

Elaborating Polyurethane Pillow Soft Mat on Polypropylene Monofilament Surface with Stepwise Surface Treatments

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Abstract The dissatisfactory mechanical compliance between stiff polypropylene (PP) and soft human tissue is one of the main factors causing the implanted complication of PP mesh devices such as chronic abdominopelvic pain and mesh exposure. This work aims to improve the mechanical compliance of PP monofilament to human tissue without compromising the mechanical properties by elaborating polyurethane pillow soft mat on the PP monofilament surface. Combining polarity pretreatment with dopamine-sedimentation, stiff PP monofilament can be wrapped up facily and tightly in soft polyurethane to obtain PU/PP complex fiber with a core-shell structure. Notably, the interfacial shear strengths (IFSS) between stepwise treated PP monofilament and PU mat can effectively increase 586% compared to raw PP. This work provides a promising surface modification strategy to improve the interfacial adhesion between PP monofilament and PU mat. The obtained novel PU/PP complex fiber with pillow soft mat would be a potential application in abdominal wall defects, hernia repair and pelvic organ prolapsed surgery.

Keywords Polypropylene monofilament; Polyurethane; Interfacial adhesion; Surface treatment; Dopamine-sedimentation

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INTRODUCTION

The excellent physicochemical properties of polypropylene (PP), such as mechanical properties, light weight and biological stability, make it as one of the most used non-degradable synthetic mesh materials for abdominal wall defects, hernia repair and pelvic organ prolapsed surgery. Despite excellent physicochemical performances, the hydrophobic surface with a high modulus of PP makes its limitation in biocompatibility and mechanical compliance to human tissue, leading to the most common complications including chronic abdominopelvic pain and mesh exposure. In recent years, considerable researches have been devoted to preparing biocompatible and elastic PP meshes through dipping different biocompatible materials or covering nanofibrous mat on meshes.^[1–5] However, membrane-coated PP meshes may cause a decrease in the porosity of devices and a sharp increase in the surface area of material contact with tissue. Evidence from the literature on vaginal and hernia mesh suggests that the surface area of the implanted (the volume of implanted polymer contact with tissue) could be proportional to the magnitude and type of the foreign body

response generated. Both animal and human studies have shown that reducing the volume of the implanted could reduce the risk of extrusion or exposure.^[6] Therefore, surface modified PP monofilament with reducing volume might be less likely to induce the risk of exposure.

However, under some deformation conditions, the internal stresses in the interface of composites material would lead to the coating delaminating. It is well known that the stability of the coating is closely related to the interfacial interaction between substrate and coating. The low-polar groups and chemically inert surface of PP cause its hydrophobic characteristics, leading to poor compatibility and weak interaction with other polymers. Hence, research on improving the amounts of polar groups on the surface of PP is important for developing high-performance PP-based complex fiber. Numerous methods have been reported for modification of chemically inert surface, such as chemical oxidation,^[7–10] layer coating,^[11–15] plasma,^[16–18] gamma irradiation,^[19–21] acid/basic treatment^[22,23] and direct fluorination.^[24–26] All these treatments aim at increasing the surface energy and inducing surface etching. Commonly, there is a risk of chemical pollution by these chemical treatments for biological applications. Direct fluorination and plasma are more convenient, safe, environmentally friendly and effective methods to obtain the long-term modified surface widely applied in surface modification of biomaterial. Especially, polydopamine (PDA) coating inspired by mussel adhesive proteins has attracted

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wide interest because of its simple fabrication process and robust coating on various kinds of surfaces, which can provide a functional surface.^[27–31] Hu *et al.* synthesized a biocompatible hydrogel functionalized with dopamine.^[32] Aided by dopamine, the adhesion of the obtained hydrogels with PP was improved. However, it is still difficult to modify raw PP by PDA co-deposition due to the lack of functional polar groups on the backbone of PP. Vijay *et al.* used plasma-assisted polydopamine-functionalized surface modification of PP resin to improve the interfacial interaction for novel polymer nanocomposites.^[33] Therefore, dopamine-sedimentation *via* a simple functional coating combining pretreatment would facilitate the effective surface functionalization of PP.

As the biological implanted materials, the host response can lead to unresolved inflammation, which can drive capsule overgrowth, pain, scarring and tissue contraction. The surface properties of the implant material are critical for host response. The biocompatibility of polymer surfaces improved by surface coating has been widely reported.^[34,35] Polyurethane (PU) is an ideal implanted material and also an excellent surface coating polymer due to its excellent properties, such as biocompatibility, non-toxicity, tailorable and elastomeric mechanical property.^[36–44] Its advantages have been demonstrated in prior animal experiments, clinical use in cardiovascular and other biomaterial applications. Hao *et al.* synthesized biodegradable waterborne phosphatidylcholine PU. The obtained PUs showed relatively high elastic modulus, excellent biocompatibility and hydrophilicity and had great potential applications for soft tissue engineering scaffolds in repair and wound healing.^[45] Zhu *et al.* fabricated PU-based nanofibrous tubular scaffold, which showed high hydrophilicity and matched mechanical properties for vascular tissue engineering.^[46] Bellon *et al.* used PU to coat PP mesh with a 26 μm thick film using a cyanoacrylate adhesive.^[47] The obtained composite mesh performed very well in terms of reduced ad-

hesion formation at the peritoneal interface.

In this work, a pillowy soft mat of PP monofilament was performed by PU through stepwise surface treatments for improving the interfacial adhesion. Stepwise procedures are performed (Fig. 1). First, the surface of PP monofilament was modified by direct fluorination or plasma treatment to incorporate suitable polar groups, such as $-\text{COOH}$ and $-\text{C}-\text{F}$ for interfacial adhesion. Second, dopamine-sedimentation *via* a simple functional coating on the polar surface for further improvement of the interfacial adhesion with the PU coating. Last, the PU was coated on the modified surface of PP monofilament to get the pillowy soft mat. Herein, we focus on discussing a safe and suitable strategy to improve the interfacial interaction between PP monofilament and PU mat. This modified PP monofilament with improving biocompatibility and mechanical compliance would be more beneficial for the applications of implanted mesh materials. The surface microstructure, chemical characteristics, mechanical property and hydrophilicity of the pretreatment PP monofilament and PU/PP complex fiber were characterized by scanning electron microscopy (SEM), Raman, micro-attenuated total reflectance Fourier transform infrared spectroscopy (micro-ATR-FTIR), X-ray photoelectron spectroscopy (XPS), wide angle X-ray diffraction (WAXD), energy dispersive spectroscopy (EDS) and water contact angle (WCA). The effect of the pretreatment on the surface of the PP monofilament was evaluated based on interfacial shear strength analysis.

EXPERIMENTAL

Materials

Isotactic polypropylene (iPP) with a $M_n=6.7\times10^4$; $M_w=2.5\times10^5$ was purchased from Lanzhou Petrochemical Company (Lanzhou, China). PP monofilament was melt spun by our research group. Dopamine hydrochloride (DA) was purchased from Sigma-Aldrich Corporation (St. Louis, MO). Hydroxymethyl

