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A simple photochemical method for surface fluorination using perfluoroketones

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ABSTRACT

Surface fluorination of conventional polymers can give them desirable surface properties similar to the expensive and difficult-to-process fluoropolymers. However, traditional surface fluorination techniques often require toxic reagents and special equipment. Here, we report a simple and effective polymer surface fluorination method by using safe and inexpensive perfluoro-2-methyl-3-pentanone (PFMP, $C_2F_5C(=O)CF(CF_3)_2$) and UV irradiation. This method is applicable to various polymer materials, and generates nanometer-thick fluorinated layer on the outermost surface, significantly changing their surface properties without changing the surface morphology.

Among various polymeric materials, fluorine-containing polymers occupy a peculiar and vital niche due to their unique properties such as extremely low surface energy, water and oil repellence, low friction coefficient and chemical inertness [1–3]. However, the application of fluoropolymers is greatly limited by their high production cost and processing difficulty. In addition, perfluoroalkyl and polyfluoroalkyl substances (PFAS) have been called for reduced use because their persistence in environment and potential harmful effects on human health [4–7]. However, a complete ban on PFAS is not realistic as fluorine-containing materials are at least currently irreplaceable in many applications [8]. Thus, new strategy is needed to retain the desirable properties of fluoropolymers while keep their fluorine content to the minimal level.

Since many applications of fluoropolymers mainly involve their surface properties, an ideal approach is to start with conventional polymer materials and simply introduce fluorine-containing moieties on their surfaces (*i.e.,* surface fluorination). During the past decades, several strategies have been developed to achieve the surface fluorination on polymer materials. For example, direct fluorination by exposing polymer surfaces to gaseous fluorine can replace surface hydrogen atoms with fluorine [9,10]. Another effective approach is plasma fluorination *via* the reaction of the plasma generated by the fluorinated gas with the polymer surfaces [11,12]. However, both direct fluorination and plasma fluorination use toxic fluorine-containing gases and require special equipment [13–15]. Surface fluorination reactions can also be achieved by reacting fluorinated reagents (*e.g.,* fluorinated silanes or fluorinated carboxylic acids) with specific functional groups on the polymer surface or by surface grafting polymerization of fluorinated monomers [16–19]. However, this approach requires pre-existing functional groups on the polymer surface, and special fluorine-containing reagents are expensive.

Here, we report a simple, mild and easy-to-operate UV photochemical method for surface fluorination, using perfluoroketone compounds as both the fluorine source and the photosensitizer. Under UV irradiation, it is well known that ketones may undergo two types of reactions: photoreduction and/or α-cleavage reactions [20,21]. In the photoreduction route, the photoexcited ketones abstract hydrogen atoms from polymers and generate polymer radicals [22]. In the α-cleavage route, the ketone compounds directly form two free radical moieties, which may also abstract hydrogen atoms to generate polymer radicals. In either case, polymer radicals can couple with the small molecular radicals, and hence transform the polymer surface C–H bonds into desirable surface functional moieties [23–27]. We hypothesized that, under suitable UV irradiation, perfluoroketones at the polymer surface can act both as a photosensitizer and source for fluorine-containing free radicals, and surface fluorination may be achieved. Furthermore, as the UV-mediated modification only occurs on the surface, it allows the fluorine content in the final product to be minimal.

In this study, we use perfluoro-2-methyl-3-pentanone (PFMP, $C_2F_5C(=O)CF(CF_3)_2$), as a model perfluoroketone compound. PFMP has been commercially produced and widely used as fire extinguishing fluids and electronics coolant liquid. Unlike other fluori-

