

# Surface Modification and Characterization of an H<sub>2</sub>/O<sub>2</sub> Plasma-Treated Polypropylene Membrane

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**ABSTRACT:** Low-pressure plasma treatments in a 13.56 MHz RF glow discharge of Hydrogen (H<sub>2</sub>)/Oxygen (O<sub>2</sub>) gas mixture were used to introduce polar functional groups onto microporous polypropylene (PP) membrane surfaces to improve the hydrophilicity and surface modification. The change in hydrophilicity and surface free energy was monitored by static contact angle measurement. Significant increased surface energy of polypropylene membranes from the H<sub>2</sub>/O<sub>2</sub> mixture gas plasma treatments was observed. The PP membrane surfaces became highly hydrophilic when exposed for only 5 s to the H<sub>2</sub>/O<sub>2</sub> mixture gas plasma. Optical emission spectroscopy (OES) was used to examine the various chemical species of low pressure plasma processing. The chemical structure and surface morphological changes on the mem-

brane surface were characterized by X-ray photoelectron spectroscopy (XPS) and confocal laser scanning microscopy (CLSM). XPS analysis showed significantly higher surface concentrations of oxygen functional groups for H<sub>2</sub>/O<sub>2</sub> mixture gas plasma-modified PP membrane surfaces than the originally unmodified PP membrane surfaces. The experimental results revealed low pressure H<sub>2</sub>/O<sub>2</sub> plasma processing is an effective method to improve the surface hydrophilicity of microporous PP membranes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: E108–E115, 2012

**Key words:** polypropylene membrane; surface characteristics; H<sub>2</sub>-O<sub>2</sub> plasma; X-ray photoelectron spectroscopy; confocal laser scanning microscopy

## INTRODUCTION

Microporous polymeric membranes are commercially available in various pore sizes and compositions to address the needs of many separation processes.<sup>1</sup> The demand for multifunctional microporous membranes has been increasing for applications in filtration, bio-recycling, purification, and water-treatment processes.<sup>2</sup> The requirements for the surface properties of membranes with appropriate properties for a specific application has encouraged the development of new, advanced methods for the membranes including chemical treatment,<sup>3</sup> polymeric-composite method,<sup>4</sup> bulk polymerization,<sup>5</sup> and graft polymerization.<sup>6</sup> The polypropylene (PP) membranes used in these applications show excellent mechanical properties, light weight, and high adaptability to complicated structures. However, the limitations of their application are their nonpolar nature

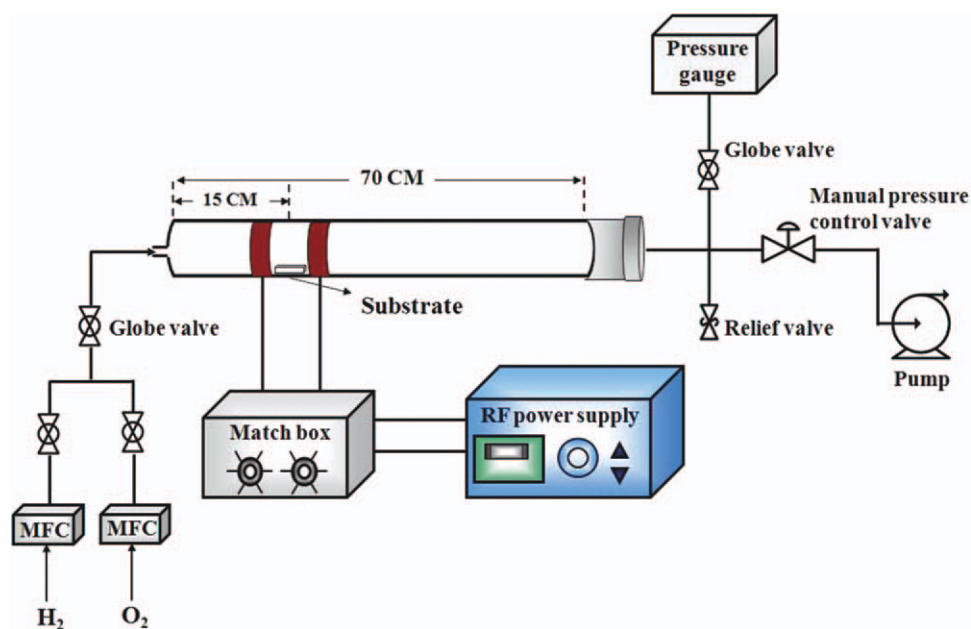
and low surface energy.<sup>7</sup> For this reason, the surface of the membrane must be rendered hydrophilic through chemically modifying the membrane surface property prior to use in separation and/or filtration.

