Polymer Journal (2016) 48, 889–896
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ORIGINAL ARTICLE

Contamination control of polymer films by two atmospheric pressure plasma jet treatments

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To control the contamination resistance of polymer surfaces, surface hydrophobization and hydrophilization were attempted by two atmospheric pressure plasma jet (APPJ) treatments. Poly(ethylene terephthalate) and cellulose films were treated by using APPJ for subsequent coating with hexamethyldisiloxane and by APPJ-induced oxidation. For comparison to the APPJ treatments, chemical wet treatments with fluorinated and polyethylene glycol-based resins were also attempted. Each treatment substantially changed the wettability of both films, depending on the surface chemical composition, as determined by X-ray photoelectron spectroscopy. The APPJ-coating and APPJ-oxidation treatments resulted in excellent water and oil repellency and high wettability, respectively. The deposition test was performed using red clay, montmorillonite and carbon black as model contaminants. The experimental results showed that the contaminant deposition onto both films in air was significantly reduced by the APPJ-coating. The removal of any contaminant from both films by aqueous cleaning was promoted by the APPJ-oxidation. The granular morphology of the film surfaces after the APPJ-coating treatment, which was observed by scanning electron microscopy, may be the underlying factor resulting in the superior contamination resistance observed, owing to a decrease in the contact area with the contaminant.

Polymer Journal (2016) **48,** 889–896; doi:10.1038/pj.2016.50; published online 18 May 2016

INTRODUCTION

Most conventional natural and synthetic polymers are relatively resistant to chemicals, lack conductivity, light in weight, significantly strong and low in cost. Because of these properties, polymers are used in numerous applications in almost every industry, including engineering, pharmacy, medicine, agriculture, food and textiles. In production and end-use processes, the presence of small particle and hydrocarbon contaminants can have a large impact on their performance. To obtain the required quality and to maintain the material performance, the contamination resistance of polymer surfaces is of fundamental interest to a wide variety of industries.[1]

In general, contamination resistance is dominated by surface energetics. Surface modification and coatings, which do not affect the desirable bulk properties of the polymeric materials, have been used to change the surface energetics to control various properties, including adhesion, wettability, printability, biocompatibility, chemical resistance and barrier properties.[2,3] Methods for surface modification include liquid (wet) chemical processes[4,5] as well as reactive gas (dry) chemical processes such as corona,[6,7] flame[8–10] and low-temperature plasma treatments.[11–17] In the case of wet processes, a large amount of finishing agents and solvents are required, which, in turn, requires high-cost drying and pollutant-treating steps. Dry processes are an eco-friendly technology that eliminates these waste liquids.

Recently, cold atmospheric plasma surface processing systems, with various gases and gas mixtures, have received considerable attention[18–22] because these systems generate plasmas in open space and they are used in high-speed in-line processing.[23–27] We have oxidized several polymer surfaces using the atmospheric pressure plasma jet (APPJ) technique and have found large increases in the surface wettability and roughness.[28–33]

However, plasma-coating technology using organosilanes has also been recently developed to decrease wettability. Hexamethyldisiloxane (HMDSO) is the preferred precursor used in plasma polymerization because of its high organic character, as well as its high vapor pressure. The plasma deposition of HMDSO mixed with different carrier gases has been extensively studied using low-pressure non-thermal plasmas.[34–36] To avoid the limitations of applying vacuum systems in plasma-enhanced thin-film depositions, an APPJ treatment has also been used.[37–39]

To enhance the contamination resistance of polymer surfaces, it is necessary to promote contaminant removal in aqueous cleaning systems as well as to prevent the contaminant deposition in air. From an adhesion viewpoint,[40] the contaminant deposition in air can be prevented by surface hydrophobization, by decreasing the wettability, whereas the contaminant removal in an aqueous solution can be promoted by surface hydrophilization, by improving the wettability. Furthermore, it is known that the surface electricity[41–44] and morphology[45,46] can affect the deposition of contaminants from the atmosphere.

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Received 6 December 2015; revised 17 March 2016; accepted 24 March 2016; published online 18 May 2016

The purpose of the present study was to obtain fundamental information with respect to contamination resistance of polymer surfaces. Two polymer films, hydrophobic poly(ethylene terephthalate) (PET) and hydrophilic cellulose films, were treated with both a dry APPJ process and a wet process to change the surface wettability. After characterization of the untreated and treated film surfaces, the contamination resistance was investigated by microscopy and is discussed in terms of surface energetics, electricity and morphology.

EXPERIMENTAL PROCEDURE

Materials

Poly(ethylene terephthalate) (PET, thickness 188 μm, Melinex, S-188, Teijin DuPont, Tokyo, Japan) and cellulose (thickness 20 μm, Rengo Co., Ltd, Tokyo, Japan) films were used in this study. The PET film was ultrasonically cleaned in water at 60 °C twice, and the cellulose film was cleaned in boiled water twice.