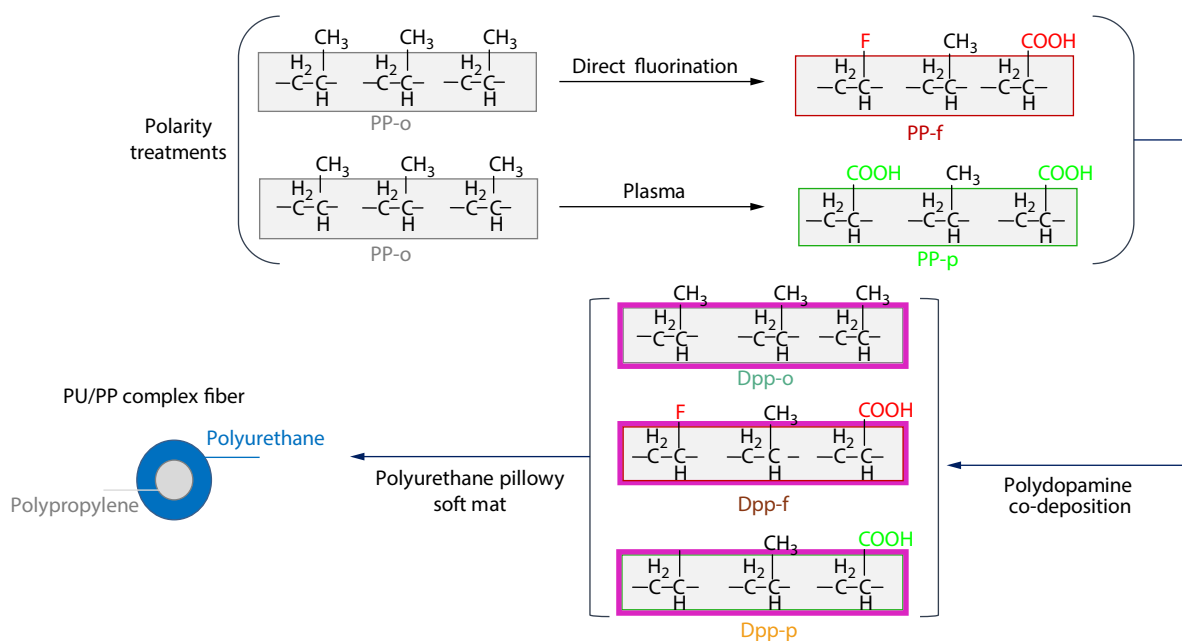


Fig. 1 The whole process of the modification of PP monofilament.

aminomethane (Tris base), the molecular biology grade, was purchased from Chengdu Kelong Reagent Corporation (Chengdu, China). Hexamethylene diisocyanate (HDI, Nantong Dahong Chemical industry limited company) was redistilled under vacuum before use. Polycarbonate (molecular weight 1000, Dow Chemical) was dehydrated at 100–108 °C under vacuum for 2 h.

Surface Functionalization of PP Monofilament

Firstly, the PP monofilament was cut into 10 cm and sonicated in ethanol for 30 min to remove the residual organic reagent. The untreated PP monofilament was denoted as PP-o.

PP monofilament was deposited in a closed stainless-steel chamber equipped with a vacuum line. 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. 20 kPa F_2/N_2 mixed gas was introduced to the chamber at 100 °C for 30 min. Then residual F_2 and byproducts in the chamber were removed by vacuum and absorbed by alkali aqueous solution at once. The direct fluorination PP monofilament was denoted as PP-f.

PP monofilament was dried in an oven at 50 °C to remove moisture. Subsequently, the dried PP monofilament was put in the plasma chamber, which was cleaned using argon gas for 30 min at a pressure of 0.4 mbar. The plasma chamber was operating at 13.56 MHz and 29.6 W for 10 min.^[16] Immediately after the completion of plasma treatment, the treated PP monofilament was exposed to the atmosphere at room temperature (25 °C) for 30 min to facilitate the efficient formation of surface hydroperoxides and peroxides. The plasma functionalized PP monofilament was denoted as PP-p.

PP monofilament was functionalized with a polydopamine (PDA) layer by pH-induced and oxidative self-polymerization of dopamine through a facile dip-coating procedure. Dopamine hydrochloride was dissolved in Tris-HCl buffer (1 mol/L, pH 8.5). Subsequently, the PP-o, PP-p and PP-f monofilaments were washed by ethanol and immersed into freshly prepared dopamine solution and shaken for 24 h at R.T. Later, the monofilaments were taken out and washed with water and ethanol, and then they were air dried for 1h. The obtained monofilaments were denoted as Dpp-o, Dpp-f and Dpp-p respectively.

Preparation of PU, Composite Specimen and PU/PP Complex Fibers

The polycarbonate urethane has attracted more and more attention owing to its better biological stability and biocompatibility *in vivo*, showing good cell proliferation and adhesion, decreased platelets activity and less inflammatory reaction. Thus, the polycarbonate urethane has a wide application in cardiovascular long-term implants.^[48]

The aliphatic diisocyanate of hexamethylene diisocyanate (HDI) has better biocompatibility.^[49,50] Therefore, HDI and poly(1,6-hexanediol) carbonate diols (PCDL) were used to synthesize PU prepolymer. In brief, PCDL (100.00 g, 10 mmol) was added into the three-necked flask and dried under vacuum at 95 °C for 2 h, HDI (25.28 g, 15 mmol) and organic bismuth (catalyst, 2 wt%) were added. Polymerization was conducted for 2.5 h under mechanical stirring at 70 °C under N₂ protection. After pre-polymerization, the obtained prepolymer was dissolved into the 2-butanone with weight ratio of 1:2 for standby (Fig. 2). PU membrane was prepared by casting PU/2-butanone solution at the concentration of 40% (W/W) onto a glass mold. The glass mold was put in a moist environment reacting with water vapor. Then the cross-linked PU was obtained.^[51,52] The solvent was evaporated at 40 °C for 24 h, and further dried under reduced pressure for another 24 h at 30 °C, yielding a transparent PU membrane with a thickness of 150±10 μm.

The adhesion property of PP monofilament with PU mat was characterized by the single pull-out test of a specimen prepared by a single fiber axially infiltrating in cylinder-shaped PU with thickness between 2–5 mm. Fiber went through the cavity in the cylinder-shaped mold with counterweight hanged at the bottom of fiber to keep the fiber vertical. Then, the curing process was operated at ambient temperature for 48 h.

The PU/PP complex fiber was made by the dipping method. The PU prepolymer was dissolved into the 2-butanone with weight ratio of 3:1. The polymer solution was used to form the coatings. The fabrication process of complex fiber by the dipping method was as follows. Firstly, the pretreatment PP monofilament was soaked in PU prepolymer solutions for 20 s. Then the monofilament was taken out to react with wa-

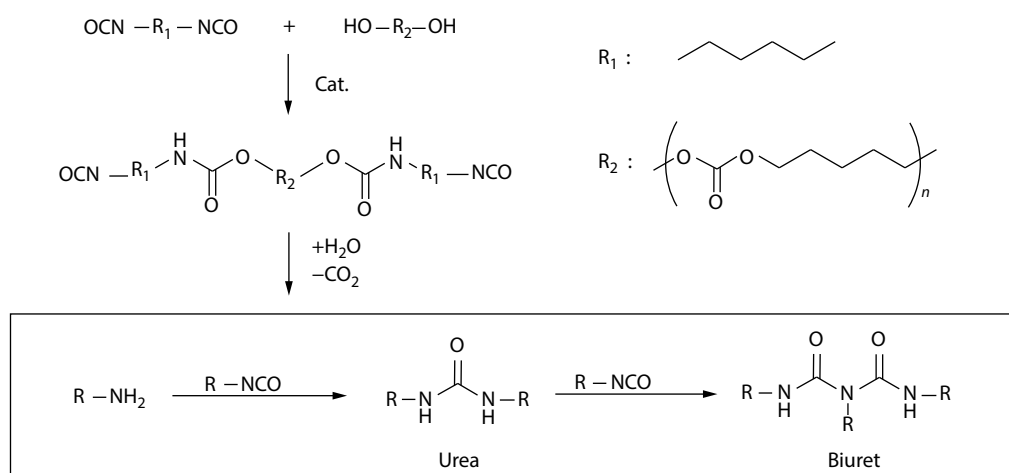


Fig. 2 Synthesis procedure of cross-linked PU.

ter vapor in the moist environment. The solvent was evaporated at 40 °C for 24 h, and further dried under reduced pressure for another 24 h at 30 °C. It is noteworthy that monofilament had to be kept horizontal during the whole fabricating process to avoid non-uniform thickness, because liquid PU prepolymer tends to deposit in the bottom, caused by gravity.

Characterization

Surface morphologies of the pristine and modified PP monofilaments were observed and investigated via scanning electron microscope (SEM, Apreo S, Thermo Fisher Scientific, U.S.A.) with an operating voltage of 2 kV. The surfaces were sputter-coated with gold (Quorum, U.K.) before observation to avoid charging.

Micro attenuated total reflectance fourier transform infrared spectroscopy (micro-ATR-FTIR, iN10MX, Thermo Fisher Scientific, U.S.A.) was used to analyze the chemical structure of the fiber surface.

