ABSTRACT: Fluorination modification is an effective way to improve the friction property of a polymer; however, current preparation of fluorine-containing polymers is limited by the high cost and complex synthesis. Here, an industrial fluorination strategy with gaseous fluorine (F_2) to achieve fluorine enrichment on the surface of a polyurethane (PU) sheet was demonstrated. Benefiting from the high reactivity and strong diffusion of F_2 gas, the as-prepared PU sample was characterized by the rich fluorinated surface with the slightly fluorinated bulk. As a result, the fluorinated PU combined the excellent mechanical properties of pristine PU with the unique function of the fluorine-containing polymer, where the fluorinated surface may function as a robust lubricating layer, contributing to remarkable promotion of friction property while maintaining the mechanical strength unchanged. The friction coefficient decreased to 0.5 at the dry condition and 0.1 at the wet condition from the initial value of 1 and 0.45 for the pristine PU sample. The surface manipulation via direct fluorination offers great opportunities to tailor the friction property while keeping the mechanical strength unchanged.

INTRODUCTION

Benefiting from tailored hard and soft segments, polyurethane (PU) presents an excellent combination of stiffness, elasticity, and abrasion resistance and thus is widely used as a sealing material to produce transport belt, bearing, valve seals, O-rings in aircraft, and marine industry. However, the friction coefficient is high with poor self-lubrication, so that in large sealing devices running under high frequency, huge stress followed by a sharp increase in friction heat often causes serious damage of the PU material. Therefore, it is critical to reduce the friction coefficient for high-performance PU sealing materials.

Currently, there are two main strategies to ameliorate the tribological performance of the PU material. One common way is to incorporate self-lubricating fillers into the PU matrix. Golaz investigated the effects of graphite, TiO_2, MoS_2, SiO_2, and ZrO_2 particles on the tribological properties of wax-containing PU composites and revealed that the lowest friction coefficient of 0.53 was achieved at 10 wt % ZrO_2 and 15 wt % MoS_2. Yang utilized the strong load-carrying ability of multiwalled carbon nanotubes and the excellent lubricant capacity of MoS_2 to greatly reduce the friction coefficient of the PU coating. However, homogenous dispersion of lubricating fillers and good interfacial interaction with the PU matrix still remain challenges, and the introduction also can change the mechanical properties of the PU bulk. Another strategy for lowering the friction coefficient is to embed fluorine-containing groups into the PU chain by copolymerizing the fluoro-comonomer. It is well-documented that the fluorine (F) atom has a small atomic radius and a strong electronegativity. When the F atoms are introduced into polymer chain, the C–F bond can completely cover the C–C main chain, providing shielding and protecting effects on the main chain. As a result, fluorine-containing polymers often have excellent thermal and chemical stabilities, antifouling behavior, and a low friction coefficient. Tonelli reacted a fluorinated macrodiol with poly(tetramethylene glycol) and 4,4’-methylene-bis-phenylisocyanate via two-step polymerization technique to synthesize a fluoro-modified PU with perfluoropolyether blocks. However, the introduction of fluorine-containing units by chemical methods involves some issues, such as time consumption and complex fabrication, limited sources and low reactivity of fluorine-containing reagents, and difficulty to control reaction conditions.
economical strategy. Due to the quick diffusion and strong reactivity, direct fluorination by reacting gaseous fluorine with surface molecules is considered as an effective industrial technology and is applied widely to modify the surface nature of most materials.\(^\text{13}\) Compared to bulk fluorination, surface fluorination proceeds at a mild condition without a complex synthesis, and the thin fluorinated layer of below 10 \(\mu\)m thickness can endow polymer articles with special nature such as barrier property, chemical resistance, friction property, adhesion, and printability while maintaining the bulk physical properties unchanged.\(^\text{14}\) Jeong adopted direct fluorination to decorate the aramid fabric surface to enhance the interfacial interaction with the polymer matrix for improving the mechanical properties of polymer composites.\(^\text{15}\) Vega-Cantu generated a fluoropolymer surface on nitrile rubber O-rings by exposure to \(\text{F}_2\) to enhance the chemical resistance to \(\text{ZnBr}_2\) brines at high temperatures and pressures.\(^\text{16}\) Direct fluorination is also used to bring down the friction coefficient of polymer products, where the fluorinated layer can act as a shielding layer to provide additional lubrication effect.\(^\text{17}\) Gao adopted direct fluorination to modify the fluoroelastomer to decrease the surface energy and ameliorate the friction properties, as evidenced by a substantial decrease in the friction coefficient from 1.04 of the untreated sample to 0.5 of the fluorinated sample.\(^\text{18}\) Peyroux introduced 3.41\% fluorine atoms on the surface of low-density polyethylene by exposing a reactive \(\text{N}_2/\text{F}_2\) gaseous mixture, providing excellent tribological properties close to those of the reference PTFE.\(^\text{19}\) Although direct fluorination has been applied successfully to elastomer, polyethylene and polypropylene, there is little published work on the friction reduction of the PU material as well as the fluorination mechanism. Here, we performed the direct fluorination of the PU sample through gaseous fluorine and compared the chemical characteristics near the surface with the pristine PU, probing the reaction mechanism of surface fluorination. Finally, the structure-property relationship of the fluorinated PU was investigated comprehensively. This study sufficiently demonstrated the potential of direct fluorination in friction reduction of the PU material, providing a low-cost, highly efficient surface modification technology for preparing high-performance PU materials.