Plasma surface modification is an effective and green process for modifying the polymer surface by introducing functional groups onto the surface of the polymeric materials. However, despite the extensive use of the plasma modification process, the surface activation of PP membranes by H<sub>2</sub>/O<sub>2</sub> plasma process has not been extensively examined and reported. Depending on the input gas used for plasma formation and the operational parameters, it can be used to activate a polymeric surface by inserting active species and/or a crosslinking process. The diverse reactive species in plasma state cause different generations of free radicals in the polymeric chain and insert functional groups onto the surface of the polymer, which tailor the surface properties of the polymeric membranes.<sup>8</sup>

In this work, microporous PP membranes were modified in 13.56 MHz RF glow discharge of (H<sub>2</sub>)/Oxygen (O<sub>2</sub>) gas mixture plasma glow discharge under different operational parameters, with the aim of improving the intrinsic low surface properties. The change in hydrophilicity of plasma-modified PP membranes was characterized by measuring the contact angle (CA). Optical emission spectroscopy (OES)

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**Figure 1** Schematic diagram of the tubular plasma reactor system. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

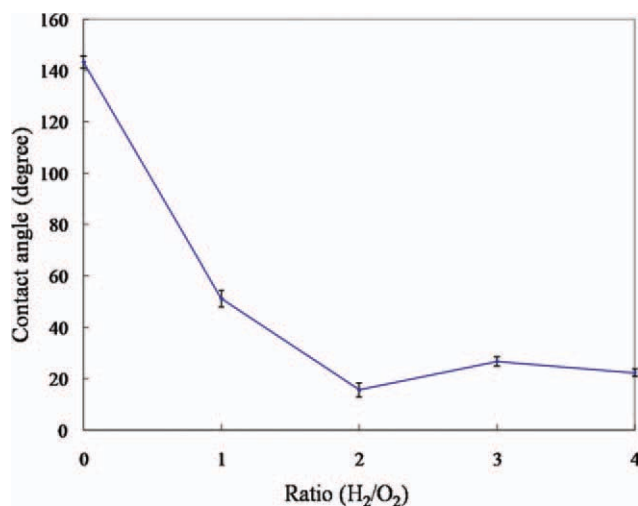
was used to examine the various chemical species to cause plasma surface modification. The surface morphology of the low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-treated PP membranes was analyzed using confocal laser scanning microscopy (CLSM). The chemical composition change of the low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-treated PP membranes surfaces were characterized by X-ray photoelectron spectroscopy (XPS). This work is the first step in exploring the potential of H<sub>2</sub>/O<sub>2</sub> plasma modification as a means of controlling the surface of microporous PP membranes.

## EXPERIMENTAL

Hydrogen (H<sub>2</sub>) and Oxygen (O<sub>2</sub>) gases used to create plasma surface modification were both industrial grade with 99.997% purity. Microporous PP membranes with a porosity of 45–50% and an average pore diameter of 0.45 μm were purchased from Ming-Young Inc. The plasma reactor system used in this investigation was a Pyrex-glass tubular reactor (6.0 cm OD, 5.3 cm ID, and 70 cm long), as shown in Figure 1. Copper coil was used for the electrical energy input of plasma power. The copper coil was placed on the Pyrex tube at a distance of 10 cm from one end, where the gas inlet was located. H<sub>2</sub>/O<sub>2</sub> gas mixtures with different ratios were used as the reactive gas for plasma surface modification. The plasma reactor was first pumped to a base pressure of 1 mTorr or below, and then H<sub>2</sub>/O<sub>2</sub> gas was introduced into the chamber at a preset flow rate and mixing ratio. The system pressure in the reactor was controlled with an MKS pressure controller. When

the system pressure reached a preset value, plasma power was applied at 13.56 MHz with a required match network unit (PFG-300RF generator Huttinger Elektronik Inc., Germany). The static contact angles of plasma treated microporous PPs were measured by projecting an image of an automatic sessile droplet resting on a membrane surface with a Magic Droplet Model 100SB Video Contact Angle System (Sindatek Instruments Inc., Taiwan). To understand the nature of the changes in the surfaces properties of PP membranes due to plasma surface modification, the dispersion and polar interaction contributing to the surface energy of the materials were calculated using the Owens-Wendt model.<sup>9</sup> The liquids used for calculating the surface energy of the untreated and plasma treated PP membranes were water and diiodomethane of known  $\gamma^p$  (polar component) and  $\gamma^d$  (disperse component). The surface energy of a solid ( $\gamma^s$ ) has two components, namely, a polar component and a disperse component. Both components contribute to the total surface energy. The polar and the disperse components are responsible for the hydrophilic and hydrophobic properties, respectively.

The major plasma diagnostic apparatus of H<sub>2</sub>/O<sub>2</sub> gas mixture plasma is an OES. This equipment consists of both instrumentation and spectrum analysis software, which was supplied by Hong-Ming Technology, Inc. The observable spectral range was 250–950 nm with a resolution of 2 nm. The OES was situated outside the quartz window, about 20 cm from the target, and fixed so the maximum light emission was detected. The surface morphology and



**Figure 2** The average contact angle values of low-pressure H<sub>2</sub>/O<sub>2</sub> plasma modified polypropylene (PP) membrane with different ratio of hydrogen–oxygen gas mixture inputs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