X-ray photoelectron spectroscopy (XPS, ESCALAB Xi, Thermo Fisher Scientific, U.S.A.), was used to investigate the chemical composition of the fiber surface with Al K α excitation radiation (1486.6 eV).

X-ray diffraction (WAXD, Rigaku, Japan) was used to characterize the crystalline structures of samples, and the diffraction patterns were recorded with the 2θ range of 5°–35°.

Raman Spectra of PP monofilaments were collected on Laser Raman Confocal Spectrometer (Raman, in Via plus, Renishaw, U.K.) with a 2 mW 532 nm excitation wavelength laser from 200 cm⁻¹ to 3500 cm⁻¹ and a nominal laser power between 1–100 mW out power, mapping was scanning range from 2300 cm⁻¹ to 3200 cm⁻¹.

Water contact angle (WCA, DSA 100M, Kruss, Germany) was used to characterize the water contact angle of samples, using the angle when water firstly encounter the fiber to represent hydrophilicity of the fiber.

Mechanical properties (tensile strength, the initial modulus, elongation at tensile strength lose 50%) of fiber were determined on Instron 1122 tensile tester (Instron, High Wycombe, England) using 20 mm long samples at room temperature and extension rate of 20 mm/min.

Shore-D hardness was determined by Zwick 3100 durometer according to the ASTM D2240 (2010) standard.

Energy dispersive spectroscopy (EDS, EDAX, Mahwah, U.S.A.) was conducted with Octane elect super to characterize the element mapping of PDA functionalized fibers.

The characterization of the interfacial shear strength between fiber and PU was measured using single pull-out strength (Fig. 3), each sample was test for 5 times and the average value was reported. The fiber after pull-out test was observed by an optical microscopy (Lecia, Germany).

The adhesive property of PP monofilament with PU coating acquired from the embedding specimen was calculated according to the following expression: $P = F/d \cdot p$. P stands for the adhesion strength in cN·dtex⁻¹·mm⁻¹; p is the linear density of a monofilament in dtex; d is the thickness of the PU matrix in mm and also indicates the depth of the fiber embedding in the matrix; F represents the max force of the fiber pulled out from the enwrapping of the PU matrix in cent Newton.

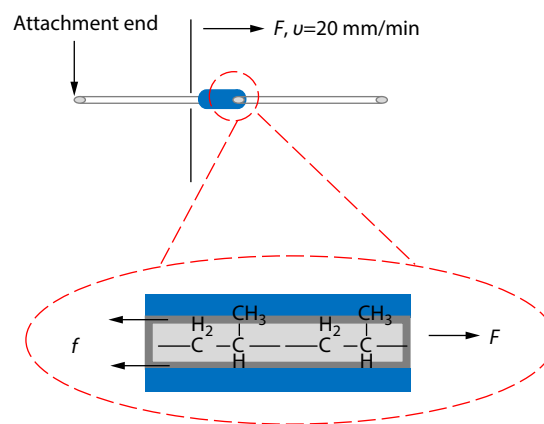


Fig. 3 Schematic of the pullout test sample.

Nanoindenter (Nanoindenter Piuma Chiaro, Optics 11 BV, Netherlands) was used to measure the surface hardness and Young's modulus. The diamond indenter was an Optics tip with a tip radius of 10.5 μ m. Three indentations are made in every sample for estimating Young's modulus.

RESULTS AND DISCUSSION

Characteristics of PP Monofilament with Polarity Treatments

It still poses a challenge to directly modify raw PP by PDA co-deposition due to the backbone of PP with no functional polar groups. Therefore, dopamine-sedimentation via a simple functional coating combining polarity pretreatment would facilitate the effective surface functionalization of PP. After the polarity pretreatments of PP monofilament by fluorination or plasma, the chemical structures of the PP monofilament surface were determined by micro-ATR-FTIR, Raman, and XPS techniques. The micro-ATR-FTIR spectra of PP-o, PP-f and PP-p were shown in Fig. 4(a). The micro-ATR-FTIR spectrum of untreated PP monofilament (PP-o) exhibits the characteristic peaks of PP polymer. On the spectrum of PP-p, it can be observed that the bands at 2960, 2870 and 1457 cm⁻¹ corresponding to CH₃ stretching vibration were nearly disappeared. The intensities of CH₂ and CH bands over 3000–2800 and 1500–800 cm⁻¹ range are markedly decreased. On the other hand, some new absorption bands exhibit at near 3400 and 1666 cm⁻¹, corresponding to —OH and —C=O stretching vibration absorption bands, indicating that many hydrophilic groups were introduced to the surface of PP-p monofilament. On the spectrum of PP-f, a diffuse band at 3460 and 1665 cm⁻¹ was assigned to —COOH. Also, a broad diffuse band over 1125 cm⁻¹ was observed, corresponding to C—F.^[24] The results indicated the presence of the —COOH and —C—F groups on the surface of monofilament PP-f.

Raman spectroscopy can provide rich information on the ordered/disordered structure of the near-surface region of the iPP matrix. The spectra of PP-f and PP-p exhibit that the intensities of characteristic bands corresponding to CH₃ (bands at 972, 998, 1168 and 2962 cm⁻¹) decrease (Fig. 4b). It suggested that after the pretreatments, the pendent methyl group was turned into the hydrophilic groups and the extra polar groups observed by micro-ATR-FTIR. The surface chain

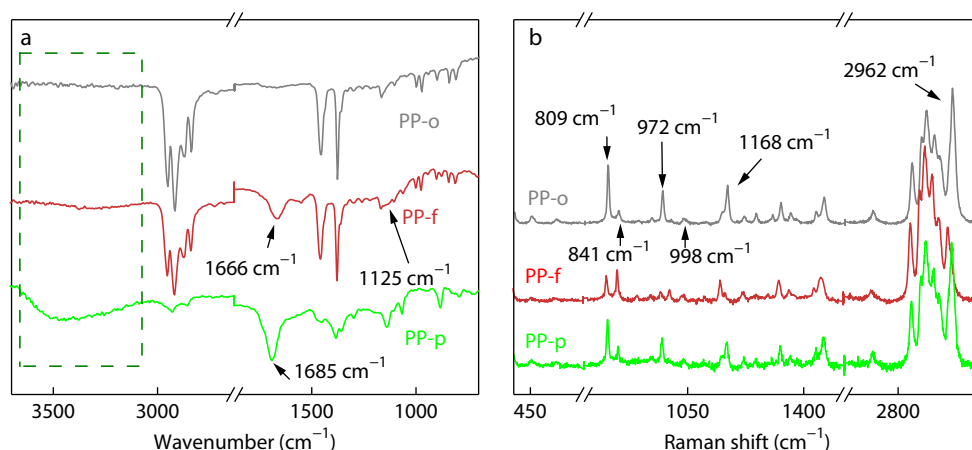


Fig. 4 The chemical structure of PP monofilament surface with different treatments: (a) micro-ATR-FTIR spectra, (b) Raman spectra.

scission behavior in the process of the pretreatment may also cause decreases in the intensity of CH_3 . The ratio of Raman bands at $841/809\text{ cm}^{-1}$ is sensitive to the molecular anisotropy in PP samples.^[53,54] Compared with PP-o, the ratio of PP-f at $841/809\text{ cm}^{-1}$ markedly rises, indicating that molecular anisotropy of fiber surfaces decreased. Obviously, the direct fluorination caused serious surface chain scission behavior. Moreover, it can be found that the locations of the characteristic bands are nearly unchanged, implying that the treatments did not affect the entity structure of the PP monofilament.

