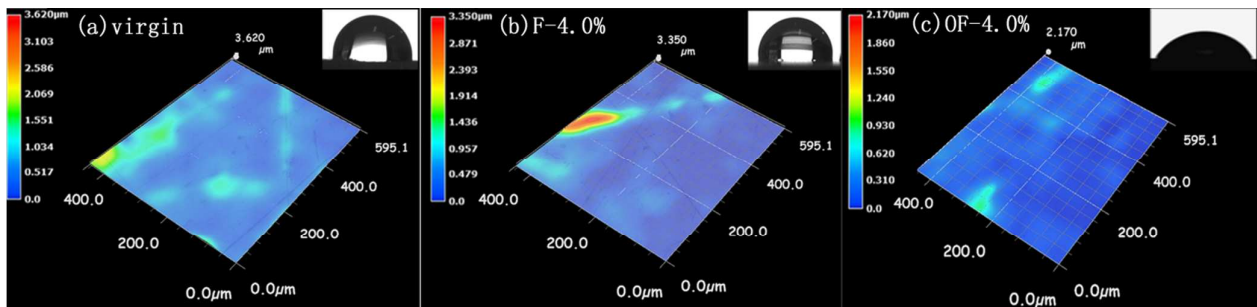


Figure 2. The surface roughness of (a) virgin, (b) F-4.0% and (c) OF-4.0% samples. The insets correspond to the water contact angle for virgin, F-4.0% and OF-4.0% samples.

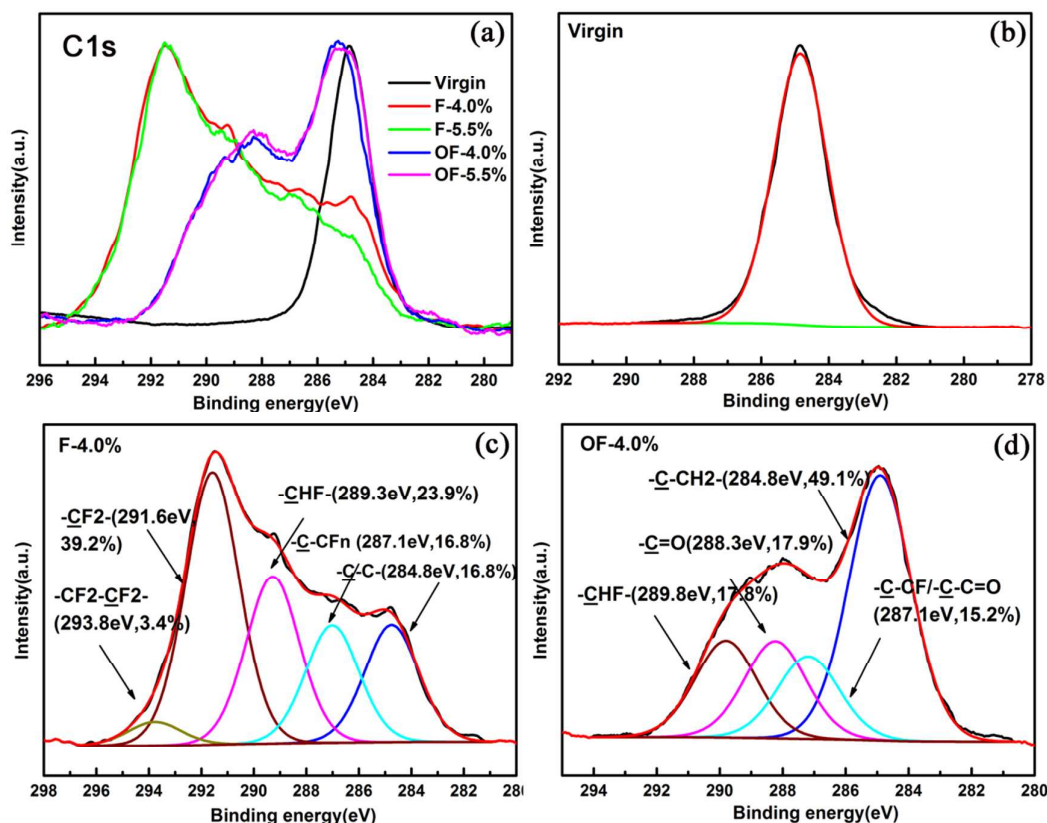


Figure 3 (a) The C1s of virgin, F-4.0%, F-5.5%, OF-4.0% and OF-5.5% UHMWPE samples, the individual C1s spectra (b) virgin, (c) F-4.0% and (d) OF-4.0% particle.

wettability of UHMWPE is mainly attributed to the greatly increasing polarity.

