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Surface characterization of microporous polypropylene membranes modified by plasma treatment

B. Bae[a], B.-H. Chun[b], D. Kim[a,*]

[a]*Department of Chemical Engineering and Polymer Technology Institute, Sungkyunkwan University, Suwon, Kyungki 440-746, South Korea*
[b]*Yonsei Institute of Automobile Technology, Yonsei University, Shinchon-dong, Seodaemoon-ku 134, Seoul 120-749, South Korea*

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Abstract

Scanning electron microscope and goniometer were used to investigate morphology and wetting property of polypropylene membrane surfaces modified by plasma treatment using different reagents. Surface morphology was significantly affected by the types of reagents. X-ray photoelectron spectroscopy and attenuated total refection-Fourier transform infrared spectroscopy were used to characterize the chemical structure of polypropylene membrane surfaces modified by Freon-116 gas plasma treatment. Many fluorine atoms were observed on the polypropylene surface, and its concentration increased to saturation with increasing plasma treatment time. The wetting behavior of plasma treated polypropylene membrane was well explained in relation with morphology and chemical structure. © 2001 Published by Elsevier Science Ltd.

Keywords: Plasma treatment; Polypropylene membrane; Surface morphology

1. Introduction

Application fields of polymeric materials are extended by modification of their surfaces [1,2]. Generally, some hydrophobic polymer surfaces can be changed to hydrophilic ones, and thus their adhesion, wetting, printing and friction properties are significantly changed to have considerable technological importance in the areas of adhesion, coating and paintings, composite fabrication and interfacial compatibility [3–5].

Wet-chemical treatment, corona discharge, exposure to flame and glow discharge plasma are well-known surface modifying techniques [6–9]. All techniques aim at the same objective — removal of surface contaminant and drastic decrease in the interfacial molecular energy to provide intimate contact between two interacting materials. Although each technique has its own advantages and shortcomings, surface modification by low-pressure plasma treatment illustrates many important advantages over other techniques: (i) environmental safety; (ii) uniformity and reproducibility; (iii) diversity of reagent gases; (iv) selective modification with minimization of bulk property change [10–12].

Polypropylene (PP) membranes are used in a variety of industrial applications — sterilisation of beverage and pharmaceutics, wastewater treatment, ultra-pure water in the semiconductor industry, desalination of sea water, electrode separation in secondary battery, etc, as they are one of the cheapest polymer membranes with acceptable thermal, mechanical and chemical stability in commercial application [13,14]. In this study, the surface of commercial PP membranes was modified by a few liquid or gas plasma to analyze and compare resulting surface characteristics. After plasma treatment, not only the morphology and chemical structures of membrane surface, but also thermal and mechanical properties of bulk polymer membranes were investigated. By this technique, significant changes in the interfacial stability between other hydrophilic molecules and PP membranes were anticipated.

2. Experimental

2.1. Raw materials

Microporous PP membranes (PP, Celgard 2500, USA) were purchased from Hoechst Celanese. The porosity was 47%, pore dimension $0.05\mu m \times 0.21\ \mu m$, and thickness 25.4 μm. A few plasma treatment reagents such as allylamine (Aldrich, USA, purity > 99%), acrylic acid (Merck,

* Corresponding author. Tel.: +82-31-290-7250; fax: +82-31-290-7272.
E-mail address: djkim@skku.ac.kr (D. Kim).

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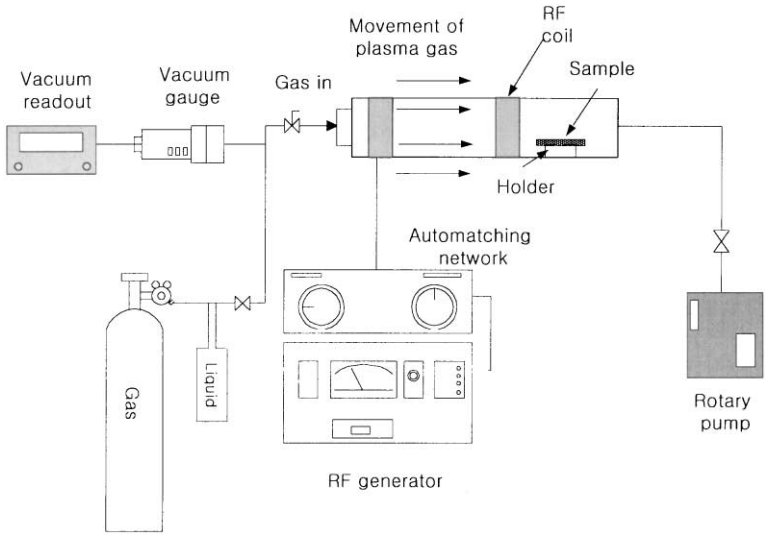

Fig. 1. Schematic of experimental apparatus.