XPS was used to investigate the chemical compositions of PP surfaces (Fig. 5). The surface element compositions from XPS spectra and functional components obtained from the deconvolution of C1s peaks are listed in Table 1. Particularly, the C1s peaks fit with four or five components, assign to C—C (284.7 eV), C—CF (286.1 eV), C=O (287.6 eV), O—C=O (288.6 eV), CHF (290.0 eV),^[24] respectively. Relatively, the more differences in the elements were observed on the surface of PP-f. Compared with PP-o, the O atom content on the surface of PP-f dramatically raises from 5.29% to 15.89%, the percentage of C=O sharply increases from 0% to 14.23% and the percentage of O—C=O also largely increases from 0% to 8.72%. Besides, PP-f shows new bonding energy peaks at 286.1 eV (C—CF) and 290.0 eV (CHF), which was confirmed the existence of extra polar group C—F. Meanwhile, PP-f and PP-p monofilament show higher O/C atomic ratios, increasing from 0.06 to 0.23 and 0.17, respectively. The results showed that high content of oxygen-containing functional groups appeared on the surface of PP-f and PP-p monofilament. In addition, the above XPS analysis also indicated that oxygen and fluorine atoms produced by plasma and direct fluorination were in the form of covalent bonds on the surfaces of PP monofilament. The higher content of oxygen-containing and extra polar groups on monofilaments surface were expected to increase the polarity, resulting in an improvement of interfacial interaction between the monofilament and PU-coating.

To further understand the surface morphology of the treated monofilaments, the SEM images of the surface of PP-o, PP-f and PP-p were shown in Fig. 6(a). It could be seen that

untreated PP monofilament (PP-o) displays a smooth surface and the PP-f and PP-p display a surface with micro-pits and grooves. Particularly, the surface etching of PP-f was the most serious. Moreover, the surface crystalline characterization of PP-o, PP-f and PP-p were measured by WAXD and the spectra were shown in Fig. 6(b). There were three distinct characteristic peaks at 2θ values of 14.0° , 16.8° and 18.4° , respectively, corresponding to (110), (040) and (130) planes of α -crystal forms of PP. Apparently, the intensity of the crystal peaks decreased after pretreatments. The crystallinity of PP-o, PP-f and PP-p were 54.5%, 32.8% and 40.5% respectively, decreasing from 54.5% to 32.8%. The results indicated that the pretreatment of the monofilaments by fluorination and plasma damaged the surface crystalline structure of monofilaments in a certain degree, which was consistent with the results of Raman. In the process of the pretreatments, the destruction of the monofilament surface crystalline structure caused the decrease of monofilament surface molecular anisotropy. Besides, the direct fluorination caused more serious damage to the PP monofilament. Since the morphology, crystallinity and orientation usually affect the mechanical properties. The mechanical properties of PP monofilaments were measured and plotted in Fig. 6(c). Compared with PP-o, the tensile properties of PP-p show negligible change with a strength of 5.67 cN/dtex, the initial modulus of 47.15 cN/dtex and elongation of 16.6%, respectively. This change was negligible because the damage caused by the plasma is limited to a depth of few nanometers. However, the tensile properties of PP-f exhibit a certain decrease from about 7% to 5.24 cN/dtex, the initial modulus of 46.03 cN/dtex and elongation of 16.0%. The direct fluorination led to a damage of micrometer depth and caused the surface chain scission behavior. Thus, the tensile properties of PP-f show a significant decline. Some imperfections in bulk monofilament were formed, leading to the decrease in tensile strength.

Characteristics and Properties of PP Monofilament with Dopamine Co-deposition

After surface pretreatment, PP monofilament was coated by dopamine-sedimentation *via* a simple functional coating. Micro-ATR-FTIR spectra firstly confirmed the formation of PDA coatings (Fig. 7a). In addition to the classic bands such as 2916

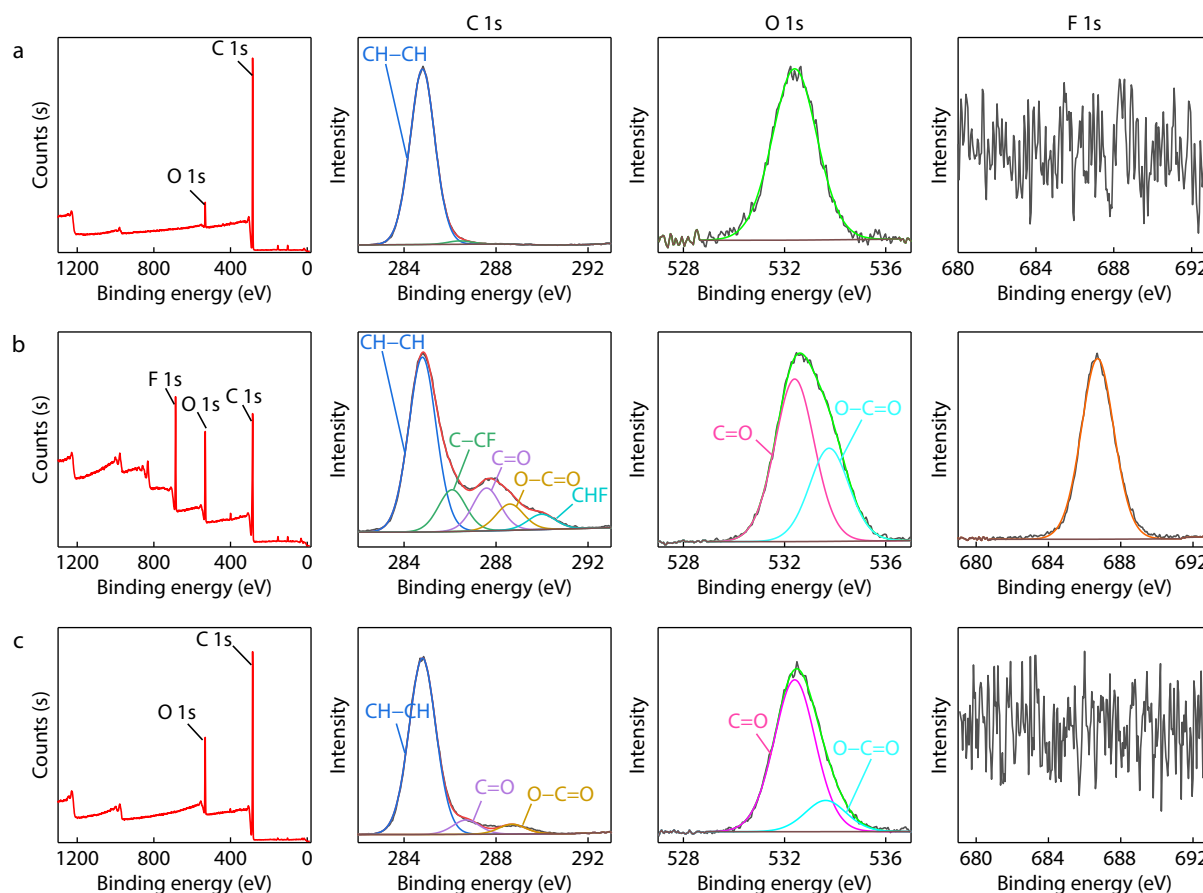


Fig. 5 XPS survey spectra and C1s, O1s and F1s spectra of PP monofilaments with different treatments: (a) PP-o, (b) PP-f and (c) PP-p.

Table 1 The XPS surface element analysis parameters and carbon-based groups content in C1s spectra of PP monofilaments.

Sample	Atomic content (%)				Atomic ratio (%)	Functional group composition (%)				
	C	O	F	N		CH-CH (284.8 eV)	C-CF (286.1 eV)	C=O (287.6 eV)	O-C=O (288.6 eV)	CHF (290.0 eV)
PP-o	93.63	5.29	—	1.08	0.06	100	—	—	—	—
PP-f	67.58	15.89	14.41	2.12	0.23	58.09	13.90	14.23	8.72	5.06
PP-p	83.94	14.63	—	1.43	0.17	87.98	—	7.14	4.89	—

cm^{-1} (C—H bands), 1457 cm^{-1} ($-\text{CH}_2$) and 1379 cm^{-1} ($-\text{CH}_3$), new bands at 1510 cm^{-1} (C=N), 1640 cm^{-1} (C=C of benzene ring) and $3000\text{--}3700\text{ cm}^{-1}$ (N—H and O—H stretch vibration) appeared in the spectra of all the PDA-coated monofilaments. After *in situ* sedimentation of PDA, the position of the characteristic bands of PP does not change, demonstrating that *in situ* sedimentation of PDA on the PP monofilament surface was a physical procedure. Compared with Dpp-o, the intensities of the bands at $3000\text{--}3700\text{ cm}^{-1}$ (N—H and O—H stretch vibration), 1510 cm^{-1} (C=N) and 1640 cm^{-1} (C=C of benzene ring) in the spectra of Dpp-f and Dpp-p display a significant increase, indicating that more —OH and —NH₂ groups of polydopamine were present on the surface of Dpp-f and Dpp-p. Further, Raman spectra were used to confirm the surface polydopamine functionalization of PP monofilament (Fig. 7b). Besides the characteristic bands of PP, two protuberant characteristic bands at 1580 and 1350 cm^{-1} attributed to the deformation of the catechol group in the polydopamine

molecules can be observed at the Raman spectra of Dpp-o, Dpp-f and Dpp-p.^[30] These results matched the results of micro-ATR-FTIR, indicating that the Dpp-o, Dpp-f and Dpp-p were successfully functionalized by polydopamine. Compared with the Raman spectrum of Dpp-o, the intensities of characteristic bands at 1580 and 1350 cm^{-1} considerably increase on the Raman spectra of Dpp-f and Dpp-p, indicating that more PDA decorating on the PP monofilament surface.

