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Polymer 46 (2005) 6976–6985
polymer
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Surface grafting polymerization and modification on poly(tetrafluoroethylene) films by means of ozone treatment

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Received 8 April 2005; received in revised form 28 May 2005; accepted 30 May 2005
Available online 1 July 2005

Abstract

Surface modification on polytetrafluoroethylene (PTFE) films was performed with sequential hydrogen plasma/ozone treatments and surface-initiated polymerization. C–H groups were introduced to the surface of PTFE films through defluorination and hydrogenation reactions under hydrogen plasma treatment. The C–H groups then served as ozone accessible sites to form peroxide groups under ozone treatment. Grafting polymerization initiating from the peroxide groups was performed on the PTFE film surface with using acrylamide, acrylic acid, glycidyl methacrylate and 2-(2-bromoisobutyryloxy)ethyl acrylate (BIEA) as monomers. With utilizing the isobutylbromide groups on the surface of PTFE-*g*-PBIEA film as initiators, sodium 4-styrenesulfonate (NaSS) was polymerized onto the PTFE film surface via atom transfer radical polymerization, to bring arborescent macromolecular structure to PTFE film surface. The chemical structures of the macromolecules on PTFE film surfaces were characterized with FTIR-ATR, SEM-EDX and XPS. The surface hydrophilicities of modified PTFE films were significantly enhanced with the modification.

Keywords: Polytetrafluoroethylene (PTFE); Surface modification; Ozone

1. Introduction

Polytetrafluoroethylene (PTFE) is an attractive material for using in flexible printed circuit boards, multi-layer electronic packages, low friction films, protective sealing and biomedical fields. The wide applications of PTFE are basing on its outstanding bulk and surface properties, such as high thermal stability, excellent chemical inertness, low dielectric constants, low water sorption, extremely frictional resistance and low surface energy [1–4]. However, the extremely hydrophobic and poor adhesive properties of PTFE limit its performance in application. To introduction particular functional groups onto the polymer film surface could improve the performance and make it promising in other practical application [5–10]. A lot of attempts focusing on improving the surface properties of PTFEs have been reported. Some approaches are chemical etching with sodium naphthalene, UV-lasers, electron and ion beams irradiation, ^{60}Co γ-rays irradiation and plasma modification [10–21]. Among these methods, plasma treatments, including plasma polymerization and plasma-induced grafting polymerization, are attractive for their high efficiency [18–21]. However, both plasma polymerization and plasma-induced grafting polymerization involves complicated processes [22]. The complicated steps of plasma grafting polymerization process in vacuum system are the knotty problem for applying in industrial manufacture. Control of the molecular weights and well-defined macromolecular architectures are almost impossible while employing the plasma techniques on PTFE surface modifications. Recently, Yu et al. reported the first attempt of bringing controlled macromolecular structures onto PTFE film surface by means of combination of plasma activation and controlled radical polymerizations (RAFT and ATRP) techniques [23]. However, the reported process is still very complicated.

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doi:10.1016/j.polymer.2005.05.116

In addition to plasma treatment, ozone treatment is another efficient method for polymer surface modification [24–28]. Generation of alkylperoxide and hydroperoxide groups, which could serve as reactive sites for further reactions and modifications, on polymer chains or polymer film surfaces has been characterized with ozone treatment [28]. The ozone treatment induced grafting copolymerization reaction exhibits some advantages over other processes. The process can be carried out at atmospheric pressure, with simple and inexpensive apparatus, which is quick and easy to use. The ozone treatment is applicable to three-dimensional objects. Controls of molecular weights and chemical structures of the polymer chains built on the surface of polymeric substrates could be achieved with molecular design and controlled polymerization techniques [29,30]. Some patents also present that ozone treatment is suitable for mass production in practical industries [31–36].

In spite ozone process is convenient for using in polymer modification, this technique is restricted for PTFE modification because of the strong bonding energy of C–F bonds in PTFE structure [37]. An attempt of applying ozone treatment to surface modification of PTFE film is reported in this work. First, a hydrogen plasma treatment was applied to PTFE films for incorporation of some C–H groups on the film surface. Therefore, the PTFE surface modified by hydrogen plasma possesses the hydrocarbon surface and PTFE bulk characteristics to susceptible to ozone treatment as other polymer. The incorporated hydrocarbon could be converted to alkylperoxide and hydroperoxide groups after ozone treatment. Surface initiated radical polymerization and atom transfer radical polymerization (ATRP) are then performed to incorporate linear and arborescent macromolecular structures to PFTE film surfaces. This approach certainly extends the scopes of surface modification for PTFE films.

2. Experimental

2.1. Materials

Dense PTFE films (Nitto Denko Co., Ltd, Japan) were cut into 25×50 mm^2 pieces for using as specimen in surface modification experiments. The specimen were washed with acetone in an ultrasonic washer and dried at room temperature under vacuum prior to use. Acryamide (AAm), acrylic acid (AAc), glycidyl methacrylate (GMA), 2-bromoisobutyl bromide (Merck Co.), sodium 4-styrenesulfonate (NaSS) (Fluka Chemie), 2-hydroxyethyl acrylate (HEA) (Aldrich Chemical Co.) and triethylamine (Tedia Co.) were used as received. The catalysts of copper(I) chloride (CuCl) and copper(II) chloride (CuCl$_2$) and the ligand of bipyridine (bPy) for ATRP reaction were purchased from Aldrich Chemical Co. and used as received. The inimer of 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA) was prepared in our laboratory [29].