For the wet chemical treatments, fluorinated water and oil repellent resin (Paraguard AF-600, Ohara Paragium Chemical Co., Ltd, Kyoto, Japan), and a polyethylene glycol (PEG)-based hydrophilizing resin (Parasolbe PET, Ohara Paragium Chemical Co., Ltd) were used. As an organic precursor for the APPJ surface coating, HMDSO (LS-7130, Shin-Estu, Tokyo, Japan) was used.

Three model particulate contaminants were chosen on the basis of the dust content in ambient air: red clay (JIS Z 8901, Kanto (Japanese) loam, class 11, The Association of Powder Process Industry and Engineering, Kyoto, Japan), montmorillonite (Alfa Aesar, Ward Hill, MA, USA) and carbon black (Sentakukagaku-kyokai, Tokyo, Japan). Ultra-pure water and extra-pure grade diiodomethane and hexadecane were used as probe liquids for evaluating wettability. An alcohol ethoxylate (AE) surfactant, with an alkyl chain length of 12 carbon atoms and an ethylene oxide chain length of 10 with a critical micelle concentration of 0.14 mmol dm^{-3},[47] was provided by the Lion Corporation, Tokyo, Japan.

The water was purified (resistivity of 18 MΩcm) using a Direct-Q UV apparatus (Millipore, Billerica, MA, USA).

APPJ surface treatment

The APPJ surface polymer coating[37,38] was performed with PAD-1 nanocoating equipment (Plasmatreat GmbH, Steinhagen, Germany). The plasma-processing parameters were determined by preliminary experiments. Nitrogen was used as a reactive gas together with HMDSO vapor. The pressure and the flow rate of nitrogen gas were regulated at 0.3 MPa and 33.3 l min^{-1}, respectively, and the flow rate of HMDSO was maintained at 0.66 g min^{-1}. The APPJ nozzle with a 5-mmϕ head was set vertically, and the film was horizontally displaced at a separation distance of 15 mm from the nozzle head. During the treatment, the APPJ nozzle was reciprocated at 160 mm s^{-1} in the horizontal direction by 3 mm feeding per 1 pitch.

The APPJ surface oxidation was carried out using plasma-pretreatment equipment (FG 1001, HTR 1001 and RD 1004, Plasmatreat GmbH).[30,48] The plasma-processing parameters used were obtained from a previous study.[28,30] The chosen reactive gas was nitrogen, which was regulated at 0.3 MPa and 20 l min^{-1}. The APPJ nozzle with a 20-mm diameter head was set vertically, and the film was placed on the sample stage 7 mm away from the nozzle head. During exposure to the APPJ, the film was reciprocated at 80 mm s^{-1} in a horizontal direction. It has been reported that the wettability of the polymer film decreases with storage after being subjected to dry processing. We found that the water contact angle remained almost constant for 3 days after the APPJ treatment.[28,30,31] In this study, the polymer films were stored for 3 days prior to performing the experiments below.

Wet processing surface treatment

The film (200 × 200 mm^2) was immersed in a 0.1-dm^3 aqueous solution containing either the fluorinated resin (3 wt%) or the PEG-based resin (5 wt%). After 10 min, the film was removed from the solution and dried at 110 °C for 2 min. The 1-min heat treatment was then carried out at 170 and 180 °C for the fluorinated and PEG-based resins, respectively.

Scanning electron microscopic (SEM) observation

The surface morphology of the films was investigated using SEM (SU1510, Hitachi, Tokyo, Japan) operated at an accelerating voltage of 5 kV. All samples were cut into 5 × 5 mm^2 pieces before being coated with a tungsten layer in a fine coater (JFC-1600, JEOL, Tokyo, Japan) for 200 s prior to characterization.

X-ray photoelectron spectroscopic (XPS) analysis

XPS was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical Ltd., Manchester, UK) equipped with a monochromatic X-ray source (Al K_α, $h\nu = 1486.7$ eV). The survey spectra were recorded using a pass energy of 80 eV and a slot aperture of 0.8 × 2.0 mm^2. Charge neutralization was used for all samples. The spectra were acquired at a photoelectron take-off angle of 90°. The pressure was maintained below 10^{-8} Pa during analysis.

Contact angle measurements

The sessile drop contact angles of water, diiodomethane and hexadecane on the PET and cellulose films were evaluated using a commercial apparatus (VCA-2500, AST Products, Billerica, MA, USA). The 2–3-μl droplet was placed on the film sample (5 × 30 mm^2). The contact angle was determined immediately as the approximate value of the advancing contact angle.[49] The measurements were repeated 10 times for the same sample and the arithmetic mean angle was calculated. The experimental error was within ± 3% for the same sample.

The measurements were performed in a room that was maintained at 20 °C and 65% relative humidity (RH).