3.2 Surface chemical composition

Table 2 The surface element content of UHMWPE particle samples

Samples	Element content (%)			Element ratio	
	C	F	O	F/C	O/C
Virgin	96.2	0	3.8	0	0.039
F-4.0%	41.2	54.2	4.6	1.316	0.112
F-5.5%	39.8	56.0	4.2	1.407	0.106
OF-4.0%	58.2	21.6	20.1	0.371	0.345
OF-5.5%	57.9	21.7	20.4	0.375	0.352

The changes for surface chemical structure induced by reactive fluorine have been characterized by XPS spectroscopy.²⁰ Table 2 shows the surface elemental analysis of UHMWPE particles with different fluorine gas components. The F/C and O/C ratios of the F-4.0% are 1.316 and 0.112, respectively, showing a lot of fluorine atoms introduced, while that of OF-4.0% are 0.371 and 0.345, respectively, indicating both fluorine-containing and oxygen-containing polar groups are introduced on the surface of UHMWPE particles. Difference in functionalities result in entirely different wettability of UHMWPE particles among water.

A detailed composition and nature of the chemical bonds of the samples are investigated by XPS spectra in Figure 3(a) that present C1s spectra of the virgin, F-4.0% and OF-4.0%, respectively. Only strong -C-C- single absorption peak at

284.8eV in the virgin C1s spectrum is observed in Figure 3(b). The F-4.0% and OF-4.0% C1s spectra are fitted to five peaks corresponding to -C-C- at 284.8eV, -C-C=O/-C-CFx at 287.1eV, -C=O at 288.3eV, -C-F at 289.8eV, -C-F₂ at 291.6eV (only for F-4.0% sample) and -CF_x-CF₂ at 293.8eV (only for F-4.0% sample) shown in Figure 3(c) and (d).²¹⁻²³ It is clear that OF-4.0% possesses more oxygen-containing groups but less fluorine-containing groups than F-4.0%. The chemical functionalities on surface-modified particles introduced by fluorination facilitate well wetting and dispersion among water.²⁴

3.3 ATR-FTIR

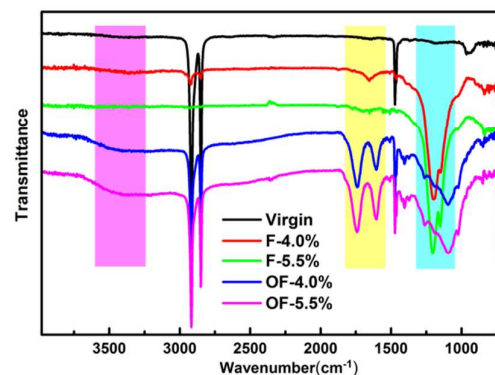


Figure 4 The ATR-FTIR spectra of virgin, F-4.0%, F-5.5%, OF-4.0% and OF-5.5% UHMWPE samples.



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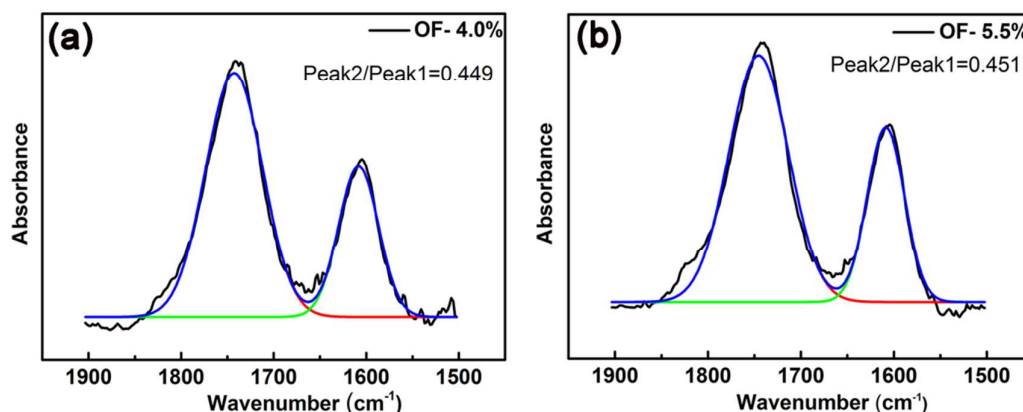


Figure 5 The ratio of -C=O to C=C (by area in the absorption peak) observed in ATR-FTIR spectra of UHMWPE at 1900-1500 cm⁻¹ for (a) OF-4.0% and (b) OF-5.5%.