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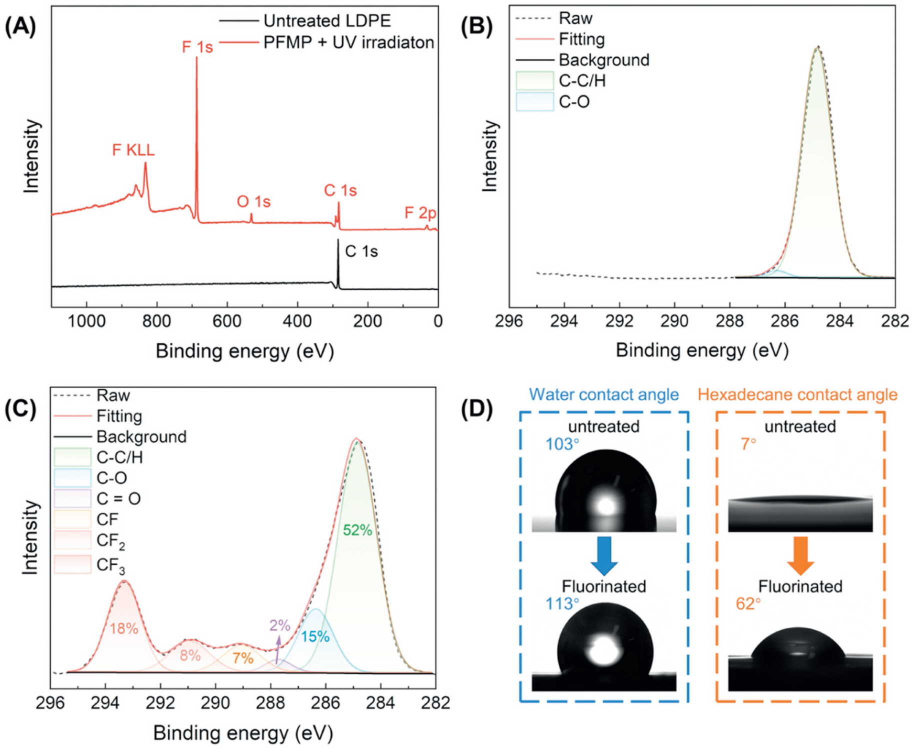


Fig. 1. (A) XPS survey spectra for the LDPE films before and after modification. (B) XPS C 1s spectrum for the untreated LDPE film and (C) LDPE fluorinated with PFMP and UV irradiation for 20 min at the room temperature. (D) Image of the WCA and HCA for the untreated and fluorinated LDPE.

nated compounds, PFMP is safe to use and does not persist in the environment [28,29], representing an ideal compound for surface fluorination. To the best of our knowledge, PFMP and other perfluoroketones have not been used for surface fluorination. Here, we show that surface fluorination is conveniently achieved by coating the surface of polymeric substrates with very little amount of PFMP and then irradiating with a low pressure mercury lamp. This mild modification method is shown to be applicable to many polymer substrates, forming nanometer-thick fluorinated layer and significantly changing their surface properties without changing the surface morphology.

In a typical experiment, 60 µL PFMP was added to the surface of a 4 × 4 cm^2 low-density polyethylene (LDPE) film, and then a biaxially oriented polypropylene (BOPP) film with high UV light transmittance was placed atop to spread the liquid PFMP uniformly (the calculated liquid thickness was about 37.5 µm). The films were then placed in between two quartz plates to fix the setup and then irradiated for 20 min (120 W low pressure mercury lamp, 15 mW/cm^2 at 254 nm). The BOPP films were for placed in between the to-be-treated polymer film and the quartz plates, in order to prevent the latter from being contaminated by the reaction mixture. After irradiation, the LDPE film was rinsed thoroughly with water, sonicated in acetone for 10 min, and subsequently dried and stored in a sealed container prior to characterization. Fig. 1A compares the XPS survey spectrum of the LDPE film before and after the treatment. The untreated LDPE film has only a characteristic XPS signal for carbon, while after the treatment a strong characteristic fluorine signal is clearly observed, followed by a carbon signal and a weak oxygen signal. It is worth noting that no fluorine signal is observed when the LDPE film is only immersed in the PFMP liquid but without UV irradiation (Fig. S1 in Supporting information), indicating that both UV irradiation and PFMP are crucial for the surface fluorination of LDPE films. Detailed investigation of the XPS C 1s spectra by curve fitting confirms the successful fluorination (Figs. 1B and C). For the pristine LDPE, the C 1s spectrum is deconvoluted into two peaks (Fig. 1B): The main peak at 284.8 eV represents the $-\underline{C}-C/H$ bonds, and a small peak at 286.3 eV represents the $-\underline{C}-O$ bonds that comes from slight surface oxidation during the film manufacturing [30]. For the PFMP + UV treated LDPE (Fig. 1C), the C 1s spectra is mainly deconvoluted into the $-\underline{C}-C/H$ peak (peak area percentage 52%), and peaks for $-\underline{C}F_3-$(18%), $-\underline{C}F_2-$(8%), $-\underline{C}F-$(7%) [31]. In addition, there are also $\underline{C}-O$ (15%) and $\underline{C}=O$ (2%) signals. According to the XPS results, the surface C, F, O atomic percentages are 51%, 45%, 4%, respectively (*i.e.,* F/C ratio 0.9). These results demonstrated that the treated LDPE surface is highly enriched with $-CF_n$ groups, especially $-CF_3$. The slight increase of oxygen on the polymer surface may be attributed to photo-oxidation [32–34]. The successful fluorination is also confirmed by ATR-FTIR analysis (Fig. S2 in Supporting information). The LDPE films immersed in PFMP without UV irradiation shows infrared spectrum identical to that of the pristine LDPE film. In contrast, the spectrum of the LDPE films treated with PFMP and UV light shows distinct absorption peak at 1238 cm^{-1} (the C–F bond stretching) and indicates LDPE surface has been fluorinated (Fig. S2) [35].