2.2. Surface activation on PTFE films

Hydrogen plasma treatment was performed with a capacity coupling electrodes (Dressler HF-Technik GmbH, Germany; model CESAR-1310) under the conditions of a hydrogen mass flow rate of 10 sccm (standard cm^3/min), a radio frequency of 13.56 MHz, a power of

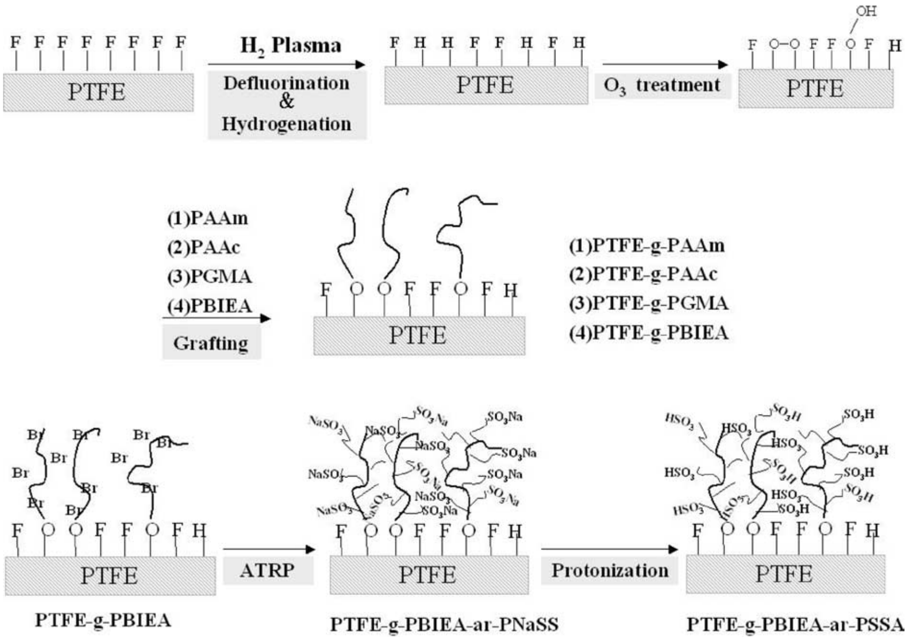

Fig. 1. A typical scheme of hydrogen plasma pretreated PTFE film surface.

50 W, a pressure of 0.1 Torr and a reaction time of 180 s. After plasma treatment, PTFE films were immersed in 80 ml isopropanol (IPA). A continuous O_3/O_2 mixture stream (flow rate: 6 l/min; O_3 concentration: 28 g/m^3) generated from an ozone generator (Ozone Group, Taiwan) was bubbled through the liquid at room temperature for about 15 min. The liquid was icy cooled; PTFE films were draw out and then dried at room temperature under vacuum.

2.3. Surface initiated grafting polymerization of PTFE films

The activated PTFE films were immersed in the 50 ml solutions of various monomers in IPA. The monomer concentrations were 20 wt% for AAm, AAc and GMA and was 10 wt% for BIEA. The solutions were degassed by argon purge and frozen degas process. The reaction system was then heated to 80 °C and then reacted at 80 °C for 24 h and then was quenched in an ice bath. PTFE films were then draw out, washed with water and acetone in an ultrasonic washer and dried at room temperature under vacuum.

2.4. Incorporation of arborescent copolymer on PTFE film surface via atom transfer radical polymerization (ATRP)

PTFE-*g*-PBIEA film was immersed in 30 ml DMSO and then purged with argon for 30 min. Sodium 4-styrenesulfonate (NaSS, 4 g), 2,2′-bipyridine (316 mg), $CuCl_2$ (27 mg) and CuCl (80 mg) were added sequentially into the liquid. The brown solution were frozen degas for three times, sealed and then reacted at 40 °C for 24 h. The