To visualize the PDA sedimentation, the surface morphologies of PP-o, Dpp-o, Dpp-f and Dpp-p were observed by SEM (Fig. 8a). The uncoated PP-o revealed a smooth surface. In contrast, PDA nanoparticles were well-decorated on the surface of PP monofilaments. The aggregates were more densely distributed on the surface of pretreated PP monofilament. Since PP is a linear chain hydrocarbon polymer and nonpolar crystalline material with hydrophobicity, it is difficult for DA to polymerize on the surface of untreated PP monofilament. Therefore, after plasma and direct fluorination pretreatment,

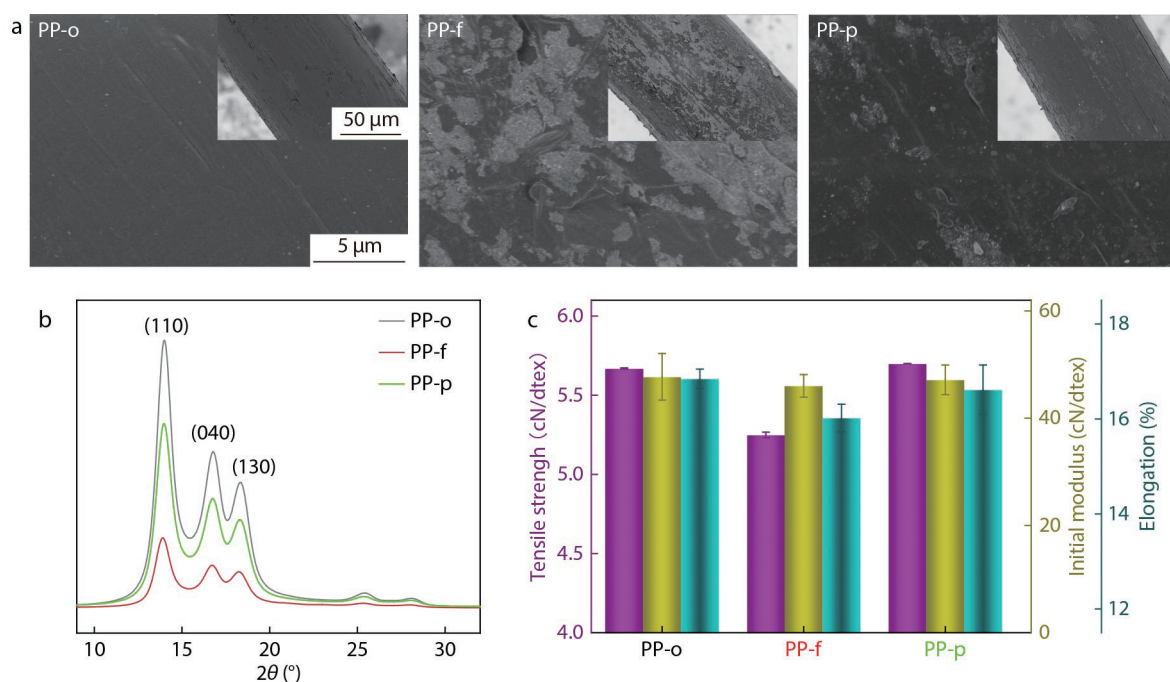


Fig. 6 (a) SEM images of different treatment monofilaments surfaces; (b) WAXD profiles of different treatment monofilaments; (c) Mechanical properties of different treatment monofilaments.

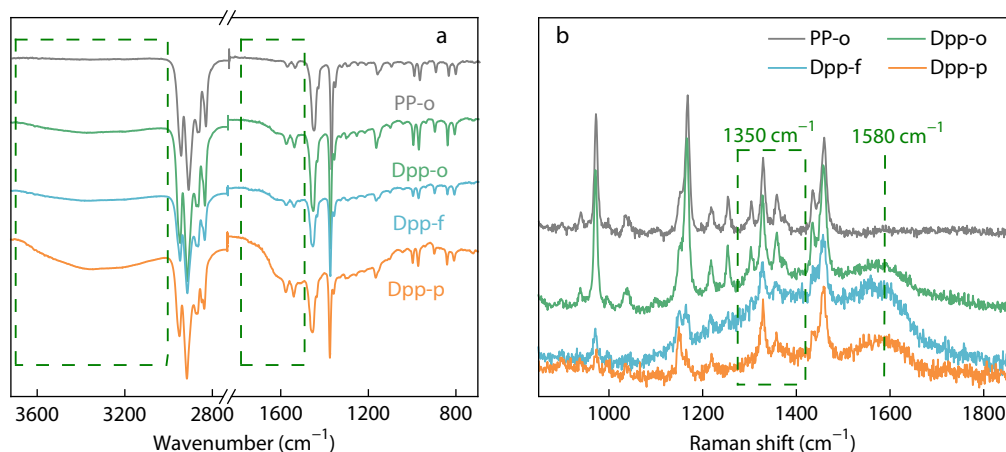


Fig. 7 Chemical composition of polydopamine functionalized PP monofilaments: (a) micro-ATR-FTIR spectra, (b) Raman spectra.

the polydopamine was easily coated on the surface of PP-f and PP-p due to the polar anchoring groups.

The surface element analysis of PDA functionalized monofilaments is shown in Table 2, and the samples were mainly composed of C, N and O elements after modification with dopamine. The surface of modified PP monofilaments with different ratios of O/C and N/C was observed. The ratio of O/C was increased from 0.10 to 0.31, while the ratio of N/C increases from 0.02 to 0.08, indicating that Dpp-f and Dpp-p strongly interacted with the dopamine molecules compared with Dpp-o. The element mapping revealed that C, N and O were homogeneously distributed throughout the surfaces of Dpp-o, Dpp-f and Dpp-p (Fig. 8b). Judging from the intensity of the presented elements with various colors for different pretreated PP monofilaments, the density of PDA distributed

on the surface of Dpp-f and Dpp-p was more than that of Dpp-o.

