

**Hydrophobic Cellulose Fiber Surfaces modified with
2,2,3,3,3-pentafluoropropylmethacrylate (FMA) by Vapor-Phase Assisted
Photo-Polymerization**

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Running Head: Simple surface modification by photo-VASP method

Abstract

We report a simple method to produce hydrophobic surface created with 2,2,3,3,3-pentafluoropropylmethacrylate (FMA) by continual vapor-phase assisted surface photo-polymerization (photo-VASP) which enabled to control the chemical and physical properties of unique substrate surfaces without any morphological change. Using the photo-VASP approach, a modification of substrate surface maintaining original properties was achieved on cellulose fibers such as a typical complicated, flexible, and soft substrate, giving a superior water-repellency without compromising the original tactile nature. In the polymerization, the substrate surface was consecutively exposed to vaporized initiator and monomer, 2,2,3,3,3-pentafluoropropylmethacrylate (FMA), under UV-irradiation to start photo-polymerization, resulting in the irradiated surface being selectively coated by polymer chains. The cellulose fibers coated by the thin polymer layer, as well as retaining its original tactile nature, demonstrated superior water-repellency exhibited by its controlled static contact angle being greater than 130° .

Key words: photo-polymerization, hydrophobicity, surfaces, thin layer coating, ESCA/XPS

In recent years, a large number of publications has focused on the ability to covalently modify surfaces by polymeric chains to tailor the interfacial properties such as repellency, wettability, friction resistance, corrosion resistance, and biomedical functions.¹⁻³ This modification can be achieved using “grafting-to” and “grafting-from” techniques, respectively. To modify substrate surfaces, organic solvents are often used based on conventional liquid processes with the solvent being completely eliminated from the final products. From the point of view of green-chemistry, organic solvent-minimized or solvent-free processes,⁴ which minimize the consumption of energy and use of chemical materials, are ideally suited for sustainable development. The liquid process for the pretreatment may also cause considerable damage to the morphology of an original surface on organic compounds. To control the surface properties without any damage to morphology, a gentle and thinly layered coating by graft polymerization techniques is required to protect substrates having a unique tactile nature, such as fibers, textile fabrics, fine powders, biological tissues, electronic devices, *etc.*

One such ideal process is vapor-phase assisted surface polymerization (VASP), a well-known solvent-minimized or solvent-free method for the thin layer coating of solid surfaces.⁵⁻⁹ Previously, we have reported on physically-controlled living radical polymerization using free-radical initiators by VASP method, resulting in the preparation of block copolymers,¹⁰ the design of fine patterns, the application to surface coatings by a fluorinated polymer¹¹ and the development of a homogeneous coating of a fine Fe-powder

surface.¹² In these studies, a small amount of organic solvent was used to pre-coat the initiators on the substrate surfaces.

However, pre-treatment by organic agents to substrate for thin-layer coating gives some damage on original properties such as flexibility, softness, and unique tactile natures. The present study describes the surface modification of cellulose fiber (cotton fabric) having unique properties by photo-VASP of fluorinated monomer in a vapor phase condition without pretreatment with organic agents. Two liquid type photo-initiators: 2-hydroxy-2-methylpropiophenone (HMPP) and benzoin isobutyl ether (BIBE) were employed for the totally vapor-phase reaction. These photo-initiators have definite saturated vapor pressures of sufficient values to vaporize, adsorb, and initiate the polymerization. In the polymerization, the substrate surfaces were consecutively exposed to vaporized initiator and monomer under UV-irradiation to start photo-polymerization. This continual vapor-phase polymerization enables us not only to change the surface properties distinguishably, but also to avoid morphological changes associated with liquid processes, so that a hydrophobic property can be added to the fabric surface without any deformation and/or alteration in its original surface morphology.