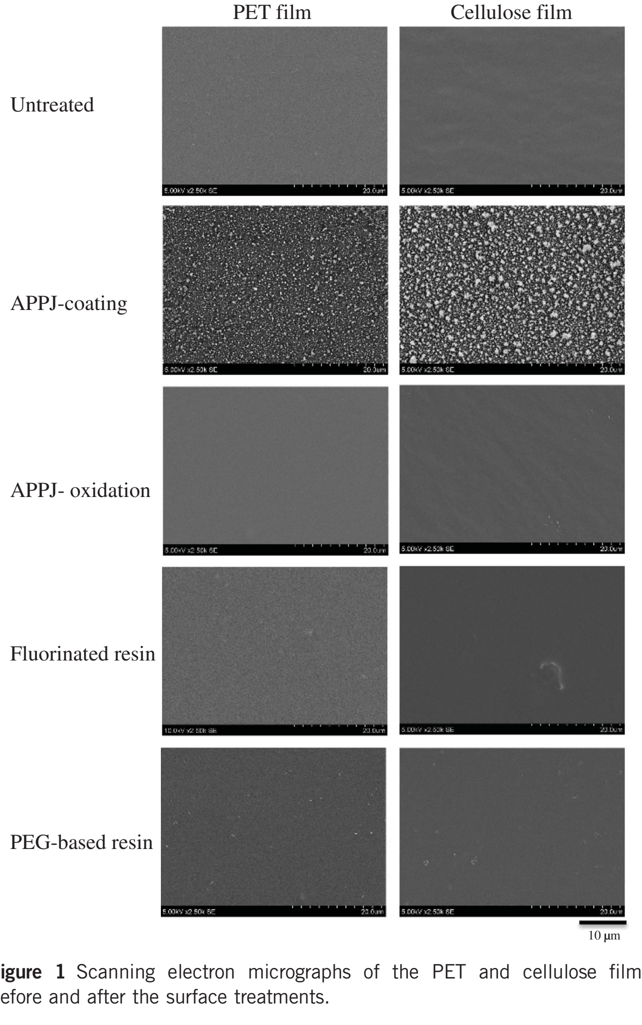

Figure 1 Scanning electron micrographs of the PET and cellulose films before and after the surface treatments.