Germany, purity > 99%), water and Freon-116 (hexafluoroethane) gas (Aldrich, USA, purity > 98%) were used.

2.2. Plasma treatment

PP membrane surfaces were modified by plasma treatment. The experimental power input from RF generator (RFX-600, Advanced Energy, USA,) was from 50 to 100 W and the treatment time from 1 to 40 min at the fixed pressure of 0.5 Torr maintained by a rotary pump (RV5 rotary vane pump, Edwards, USA). The gas flow rate was 5 sccm (standard cm^3/min). A pressure gauge (622A11TD2, MKS, USA) was used to monitor operating pressure. The plasma reactor volume was 3320 cm^3. The plasma generating equipment is schematically depicted in Fig. 1.

2.3. Surface characterization of plasma treated PP membranes

The chemical structure and morphology of plasma treated PP membrane surfaces were investigated using several apparatus. X-ray photoelectron spectroscopy (XPS, VG ESCALab 220i-XL, UK) with non-monochromated Al Kα excitation (1486.6 eV), operated in the constant analyzer energy mode was used for chemical analysis. The spectrometric energy scale was calibrated applying the procedure with binding energy data recommended by Beamson and Briggs [15]. Attenuated total refection-Fourier transform infrared spectroscopy (ATR-FTIR, Magna IR 560, Nicolet, USA) with germanium (45°) crystal was also used. Scanning electron microscope (SEM, XL30ESEM-FEGUN (FEI), Philips) was used for morphology analysis.

2.4. Measurement of wetting properties

Goniometer (Model G-1, 113-110-0, Erma, USA) was used to investigate wetting properties of plasma treated PP surface. Advancing and/or receding angles of de-ionized water on both the plasma treated and virgin PP membrane surfaces were measured at room temperature for different plasma treatment reagents.

2.5. Measurement of thermal and mechanical properties

Thermal and mechanical properties of membranes before and after plasma treatments were analyzed. Thermal stability was measured using the thermogravimetric analyzer (TGA, Perkin–Elmer TGA7, USA). TGA measurements were performed at the scanning rates of 30°C/min in the presence of nitrogen gas.

Tensile properties were measured at room temperature under constant humidity of 20% using a universal tensile machine (SFM-20, United Calibration, USA) with the full-out velocity of 500 mm/min. The measurements were conducted according to ASTM D 638. The sample thickness was 25.4 μm. Measurements were performed five times per each sample and the average value was obtained for its determination.

3. Results and discussion

3.1. Effect of reagent types on the surface morphology of plasma treated PP membranes

Fig. 2(a)–(e) shows the microphotographs of PP membrane surfaces modified by plasma treatment with no gas, acrylic acid, allylamine, water and Freon-116. In Fig. 2(a), the pores in the dimension of 0.21×0.05 μm were clearly observed for original PP films. Plasma treatment with acrylic acid and water for 40 min resulted in the significant change in the surface morphology. SEM data illustrated deterioration of membrane pores due to