## EXPERIMENTAL SECTION

**Materials.** PU sheets with a urethane-based hard segment and a poly(\(\varepsilon\)-caprolactone) soft segment were provided kindly by Wanhua Chemical Group.

**Sample Preparation.** The 25 cm \(\times\) 25 cm \(\times\) 0.2 cm PU sheets were placed into the fluorination device (Jiangsu Rotam Boxmore Packaging Co., Ltd., China), and then the air was removed. Next, the \(\text{F}_2/\text{N}_2\) gaseous mixture (20 vol \% for \(\text{F}_2\)) was injected, and the pressure was elevated to 500 mbar. The temperature of the fluorination process was kept constant at 50 °C for 2.5 h. The sample was named as F-PU.

**Characterization.** Scanning Electron Microscopy Observation. The surface and cross-sectional morphologies of the films were observed by a FEI Inspect FSEM instrument (FEI, USA) with an acceleration voltage of 5 kV. The elemental compositions were characterized by energy-dispersive X-ray spectrometry (EDS) combined with scanning electron microscopy (SEM). The view field illustration is shown in Figure 1.

**Fourier Transform Infrared Spectroscopy.** The chemical compositions of the PU films were investigated in the attenuated total reflection mode using a Nicolet 20SXB FTIR spectrometer (Thermo Fisher Scientific Inc., USA). The spectra were collected from 4000 to 650 cm\(^{-1}\).

**X-ray Photoelectron Spectroscopy.** The surface nature was analyzed by an AXIS ULTRA DLD multifunctional X-ray photoelectron spectrometer (Shimadzu/Kratos Ltd., Manchester, UK) with the excitation at 1486.8 eV from an Al K alpha.

**Contact Angle.** The contact angles (CAs) of the films were investigated by a Kruss DSA25 optical contact angle analyzer (Hamburg, Germany) at room temperature with 5 \(\mu\)L of water and ethanediol droplets.

**Friction Properties.** The friction coefficients were measured with a M-200 friction and wear testing machine (Guance Jingdian Instrument Equipment Co., Ltd., Beijing). The load applied was 5 kg, and the sliding speed was 50 rpm. In order to test the friction coefficient at the wet condition, a water droplet of about 0.05 mL was dripped on the sample surface, and then the friction coefficients were measured at the same condition.