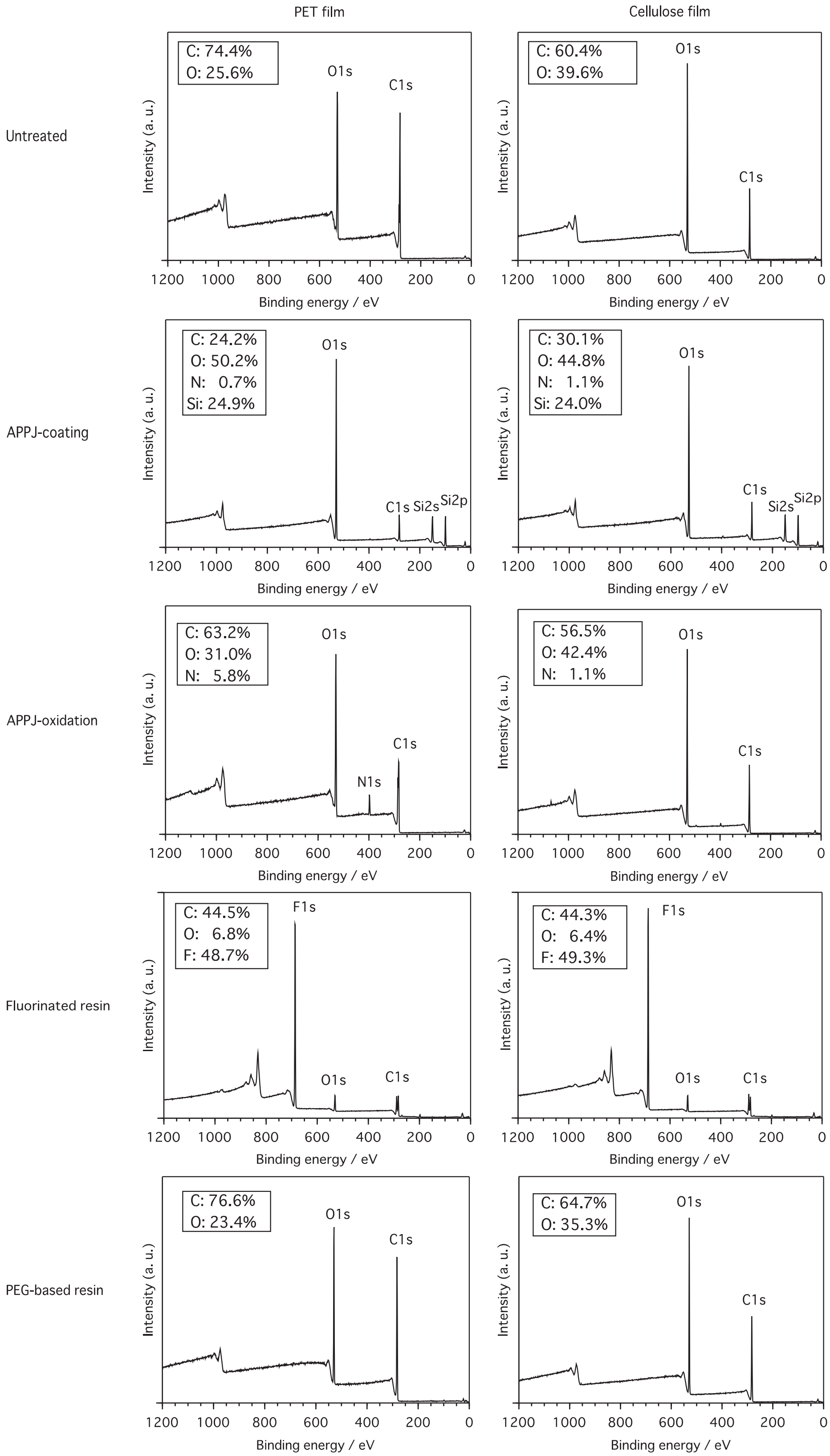

Figure 2 The XPS survey spectra of the PET and cellulose films before and after the surface treatments.

Static electricity evaluation

Triboelectric charge accumulation testing was performed with an electrostatic electrometer (SK-030/200, Keyence Corp., Osaka, Japan). After reduction of electrostatic charges < -0.5 mV using a compact ionizer (APDIT, AS ONE, Japan), the film (100×100 mm^2) was rubbed 10 times at 1 cycle s^{-1} with cotton fabric (JIS Test Fabric, Japanese Standards Association). The change in the electrostatic potential with time was recorded immediately after hanging the film 70 mm away from the sensor. The measurements were carried out in a room maintained at 20 °C and 65% RH.

Contaminant-deposition experiments

The contaminant deposition on the film in air was investigated in reference to JIS L1919, A-1.[50] A polyethylene cylindrical bottle (90 mmϕ × 190 mm) containing the films (40×40 mm^2) and the particulate contaminant was rotated at 60 r.p.m. for 20 min. The same batch contained the PET or cellulose films, untreated and treated (a total of five films), as well as 0.03 g of red clay, 0.03 g of montmorillonite or 0.01 g of carbon black, which was determined by preliminary experiments. The contaminant-deposition experiments were performed in a room maintained at 20 °C and 65% RH.

The contaminant deposition onto the film was evaluated by binary processing of microscopic images. A biological microscope (CKX41, Olympus, Tokyo, Japan), a complementary metal-oxide-semiconductor camera (Lu275, Lumenera, Nepean, ON, Canada), image-tiling software (e-Tiling, Mitani Corporation, Fukui, Japan), and 2D image-analysis software (WinRoof Ver. 6, Mitani Corporation) were used for the evaluation. Microscopic images were retrieved over five different areas (0.13 mm^2 per area) on the film. The image obtained was converted from an original gray-scale digital image with 256 possible intensity levels to a binary image using an appropriate threshold level (~105 in most cases).[51] The surface coverage of the deposited particles on the film was automatically calculated as a measure of the contaminant deposition.

The deposition experiments were repeated 4–8 times under the same experimental conditions.

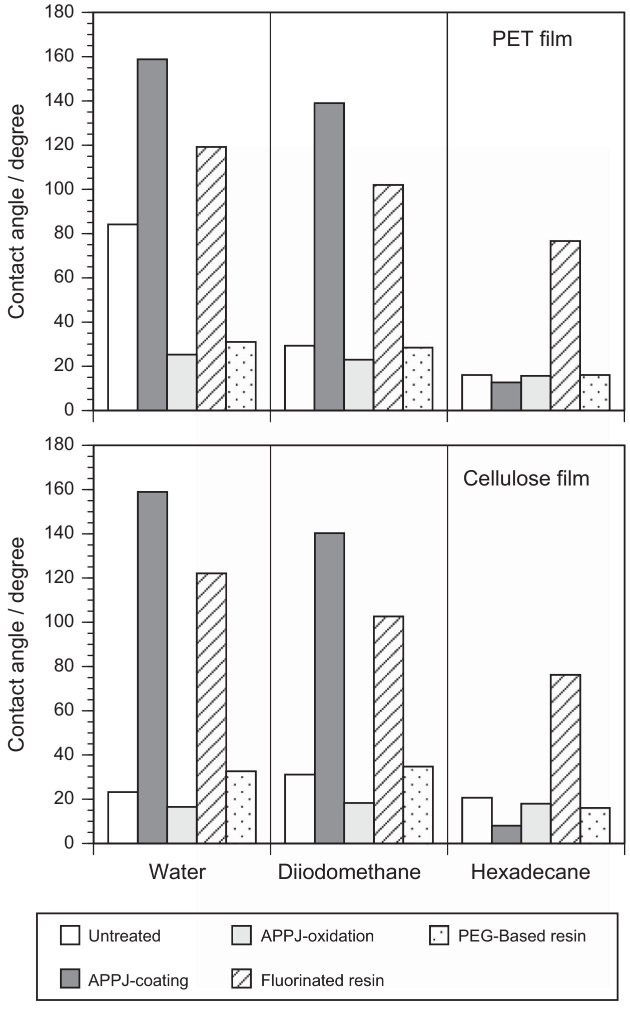

Figure 3 Liquid contact angles on the PET and cellulose films before and after the surface treatments.