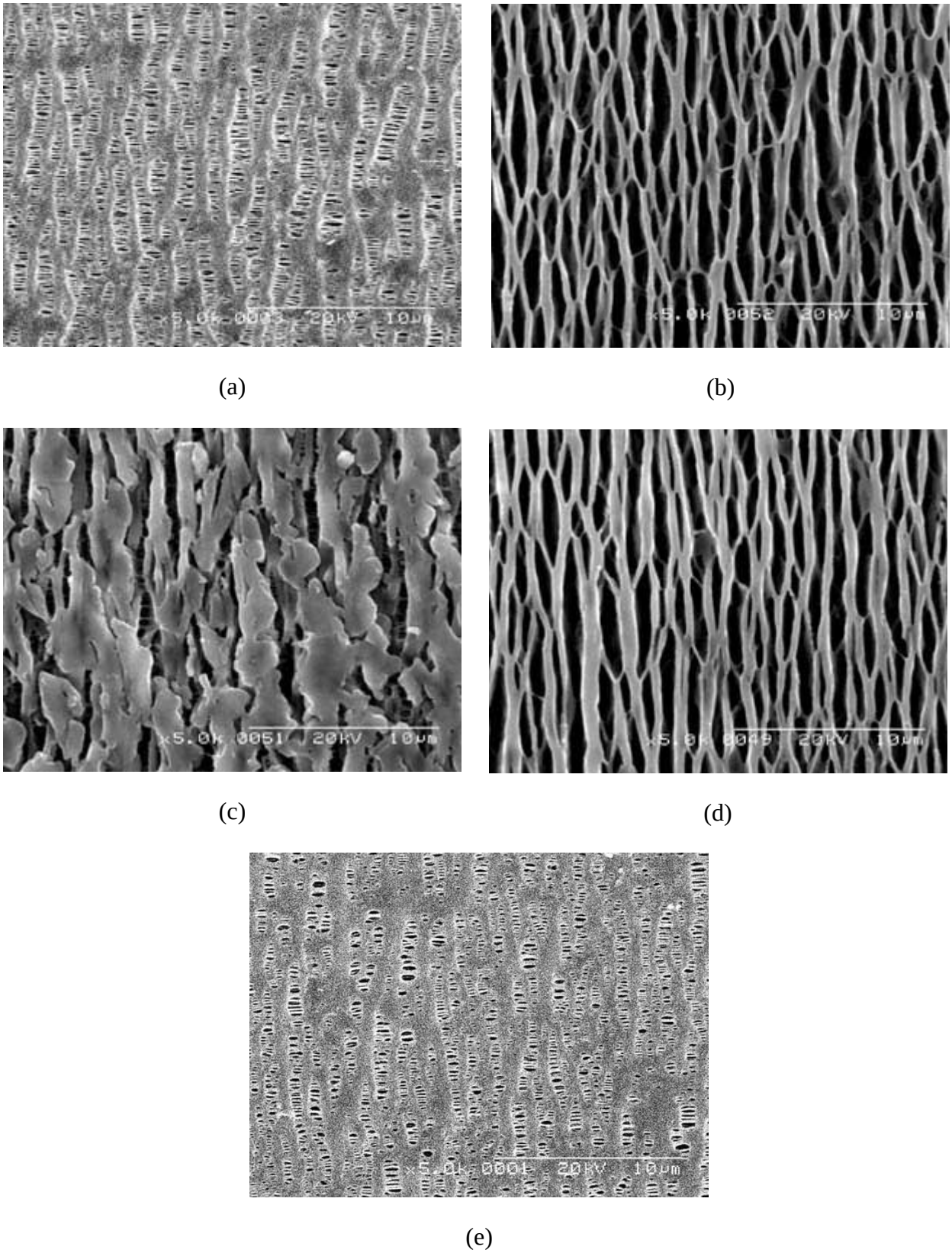

Fig. 2. SEM photographs after plasma treatment for 40 min: (a) no gas; (b) acrylic acid; (c) allylamine; (d) water; (e) Freon-116, respectively.