**Cyclic Mechanical Properties.** The tests were divided into cyclic tensile, compressing, and bending with different sample dimensions (2 mm \(\times\) 15 mm for tensile; 10 mm \(\times\) 10 mm for compressing; 2 mm \(\times\) 15 mm for bending). Then, the specimens were measured by a Boss 3220 SERIES II electronic universal testing machine (Bose, USA) with strains of 20, 10, and 100\% for 500 cycles, and the frequency was 1 Hz.

**Thermogravimetric Analysis.** The samples were measured in the temperature range of 40–700 °C with a constant heating rate of 10 °C/min using a Q50 thermal gravimetric analyzer (TA Instruments Co. Ltd., New Castle, DE, USA).

## RESULTS AND DISCUSSION

**Fluorination-Enabled Structure.** The element compositions and distributions in the sample were analyzed by EDS combined with SEM. As shown in Figure 2, the surface of the PU sheets became slightly rougher after fluorination. Moreover, it was found that direct fluorination was an effective way to introduce F elements to the PU sample. Figure 2 also presents the elemental distributions from EDS analysis scanned over the pristine PU surface, fluorinated PU surface, and cross section. One should note that few fluorine elements were present on the surface of the pristine PU where trace amounts of fluorine (1.89\%) may originate from the signal noise. In addition to the C, N, and O elements contained in the PU sample itself, rich F elements appeared after fluorination treatment with \(\text{F}_2\) gas. Moreover, different chemical compositions between the surface and bulk were observed. The mapping images of F elements (Figure 2g and
k) clearly revealed that the F element was mainly distributed on the surface rather than in the bulk. Compared to the high F content of 14.92 wt % on the surface, a clear decrease in F elements on the cross section (2.9 wt %) supported the preferential attachment of F element onto the surface. Considering the high reactivity and strong diffusion rate of F₂ gas as well as the amorphous characteristics of the PU matrix, it should be reasonable that the bulk sample was partially fluorinated.

In order to reveal the surface fluorination mechanism, IR and X-ray photoelectron spectroscopy (XPS) analyses were combined to characterize the variation of the surface chemical bonds after fluorination treatment. Figure 3 shows the IR spectra of the pristine PU sample and the fluorinated sample. For the pristine PU sample, the characteristic peaks appeared at 3334, 2951, 1725, and 1530 cm⁻¹ corresponding to N–H stretching vibration, C–H aliphatic stretching vibration, C=O stretching vibration, and N–H bending vibration, respectively. After fluorination treatment, the characteristic peaks from the C–H stretching vibration and N–H bending vibration became weaker compared to the invariable peak at 964 cm⁻¹ corresponding to the standard C–C stretching vibration, while the new absorption peaks at 737 cm⁻¹ from the C–F rocking and wagging vibrations were excited, implying that the fluorine element was introduced to the PU sample. One also notes that there were multi broad peaks over 3000–3600 cm⁻¹ corresponding to the formation of the −OH group and the accompanying hydrogen bonding with −NH groups. The −OH group was related to the fluorination of the −CONH− group followed by the resulting −COF group hydrolysis. For example, Leu investigated the −COF group formation followed by partial hydrolysis into the −COOH group in the fluorinated polyimide and poly(methyl-methacrylate) surfaces.