Contaminant-removal experiments

The deposition of each particulate contaminant onto the film prior to the contaminant-removal experiment was carried out as described above. After storage for 24 h in a room maintained at 20 °C and 65% RH, the film was cleaned by the perpendicular immersion into a 0.02 dm^3 detergent solution containing $[\mathrm{AE}] = 0.16$ mmol dm^{-3} and $[\mathrm{NaCl}] = 1$ mmol dm^{-3}. As a mechanical action for contaminant removal, an agitation action at 600 r.p.m. was applied with a magnetic stir bar (1.5 mmϕ × 10 mm). The cleaning temperature was set to 25 ± 1 °C. After cleaning for 5 min, the film was removed from the detergent solution and dried in air without rinsing to avoid removing any further contaminants remaining on the flat film after the cleaning process was performed.

The contaminant surface coverage of the film after cleaning was determined by using microscopic image analysis as mentioned above. The removal efficiency was calculated from the contaminant surface coverage before and after cleaning.[51]

The removal experiments were repeated 4–8 times under the same experimental conditions.

RESULTS AND DISCUSSION

Surface morphology and chemical composition of films

Figure 1 shows the SEM images of the PET and cellulose films before and after treatment. For both films, the untreated surfaces were very smooth. Some irregular traces were observed on the film surfaces treated with the fluorinated and PEG-based resins. Although the film surface was rinsed with water after the wet chemical treatment, the traces did not disappear. After the APPJ-coating treatment, the surface morphology of both films became granular. Similar results have been reported for plasma polymerization using HMDSO.[52–56] However, the film surfaces after the APPJ-oxidation were found to be as smooth as the untreated films.

The XPS wide scan spectra are shown in Figure 2. The obtained surface atomic compositions are inserted in the figures. After the APPJ-coating, the amount of silicon was detected to be approximately half that of oxygen, which confirms the successful deposition of silicon oxides, predominantly SiO_2, onto the polymeric substrates at atmospheric pressure.[37,38,57,58] In the case of the films treated by the plasma-oxidation, the oxygen concentration increased by several percent and was accompanied by the appearance of a nitrogen peak. This observation suggests that polar functional groups had successfully been produced on the polymeric surfaces.

A fluorine concentration of ca. 50% was found for both films treated with the fluorinated resin. A slight decrease in the O/C ratio owing to the treatment with the PEG-based resin was observed in both cases. In contrast, the cellulose and PET films after treatment with the PEG-based resin exhibited a different O/C ratio. This observation suggests that the films were not perfectly covered with the PEG-based resin or that the thickness of the PEG-based resin layer was smaller than several nanometers, as detected by XPS. For either film, a slight decrease in the O/C ratio owing to the treatment with the PEG-based resin was observed.