Water contact angle measurement was used for the characterization of the surface wetting properties, which is a common method to evaluate the polarity of the substance. Compared with PP-o, the water contact angles of surface modified monofilaments were significantly reduced (Fig. 9a). PP-o owned the highest value of WCA (109.9°) and showed a hydrophobic surface. After polarity treatments and dopamine co-deposition, the WCA values of PP-f, PP-p, Dpp-f and Dpp-p were 95.6°, 74.9°, 63.0° and 65.0°, respectively. It can be found that the wettability of surface modified monofilaments increased with the introduction of the hydrophilic groups —COOH and extra polar groups C—F on the monofilament surface. And the hydrophilic groups and polar group can also

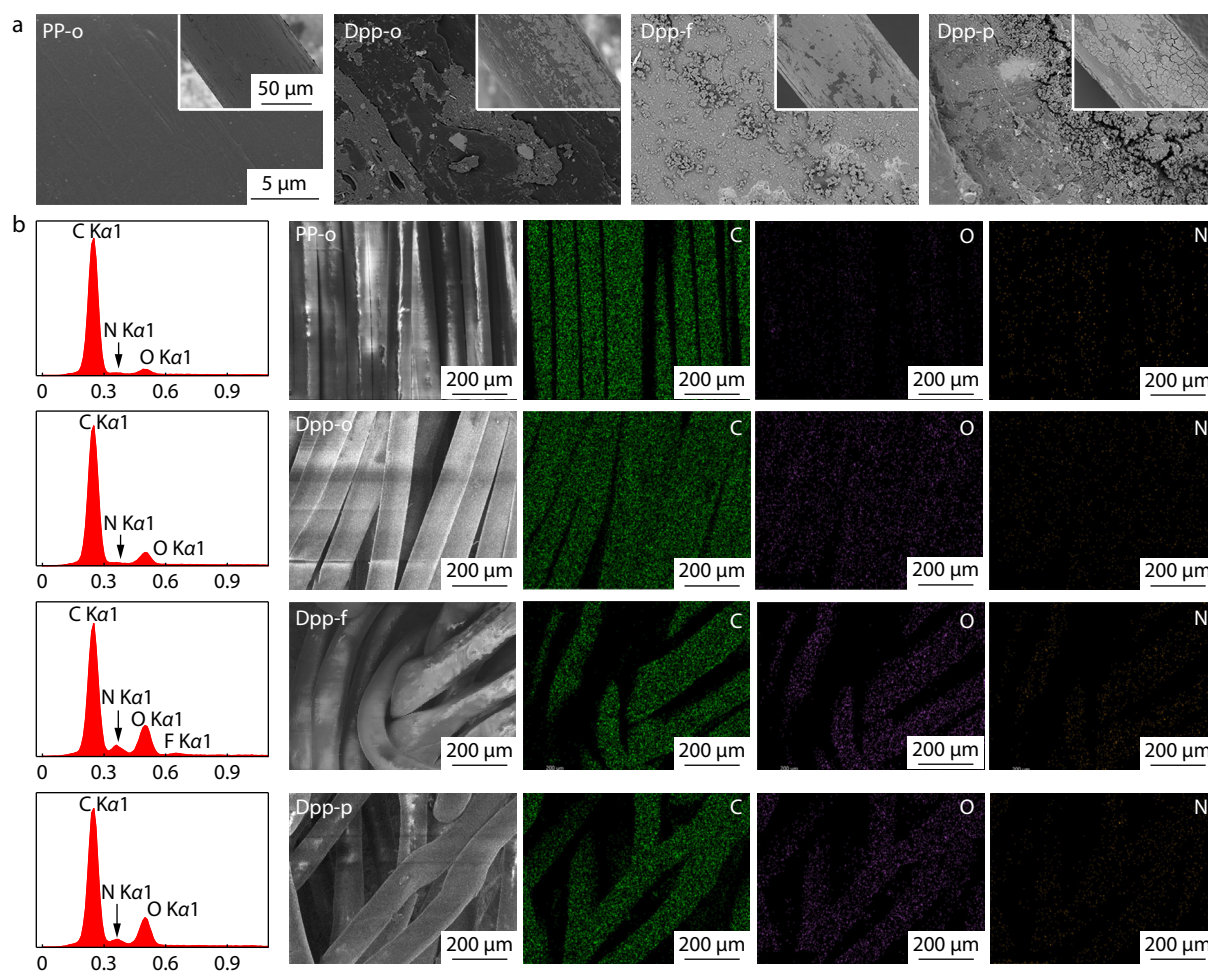


Fig. 8 (a) Surface morphology of polydopamine functionalized PP monofilaments; (b) EDS mapping of polydopamine functionalized PP monofilaments.

Table 2 EDS surface elemental analysis parameters of polydopamine functionalized PP monofilaments.

Element	Weight content (%)			
	PP-o	Dpp-o	Dpp-f	Dpp-p
C	94.02	88.66	70.85	76.42
N	—	2.16	5.79	5.65
O	4.41	9.18	21.74	17.93
F	—	—	1.62	—
O/C	0.05	0.10	0.31	0.23
N/C	—	0.02	0.08	0.07

improve the interfacial bonds between PDA and PP, which may increase the concentration of PDA on PP monofilament surface with higher hydrophilicity. Although the hydrophilicity of C—F was lower than that of —COOH, the high polarity of C—F significantly improved the interfacial bonds between PDA and PP monofilament, so that the Dpp-f could be coated with a larger amount of PDA with the highest hydrophilicity.

Since the interfacial wettability of monofilament would have a great influence on the interfacial adhesion. The PDA-coated monofilaments were subsequently embedded PU matrix to explore the interfacial bond properties between PP monofilament and PU matrix. Single fiber pullout tests are

performed (Fig. 3) and the interfacial shear strengths (IFSS) of various single fibers with PU coating are shown in Fig. 9(b) and Table 3. The pull-out strength of untreated PP monofilament/PU composites was $1.69 \text{ cN-dtex}^{-1}\cdot\text{mm}^{-1}$. After plasma treatment and fluorination, the pull-out strength of PP-f and PP-p increases by 388% and 298%, respectively, up to 8.25 and $6.72 \text{ cN-dtex}^{-1}\cdot\text{mm}^{-1}$. The pull-out strength of polydopamine functionalized PP monofilament (Dpp-o) shows a little higher improvement of 54% compared to PP-o.

Notably, Dpp-f achieved the best interfacial properties with a corresponding increase of 586% to $11.60 \text{ cN-dtex}^{-1}\cdot\text{mm}^{-1}$ in pull-out strength. And Dpp-p also performed an increase of 473% up to $9.69 \text{ cN-dtex}^{-1}\cdot\text{mm}^{-1}$. Stepwise surface modification combining pretreatment and dopamine-sedimentation *via* a functional coating would effectively improve the interfacial interaction between PP and PU coating.

The residual matrix on fiber after the single fiber pull-out test can be used to measure the adhesion of the composites. The more residual matrix left, the better the adhesion is.^[55–59] Therefore, the content of residual matrix on fiber after the pull-out test is a signal of adhesive properties of the composites. The morphologies of the fiber surface of these composites after the pull-out test are exhibited in Fig. 9(c). The sur-