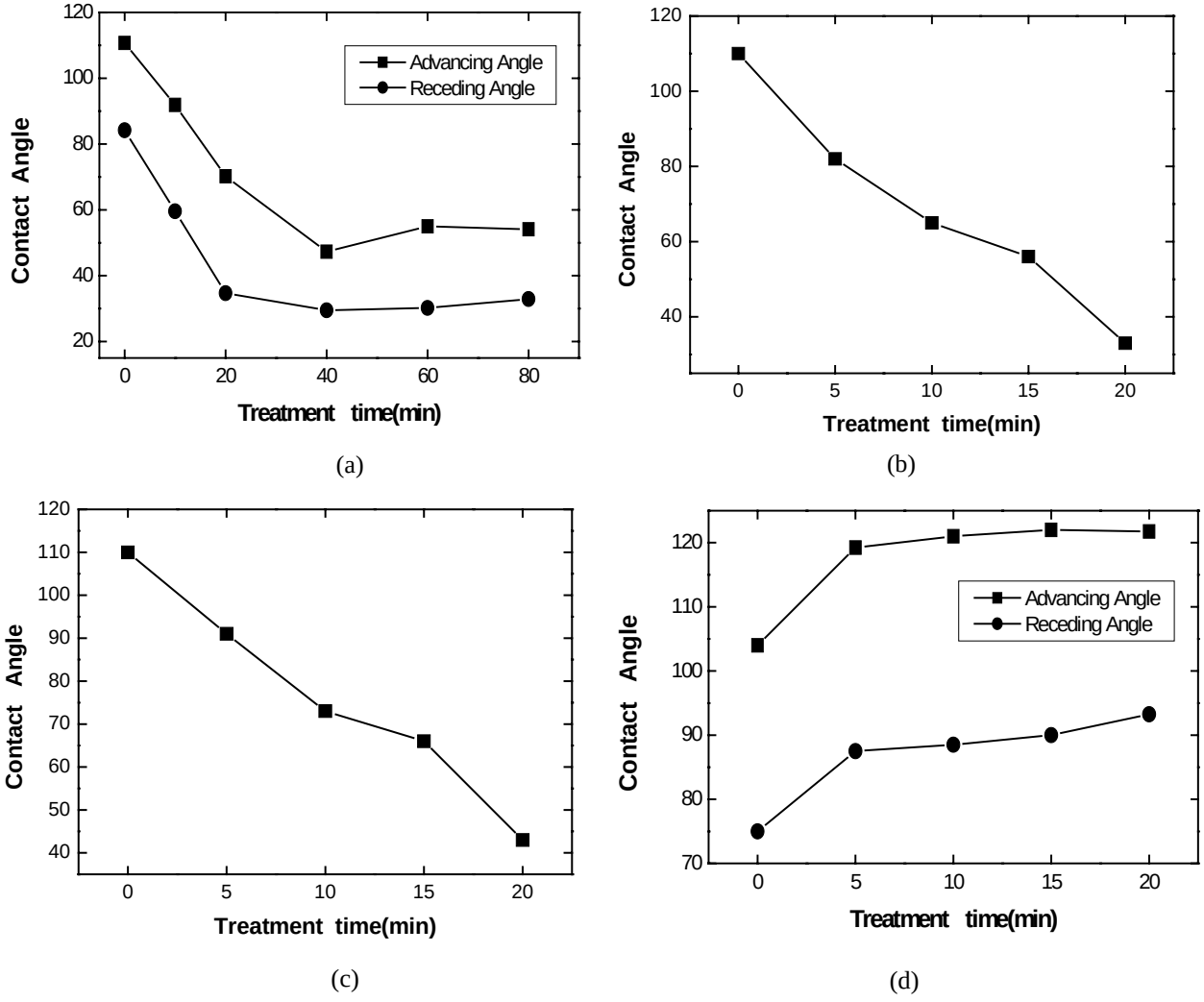

Fig. 3. Water contact angle of plasma treated PP membrane: (a) allylamine; (b) water; (c) acrylic acid; (d) Freon-116, respectively.

the oxidation associated with oxygen containing gases, resulting in significant reduction of mechanical strength.

Allylamine and Freon-116 gases induced different surface morphologies. Plasma treatment of allylamine, produced thin film barriers on the membrane surface via polymerization reaction, but Freon-116 gas plasma treatment made no change in its surface morphology. No deterioration of pores was observed even upto 40 min treatment with Freon-116 gas. Plasma treatment of Freon-116 gas on the PP membrane surface was expected to graft fluorocarbon molecules on its surface. More detailed analysis was given in Section 3.3.

3.2. Effect of reagents on the wetting properties of PP membranes modified by plasma treatment

Fig. 3(a)–(d) shows the contact angles of water on the PP membrane surface modified by plasma treatment for different duration of time with different reagents of allylamine, water, acrylic acid and Freon-116, respectively. Because of the hydrophilicity of poly(allylamine) grafted on PP surface, the contact angle decreased with increasing treatment time. Both advancing and receding angles decreased linearly up to 40 min, but no further change was observed after then.