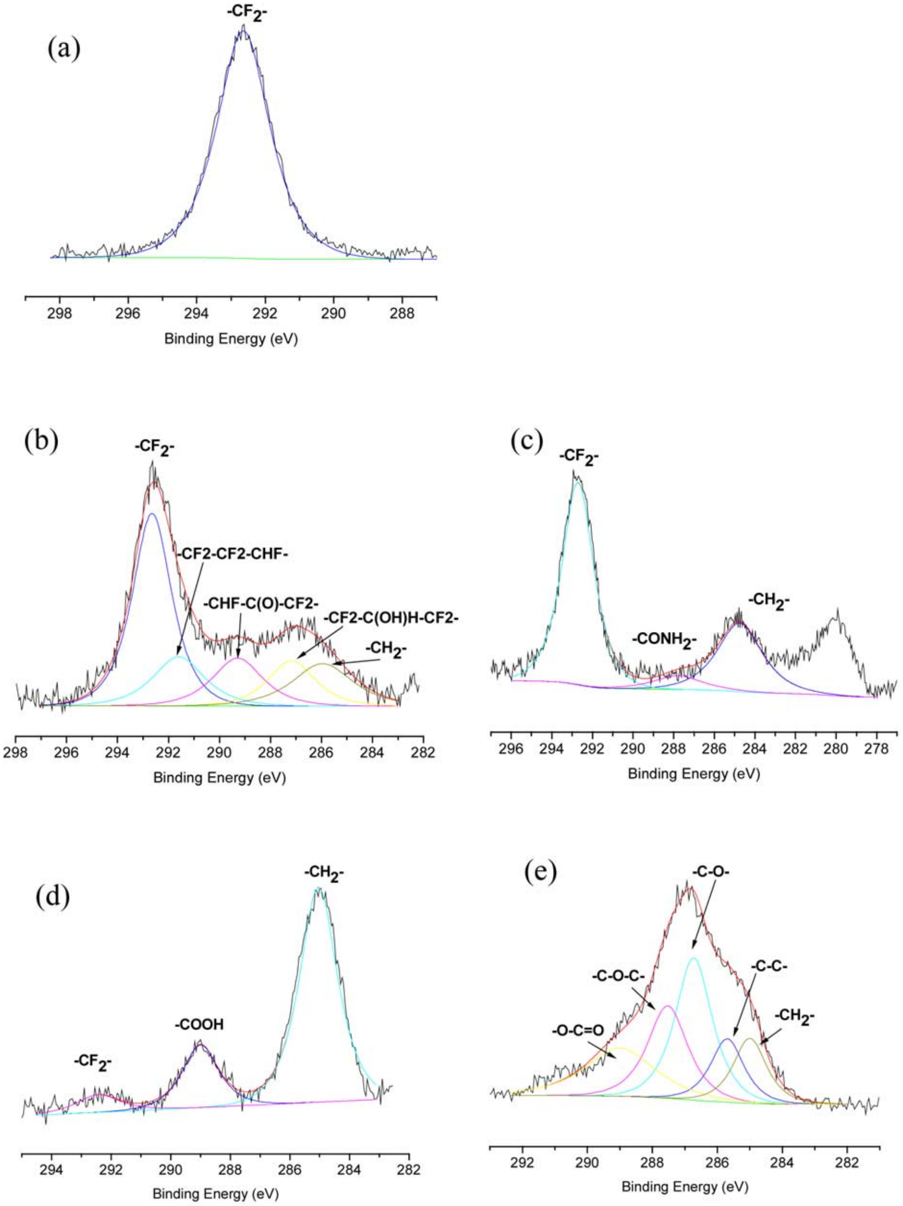

Fig. 2. C_{1s} core-level XPS spectra of (a) pristine PTFE; (b) hydrogen plasma treated PTFE; (c) PTFE-*g*-PAAm; (d) PTFE-*g*-PAAc; (e) PTFE-*g*-PGMA film.

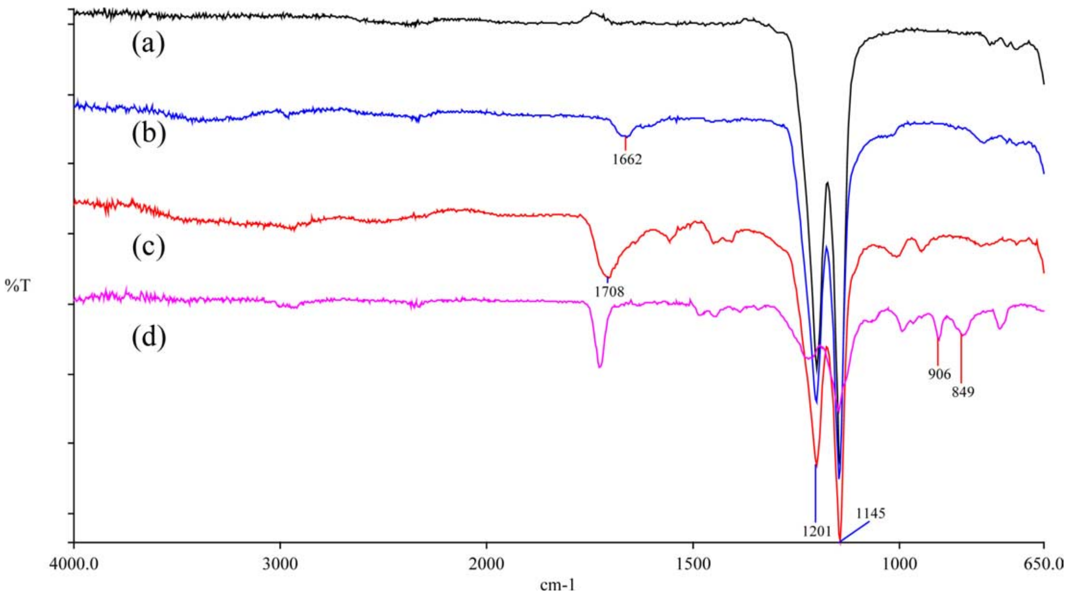

Fig. 3. FTIR-ATR spectra of PTFE films of (a) pristine film and grafted copolymerization with (b) AAm; (c) AAc; (d) GMA.

PTFE films were draw out, washed with acetone and distilled water for several times and then dried at room temperature under vacuum to give the sample of PTFE-*g*-PBIEA-*ar*-PNaSS. Treating the sample with 1 M $HCl_{(aq)}$ solution at room temperature for 5 h converted the sodium sulfonate groups to hydrogen sulfonate groups to result in the sample of PTFE-*g*-PBIEA-*ar*-PSSA.

2.5. Characterization

Water contact angles were measured with an angle-meter (Automatic Contact Angle Meter, Model CA-VP, Kyowa Interface Science Co., Ltd Japan) at room temperature. The distilled water was dropped on the sample surface at 10 different sites. The average of ten measured values for a sample was taken as its water contact angle. Scanning electron micrographs were recorded with a JEOL JSM-5410 SEM equipped with an energy dispersive X-ray spectroscopy (EDX, JEOL JSM 6000). Atomic force microscope measurements were observed with a Digital Instrument DI 5000 AFM. FTIR-ATR spectra were obtained with a Perkin–Elmer Spectrum One FTIR equipped with a multiple