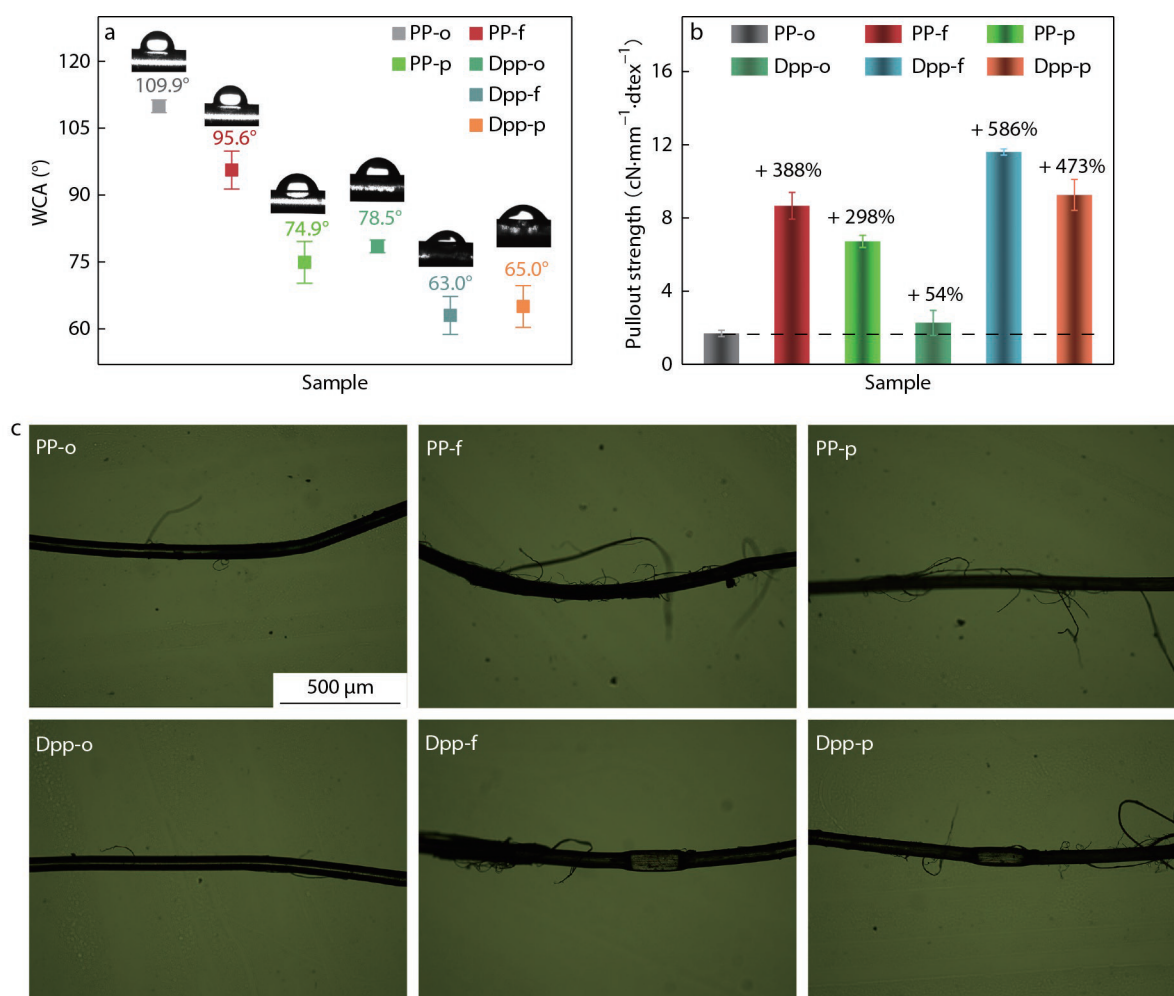


Fig. 9 (a) The interfacial shear strength of single fibers with PU coating; (b) WCA of fibers surface with different treatment; (c) Surface morphology of single fiber after pull-out.

Table 3 The interfacial shear strengths (IFSS) of pull-out single fiber from PU matrix.

Sample	IFSS (cN·dte ⁻¹ ·mm ⁻¹)	Increment of IFSS (%)
PP-o	1.69±0.02	0
PP-f	8.25±0.17	388
PP-p	6.72±0.03	298
Dpp-o	2.61±0.05	54
Dpp-f	11.60±0.01	586
Dpp-p	9.69±0.08	473

face morphologies of PP-f, PP-p, Dpp-f and Dpp-p monofilament exhibit apparent microfibril structure. It can be observed obviously that the fibers were damaged after the pull-out test. Vividly, the surface modified monofilaments were damaged more seriously than the PP-o and Dpp-o monofilaments. This fracture behavior on pretreated fibers would certainly consume more energy and thus improve the IFSS value. Furthermore, micro-ATR-FTIR was used to confirm the residual PU matrix after the pull-out test (Fig. 10). It can be observed that all fibers have characteristic bands of PP at 2916 cm⁻¹ (C—H bands), 1457 cm⁻¹ (—CH₂) and 1379 cm⁻¹ (—CH₃). At the spectra of PU, the band at 2270 cm⁻¹ (—NCO)

disappeared, indicating that the isocyanate groups were consumed as the curing process. The band around 3317 cm⁻¹ demonstrated the formation of urea and biuret linkages. The band of 1735 cm⁻¹ was attributed to the formation of urethane linkage containing carbonyl groups. Meanwhile, the bands around 1680–1530 cm⁻¹ represented asymmetric and symmetric O=C stretching vibration in the urea and biuret linkages. The characteristic band at 1538 cm⁻¹ was observed, corresponding to N—H. The C—O—C stretching vibration of acrylic ester groups was detected at 1238 cm⁻¹.^[52,60] Besides, at the spectra of PP-f, PP-p, Dpp-f and Dpp-p monofilaments the peaks at 3317 cm⁻¹ (N—H), 1735 cm⁻¹ (C=O), 1680–1530 cm⁻¹ (O=C—N), 1538 cm⁻¹ (N—H), 1238 cm⁻¹ (C—O—C) appeared, corresponding to the characteristic bands of PU matrix. Moreover, the intensity of all these new bands became stronger after stepwise treatments, due to the monofilament surface containing more residual PU matrix. Obviously, the surface of Dpp-f monofilament contained more PU matrix than that of PP-f monofilament, similar increase between the surface of Dpp-p and PP-p are revealed. The result indicated that the polarized pretreated monofilaments have an influence on the co-deposition of PDA, which might affect the interaction between the pretreated PP monofilament and

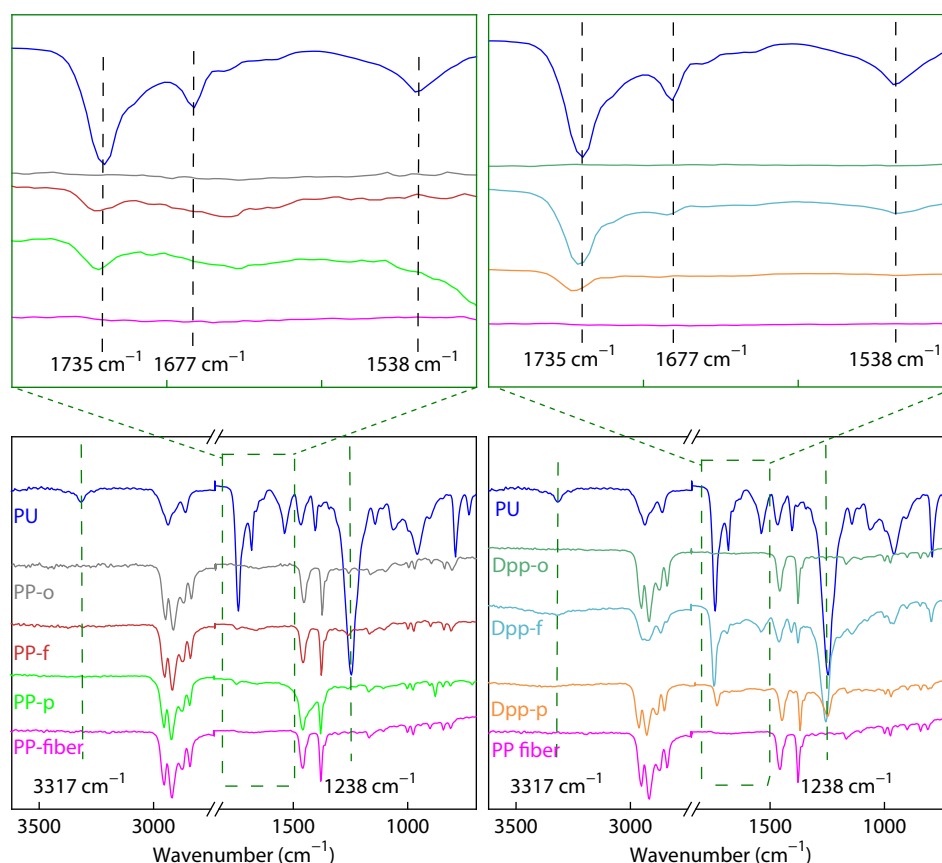


Fig. 10 Micro-ATR-FTIR spectra of the single fiber surface after the pull-out test.

dopamine molecules. Therefore, combined surface pretreatment with PDA co-deposition could effectively increase the interfacial adhesion between PP and PU. However, the direct fluorination treatment would cause a large decrease in the mechanical property of PP monofilament. The plasma treatment would achieve the goal for simultaneously introducing numerous functional polar groups and retaining the fibers mechanical properties.