The changes for surface chemical structure have been also corroborated by ATR-FTIR spectroscopy. ATR-FTIR spectra show that the chemical structure of a fluorinated layer is dependent on fluorine gas components. As presented in **Figure 4**, the characteristic peaks at 2916 and 2849 cm⁻¹ are observed in all of the samples, which are assigned to C-H vibrations of CH₂ groups. One of notable features in the ATR-FTIR spectra of F-4.0% is a very obvious band at 1197.4 cm⁻¹ with a shoulder band at 1146.7 cm⁻¹, corresponding to -C-Fx groups. The C-H vibrations at 2916 and 2849 cm⁻¹ greatly reduce and completely disappear in F-5.5% sample. The surface structure of F-4.0% is similar to a counterpart of Teflon structure and shows hydrophobic properties. The spectrum of OF-4.0% and OF-5.5% substantially differs from that of F-4.0% and F-5.5%. The -C-Fx band in OF-4.0% and OF-5.5% is a very broad diffuse band over 1000-1300 cm⁻¹ region. That means different relative percentage of fluorine-containing groups.⁴

Furthermore, there are three new peaks observed at near 3500, 1735 and 1608 cm⁻¹, attributed to -OH, C=O and C=C bonds, respectively, indicative of forming various oxygen-containing polar groups on the particle surface.²⁵ It is interesting that the ratio of C=C to -C=O (by area in the absorption peak) observed in FTIR spectra is kept at around 0.45 shown in **Figure 5**.

The most interesting finding is that many double bonds are formed through fluorine-activation. The formation process of double bonds is still confused. **Figure 6** shows that there is only C-F group in F-4.0% and F-5.5%. Poor wettability and white color of UHMWPE particles are presented in **Figure 1**, and the surface structure does not change with time and shows well stability. However, what is different in the case of fluorination with substantial oxygen introduced. The samples taken immediately from the reactor, denoted as fresh OF-4.0%, has

many -COF groups (1840.7 cm⁻¹, **Figure 6**) that can be easily transformed into -COOH groups by hydrolysis in the presence of atmospheric moisture or water.²⁶ The -COF groups disappear completely after 12 h in OF-4.0%, and the formation of a double bond is accompanied in **Figure 6**, which is similar to the transformation of unstable end-groups in perfluorinated copolymers. The unstable -C(=O)OH group can be transformed into -CF=CF₂.¹⁴ Therefore, the partial decarboxylation behavior may occur from polymeric backbone when adjacent to the C-F bond with strong attracting electron effect, resulting in the formation of CH=CH structure and byproduct of HF and CO₂.^{15, 17} The possible formation process of double bonds on the surface chemical structure is illustrated in Schematic diagram 1.

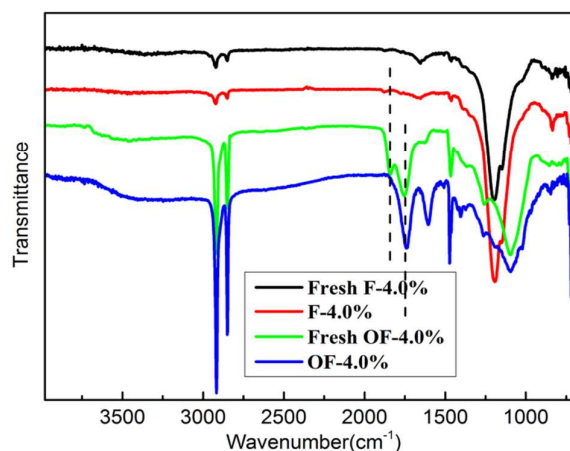
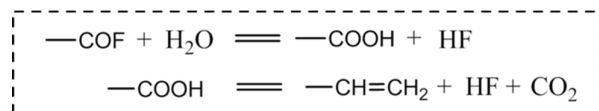


Figure 6 The ATR-FTIR spectra of Fresh F-4.0% and Fresh OF-4.0% samples that were taken immediately from the reactor, and F-4.0% and OF-4.0% samples stored for 12h after taken from the reactor.