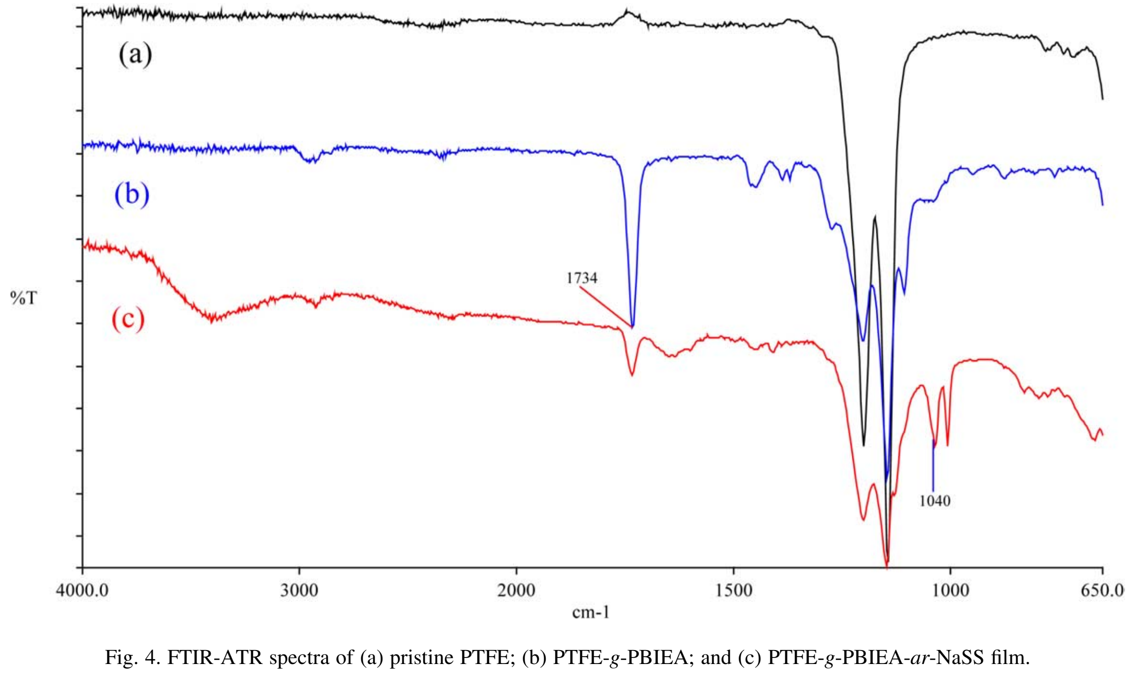

Fig. 4. FTIR-ATR spectra of (a) pristine PTFE; (b) PTFE-*g*-PBIEA; and (c) PTFE-*g*-PBIEA-*ar*-NaSS film.

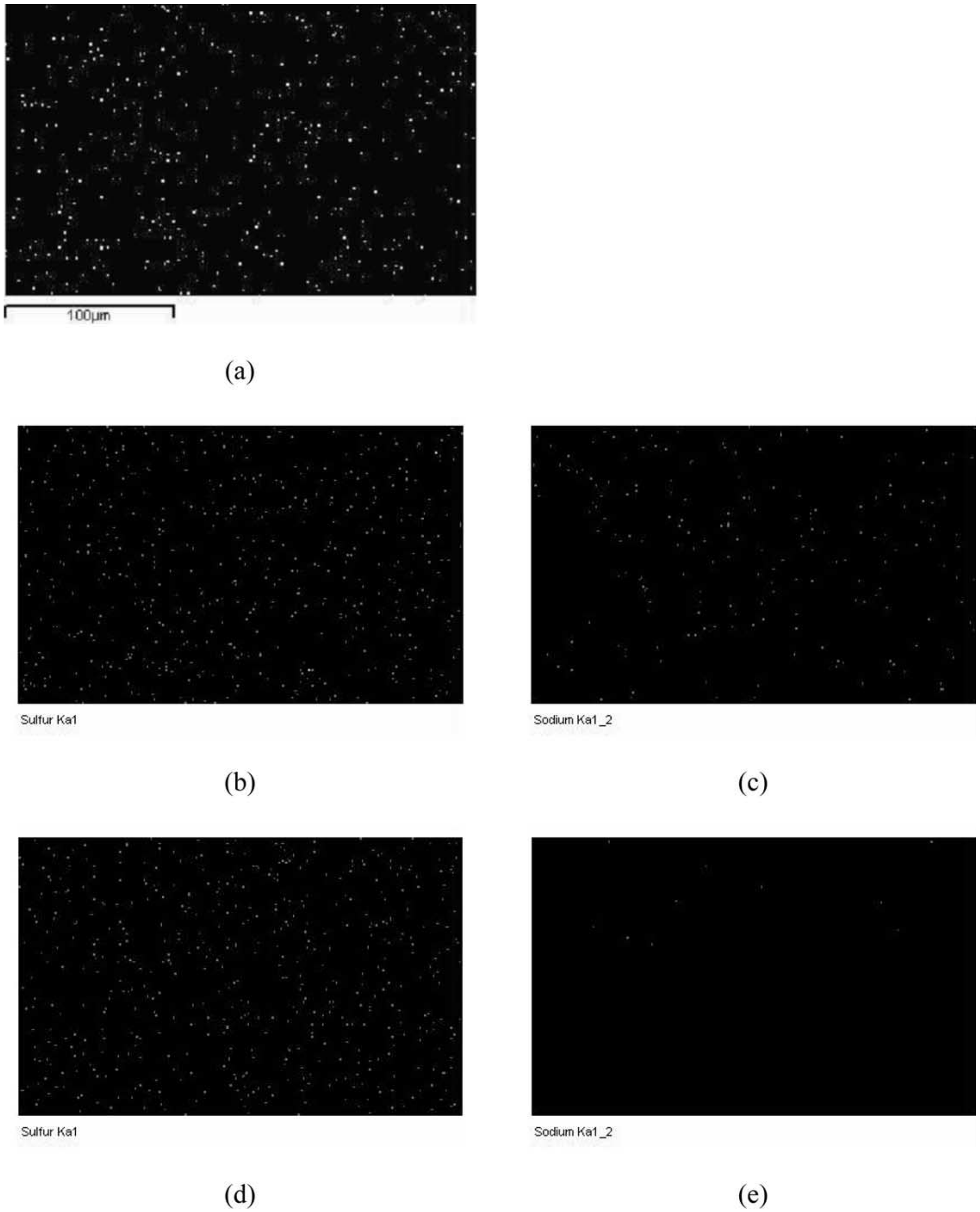

Fig. 5. SEM-EDX elemental mapping micrographs of the PTFE film surfaces: (a) bromine mapping on PTFE-*g*-PBIEA film, (b) sulfur mapping on PTFE-*g*-PBIEA-*ar*-NaSS film, (c) sodium mapping of PTFE-*g*-PBIEA-*ar*-NaSS film, (d) sulfur mapping on PTFE-*g*-PBIEA-*ar*-PSSA film and (e) sodium mapping on PTFE-*g*-PBIEA-*ar*-PSSA film.