The XPS measurements verified the fluorine enrichment on the PU surface upon fluorination treatment, as illuminated in Figure 4. The survey spectra showed that no peak assigned to the fluorine element was detected in the pristine PU sample, while the F-PU sample contained the F peak in a range of 682–692 eV. The F content in the F-PU sample was 21.7%, higher than the EDS result in Figure 2h. This increase essentially originated from the different test depth of XPS (10 nm) and EDS measurements (1 μm). This also supported the surface fluorination with little effect on the bulk. Further, the detailed spectra in C₁s, N₁s, and O₁s regions were shown to reveal different chemical bonding states in the PU and F-PU samples, with different profiles composed of the deconvoluted peaks (Figure 4b–d and f–h). For the C₁s XPS spectra, one can observe two additional CHF and C–F peaks at 287.5 and
290.2 eV besides the peaks of C–C, C–N, and C–O groups at 284.8, 285.7, and 289.7 eV. The formation of the fluorine-containing groups signified that direct fluorination introduced the F element onto the PU surface. Turning to the N 1s range, a single peak at 400.3 eV corresponding to the C–N group was observed in the pristine PU sample, in good agreement with the typical XPS result of the reported PU sample. After fluorination, the shift to higher energy indicated the formation of new N species, which can be attributed to strong electron-withdrawing substituents of F and O atoms attached to N atoms. Accordingly, 401.6 and 403.2 eV were assigned to the N–O group and the N–F group. The formation of N–F groups suggested that F replaced H in the N–F, while the N–O group reflected partial hydrolysis of the C–N bond, as evidenced by the presence of N–F and O–H groups.

Fluorination-Enabled Surface Property. The introduction of C–F bonds and –COOH groups into the F-PU surface via direct fluorination modified the surface nature. Figure 5 displays the CAs of the samples with deionized water and ethanediol. The pristine PU sample was highly hydrophobic, and the CAs of water and ethanediol were 114.7 and 90.1°. Direct fluorination reduced the two values to 51.5 and 29.8° and increased the surface energy from 19.3 mN/m of the pristine PU sample to 47.9 mN/m so that the resulting F-PU sample became hydrophilic.
energy and hydrophobic property of the typical fluorine-containing polymer, the hydrophilic nature was essentially attributed to the $-\text{COOH}$ group generated by the cleavage of the $\text{C}^{-}\text{N}$ bond.

**Fluorination-Enabled Friction Property.** By integrating individual virtues of PU and the fluorinated polymer, the resulting F-PU sample exhibited excellent comprehensive properties. The variation of friction coefficient at dry and wet conditions was evaluated. As shown in Figure 6a–c, the F-PU sample exhibited a lower friction coefficient than the pristine PU sample. At the dry wearing process, the pristine PU was characterized with a high friction coefficient of 1–1.5. The increase in the friction coefficient should be attributed to the friction heat generated during the tribological test. Moreover, the triboelectric property was determined by the surface nature. Inheriting the merits of the F-containing polymer, the fluorinated surface endowed the F-PU sample with excellent self-lubricating property, decreasing the friction coefficient to 0.5–0.7.

When water was introduced into a polymer–metal sliding interface, the friction coefficient of the two samples decreased sharply, originating from the additional slippage function provided by water located at the specimen/the counterpart cylinder interface. However, the pristine PU sample was characterized by poor stability. Within the first 30 s of the test, the friction coefficient kept a low value of $\sim$0.5 and quickly increased to $\sim$1.5. The drastic fluctuation of the friction coefficient was derived from the water-repellent property initiated by the hydrophobic nature of the PU sample. In this case, the loaded water absorbed ineffectively onto the surface, resulting in a gradual decrease of water at the interface during the testing process (Figure 6d). Finally, the additional sliding against the counterpart cylinder conferred by water disappeared, and the value became similar to the value tested under dry conditions. On the contrary, the $-\text{COOH}$ groups in the F-PU surface caused the hydrophobicity-to-hydrophilicity transformation, favorable to the water spread and fixation on the surface. Therefore, at the wet wearing process, the added water was immobilized tightly on the sample surface and served as a stable lubricating layer, keeping the friction coefficient at $\sim$0.1. As shown in Figure 6d, the water presented good spread at the F-PU surface after 20 cycles.

**Bulk Properties of Fluorinated PU.** Because direct fluorination only achieved the F enrichment on the surface, the bulk properties can be well maintained. Figure 7 evaluates the resistances of the PU and F-PU samples to various mechanical deformations (tensile, compression, and bending stress), with the corresponding results. It can be found that although the F-PU sample exhibited excellent friction resistance, the mechanical properties of the bulk were nearly unchanged. For example, the tensile modulus was 3.5 MPa, approaching 3.3 MPa of the PU sample. The small thickness of the fluorinated layer should be responsible for the similar mechanical properties. It is worth pointing out that the F-PU
sample also preserved the original fatigue performance, with stable mechanical strength in ∼500 cycles, as was presented in Figure 7a.