Schematic diagram 1 The possible formation process of double bonds on the surface chemical structure on UHMWPE

UHMWPE with those functionalities can be used as precursor, offering a pathway to the subsequent derivatization reactions for further covalent functionalization of UHMWPE. The C=C bonds produced during fluorine-activated process is one of important functionalities, which can be used for further functionalization by addition reaction with F_2 , Br_2 , etc. The OF-4.0% and OF-5.5% samples were re-fluorinated with only fluorine-nitrogen mixture (0.2 bar, 20 min) at room temperature. **Figure 7** presents that the ATR-FTIR spectra and XPS C1s spectra of re-fluorinated UHMWPE. As shown in **Figure 7(a)** and **7(b)**, the C=C at 1608 cm^{-1} disappears after re-

fluorination, and the C=O at 1739.9 cm^{-1} and 1741.2 cm^{-1} shifts to 1754.8 cm^{-1} and 1753.5 cm^{-1} due to the break of conjugated structures that associates with C=O and C=C. Accordingly, the color of UHMWPE particles turns into pristine white color shown in **(Figure 7(b), inset)**. It is speculated that the addition reaction with F_2 may occur during the process of re-fluorination at room temperature. Meanwhile, there is another evidence that supports the speculation of the formation of C=C groups shown in **Schematic diagram 1**.

Surface chemical change induced by re-fluorination was also characterized by XPS measurement. The chemical composition changes are tabulated in **Table 2**. The ratios of F/C in two samples arise from 0.375 and 0.360 to 0.641 and 0.637. There is almost no change in the O/C ratios in both samples. A typical change in XPS C1s is shown in **Figure 7(c)** and **Figure 7(d)** before and after re-fluorination. It can be concluded that the addition reaction is dominant during the OF-4.0% and OF-5.5%

Table 3 The surface element analysis for OF-4.0% and OF-5.5% before and after re-fluorination

Samples	Element content (%)			Element ratio		Chemical formula
	C	F	O	F/C	O/C	
OF-4.0%	57.9	21.7	20.4	0.375	0.352	$\text{C}_1\text{F}_{0.375}\text{O}_{0.352}$
Re-fluorinated OF-4.0%	49.9	32.0	18.1	0.641	0.365	$\text{C}_1\text{F}_{0.375}(\text{F}_2)_{0.133}\text{O}_{0.365}$
OF-5.5%	58.1	20.9	21.0	0.360	0.361	$\text{C}_1\text{F}_{0.360}\text{O}_{0.361}$
Re-fluorinated OF-5.5%	49.6	31.6	18.8	0.637	0.379	$\text{C}_1\text{F}_{0.360}(\text{F}_2)_{0.139}\text{O}_{0.381}$