internal reflectance apparatus and a ZnSe prism as an internal reflection element. X-ray photo spectroscopy (XPS) analysis was conducted with using a VG MICROTECH MT-500 ESCA (British) using a Mg K_α line as a radiation source. The background pressure in the analytical chamber was 1.0×10^{-5} Pa and the take-off angle of the photoelectrons was 90° with respect to the sample surface.

3. Results and discussion

3.1. Applying ozone treatment to PTFE surface modification

The fully fluorinated PTFE polymer is not susceptible to ozone treatment, owing to the strong bonding energy of C–F bonds. To make ozone treatment be efficient for PTFE modification, PTFE films were first treated with hydrogen plasma. Hydrogen plasma treatment effectively changes the surface chemical compositions of PTFE films by means of defluorination and hydrogenation reactions [38]. Under mild conditions, some C–F bonds on the surface of PTFE film are converted to C–H bonds after hydrogen plasma treatment. These C–H bonds were O_3 accessible, so as to serve as reactive cites in ozone treatment to form peroxide groups onsite. The peroxide groups formed on the surface of PTFE film were utilized as the initiating points for further free radical grafting polymerization. Fig. 1 schemes this approach of PTFE surface modification.

The surface chemical structures of the PTFE films were observed with XPS measurements (Fig. 2). Only a peak at 292.7 eV attributing to CF_2 species was observed for pristine PTFE. After hydrogen plasma treatment, the appearance of a new peak at 285 eV indicated the formation of $–CH_2–$ species on the treated PTFE film surface. Other peaks at 291.5, 289.2 and 287.2 eV were also observed with the XPS spectrum of plasma treated PTFE films and these three peaks were assigned as the contributions of $–CF_2–CF_2–CHF–$, $–CHF–C(O)–CF_2–$ and $–CF_2–C(OH)H–CF_2–$ species, respectively. The oxygen-containing groups formed from the reaction between the activated PTFE surface and air.

Surface-initiating polymerization on the hydrogen plasma treated PTFE film was examined with using AAm as a monomer. However, no AAm polymer chains were observed with the obtained sample to verify that the hydrogen plasma treated PTFE film surface did not possess peroxides or free radicals to initiate the AAm polymerization. On the other hand, vinyl monomers including AAm, AAc and GMA were successfully polymerized onto the surfaces of O_3 treated PTFE films. The performance of grafting polymerization was first characterized FTIR-ATR and the spectra are shown in Fig. 3. The pristine and modified PTFE films showed very different spectra in FTIR-ATR analysis to imply the occurrence of modification. The acryamide structure in PTFE-*g*-PAAm film was characterized with the absorption peak of carbonyl group in amide (–NH–C=O) at 1662 cm^{-1}. Meanwhile, the structures of PTFE-*g*-PAAc and PTFE-*g*-PGMA were characterized with the absorption peaks of –C=O in acrylic acid groups (1708 cm^{-1}) and the peaks of oxirane rings in GMA (849 and 906 cm^{-1}), respectively. Further characterization on the modified PTFE films was conducted with XPS analysis and the spectra obtained were shown in Fig. 2. The grafted AAm, AAc and GMA polymer chains on the surfaces of modified PTFE films were observed with the presence of the $–CONH_2$, –COOH and oxirane ring species, which exhibited C_{1s} component at the bonding energies of 287.4 eV (Fig. 2(c)), 288.7 eV (Fig. 2(d)) and 287.5 eV (Fig. 2(e)), respectively [3]. The grafted amount of acrylates onto PTFE surface was obtained from the weight differences of the membranes before and after grafting copolymerization. The grafted amounts were 0.1, 0.3 and 12.6 mg/cm^2 for AAm, AAc and GMA, respectively. The above results directly demonstrated the success of utilization of ozone treatment for PTFE surface modification via surface-initiated grafting polymerization.

3.2. Building molecular architecture on PTFE film surface through ATRP

Introduction of control macromolecular architectures to substrate surfaces received wide studies in recent years. Living polymerization system is efficient in controlling polymer chain length and structure. Atomic transfer radical polymerization (ATRP) has shown versatility and ability on building macromolecular architecture on material surfaces. To employ ATRP in modification of PTFE film surface, BIEA was polymerized onto the PTFE film surfaces with the same manner of the above-mentioned method. The bromoisobutyl groups in the grafted PBIEA chains then served as initiating sites for further atom transfer radical polymerization with using NaSS as a monomer. The grafted polymer chain could be an arborescent structure possessing a linear PBIEA chain with many PNaSS side moieties [32]. The modified PTFE film obtained was coded as PTFE-*g*-PBIEA-*ar*-PNaSS. Further treating PTFE-*g*-PBIEA-*ar*-PNaSS with a hydrochloride aqueous solution converted sodium sulfonate groups to sulfonic acid groups to result in