Further, the thermal stabilities of the PU and F-PU samples were compared by thermogravimetric analysis (TGA), as shown in Figure 8. One can observe that the two PUs exhibited a two-stage decomposition process, where the first
degradation step at 360 °C corresponds to the cleavages of the urethane bonds in hard segments, while the second step at 370–450 °C corresponds to the scission of soft segments. Moreover, the initial decomposition temperature and the maximum degradation rate remained similar, suggesting that the fluorinated layer was very thin, so that the thermal stability was influenced hardly.

Accordingly, it can be concluded that compared to the other preparation methods of fluorinated PU, this direct fluorination is featured with low energy consumption and a simple and mild process and can offer adequate strong coating of F elements onto the sample without affecting the bulk, holding promising potential in industrial fabrication of high-performance self-lubricating PU materials.

## CONCLUSIONS

In this study, direct fluorination of the PU sample through F gas was adopted to achieve fluorine enrichment on the PU surface. As a result, a fluorinated layer was constructed by F substitution of H atom in the −CH2− segments, and the hydrophobicity-to-hydrophilicity transformation was initiated by the cleavage of the C–N bond. Benefiting from the rich fluorinated surface and water fixation, the fluorinated PU sample exhibited excellent comprehensive properties. The friction coefficient decreased to 0.5 at the dry condition and 0.1 at the wet condition from the initial value of 1 and 0.45 for the pristine PU sample, while the mechanical strength and thermal property kept unchanged. This study sufficiently demonstrated the potential of direct fluorination in friction reduction of the PU material, providing a low-cost, highly-efficient surface modification technology for preparing high-performance PU materials.

## AUTHOR INFORMATION

**Corresponding Authors**

Changhua Yang — State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China;
Email: yangchanghua18@163.com

Ming Nie — State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China; orcid.org/0000-0001-8386-7547; Phone: +86-28-85405133; Email: poly.nie@gmail.com; Fax: +86-28-85405133

**Author**

Xue Yang — Institute of Noise and Vibration, Naval University of Engineering, Wuhan 430033, China; Key Laboratory on Ship Vibration & Noise, Wuhan 430033, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c03019

**Notes**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work is financed by the National Natural Science Foundation of China (52171323) and the State Key Laboratory of Polymer Materials Engineering (sklpme2019-2-11).