EXPERIMENTAL

Materials. Photo-initiator: 2-hydroxy-2-methylpropiophenone (HMPP, 97%) and benzoin

isobutyl ether (BIBE, >95%) were purchased from Aldrich and Tokyo Chemical Industry Co., Ltd., respectively, and used as received. Free radical initiator: 2,2'-azobis(isobutyronitrile) (AIBN, >99%) was purchased from Otsuka Chemical Inc. and recrystallized from methanol. Monomer: 2,2,3,3,3-pentafluoropropylmethacrylate (FMA) from Daikin Finechemical Laboratory, Ltd. was purified by distillation just before use. Polymerization inhibitor: 4-tert-butylpyrocatechol was purchased from Wako Pure Chemical Industries, Ltd. and used as received. All solvents were commercially obtained and used as received. Cotton fabrics (JIS technical standard grade) were purchased from the Japanese Standard Association. Any surface treatment reagents and additives were removed from the cotton fabrics with Soxhlet apparatus using tetrahydrofuran (THF) as a solvent for 24 h after which the fabrics were dried for 12 h at 25 °C.

Measurements

¹H-NMR spectra were measured on a 300-MHz JEOL AL-300 spectrometer. Acetone-*d*₆ was used as a solvent and the chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane (TMS) unless otherwise noted. Fourier transform infrared (FT-IR) spectroscopy was performed using a JASCO FT-IR 460 plus spectrometer. Transmission spectra were measured from a KBr disc coated with polymer samples. Scanning electron microscopy (SEM) observation of polymer coatings on cotton fabric surfaces was performed

with a HITACHI S3000N scanning microscope at an accelerating voltage of 25.0 kV. The microscope was operated at a specimen chamber pressure of 80 Pa without any electron conductive layer of gold or carbon.

Molecular weights of polymers were measured on a TOSOH HLC-8220 gel permeation chromatography (GPC) system with refractive index (RI) and ultraviolet (UV, $\lambda = 254$ nm) detectors under the following conditions: TSKgel Super HM-H linear column (linearity range, $1 \times 10^3 - 8 \times 10^6$; molecular weight exclusion limit, 4×10^8), tetrahydrofuran (HPLC grade) eluent at a flow rate of $0.6 \text{ mL} \cdot \text{min}^{-1}$, and column temperature of 40°C . The calibration curves for GPC analysis were obtained using polystyrene standards with a low polydispersity (7.70×10^2 , 2.43×10^3 , 3.68×10^3 , 1.32×10^4 , 1.87×10^4 , 2.93×10^4 , 4.40×10^4 , 1.14×10^5 , 2.12×10^5 , 3.82×10^5 , 5.61×10^5 , 2.00×10^6 , Aldrich).

Static contact angle was measured on a Drop Master 500 from Kyowa Interface Science Co., Ltd. to a $2.0 \mu\text{l}$ water droplet at five randomly selected points on the sample surface.

Photo-VASP. Photo-VASP of FMA was carried out in an H-shaped glass tube reactor with a vacuum stopcock, a quartz plate cap, and a glass filter separator (pore size $20\text{-}30 \mu\text{m}$) at the bridge part (Figure SM-1). UV-irradiation was performed with a point light source from a 320 W high-pressure mercury lamp (MORITEX Co., MUV-202-U) ($\lambda = 280\text{-}320 \text{ nm}$).

In a typical procedure, initiator: HMPP (1.0 ml, 5.6 mmol) was placed in the bottom of the small leg of the H-shaped glass tube. The cotton fabric sample ($35 \times 30 \text{ mm}^2$; average weight: 103.52 mg) was set on a stage in the bottom of the large leg of the H-shaped glass tube. HMPP in the tube was subjected to a freeze-pump-thaw cycle conducted three times and then sealed in *vacuo*. Adsorption of vaporized HMPP on the sample surface was carried out in a saturated vapor of HMPP ($6.0 \times 10^3 \text{ Pa}$) in an oven at 40°C for 1 h. After the initiator adsorption, the remaining HMPP was sucked out using a syringe through the glass stopcock under an Ar atmosphere. Then, a mixture of FMA (2.0 ml) and 4-tert-butylpyrocatechol (20 mg) as an inhibitor was introduced into the bottom of the small leg. The FMA/inhibitor solution in the tube was subjected to three freeze-pump-thaw cycles and then sealed in *vacuo*. Photo-polymerization was carried out in a saturated vapor of FMA ($21.5 \times 10^3 \text{ Pa}$) at 40°C under UV-irradiation at a distance of 5 cm from the cotton fabric surface through the quartz plate cap (illumination intensity on the sample surface was $13 \text{ mW}\cdot\text{cm}^{-2}$ ($3.2 \times 10^3 \text{ lux}$) through the saturated FMA vapor). After conducting photo-polymerization for a prescribed time, the monomer vapor and adsorbed monomer molecules were eliminated under vacuum for 24 h at room temperature. The static contact angle between the obtained fabric sample surface and a water droplet was measured, after which the coatings on the surface were extracted by Soxhlet extraction with THF for 24 h to analyze the chemical structure of the product by FT-IR, ^1H -NMR, and GPC.