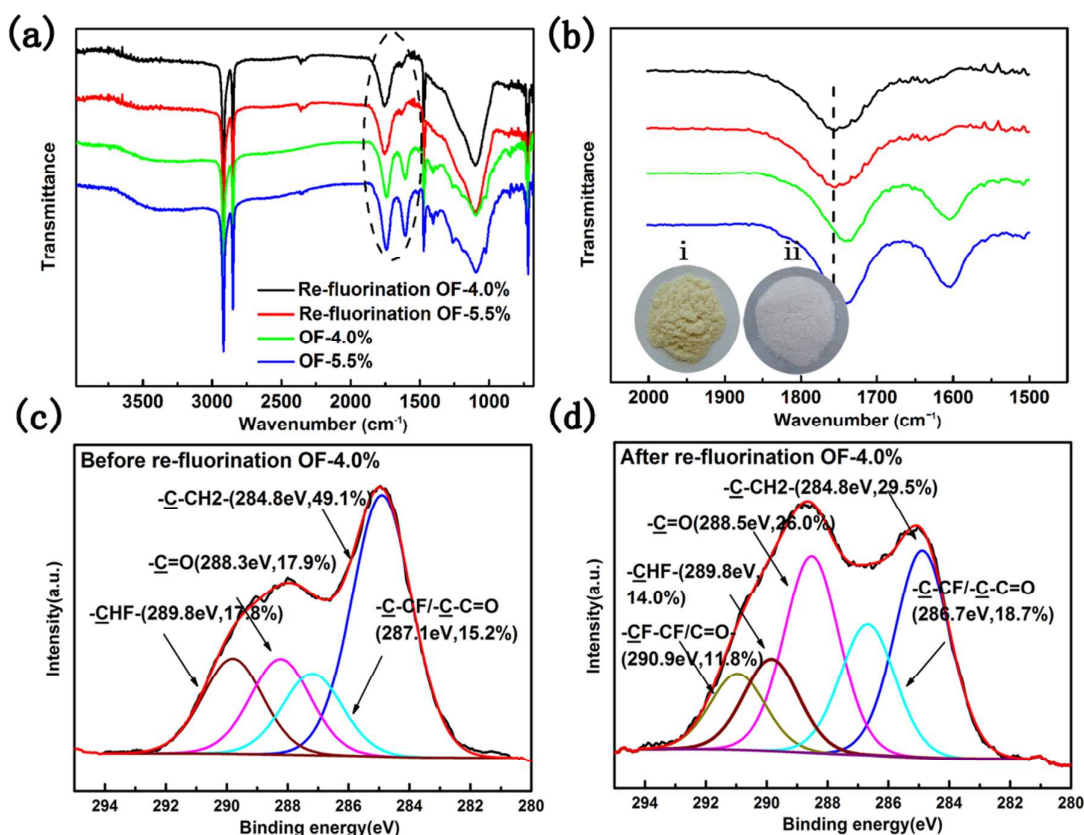


Figure 7 (a) The whole ATR-FTIR spectra of OF-4.0% and OF-5.5% UHMWPE re-fluorinated with only fluorine-nitrogen mixture (0.2 bar, 20 min) at room temperature. (b) The ATR-FTIR spectra of re-fluorinated OF-4.0% and OF-5.5% samples only at $1500\text{--}1900\text{ cm}^{-1}$. The insets correspond to the color of UHMWPE samples for 4.0% before (i) and after (ii) re-fluorination. XPS C1s spectra of UHMWPE before (c) and after (d) re-fluorination for OF-4.0% samples.

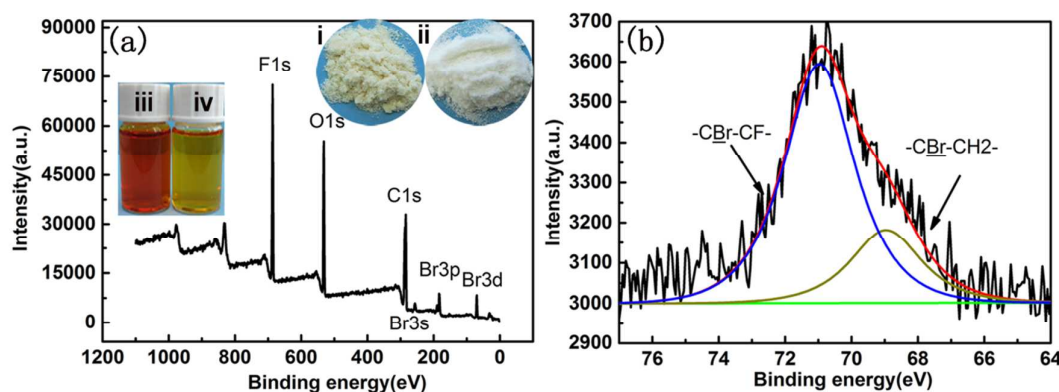


Figure 8 (a) XPS survey scans and (b) XPS Br_{3d5/2} for brominated OF-4.0%-UHMWPE. The insets correspond to the color of OF-4.0% UHMWPE particles before (i) and after (ii) immersed in Br₂/H₂O solution for several hours; the color of bromine water solution before (iii) and after (iv) UHMWPE particles immersed.

samples re-fluorinated process. The elemental ratio in the OF-4.0% and re-fluorinated OF-4.0% is C₁F_{0.375}O_{0.352} and C₁F_{0.641}O_{0.365}. Since a double bond can be reacted with two fluorine atoms in the addition reaction, the composition ratio including fluorine molecule is also written as C₁F_{0.375}(F₂)_{0.133}O_{0.365}. If the increase in fluorine during the re-fluorination is all from the addition reaction, the ratio of C=C among carbon-carbon backbone is 0.133.