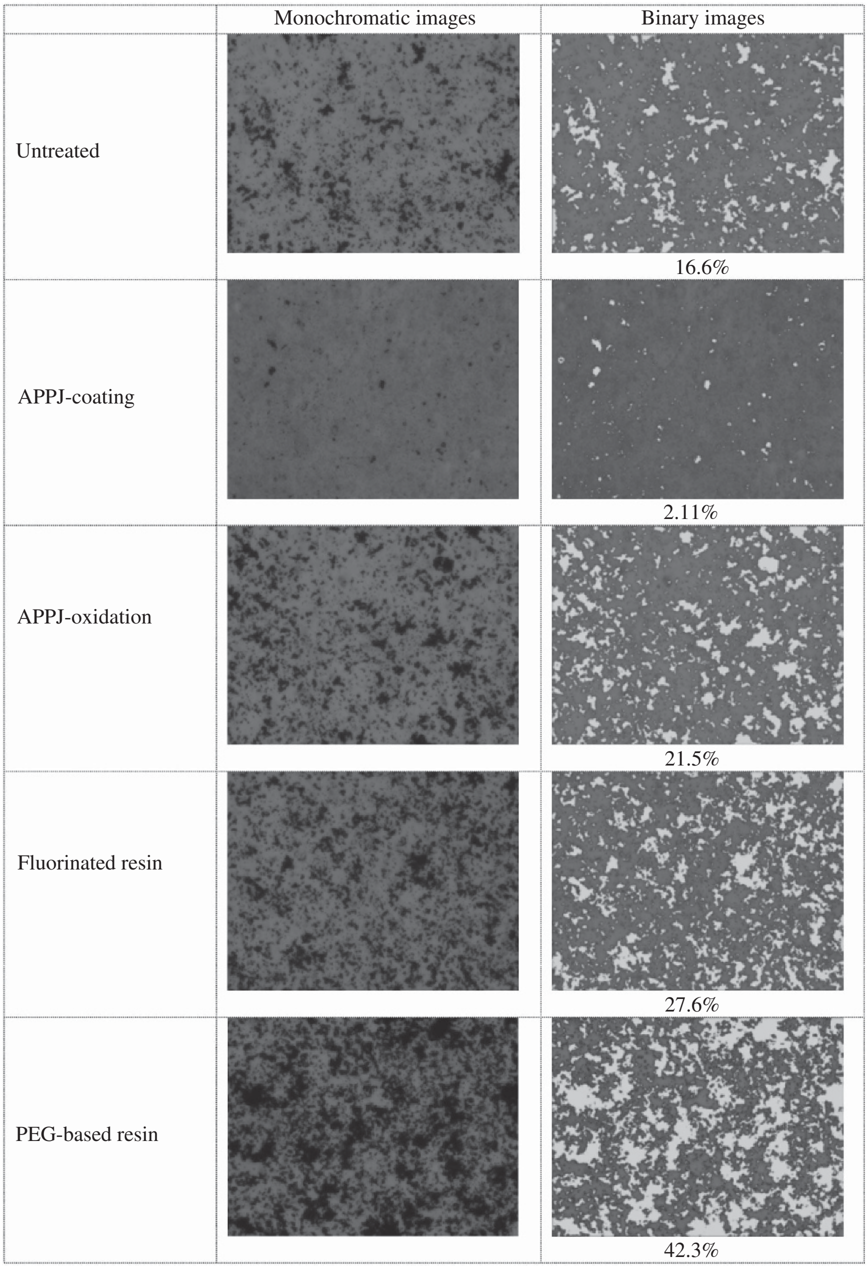

Figure 4 Microscopic images (left figures) of red clay deposited on the PET film before and after the surface treatments, their binary images (right figures) using a threshold level of 105 and the surface coverage (%) of red clay deposited onto the PET film. A full color version of this figure is available at the *Polymer Journal* online.

Wettability of films

Figure 3 shows the contact angles of three liquids on the PET and cellulose films before and after treatment. As expected, the contact angle of water on the hydrophobic pristine PET film decreased after treatment with APPJ-oxidation and the PEG-based resin. For the hydrophilic cellulose film, such treatments did not significantly change the measured contact angles.

The contact angle of water on both films increased as expected after the treatment with the APPJ-coating and the fluorinated resin. The APPJ-coating in particular exhibited excellent water repellency. However, the contact angles of the oily substances, including diiodomethane and hexadecane, were relatively large after treatment with the fluorinated resin. For films treated with the APPJ-coating, the contact angle of diiodomethane was very large but that of hexadecane was very low, showing superoleophilic properties. de Givenchy *et al.*[59] have reported that a poly (dimethyl siloxane) plate surface roughened by sulfuric acid corrosion exhibits contact angles of 130, 110 and 30° with water, diiodomethane and hexadecane, respectively. These results are in agreement with the contact angle behavior observed in the present study.

Notably, the contact angles measured on the PET and cellulose films after each treatment were very similar. These experimental findings indicate that the SiO_2 film produced by the APPJ-coating, PEG-based resin and fluorinated resin completely covered the film surfaces.

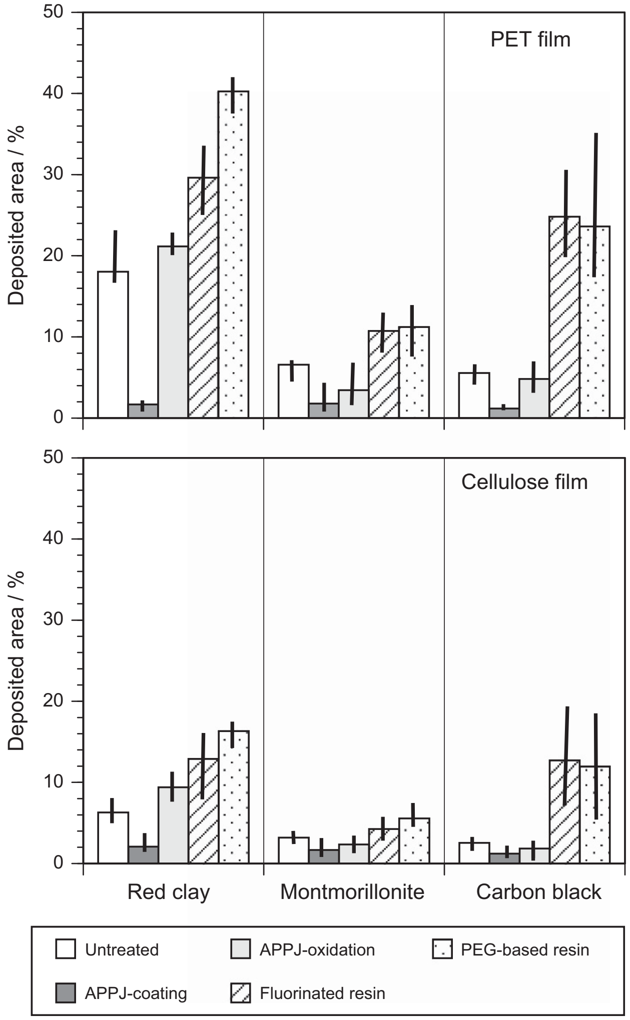

Figure 5 Surface coverage of the deposited particulate soil on the PET and cellulose films before and after the surface treatments, determined by microscopic image analysis.