To estimate the amount of the adsorbed HMPP just before the polymerization, the fabric sample was soaked in 25 ml of acetonitrile for 24 h at room temperature. The amount of the adsorbed initiator was estimated from a UV-visible spectrum of the extracted solution based on a calibration curve.

Result and Discussion

Continuous vapor-phase polymerization on cotton fabric surfaces

Wettability modification of cotton fabric as a typical cellulose fiber was carried out by photo-VASP of FMA with HMPP or BIBE as photo-initiators under UV-irradiation. To maintain the original surface morphology of the cotton fabric, the photo-VASP was achieved with a vaporized initiator and monomer. Figure 1 shows the expected mechanism of the photo-VASP process step by step. This process is started by step (a): distribution and adsorption of vaporized initiator on the substrate surface and followed by step (b): exchange of the content in the vapor phase from initiator to monomer molecules. Step (c), the photolysis of the absorbed initiator occurs under UV-irradiation to generate active species (Scheme 1) and then in step (d), the generated active species induce the polymerization of monomers provided from the vapor-phase on the surfaces.

[Figure 1 goes here]

[Scheme 1 goes here]

The amount of adsorbed initiators on the fabric surface after step (a) for 1 h at 40 °C

was estimated from UV-spectra of extracted solutions by acetonitrile, resulting in a 0.97 (HMPP) and 0.0089 (BIBE) $\mu\text{mol/fabric sample}$. Photo-VASP of FMA (steps (c)~(d)) was carried out at 40 °C under UV-irradiation at various reaction times and illumination intensities in a range of 6~77 $\text{mW}\cdot\text{cm}^{-2}$ (Table 1). Results of the polymerization are listed in Table 1. In the cases using HMPP, the total sample weight increased with time, indicating the polymer accumulation on the sample surface. GPC analysis of the extracted products showed a steady increase in the molecular weight with time, resulting in a weight-average molecular weight, M_w , of greater than 1,000,000 after 6 h of the reaction. On the other hand, no accumulation was obtained without HMPP (sample 1-6). In the absence of UV-irradiation, a small amount of oligomeric product (2.0 mg, $M_w = 480$) was obtained after a long period (12 h) (sample 1-7). Thus, it is clear that PFMA production on the fabric surface was achieved in the presence of both initiator and UV-irradiation. Photo-VASP with BIBE was also carried out under various luminescent intensities and irradiation periods, resulting in a similar accumulation of PFMA on the fabric surface with the contribution from irradiation intensity having a considerable effect on both yield and molecular weight of accumulated polymer.

[Table 1 goes here]

The products accumulated on the substrate surfaces were characterized by FT-IR, $^1\text{H-NMR}$, and GPC in comparison with authentically prepared PFMA ($M_n = 29,000$, $M_w = 49,000$) in a bulk polymerization with AIBN at 80 °C for 1 h. The VASP products were

extracted with THF by using Soxhlet apparatus at reflux temperature for over night to remove free polymers accumulated on surfaces. After the extraction, ^1H -NMR and FT-IR spectra of the extracted polymer from sample 1-3 showed the same profiles as spectra of PFMA obtained by bulk-polymerization (see Figures SM-2 and SM-3 in Supplementary materials); for example, a broad singlet at 4.65 ppm assigned to $-\text{COOCH}_2\text{C}_2\text{F}_5$ in the ^1H -NMR spectrum and characteristic peaks at 1756 cm^{-1} assigned to $\nu_{\text{C=O, ester}}$, as well as 1170 and 1218 cm^{-1} assigned to $\nu_{\text{C-F}}$ ¹³ in the FT-IR spectrum were all found to be the same. These analytical results agreed with previously reported values of PFMA.¹⁴ The molecular weight of the extracted polymers were in a range of $28,600 \sim 1,160,000$ in M_w with large polydispersity values of $2.6 \sim 4.9$, consistent with the peculiar structural property of photo-VASP-products as previously reported.^{10, 12, 15}