Aliphatic double bond is sensitive to Br₂. Addition reactions easily occur between elemental bromine and double bonds, by which it is easy to introduce carbon-bromine bonds.²⁷ The bromination reaction was carried out using Br₂/H₂O solution (3wt % for Br₂). The 4.0%-UHMWPE sample was immersed into Br₂/H₂O accompanied by bath sonication for several hours, and then collected on a filter. The bromine-functionalized

UHMWPE particles were washed in Soxhlet extractor using deionized water and ethanol, and dried overnight in a vacuum oven at 70°C. The color of UHMWPE particles turns into pristine white color shown in **Figure 8 a (ii)**, and the color of bromine water becomes shallower in **Figure 8a (iv)**.

Table 4 The surface element content change for 4.0%-UHMWPE sample before and after immersed in bromine water, before and after amination with ethylenediamine

Samples	Element content (%)				
	C	F	O	N	Br
OF-4.0%	57.9	21.7	20.4	-	-
brominated-4.0%	59.4	20.4	18.1	-	2.1
aminated-4.0%	66.3	9.5	14.2	10.0	-

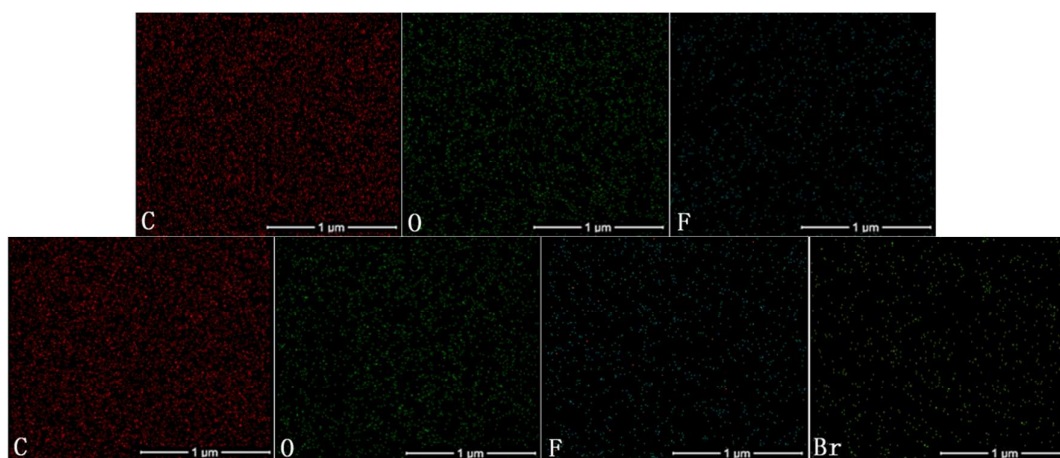


Figure 9 EDX cartography of UHMWPE films (OF-4.0% UHMWPE above, brominated OF-4.0% UHMWPE at the bottom). Attribution to C, O, F and Br elements is indicated at the left bottom corner of each