Characteristics of PU/PP Complex Fiber

Dpp-p monofilament was chosen to dip the PU prepolymer to prepare the representative PU/PP complex fiber. Micro-ATR-FTIR spectra, DSC and TGA curves firstly confirmed the characteristics of PU coating (Fig. 11a). The ATR-FTIR spectrum of PU coating shows that it was a typical polycarbonate PU. The DSC curve reveals that the PU has a microphase separation structure and several phase transition temperatures. The peak around -34.36°C assigned to the glass transition of PCDL soft segment and 11.10°C is the glass transition temperature of the PCDL mixed with the hard segment. The temperatures at 61.33 and 84.19°C are the multiple melting peaks of the hard segment. The phase separation endowed the PU with excellent elastic. The initial thermal degradation temperature (T_{id} , 5% weight loss temperature) of PU was 290.0°C . These results showed that the PU coating had a high degree of microphase separation, good elasticity and stability. Fig. 11(b) shows the SEM images of the cross-section of PU/PP complex fiber with a classic core-shell structure consisting of inner PP and outer PU. The chemical structures of the complex fiber surface were determined by

micro-ATR-FTIR, Raman and EDS techniques. The FTIR line scanning of the cross-section of PU/PP complex fiber shows that the specific band for PU around 1735 cm^{-1} appears at the zone from point 1 to 3 and disappears at the core area from point 4 to 11 (Fig. 11c). In addition, Raman mapping of PU/PP complex fiber shows the characteristic band at 2840 cm^{-1} , corresponding to symmetric CH_2 stretching vibration of PP, which only presents at the core of the complex fiber (Fig. 11d). Further, the element mapping of the PU/PP complex fiber revealed that C was homogeneously distributed throughout the cross-section of complex fiber. The atoms of N and O are nearly distributed on the shell of the PU/PP the complex fiber (Fig. 11f). All the results indicated that PU was successfully coated on the surface of PP monofilament to obtain PU/PP complex fiber with a core-shell structure.

PP is one of the most used non-degradable synthetic mesh materials for abdominal wall defects, hernia repair and pelvic organ prolapsed surgery. The hydrophobic surface with high modulus of PP makes its limitation in biocompatibility and mechanical compliance to human tissue, resulting in some complications including chronic abdominopelvic pain and mesh exposure. After coated PU, the surface hydrophilicity increases and the value of WCA of PU/PP complex fiber reduces sharply from 109.9° to 61.7° (Fig. 11e). More importantly, the surface hardness and Young's modulus of aliphatic PU were significantly lower compared to PP. As shown in Fig. 11(e), the hardness of aliphatic PU is 34.0 ± 2.0 D and the Young's modulus is 76.80 ± 7.22 MPa, while the shore hardness of PP mem-

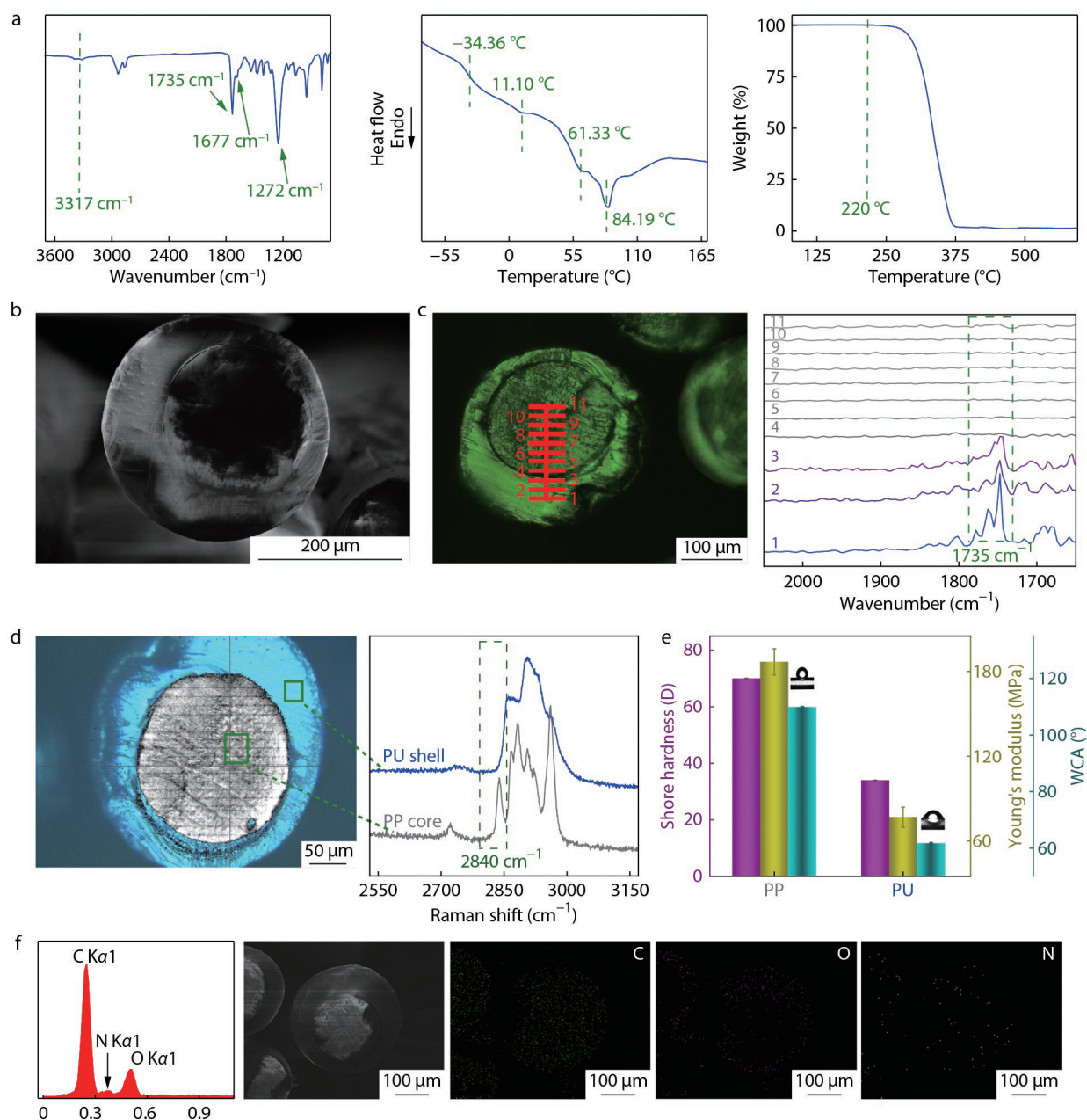


Fig. 11 The characteristics of PU/PP complex fiber. (a) The characteristics of PU coating; (b) SEM image of fracture surface; (c) Micro-ATR-FTIR spectra; (d) Raman mapping; (f) EDS mapping; (e) Young's modulus and shore hardness.

brane is 70.0 ± 1.0 D and the Young's modulus is 186.75 ± 9.28 MPa. Stiffness, the ability to resist deformation under load, is an important property for meshes to sustain physiological loading, which can directly affect cell behavior. The pillow surface modification PP monofilament by PU would benefit the improvement of biocompatibility and mechanical compliance to reduce the morbidity of chronic abdominopelvic pain and mesh exposure. Herein, we focus on discussing the efficient way to obtain PU/PP complex fiber with core-shell structures and strong interfacial adhesion. The following investigation on cell behavior and histocompatibility of PU-modified PP monofilament will be soon reported in our subsequent work.

CONCLUSIONS

In this work, the raw PP monofilament was firstly pretreated by direct fluorination and plasma treated, then PDA-deposition was further used to modify the surface characteristics of PP monofilament. At last, the PU/PP complex fiber was fabricated to test the interfacial shear strength. The pretreatment of PP introduced multiple polar groups, including $-\text{COOH}$ and $\text{C}-\text{F}$ bond, which significantly improved the wettability of PP monofilament. The interfacial shear strength analysis was proved that combining the pretreatment of direct fluorination or plasma treatment with PDA-deposition notably improved the interfacial interaction between PP monofilament and PU

coating. However, the direct fluorination treatment would cause a certain decrease in the mechanical property of PP monofilament. The plasma treatment would achieve the goal for simultaneously introducing numerous functional polar groups and retaining the fibers mechanical properties. Above all, this work suggests that stepwise surface modified PP monofilament with polar functional groups combining plasma pretreatment and dopamine-deposition is a promising technique to promote the interfacial adhesion between PP and PU, and the obtained novel PU/PP complex fiber with pillowy soft mat will be a potential application in abdominal wall defects, hernia repair, and pelvic organ prolapsed surgery.

NOTES

The authors declare no competing financial interest.

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