As listed in Table 1, the PFMA production with HMPP gradually increased from 2.7 to 7.5 mg over a period of up to 5 h. Over 5 h, a significant increase in polymer accumulation (410.8 mg) was found as shown in sample 1-5 (reaction time 6 h), accompanying an extreme increase in molecular weight. This suggests that the propagation reaction was extremely accelerated once the reaction time exceeded 5 h. A similar phenomenon was observed in a previous study of VASP.¹⁰ Thus, this acceleration must be caused by various factors, such as an increase in the adsorption and absorption area of monomer molecules and the suppression of termination reactions caused by the isolation of active chain-ends on the top surface of

deposits as reported previously.¹¹

Multi-modal profiles with the wide polydispersity values were exhibited as typical profiles of photo-VASP products. In spite of the multi-modal profiles, it was found that the molecular weight tended to increase monotonously with the reaction time and polymer yield, demonstrating the continuous propagation characteristics in photo-VASP.¹⁰

Properties of modified surfaces

A typical surface property of the cotton fabric is its wettability, showing a smooth absorption of water droplets on the surface arising from original natures. A surface deposited by PFMA is expected to give improved water-repellency due to the low surface free energy of PFMA.¹⁶ Moreover, it is well known that surface roughness remarkably affects the apparent hydrophobicity by the lotus effect.¹⁷ Thus, the hydrophobic change in the surface property of the cotton fabric, in retaining its unique morphology, leads us to expect the surface having a superior water-repellency. Figure 2 shows a water droplet on the treated surface and reverse surface of cotton fabrics after photo-VASP of FMA. The photo-VASP-treated surface exhibits a superior water-repellency, as demonstrated by the round-shaped water droplet held on its characteristically surface (Figure 2a). On the other hand, the reverse surface, which did not undergo UV-irradiation, retains the normal hydrophilic property of cotton fabrics, resulting in quick absorption of the water droplet (Figure 2b). These results indicate that the

UV-irradiated surface was selectively changed into a superior hydrophobic surface by photo-VASP, retaining its original surface morphology.

[Figure 2 goes here]

To evaluate the wettability changes in surface properties of the cotton fabrics, the static contact angle value to a water droplet was measured on the surface. Results are listed in Table 1. Original cotton fabrics easily absorbed water droplets due to their naturally superior hydrophilic property (contact angle 0°).¹⁵ After the adsorption of initiator, no change in the property was observed, with the same quick absorption of water droplets (ref. 1 and 2 in Table 1). After photo-VASP of FMA, the hydrophilic property of the surface discontinuously changed into a hydrophobic one, so that the water droplet was held on the surface maintaining its round shape (contact angle $> 130^\circ$) (samples 1-2~1-5 and 2-2~2-3 in Table 1).

The relationship between the PFMA accumulation and the water-repellency was illustrated in Figure 3 using three typical examples. In the case of sample 2-1 (accumulation: 0.6 mg, $57 \mu\text{g}\cdot\text{cm}^{-2}$), a water droplet was rapidly absorbed within 30 s into the fabric body, showing a sudden drop in the contact angle value. On the surface of sample 2-2 (2.1 mg, $200 \mu\text{g}\cdot\text{cm}^{-2}$), a water droplet was held for 5~10 min maintaining its round shape, but thereafter gradually being absorbed into the fabric due to the combined effects of capillary action and the internal native property of fabric. Sample 1-2 (3.5 mg, $333 \mu\text{g}\cdot\text{cm}^{-2}$) also displayed the same absorption behavior. In the case of sample 2-3 (36.8 mg, $3500 \mu\text{g}\cdot\text{cm}^{-2}$) in Figure 3, the

hydrophobicity was sufficient to allow the water droplet to retain its roundness on the surface for over 10 min. Similar results were obtained on the surfaces of samples 1-3 (6.6 mg, 629 $\mu\text{g}\cdot\text{cm}^{-2}$) and 1-4 (7.5 mg, 714 $\mu\text{g}\cdot\text{cm}^{-2}$). These results suggest that there is a critical value in an accumulation range of 333~629 $\mu\text{g}\cdot\text{cm}^{-2}$, at which the repelling property changes discontinuously.