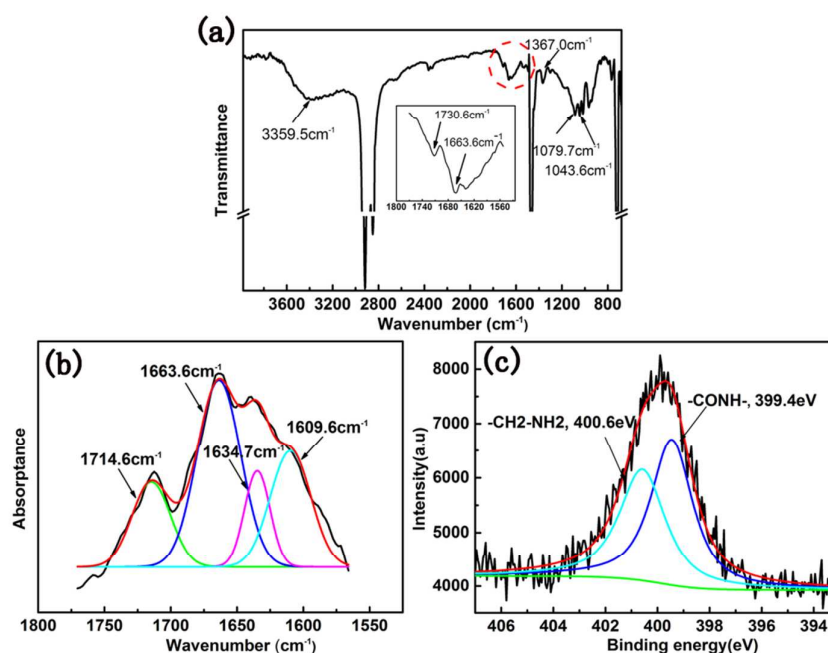


Figure 10 (a) The whole ATR-FTIR spectrum, (b) ATR-FTIR absorption spectrum at 1550–1775 cm^{-1} , and (c) The curve fitting of the N1s spectrum of aminated 4.0%-UHMWPE sample.

The Br peak is obviously observed at XPS survey scans shown in **Figure 8(a)**. Calculating the content of elements on surface of UHMWPE by area of each element, the content of Br is about 2.1 % in **Table 4**, indicating the presence of carbon-bromine bond. It is found that the bromine peaks are fitted to two peaks, centered at 69.3 and 71.0 eV, indicating two different types of C-Br groups, which are assigned to -CBr-CH₂- and -CBr-CF-, respectively.^{28, 29} The distribution of various elements marked with different colors was also detected by EDX cartography (see **Figure 9**), and Br element is uniformly dispersed on the surface. However, due to large size of bromine atom, the addition reaction may occur only upper of fluorinated layer, so there is only a small amount of bromine measured by XPS. Related literatures reported that brominated UHMWPE surfaces, used as starting material, can be further modified to other functionalities through nucleophilic substitution reactions using thiolates, providing a new route for the introduction of desired functionalities to the UHMWPE surface.^{29, 30}

Amino-functionalized reaction was conducted on 4.0%-UHMWPE containing carboxyl groups derived from fluorine-activated behavior. **Figure 10** shows the ATR-FTIR spectrum and XPS N1s spectrum of aminated UHMWPE. A new band emerges at 1663.6 cm^{-1} due to the formation of amide linkages, and 1043.6 cm^{-1} is ascribed to the C-N characteristic stretching

vibrations, while the peak at 3359.5 cm^{-1} can be assigned to the N-H stretching vibrations. In addition, peaks at 1714.6 cm^{-1} and 1609.6 cm^{-1} are the C=O stretching mode of unreacted carboxyl groups and C=C absorption peak in **Figure 10(b)**.³¹ Further evidence for the amino-functionalization coming from the XPS spectrum of amino-functionalized UHMWPE that could reveal the surface chemical state is shown in **Figure 10(c)**. Calculating the content of elements on surface of UHMWPE by area of each element, we can find that the content of N is about 10 %, indicating the presence of -NH groups in **Table 3**. It is found that the N 1s can be fitted to two line shapes with binding energies at 399.4 and 400.6 eV, which are assigned to -CONH- and CH₂-NH₂ in **Figure 10(c)**, respectively.^{32, 33} So far, combining the results of FTIR and XPS analysis, we can confirm that amino groups have been successfully grafted onto the surface of UHMWPE.

Conclusions

The fluorine-activated strategy developed in this work has been successfully applied to improve the surface properties of UHMWPE. A large number of carboxyl groups, double bonds and -C-Fx polar groups are covalently bonded to the macromolecular chain structure based on fluorine-activated process, greatly increasing the surface polarity and wettability.

Carbon-bromine bonds and amino groups have been successfully grafted onto the surface of UHMWPE through subsequent derivatization reactions with bromine and amine-terminated molecules. The fluorine-activated behavior under oxygen atmosphere is thus considered as the effective step toward high-density various surface functionalization.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51573105) and State Key Laboratory of Polymer Materials Engineering (Grant No. sklpme 2014-2-04). The authors acknowledge Analytical & Testing Centre of Sichuan University for characterization.

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