The surface fluorination of the LDPE film results in significant increase in its *n*-hexadecane contact angle (HCA) from 7.0° to 62.3° (Fig. 1D), which is even higher than the HCA (46°) of polytetrafluoroethylene (PTFE) [36]. Its water contact angle (WCA) also increases from 103.2° to 113.7°, which is within the range of PTFE WCA values reported in the literature (98°–130°) [37]. The stability of the fluorinated surface is evaluated by soaking the treated films in different solvents (organic solvents, acidic and alkali aqueous solutions) for 24 and 72 h, and no significant change is observed in their HCA and WCA values (Fig. S3 in Supporting information).

We then investigate the effect of irradiation time on the F/C ratios and contact angle of the fluorinated LDPE surface. As shown in Fig. 2A and Fig. S4 (Supporting information), the surface F/C ratio almost linearly increases with irradiation time, and reaches a plateau value of 0.9 after 20 min. Fig. 2B shows the water and *n*-

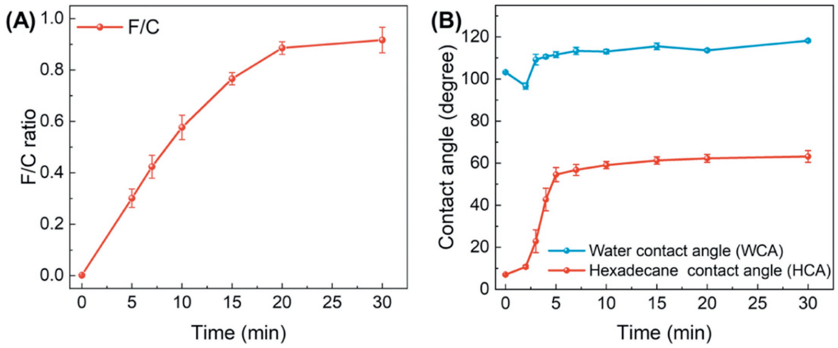


Fig. 2. (A) Surface F/C ratios of LDPE films as a function of UV irradiation time. (B) Water/ hexadecane contact angles of these LDPE films as a function of UV irradiation time.

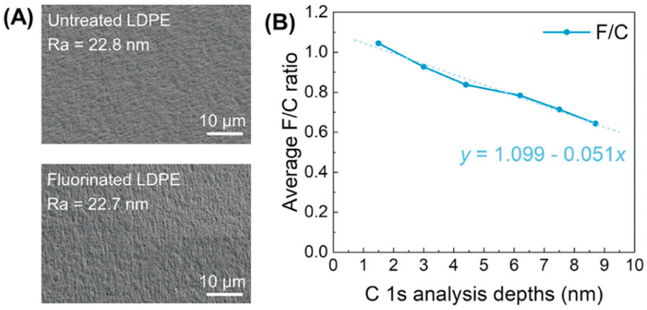


Fig. 3. (A) SEM images for the untreated LDPE film and LDPE fluorinated with PFMP and UV irradiation for 30 min. (B) The F/C ratio of LDPE films fluorinated with PFMP and UV irradiation for 20 min under different analysis depths.

hexadecane contact angles of these LDPE films. The HCA increases rapidly from 7° to 55° after only 5 min of irradiation (the F/C ratio of the corresponding film surface is 0.3). Longer treatment time does not result in further increase in HCA, even though the F/C ratio continues to increase. Similarly, the WCA increases slightly by 10° after irradiation for 5 min, and then barely changed afterwards. These contact angle data suggest that the surface layer of the polymer is rapidly fluorinated after 5 min of irradiation. The initial slight drop of the water contact angle at $t = 2$ min was probably due to the aforementioned photo-oxidation reaction.