## REFERENCES

1. Chattopadhyay, D. K.; Raju, K. V. S. N. Structural Engineering of Polyurethane Coatings for High Performance Applications. Prog. Polym. Sci. 2007, 32, 352–418.
2. Kim, Y.-S.; Lee, J.-S.; Ji, Q.; McGrath, J. E. Surface Properties of Fluorinated Oxetane Polyol Modified Polyurethane Block Copolymers. Polymer 2002, 43, 7161–7170.
3. Wu, H.; Li, X.; Gao, X.; Chen, D.; Li, Z. Development and Application of Water Sealing Technology for Gas Drainage Boreholes. ACS Omega 2022, 7, 733–743.
4. Jiao, X.; Feng, Z.; Jiao, Q.; Xu, L.; Li, C.; Guo, B.; Feng, C.; Zhao, Y. Fluorinated Polyurethane-based Enamelled Wires with a Low Friction Coefficient. ACS Omega 2021, 6, 4719–4725.
5. Wang, S.; Yang, X.; Su, W.; Li, Y. Fabrication of Polyurethane-based Composites Used in Water-lubricated Bearings. Adv. Polym. Technol. 2014, 33, 21421.
6. Yang, X.; Zhang, Z.; Zhang, T.; Nie, M.; Li, Y. Improved Tribological and Noise Suppression Performance of Graphene/Nitrile Butadiene Rubber Composites via the Exfoliation Effect of Ionic Liquid on Graphene. J. Appl. Polym. Sci. 2020, 137, 49513.
7. Golaz, B.; Tetouani, S.; Diomidis, N.; Michaud, V.; Mischler, S. Processing and Tribology of Thermoplastic Polyurethane Particulate Composite Materials. J. Appl. Polym. Sci. 2012, 125, 3745–3754.
8. Zhang, Z. Z.; Yang, M. M.; Yuan, J. Y.; Guo, F.; Men, X. H. Friction and wear behaviors of MoS2-multi-walled-carbonnanotube hybrid reinforced polyurethane composite coating. Friction 2019, 7, 316–326.
9. Lin, C.; Tian, Q.; Chen, K.; He, G.; Zhang, J.; Liu, S.; Almasy, L. Polyester Bonded Explosives with Highly Tunable Creep Resistance Based on Segmented Polyurethane Copolymers with Different Hard Segment Contents. Compos. Sci. Technol. 2017, 146, 10–19.
10. Yang, W.; Cheng, X.; Wang, H.; Liu, Y.; Du, Z. Surface and Mechanical Properties of Waterborne Polyurethane Films Reinforced by Hydroxyl-terminated Poly(2-fluorooalkyl methacrylates). Polymer 2017, 133, 68–77.
11. Yi, L.; Meng, X.; Tian, X.; Zhou, W.; Chen, R. Wettability of Electrospun Films of Microphase-separated Block Copolymers with 3,3,3-trifluoropropyl Substituted Siloxane Segments. J. Phys. Chem. C 2014, 118, 26671–26682.
12. Tonelli, C.; Ajrola, G. New Fluoro-modified Thermoplastic Polyurethanes. J. Appl. Polym. Sci. 2003, 87, 2279–2294.
13. Fu, K.; Lu, C.; Liu, Y.; Zhang, H.; Zhang, B.; Zhang, H.; Zhou, F.; Zhang, Q.; Zhu, B. Mechanically Robust, Self-healing Super-hydrophobic Anti-icing Coatings Based on a Novel Fluorinated Polyurethane Synthesized by a Two-step Thiol Click Reaction. Chem. Eng. J. 2021, 404, 127110.
14. du Toit, F.; Sanderson, R. Surface Fluorination of Polypropylene: 1. Characterisation of Surface Properties. J. Fluorine Chem. 1999, 98, 107–114.
15. Kharitonov, A. P.; Simbirseva, G. V.; Bouznik, V. M.; Chepeuzhov, M. G.; Dubois, M.; Guérin, K.; Hamwi, A.; Kharbache, H.; Masin, F. Modification of Ultra-high-molecular Weight Polyethylene by Various Fluorinating Routes. J. Polym. Sci. Pol. Chem. 2011, 49, 3559–3573.
16. Kharitonov, A. P.; Simbirseva, G. V.; Bouznik, V. M.; Chepeuzhov, M. G.; Dubois, M.; Guérin, K.; Hamwi, A.; Kharbache, H.; Masin, F. Modification of Ultra-high-molecular Weight Polyethylene by Various Fluorinating Routes. J. Fluorine Chem. 2005, 126, 251–263.
17. Jeong, E.; Lee, B. H.; Doh, S. J.; Park, I. J.; Lee, Y.-S. Multifunctional Surface Modification of an Aramid Fabric via Direct Fluorination. J. Fluorine Chem. 2012, 141, 69–75.
18. Vega-Cantú, Y.; Hauge, R.; Norman, L.; Billups, W. E. Enhancement of the Chemical Resistance of Nitrile Rubber by Direct Fluorination. J. Appl. Polym. Sci. 2003, 89, 971–979.
19. Kharitonov, A. P. Practical Applications of the Direct Fluorination of Polymers. J. Fluorine Chem. 2000, 103, 123–127.
(20) Gao, J.; Xu, X.; Fan, C.; Wang, X.; Dai, Y.; Liu, X. Surface Modification of Fluoroelastomer by Direct Fluorination with Fluorine Gas. Mater. Lett. 2014, 121, 219–222.