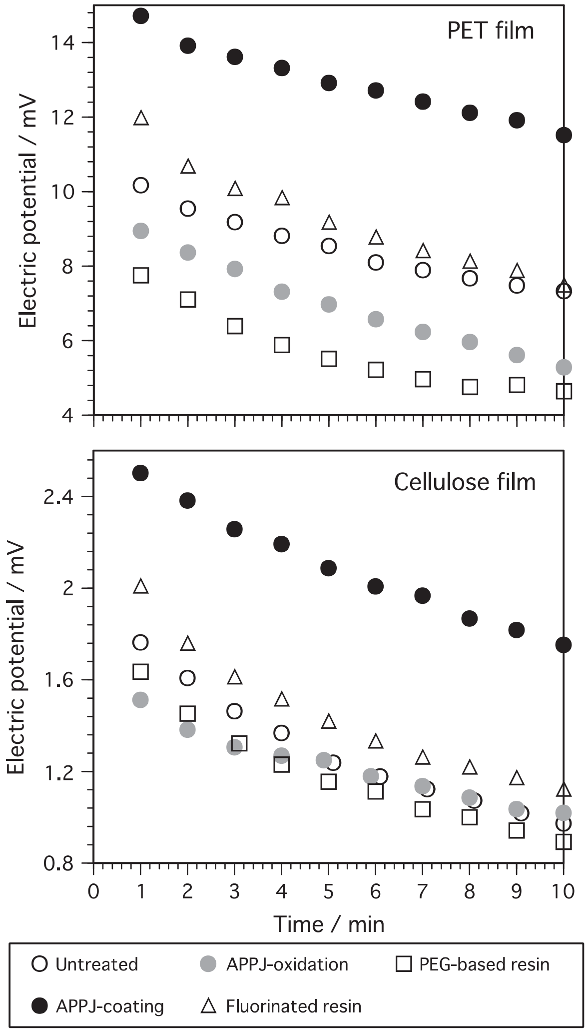

Figure 6 Changes in the electric potential of the PET and cellulose films before and after the surface treatments after rubbing with cotton fabric with time.

Effect of surface treatment on contaminant deposition

Figure 4 (left figures) shows the gray-scale digital images of the untreated and treated PET films after deposition of red clay in air. The converted binary images are also shown in Figure 4 (right figures) together with the surface coverage by red clay on the PET film. The deposition of red clay decreased after the APPJ-coating and increased after the wet treatment with the fluorinated and PEG-based resin.

The surface coverage of three particulate contaminants deposited onto the PET and cellulose films are summarized in Figure 5. A similar tendency was obtained between the PET and cellulose films with respect to the effects of the contaminant species and the treatment process, although the amount of contaminant deposited on the cellulose film was small in comparison with that deposited on the PET film. The deposition of contaminants was prevented by the APPJ-coating and was promoted by the wet treatments with the fluorinated and PEG-based resins. The surface hydrophilization by the APPJ-oxidation did not significantly affect the contaminant deposition. The change in contaminant deposition owing to treatment with the fluorinated resin and APPJ-oxidation are not consistent with the expectations from adhesion.[40] Therefore, there is another dominant factor that influences the contaminant-deposition behavior observed in the present study.

It is well known that the accumulated static electricity can influence the contaminant deposition onto the polymer surface.[41] Figure 6 presents the electrostatic potential on the film surface as a function of time after rubbing with cotton. The hydrophobic PET film showed a large frictional electrification before and after the treatments in comparison with hydrophilic cellulose, leading to a large deposition of contaminants, as shown in Figure 5. For both films, the frictional electrification decreased after surface hydrophilization with APPJ-oxidation and the PEG-based resin. Water molecules adsorbed onto the functional groups produced on the film surface may mitigate the accumulation of electric charge. This decrease in the electric charge did not have a significant effect on the contaminant-deposition behavior of APPJ-oxidation when compared with hydrophilization. After hydrophobization with APPJ-coating and the fluorinated resin, the frictional electrification increased as expected, particularly in the case of APPJ-coating. We analyzed the SiO_2 layer on the PET film, which was prepared by APPJ-coating in the present system and found that the outer layer of the SiO_2 film consists of -Si-$(CH_3)_3$ derived from HMDSO.[60] The outer layer may have a large influence on the