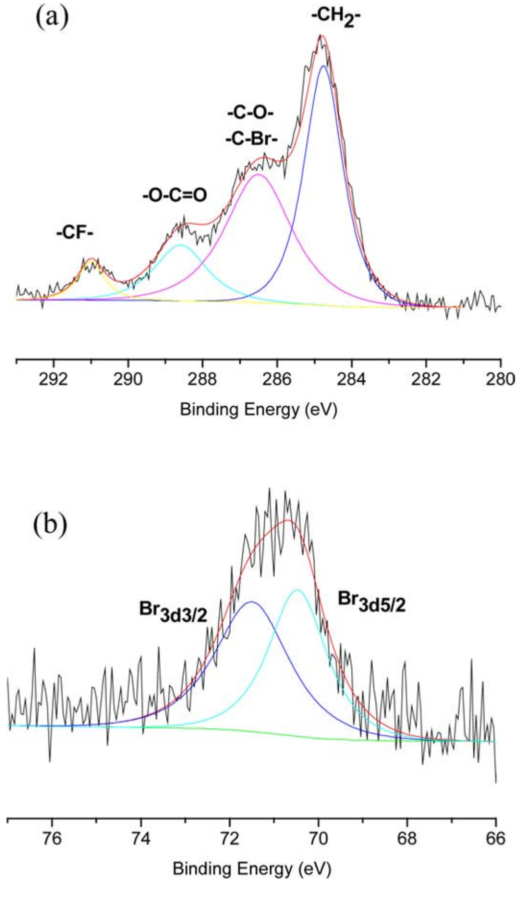

Fig. 6. XPS spectra of (a) C_{1s} core-level and (b) Br_{3d} core-level of PTFE-*g*-PBIEA film.

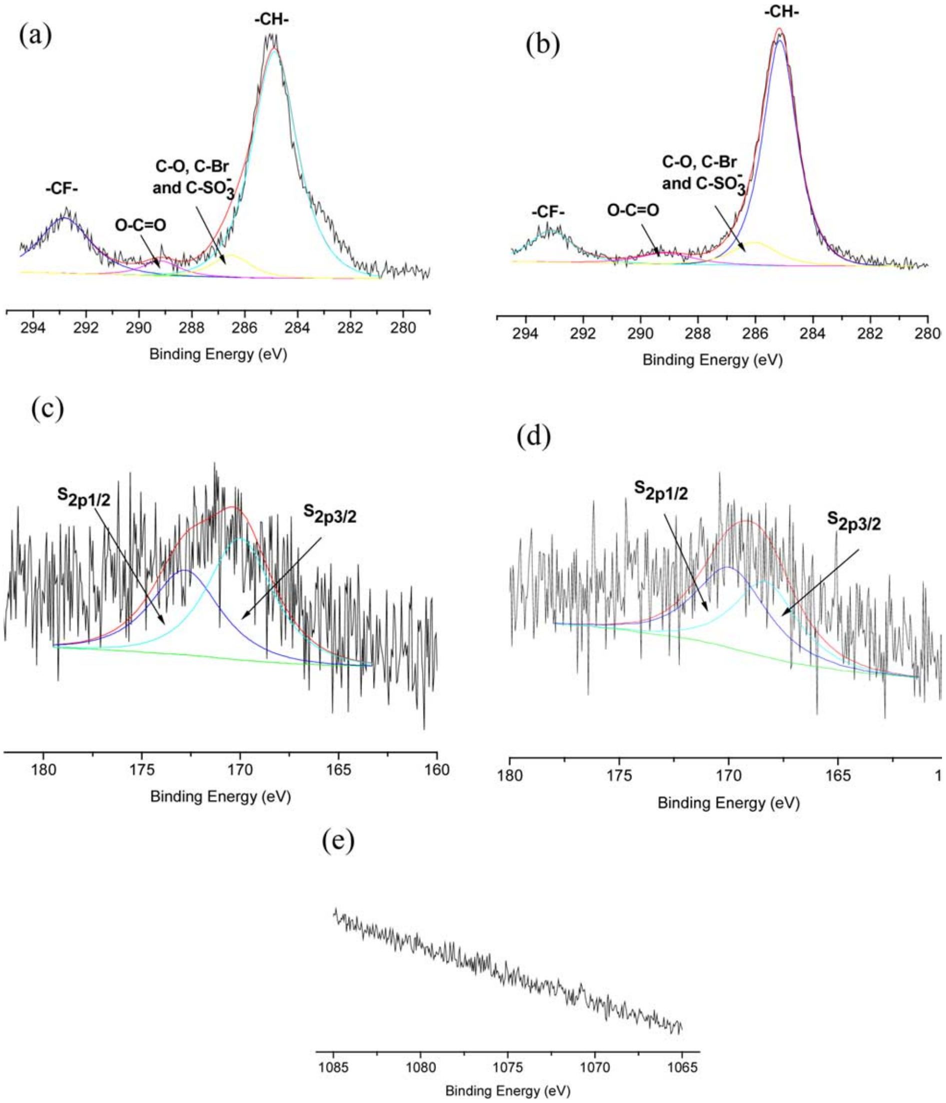

Fig. 7. XPS spectra of modified PTFE film surfaces. C_{1s} core-level spectra of (a) PTFE-*g*-PBIEA-*ar*-PNaSS film and (b) PTFE-*g*-PBIEA-*ar*-PSSA film; S_{2p} core-level spectra of (c) PTFE-*g*-PBIEA-*ar*-PNaSS film and (d) PTFE-*g*-PBIEA-*ar*-PSSA film; Na_{1s} core-level spectra of (e) PTFE-*g*-PBIEA-*ar*-PSSA film.