The surface morphology of LDPE films before and after treatment are characterized by scanning electron microscope (SEM) and atomic force microscope (AFM). As shown in Fig. 3A, SEM images of both untreated and fluorinated LDPE show relatively smooth surfaces without significant difference between the two. The surface roughness (root mean square, RMS, calculated by AFM, as shown in Fig. S5 in Supporting information) before and after 30 min irradiation are almost the same, 22.8 nm and 22.7 nm, respectively. These results prove that this photochemical method, using low-pressure mercury lamps as the UV source, does not change the surface morphology, which is consistent with the literature [38,39].

In order to see how deep the fluorination reached below the outmost surface layer, the treated LDPE surface are further analyzed with angle-resolved XPS (Fig. 3B). Different photoelectron take off angles from 10° to 90° correspond to analysis depths from 1 nm to 9 nm [40]. As the depth of analysis increases, the F/C ratio decreases almost linearly (Fig. 3B) which can be extrapolated to zero at the analysis depth about 20 nm. The results confirm that irradiation treatment only affects the outermost layers (in the order of 10^1 nm) of the sample.

Next, we explore the applicability of this surface fluorination methods to other polymer surfaces. BOPP, polyurethane (PU) and nylon 66 (PA66) are irradiated with PFMP. Compared to the XPS spectra of the corresponding pristine polymers, there is a significant increase in CF_n on the surfaces of BOPP, PU and PA66 after irradiation for 20 min, and their F/C ratios all reach about 0.6 (Fig. S6 in Supporting information). After the treatment, the WCAs and HCAs of these polymer films also increase to approximately 110° and 60°, respectively, similar to the fluorinated LDPE (Fig. 4). The surface free energy of these polymers before and after fluorination are also characterized (Table 1 and Table S1 in Supporting information), which all drastically decrease compared with the untreated surface and even slightly lower than the PTFE surface free energy (18–19 mJ/m^2) [41].

Table 1
Surface free energies for the pristine and fluorinated polymers.

Polymer	γ_S (mJ/m^2)	
	Pristine	Fluorinated
LDPE	28.1	13.7
BOPP	23.7	15.2
PU	42.6	14.9
PA66	45.6	17.1

As a commercially-used fire extinguishing reagent, PFMP has been mainly studied for its atmospheric chemistry with concerns over its persistence and possible effect on ozone depletion [42–45]. Based on the known PFMP photochemistry and our understanding of UV polymer surface modification chemistry, a possible reaction mechanism is depicted in Scheme 1. As mentioned before, two types of reactions of PFMP may take place under UV irradiation. In Pathway I, PFMP undergoes α-cleavage and produce perfluoroisopropyl and perfluoroethyl radicals [42]. These fluorinated radicals, especially the perfluoroisopropyl radicals, have a high hydrogen atom abstraction reactivity [46]. Thus, the fluorinated radicals may abstract hydrogen atoms from the polymer and generate surface radicals. In Pathway II, PFMP in the photoexcited state undergoes photoreduction, abstract hydrogen atoms from the polymer surface, and consequently generate fluorinated radicals with a hydroxyl group and polymer surface radicals. Eventually, the surface radicals couple with these fluorine-containing radicals, achieving surface fluorination. Since the XPS data indicate no correlation between the oxygen and fluorine content at the treated surface, we suspect that Pathway II is at least not dominating, and Pathway I might be the more important reactions.

Finally, we explore the potential applications of these fluorinated polymers in terms of oil repellence. As shown in Fig. 5, soybean oil in which Sudan I is added for visual contrast spread easily on and soak into the untreated BOPP films. In contrast, after the double-sided fluorinated BOPP films are immersed in the same soybean oil and taken out, the oil on the surface shrinks