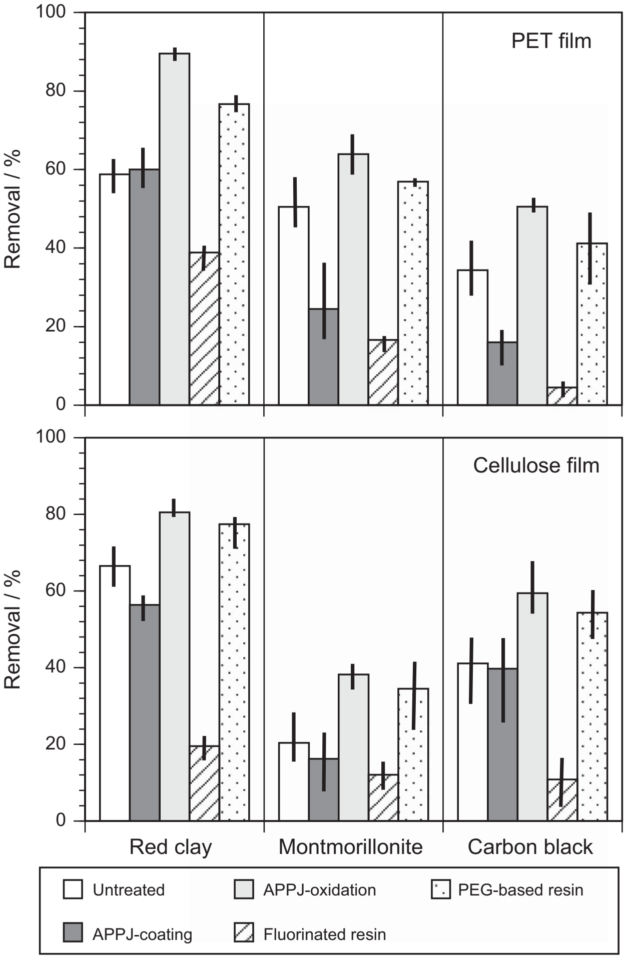

Figure 7 Removal efficiency of particulate soil from the PET and cellulose films before and after the surface treatments, determined by microscopic image analysis.

frictional electrification behavior. Nevertheless, APPJ-coating markedly prevented the contaminant deposition (Figure 5). It is believed that the granular surface morphology (Figure 1) decreased the contact region between the film and particulate contaminant, resulting in the observed reduction in contaminant deposition.[45,46,61] However, considerable contaminant deposition on the film treated with the fluorinated resin cannot be explained in terms of frictional electrification.

Effect of surface treatment on contaminant removal

The removal efficiencies of four contaminants from the untreated and treated PET and cellulose films in the detergent solution are given in Figure 7. In general, soil removal in an aqueous solution from substrates characterized by a high wettability is favorable.[62,63] For any film and contaminant, the contaminant removal was promoted after hydrophilization, as expected. APPJ-oxidation significantly improved the removal of contaminants compared with surfaces treated with the PEG-based resin, which is consistent with the water wettability in Figure 3. On the other hand, hydrophobization with APPJ-coating and the fluorinated resin resulted in a decrease in the removal of contaminants. In comparison to the fluorinated resin, the decrease of the contaminant removal after APPJ-coating was relatively small between any soil and film as a result of the decreased contact region, as mentioned above.

The results in Figure 7 show that the change in the contaminant removal owing to the surface treatment can be explained in terms of surface energetics.

CONCLUSIONS

The APPJ and wet chemical treatments markedly changed the wettability of the PET and cellulose films, depending on the surface chemical composition detected by XPS analysis. In particular, APPJ-coating with HMDSO resulted in excellent repellent properties toward water and diiodomethane. Contaminant deposition onto the films, as determined by binary processing of microscopic images, was significantly prevented by APPJ-coating and was promoted by the wet processes with the fluorinated resin, as well as the PEG-based resin. As expected, contaminant removal from the films in an aqueous detergent solution was promoted by surface hydrophilization through APPJ-oxidation and the PEG-based resin and was prevented by surface hydrophobization through APPJ-coating and fluorinated resin. The experimental results confirm that the contamination resistance of polymer surfaces is controlled predominantly by surface energetics, but there is another dominant factor, particularly when contaminant deposition occurs in air. SEM observations showed a granular morphology of the film surfaces after APPJ-coating, and this was accompanied by superior contamination resistance owing to a decrease in the contact region between the film and the contaminant. APPJ treatment is superior to the wet chemical treatment in terms of the improvement in contamination resistance of the polymer surface.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

We thank Nihon Plasmatreat Inc. for sample preparation through APPJ-coating as well as Miss Natsumi Togawa of Nara Women's University for her experimental assistance. We also thank Teijin DuPont, Rengo Co., Ltd, Lion Corporation and Ohara Paragium Chemical Co., Ltd for providing the PET and cellulose films, the non-ionic surfactants and the two resins, respectively. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan via a Grant-in-Aid for Scientific Research (B) (grant number 26282012).

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