The surface morphology (roughness, texture and heterogeneity) can be a cause of contact angle hysteresis [16–19]. It seems in Fig. 3, that the surface roughness of PP film treated by allyamine plasma became more increased than that of untreated one, and the texture of PP film treated by water and acrylic acid plasma become looser than that of untreated one. It is well known that the equilibrium contact angle observed (θ_w) on a rough surface (or Wenzel's angle) is smaller than that (θ) done on a smooth surface, if θ is less than 90° [16]. The observed contact angle on the PP film treated by allyamine plasma might be smaller than the contact angle observed on the smooth surface. The

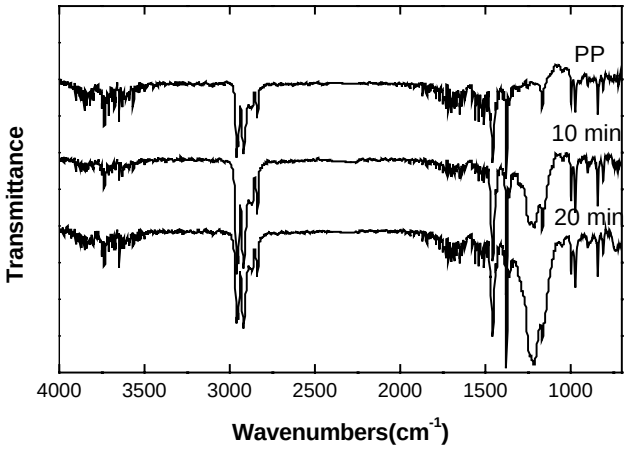

Fig. 4. FTIR-ATR spectra of Freon-116 gas treated PP membranes for 0, 10 and 20 min, respectively.

effects of surface roughness and texture on contact angle hysteresis will be studied more.

Both acrylic acid and water also reduced contact angle with increasing plasma treatment time up to 20 min, as hydrophobic characteristics of PP membrane surface was hydrophilically modified due to their polarity. Among these three reagents, water produced the minimum contact angle of 32°.

Wetting properties of PP membranes treated by Freon-116 gas were completely different from those by other reagents. For Freon-116 gas, both advancing and receding angles increased with treatment time, but no significant change was observed after the treatment time of 5 min. This result indicates that the PP membrane surface was more hydrophobically reformed via formation C–F bonds with more plasma treatment. But the hydrophobicity of this membrane surface was hardly affected after 5 min when the certain level of C–F bonds were formed, even though more