[Figure 3 goes here]

In spite of displaying such a superior hydrophobic property, the PFMA-coated fabrics retained their original tactile nature. However, in the case of sample 1-5, the original tactile nature was lost and a hard solid-like surface was produced as a result of excess accumulation of PFMA (410.8 mg, 39 $\text{mg}\cdot\text{cm}^{-2}$) on the surface. This means that the homogeneous accumulation of polymer was successfully applied to cellulose fiber by the photo-VASP method at a short time.

The reference samples 1-6 and 1-7 showed quick absorption of water droplets just like the native cotton fabric because of the absence of initiator, or failure to accumulate sufficient polymer. Therefore, the superior water-repellency and preserved tactile nature were achieved by a polymer accumulation of thicker than 333 $\mu\text{g}\cdot\text{cm}^{-2}$. This clearly indicates that the hydrophobic property is based on a feature of the surface layer.

Changes in surface morphology after photo-VASP

Changes in the morphology of cotton fabric surface before and after photo-VASP of FMA were examined by SEM observation. Figure 4 shows a typical SEM image of the treated surface (sample 1-4) after photo-VASP. No change in the morphology of the treated surface was observed, indicating that the original fabric surface has been preserved. This is because of the expected homogeneous thin-layer covered with the enough amounts of polymer accumulation ($714 \mu\text{g}\cdot\text{cm}^{-2}$) for the water repellency. On the other hand, a large accumulation of PFMA on the surface (sample 1-5, $39000 \mu\text{g}\cdot\text{cm}^{-2}$) caused the original surface morphology to be lost, resulting in a covering up of the fine structure of the fabric surface (see Figure SM-4 in Supplementary materials).

[Figure 4 goes here]

The cotton fabric substrate (macroscopic dimensions of $35 \times 30 \text{ mm}^2$) must have a huge actual surface area. Considering the weight ratio of accumulation to the substrate (average weight: 103.5 mg), the required amount of covering to give the superior water-repellency must be larger than 3.5 mg per sample ($333 \mu\text{g}\cdot\text{cm}^{-2}$). The accumulated polymers may include free and/or combined chains. To determine the free/combined PFMA components, the accumulated free polymer was dissolved out by THF as a good solvent. SEM images before and after the extraction of free polymer on sample 2-3 (accumulation: 36.8 mg, $3500 \mu\text{g}\cdot\text{cm}^{-2}$) are shown in Figure 5. After the extraction, the sample weight became nearly equal to the original substrate weight, meaning that almost all the accumulated polymer

chains were in the form of free deposits on the surface. In Figure 5, it is clear that the polymer deposits covered the fiber surfaces after the photo-VASP (Figure 5a), whereas the extracted fiber surfaces recovered their original smooth morphology (Figure 5b). From dimension analyses on the SEM images, the PFMA coatings had a thickness of around 2~3 μm even when accumulated by 3500 $\mu\text{g}\cdot\text{cm}^{-2}$.

Interestingly, the extracted cotton surface also showed a high static contact angle value of 138.3° (SD=5.3°) to a water droplet. This retention of hydrophobicity even after the extraction of free polymer chains indicates that the grafting of PFMA chains from/on the cotton surface occurred via chain-transfer reactions such as hydrogen abstraction by generated and growing chain-end radicals during the photo-VASP. A similar phenomenon was reported by Ogiwara et al.¹⁸, where the graft copolymerization of methyl methacrylate occurred on cellulose substrates under UV-irradiation. The grafting must be affected by the extent of photo-initiator adsorption, intensity of irradiation, and surface-covering rate of accumulated polymer chains. Moreover, this finding suggests, importantly, that the superior water-repellency is expressible by the imparting of an extremely thin-layer coating of top surface of substrate.