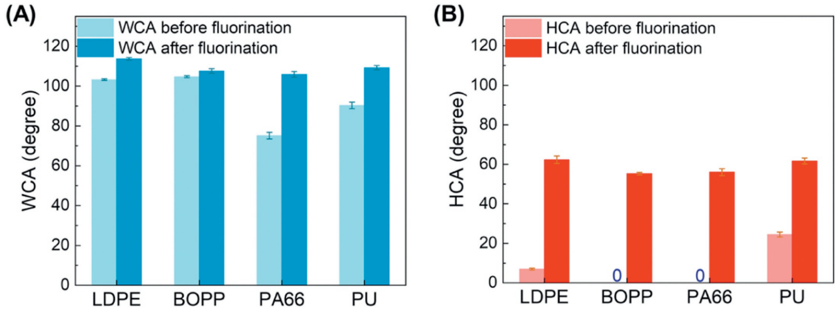
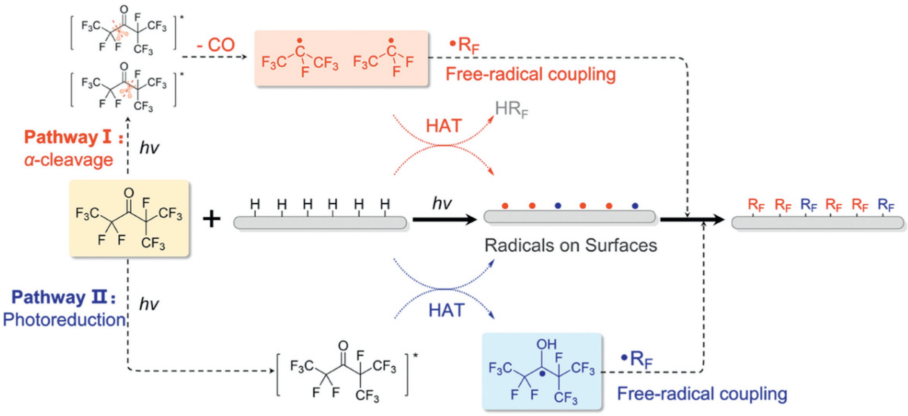


Fig. 4. The (A) water contact angles and (B) hexadecane contact angles for the untreated and fluorinated polymers.



Scheme 1. Proposed mechanism of surface fluorination using PFMP under UV irradiation.

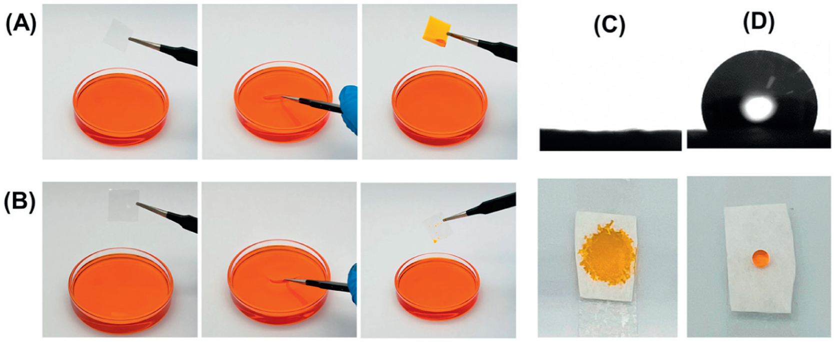


Fig. 5. Images of untreated (A) and double-sided fluorinated (B) BOPP after immersing in soybean oil. Image of the HCA and the surface after being dripped with soybean oil for the untreated (C) and fluorinated (D) non-woven fabric.

sponteaneously into droplet, which in turn slides off, recovering a clean film surface. We also test the effect of surface fluorination on improving the oil resistance of nonwoven fabric (NWF). The untreated NWF is superoleophilic, and soybean oil added to its surface quickly penetrates to the interior and contaminate a large area. After the NWF is treated with PFMP, the HCA reaches 114°, and the same volume of soybean oil added to its surface form stable droplets, avoiding the contamination by oil stains.

In conclusion, we reported a facile and efficient approach to achieve surface fluorination of polymeric materials by using the safe and inexpensive PFMP and low energy UV irradiation. This method has the following advantages: (1) safe and convenient, no toxic or expensive reagents/special equipment is required; (2) only the outmost surface layer is modified, without changing the surface physical structure; (3) suitable for many materials with C–H bond on its surface; (4) economically viable by using low pressure mercury lamps with low power consumption. Furthermore, currently perfluoroalkyl and polyfluoroalkyl substances (PFAS) are being banned or restricted from production and use due to their potential environmental and health hazards, and their replacement for many applications (*e.g.,* oil resistant materials) is urgently needed. Our approach may be an effective solution to this problem, by creating a very thin fluorine-containing layer to the surface of common polymers. However, we do realize that, though only small amount of PFMP is used for the surface modification and its reaction product is also supposedly little, the environmental effect in the long term should be studied before this technology is put into practice.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.109339.

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