the acid type PTFE film coded as PTFE-*g*-PBIEA-*ar*-PSSA. The modified surfaces were characterized with FTIR-ATR. An absorption band at 1740 cm^{-1} attributed to the ester carbonyl group of PBIEA chains [31] was observed for PTFE-*g*-PBIEA to demonstrate the performance of BIEA grafting polymerization on the surface of PTFE film. The incorporated PNaSS chains on the PTFE-*g*-PBIEA-*ar*-PNaSS film surface was observed with the absorption bands of sulfonate groups at 1040 cm^{-1} and of phenyl groups at 1596 cm^{-1} (Fig. 4(c)). The grafted polymer chains on the surfaces of PTFE films were also observed with element mapping analysis performed by an SEM-EDX instrument. Some typical micrographs were shown in Fig. 5. Certain amounts of bromine were observed with the PTFE-*g*-PBIEA film surface. The homogeneous distribution of bromine in the observation window indicated that the PBIEA chains homogeneously covered the surface of PTFE-*g*-PBIEA film. Similar results were also observed with sulfur and sodium mapping analysis on PTFE-*g*-PBIEA-*ar*-PNaSS film, to demonstrate that the PNaSS chains were homogeneously introduced to the surface of PTFE film. Moreover, sodium was not observed with the acid form of PTFE-*g*-PBIEA-*ar*-PSSA film and sulfur was still observed. The disappearance of sodium signal in EDX element mapping confirmed the transformation of PTFE-*g*-PBIEA-*ar*-PNaSS film to its acid form of PTFE-*g*-PBIEA-*ar*-PSSA.

Further characterization on the surfaces of PTFE films was performed with XPS measurements. Fig. 6 shows the XPS spectra measured on PTFE-*g*-PBIEA film. The C_{1s} core-level spectra possessed four component peaks corresponding to $–CH_2–$ (284.8 eV), C–O and C–Br (286.6 eV), O=C–O (288.7 eV) and $–CF_2–$ (292 eV) species, respectively. The first three peaks associated to the chemical structure of PBIEA chains grafted on the surface of PTFE film. On the other hand, the Br_{3d} core-level spectrum, as shown in Fig. 6(b), provided a direct observation of PBIEA chains for PTFE-*g*-PBIEA film, especially with the appearance of $Br_{3d5/2}$ peak at 70.5 eV which attributes to covalently bonded bromine [31]. XPS spectra of PTFE-*g*-PBIEA-*ar*-PNaSS and PTFE-*g*-PBIEA-*ar*-PSSA films are shown in Fig. 7. In addition to C–O and C–Br species, $C–SO_3$ species were also observed at about 286.5 eV with the C_{1s} core-level spectra of these two samples (Fig. 7(a) and (b)) [31]. The S_{2p} spectra of both samples also showed a combination peak of $S_{2p1/2}$ and $S_{2p3/2}$ peaks at about 170 eV of bonding energy, to further demonstrate the presence of sulfonate groups on the surfaces of PTFE-*g*-PBIEA-*ar*-PNaSS and PTFE-*g*-PBIEA-*ar*-PSSA films. Moreover, no peaks were observed in the Na_{1s} core-level spectrum of PTFE-*g*-PBIEA-*ar*-PSSA film (Fig. 7(e)), to demonstrate that the sodium sulfonate groups of PTFE-*g*-PBIEA-*ar*-PNaSS film were completely converted to sulfonic acid groups after $HCl_{(aq)}$ treatment. From the results obtained from FTIR-ATR, SEM-EDX and EDX measurements it was concluded that building arborescent PBIEA-ar-PSSA molecular architecture on the PTFE film surface was successfully performed.

3.3. Surface property and morphology of modified PTFE film

One major targets of PTFE modification is to bring high hydrophilicity to its surface so as to enhance its adhesion property to other materials. The surface hydrophilicity of the modified PTFE film was examined with water contact angle. The results are collected in Table 1. The hydrophobic surface of pristine PTFE film exhibited a large water contact angle of 120°. After bringing PNaSS onto PTFE surface the water contact angle dropped to 61°. Converting the sodium sulfonate groups on the film surface to sulfonic acid form further dropped the water contact angle to 26°. This small water contact angle of PTFE-*g*-PBIEA-*ar*-PSSA film surface demonstrated its high surface hydrophilicity, which was contributed from the polarity of the grafted $-SO_3H$ groups. Moreover, formation of hydrogen bonds between the sulfonic acid groups and water molecules also contributed to the extremely high surface hydrophilicity of PTFE-*g*-PBIEA-*ar*-PSSA film. The surface hydrophilicity of PTFE film depended both on the chemical structures and amounts of the grafted polymer chains. The effect of chemical structure on the surface hydrophilicity of PTFE film was observed in this work with above discussion. On the other hand, increasing the grafted amounts of hydrophilic groups would increase the surface hydrophilicity of PTFE film. However, this factor might not be so significant in this work.

Table 1
Surface contact angle with water of pristine, PTFE-*g*-PBIEA, PTFE-*g*-PBIEA-*ar*-PNaSS and PTFE-*g*-PBIEA-*ar*-PSSA films

Membrane	Contact angle (°)
PTFE	120
PTFE-*g*-PBIEA	82
PTFE-*g*-PBIEA-*ar*-PNaSS	61
PTFE-*g*-PBIEA-*ar*-PSSA	26

The surface morphologies of modified PTFE films were observed with SEM micrographs. A somewhat roughness was observed with the pristine PTFE film surface (Fig. 8(a)). After grafting polymerization of BIEA and NaSS, the roughness of the resulting film surfaces decreased, as shown in Fig. 8(b) and (c), However, nano-scale observation on the surface topography and roughness of the pristine and modified PTFE films were conducted with AFM measurements. Both of the images (Fig. 9) and the surface roughness (Table 2) showed that the surface roughness of the modified