[Figure 5 goes here]

XPS analysis of photo-VASP-treated fabrics surfaces

To confirm PFMA covering and grafting on substrate by photo-VASP, the chemical composition of the surface layer was characterized by X-ray photoelectron spectroscopy (XPS). Figure 6 shows wide scan XPS spectra of sample 2-2 and the original cotton surfaces. In the spectrum of sample 2-2, an F1s signal with a binding energy (BE) of 690 eV attributed to F atoms in PFMA was clearly observed. On the other hand, no F1s signal was observed in the spectrum of the original cotton surface.

Figure 7 shows C1s core-level spectra of original cotton and sample 2-2 surfaces before and after the extraction by a Soxhlet apparatus using THF as a solvent. The C1s signals of original cotton in Figure 7a consist of a main component with a BE of 286.25 eV and a minor component with a BE of 284.25 eV attributable to component carbons of cellulose.¹⁹ In Figure 7b, the C1s signals were dominated by component carbons of PFMA. Higher BE signals in a range of 287 ~ 295 eV indicate the presence of CF₃, CF₂, C=O, and C-O species on the photo-VASP treated surface. A nearly equivalent XPS profile was obtained from the extracted sample 2-2 surface. This result clearly revealed the PFMA chains as an grafted ultra-thin-layer on cellulose fiber.²⁰

[Figure 6 goes here]

[Figure 7 goes here]

CONCLUSION

Photo-VASP performed continuously in the vapor-phase was demonstrated through the successful alteration of the surface property of cellulose fiber maintaining an original surface morphology. The cellulose fabrics as a typical unique substrate were consecutively exposed to vaporized initiator and FMA monomer under UV-irradiation to start the photo-polymerization, resulting in the selective accumulation of PFMA on the irradiated surface. Both the radical initiator and the UV-irradiation were essential for the successful accumulation by the photo-VASP. The treated substrate surfaces showed superior water-repellency with a static contact angle value larger than 130° . In spite of the addition of the polymer coating to give a superior water-repellency, the cellulose fiber retained its original tactile nature when the deposition was controlled within a proper range of polymer accumulation. These results allowed us to control properties of many kinds of complicated, artificial and/or natural polymer surfaces by photo-VASP using various monomers and initiators. Thereby, many kinds of surfaces with new functionalities may be constructed without compromising their original delicate surface morphologies, because of the thin-layer coating by the photo-VASP.

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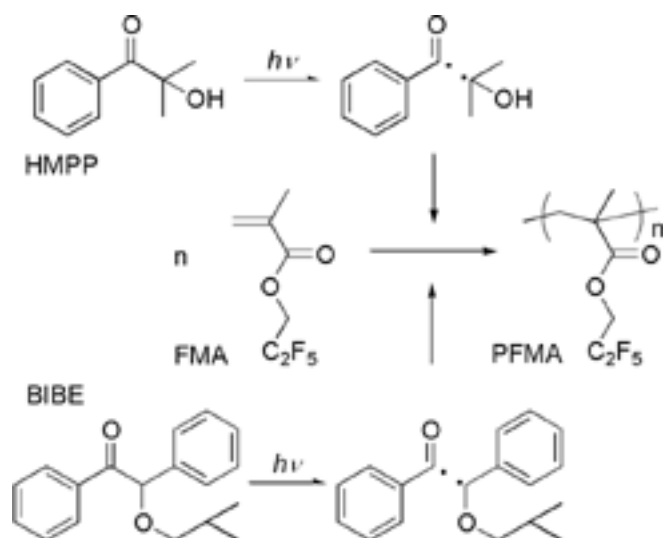
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Figure and Scheme



Scheme 1. Photolysis of HMPP and polymerization of FMA.

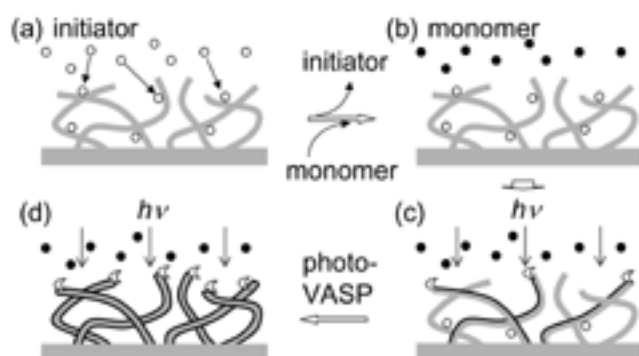


Figure 1. Expected mechanism of photo-VASP process under UV-irradiation: (a) distribution and adsorption of vaporized initiator on cotton fabric surface; (b) exchange of initiator vapor to FMA vapor; (c) distribution and adsorption of vaporized FMA on cotton fabric surface; (d) polymerization of adsorbed FMA molecules under UV irradiation.