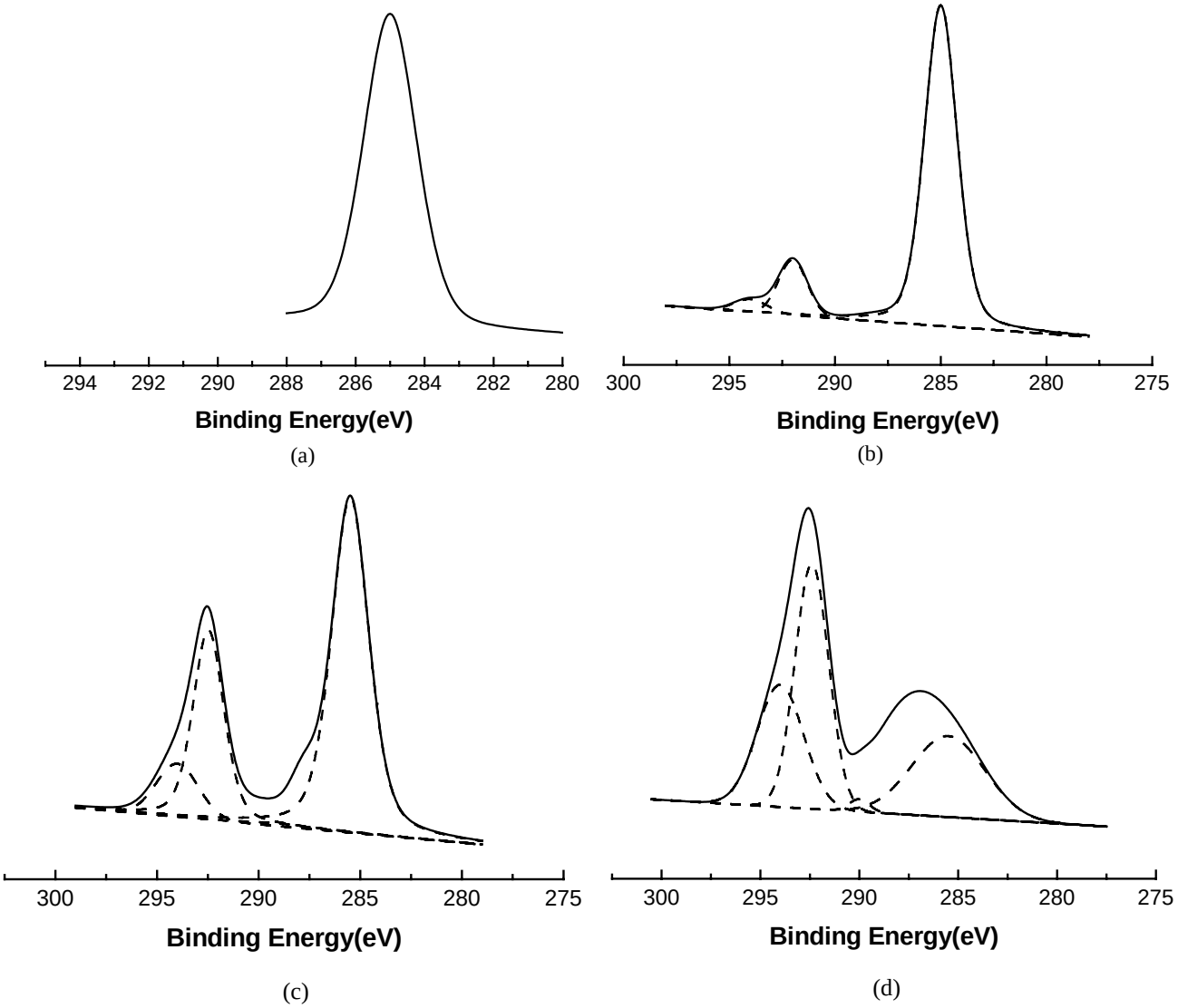

Fig. 5. C_{1s} XPS spectra of PP membranes treated by Freon-116 gas plasma for: (a) 0 min (b) 5 min (c) 10 min and (d) 20 min, respectively.

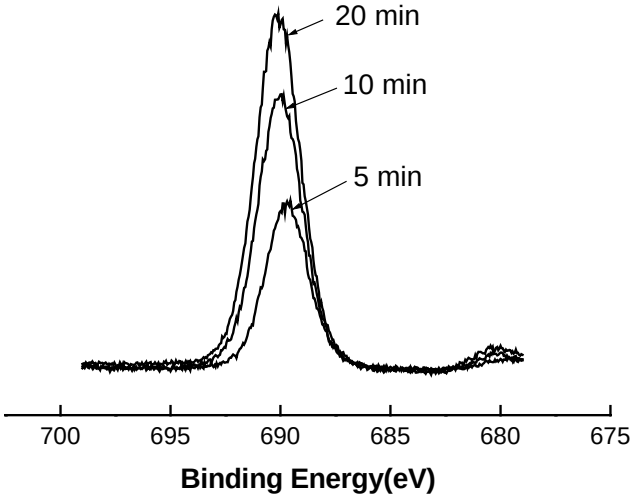

Fig. 6. F_{1s} XPS spectra of PP membranes treated by Freon-116 gas plasma for 5, 10 and 20 min, respectively.

fluorine molecules were observed on the PP film surface by further plasma treatment (refer to ATR-FTIR and XPS data in Figs. 4–6).

3.3. Chemical structure of Freon-116 gas plasma modified PP membranes

Fig. 4 shows ATR-FTIR spectra of PP membranes modified by Freon-116 plasma treatment for different times. The band arising around 1300 cm^{-1} was originating from C–F bond stretching. Increasing intensity of this band with increasing plasma treatment time indicates that more C–F bonds were replaced for C–C/C–H bonds on the PP membrane surface. Carbon radicals on PP surface were produced by Freon-116 gas plasma, and new C–F bonds were generated through the chemical reaction between the carbon radicals in PP surface and carbon atoms in Freon-116 molecules. No direct reaction between the carbon radical in PP membranes and fluorine atoms in Freon-116 were anticipated because of high bonding energy of C–F in Freon-116 molecules.