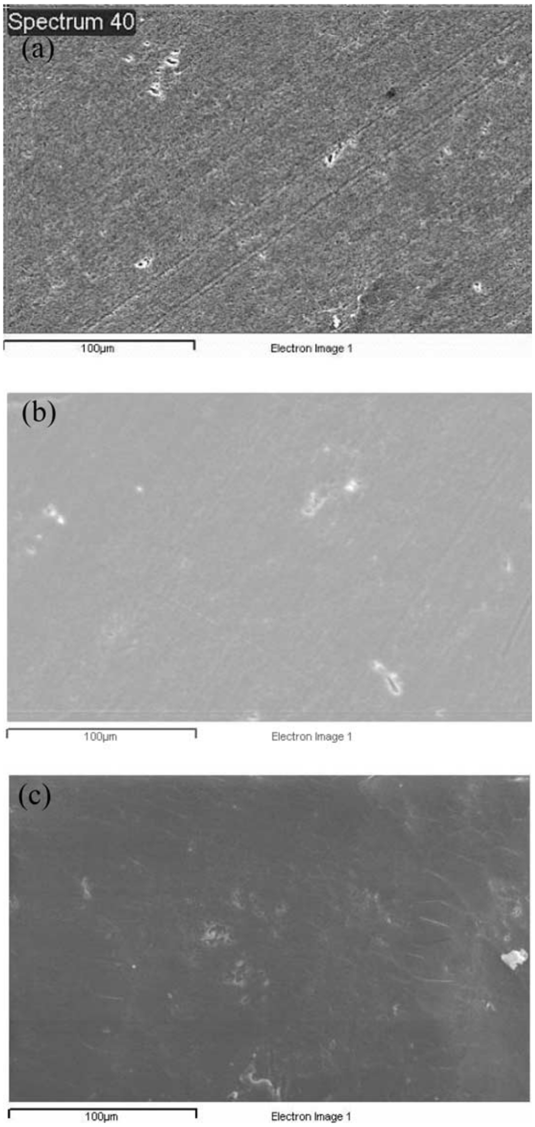

Fig. 8. SEM micrographs of (a) pristine PTFE, (b) PTFE-*g*-PBIEA and (c) PTFE-*g*-PBIEA-*ar*-PSSA film.

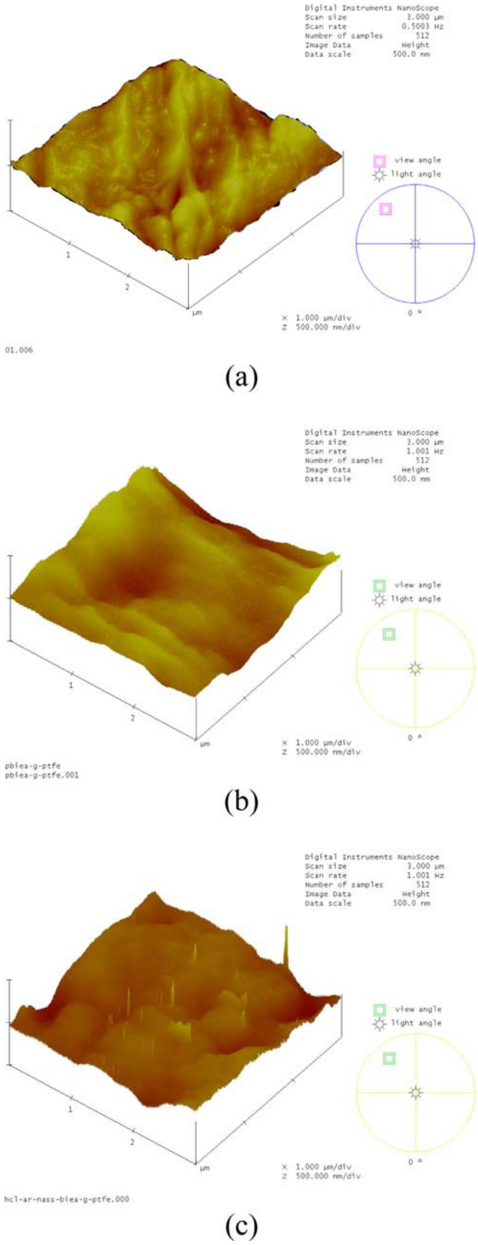

Fig. 9. AFM image of (a) pristine PTFE, (b) PTFE-*g*-PBIEA and (c) PTFE-*g*-PBIEA-*ar*-PSSA film.

Table 2
Surface roughness value of the pristine, PTFE-*g*-PBIEA and PTFE-*g*-PBIEA-*ar*-PSSA film

Membrane	R_{ms}[a]	R_{a}[b]	$R_{\max}$[c]
PTFE	29.9	24.0	198.8
PTFE-*g*-PBIEA	64.1	48.7	451.6
PTFE-*g*-PBIEA-*ar*-PSSA	87.3	68.1	967.3

[a] Root mean square (RMS) of *z* values.

[b] Mean roughness.

[c] Mean difference between the five highest peaks and the five lowest values.

PTFE films was higher than that of the pristine PTFE film. In addition, the grafted polymers on the PTFE film surfaces were also directly observed with their AFM images.

4. Conclusion

A novel modification approach of modification on PTFE film surface was successfully performed with utilization of ozone treatment. Grafted linear and arborescent polymer structures were incorporated onto the PTFE surfaces through surface-initiated radical polymerization and atom transfer radical polymerizations. PTFE films exhibiting a small water contact angle of 21° and very high surface hydrophilicity were obtained to ensure their good adhesive properties.

Acknowledgements

Financial supports on this work from the Ministry of Economic Affairs and the National Science Council, Taiwan are highly appreciated. The authors also thank Prof E.T. Kang (National University of Singapore, Singapore) for his helpful discussion on ozone treatment techniques.

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