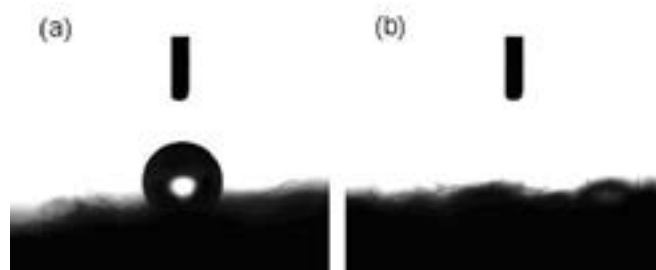


Figure 2. Microscopic images of water droplets on (a) photo-VASP-treated surface with FMA/HMPP under UV-irradiation and (b) the reverse surface without UV-irradiation.

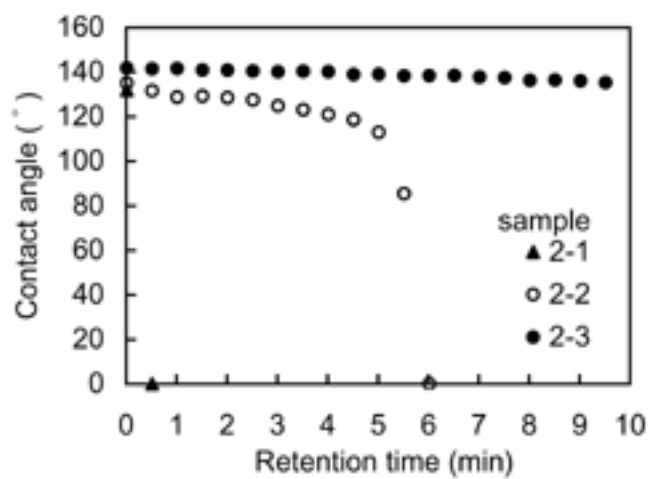


Figure 3. Changes in contact angle to water droplet on cotton fabric surfaces treated by photo-VASP of FMA.

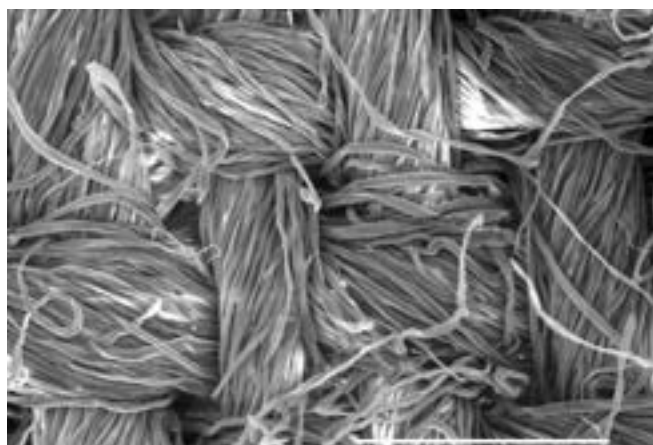


Figure 4. SEM image of cotton fabric surface treated by photo-VASP of FMA. Sample 1-4. Bar 500 μm .