(21) Peyroux, J.; Dubois, M.; Tomasella, E.; Batisse, N.; Kharitonov, A. P.; Flahaut, D.; Romana, L.; Thomas, P. Surface Modification of Low-density Polyethylene Packaging Film via Direct Fluorination. Surf. Coat. Technol. 2016, 292, 144–154.

(22) Alessandro, C.; Marcella, G.; Fabio, D.; Fabio, S.; Armandodoriano, B. Azo-pigments effect on UV degradation of contemporary art pictorial film: A FTIR-NMR combination study. Polym. Degrad. Stab. 2017, 140, 74–83.

(23) Ge, Z.; Zhang, X.; Dai, J.; Li, W.; Luo, Y. Synthesis, Characterization and Properties of a Novel Fluorinated Polyurethane. Eur. Polym. J. 2009, 45, 530–536.

(24) Shi, S.; Yang, C.; Nie, M. Enhanced Interfacial Strength of Natural Fiber/Polypropylene Composite with Mechanical-interlocking Interface. ACS Sustainable Chem. Eng. 2017, 5, 10413–10420.

(25) Kharitonov, A. P.; Moskvin, Y. L.; Teplyakov, V. V.; Le Roux, J. D. Direct Fluorination of Poly(vinyl trimethylsilane) and Poly(phenylene oxide). J. Fluorine Chem. 1999, 93, 129–137.

(26) Cheng, Z.; Wu, P.; Gao, J.; Wang, X.; Ren, M.; Li, B.; Luo, L.; Liu, X. Structural Evolution of Fluorinated Aramid Fibers with Fluorination Degree and Dominant Factor for Its Adhesion Property. J. Fluorine Chem. 2016, 188, 139–146.

(27) Leu, J.; Jensen, K. F. Fourier Transform Infrared Studies of Polyimide and Poly(methyl-methacrylate) Surfaces during Downstream Microwave Plasma Etching. J. Vac. Sci. Technol., A 1991, 9, 2948–2962.

(28) Lee, J. H.; Kim, K. H.; Choi, M.; Jeon, J.; Yoon, H. J.; Choi, J.; Lee, Y.-S.; Lee, M.; Wie, J. J. Rational Molecular Design of Polymeric Materials Toward Efficient Triboelectric Energy Harvesting. Nano Energy 2019, 66, 104158.

(29) Wu, L.; Chen, X.; Zou, L.; Hu, D. X-Ray Photoelectron Spectroscopy and Atomic Force Microscopy of High-solid Polyurethane Resins. Int. J. Polym. Anal. Charact. 2003, 8, 83–98.

(30) Solomun, T.; Schimanski, A.; Sturm, H.; Illenberger, E. Efficient Formation of Difluoramino Functionalities by Direct Fluorination of Polyamides. Macromolecules 2005, 38, 4231–4236.

(31) Prorokova, N. P.; Kumeeva, T. Y.; Vavlrova, S. Y. Improving the Wettability of Polyester Fabric with Using Direct Fluorination. J. Fluorine Chem. 2019, 219, 115–122.

(32) Cheng, Z.; Wu, P.; Li, B.; Chen, T.; Liu, Y.; Ren, M.; Wang, Z.; Lai, W.; Wang, X.; Liu, X. Surface Chain Cleavage Behavior of PBIA Fiber Induced by Direct Fluorination. Appl. Surf. Sci. 2016, 384, 480–486.

(33) Chattopadhyay, D. K.; Webster, D. C. Thermal Stability and Flame Retardancy of Polyurethanes. Prog. Polym. Sci. 2009, 34, 1068–1133.