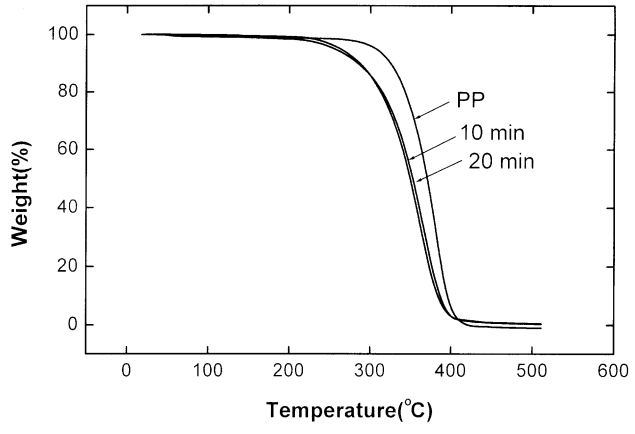

Fig. 7. TGA data of PP membranes treated by Freon-116 gas plasma for 0, 10 and 20 min, respectively.

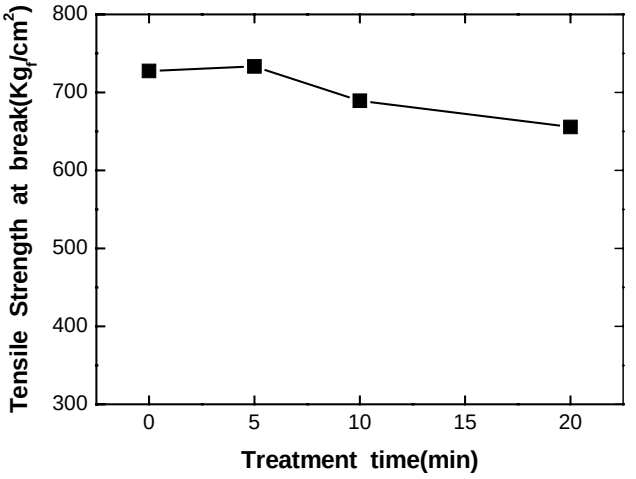

Fig. 8. Tensile strength of PP membranes treated by Freon-116 gas plasma for 5, 10 and 20 min, respectively.

This chemical analysis by ATR-FTIR was well complemented by the XPS results shown in Figs. 5 and 6. Fig. 5 shows carbon 1s (C_{1s}) spectra of PP membrane surfaces modified by Freon-116 gas plasma. The C_{1s} peaks at the binding energy of around 285 eV are corresponding to carbon atoms bonding to carbon (C–C bonds), and those of around from 288 to 294 eV, carbon atoms bonding to fluorine (C–F bonds) $-CF_3$ bond at 294 eV, $-CF_2$ bond at 292 eV, –CF bond at 290 eV, and $-C-CF_x$ bond at 288 eV. The peak intensity originating from C–C bonds decreased with increasing plasma treatment time, but that from $C-F_x$ bonds vice versa. The atomic ratio of fluorine (F) to carbon (C) increased from 0.869 to 1.934 as plasma treatment time increased from 5 to 20 min. In Fig. 6, the fluorine 1s peak originating C–F bond was illustrated at the binding energy of 690 eV. Its intensity increased with treatment time.

3.4. Thermal and mechanical properties of PP membranes modified by plasma treatment with Freon-116

The TGA data in Fig. 7 supported Fig. 2(e) where no significant deterioration of morphology of PP membranes was observed by plasma treatment. Both virgin and plasma treated PP membranes were thermally stable up to 200°C, even though slight weight loss was observed above 220°C for the plasma treated PP samples. This was probably due to the degradation of small amount of short molecules not strongly bound to PP surface.

Fig. 8 shows tensile strength of PP membranes before and after plasma treatment. Also, no significant difference was observed in mechanical strength between the two types of PP membranes.

4. Conclusions

Commercial PP membrane surfaces were modified by

plasma treatment with several different reagents. Microphotographs obtained from SEM illustrated great difference in morphologies according to the types of gas — deterioration of pores by oxygen containing chemical species such as acrylic acid and water, grafting polymerization by allylamine, but no morphological change by Freon-116. The wetting properties measured by goniometer were also significantly affected according to the types of plasma treatment species. Both highly polar species like acrylic acid and water and graft polymerizable monomer like allylamine decreased the contact angle, but C–F bond inducing Freon-116 gas vice versa, and its inclination was enhanced with plasma treatment time. Variation of surface chemistry of PP membranes being modified by Freon-116 was monitored using XPS and ATR-FTIR. Formation of C–F bonds on the PP surface was observed and treatment time effect on its behavior was in good accordance with the wetting behavior.

Acknowledgements

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