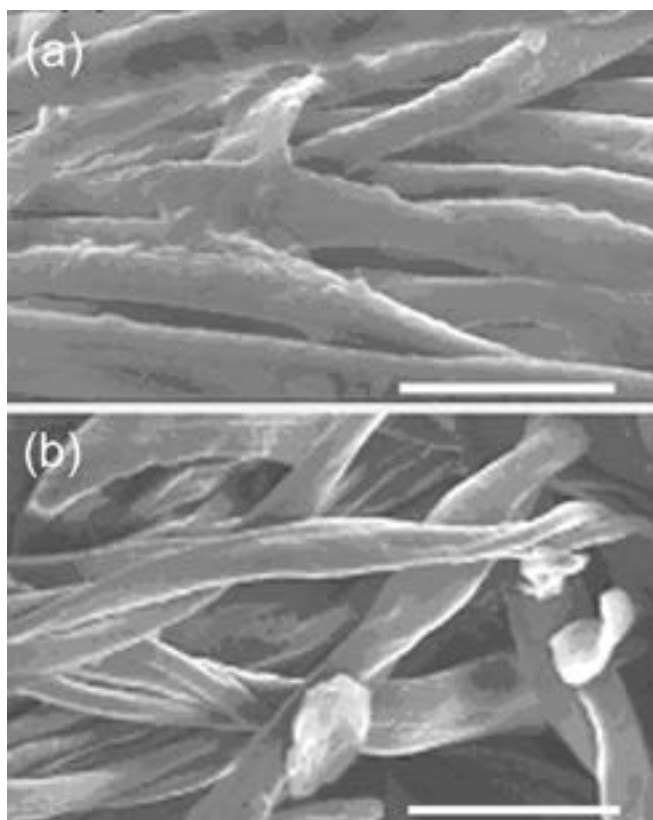


Figure 5. SEM images of cotton fabric surface of sample 2-3 (a) before and (b) after extraction of free polymer by THF. Bar 50 μm .

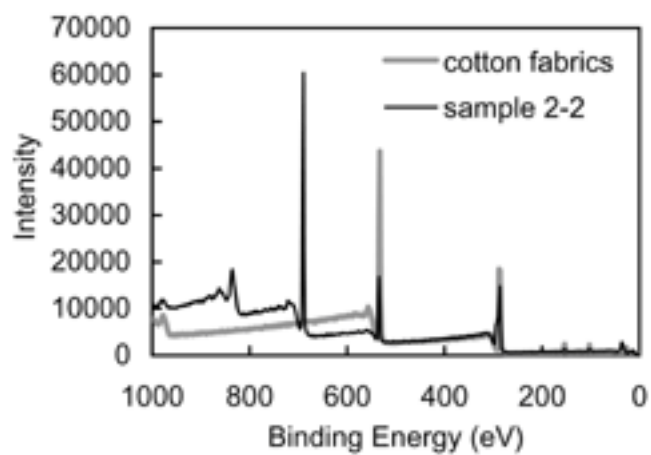


Figure 6. XPS wide scan spectra of sample 2-2 and original cotton fabric surfaces.

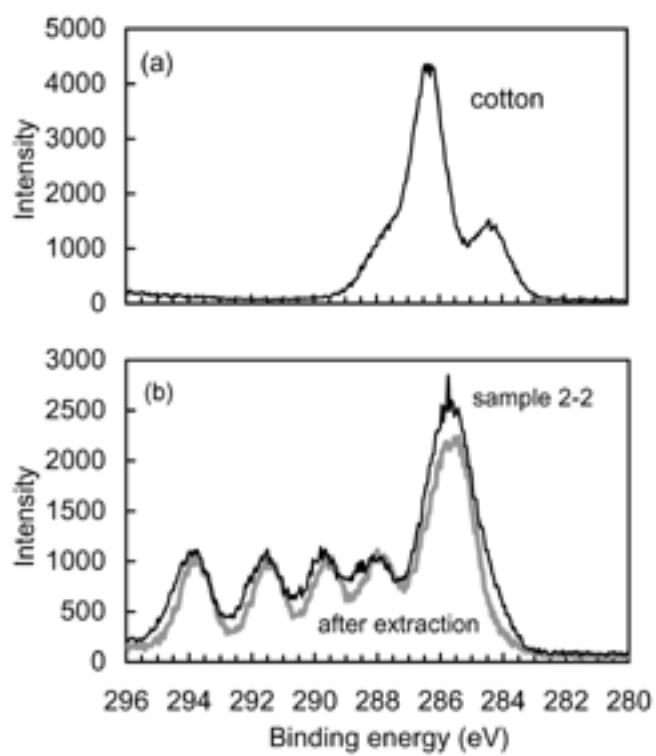


Figure 7. XPS C1s core-level spectra of (a) original cotton and (b) photo-VASP-treated sample 2-2 surfaces. Extraction: Soxhlet extraction for 24 h with THF.