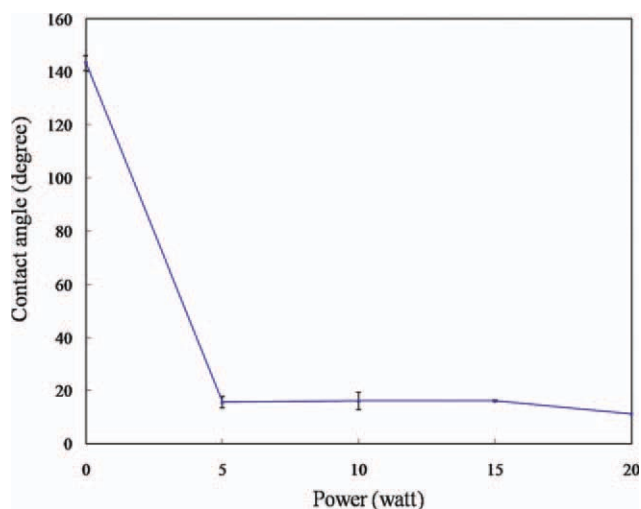
roughness of the plasma treated microporous PPs were examined by CLSM, respectively. The plasma treated microporous PP membranes were analyzed with a CLSM (VK9700, Keyence Corp., Japan) with a computer-controlled laser scanning assembly attached to the microscope. The images were processed with VK Viewer control software. XPS measurements were carried out on a VG Scientific Microlab 310F system, using nonmonochromatic Mg K $\alpha$ -radiation ( $h\nu = 1253.6$  eV) and Al K $\alpha$ -radiation ( $h\nu = 1486.6$  eV) operated at 25 kV. Spectra were acquired with the angle between the direction of the emitted photoelectrons and the surface of microporous PP membranes equal to the take-off analysis angle of 70°.

## RESULTS AND DISCUSSION

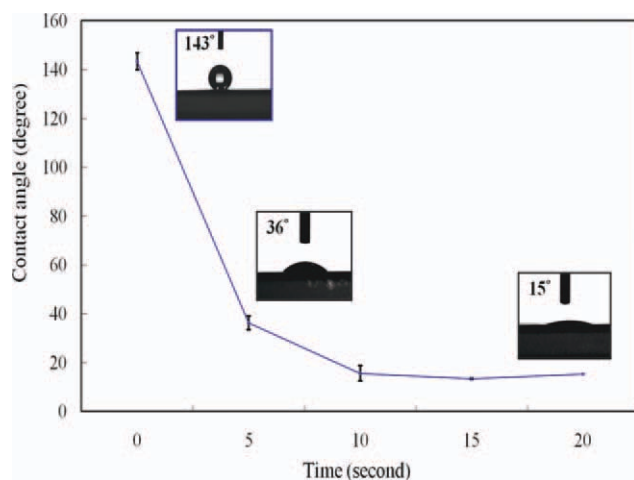
Figure 2 shows the change in the static contact-angle measurement with respect to the ratio of hydrogen content in the H<sub>2</sub>/O<sub>2</sub> gas mixture at RF power 5 Watt, H<sub>2</sub>/O<sub>2</sub> flow rate of 10 sccm, and 100 mTorr, 10 s. Figure 2 shows the static contact-angle values of low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-modified PP membrane gradually decreased with the increasing ratio of hydrogen content in the H<sub>2</sub>/O<sub>2</sub> gas mixture. The increase in the hydrogen content of the mixed gases (H<sub>2</sub>/O<sub>2</sub>) led to increased surface concentration of the polar functional groups on the PP membrane. However, the static contact-angle value of greater hydrogen content in the H<sub>2</sub>/O<sub>2</sub> gas mixture (3 : 1 and 4 : 1) contribution in the H<sub>2</sub>/O<sub>2</sub> plasma-treated PP membrane was higher than that in the H<sub>2</sub>/O<sub>2</sub> (2 : 1) plasma-modified PP membrane. As a result, the polar contribution in the H<sub>2</sub>/O<sub>2</sub> plasma of more

hydrogen content in the H<sub>2</sub>/O<sub>2</sub> gas mixture treatment became smaller than that in the low hydrogen content in the H<sub>2</sub>/O<sub>2</sub> gas mixture treatment. This can be demonstrated by the fact H<sub>2</sub>/O<sub>2</sub> (2 : 1) gas mixture plasma gradually increases the hydrophilicity of polymeric surface with respect to the pseudo water-vapor (H<sub>2</sub>O) plasma effect on polymeric surface modification. It is believed the reactive species in the H<sub>2</sub>/O<sub>2</sub> plasma gas phase, which can react with the activated surface, become abundant. Therefore, the suitable hydrophilic property of plasma-modified PP membrane was achieved by a H<sub>2</sub>/O<sub>2</sub> gas mixture of 2 : 1 ratio.

The surface modification of the PP membrane with low-pressure H<sub>2</sub>/O<sub>2</sub> plasmas was studied as a function of the RF plasma power level. Figure 3 shows the contact-angle change values of the low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-modified PP membrane with the RF plasma power level. The changes in the contact-angle change of low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-modified PP membrane significantly increased after a very short treatment time (5 s). The most efficient RF plasma power level was 5 W, where an effective surface modification was achieved on the PP membrane with low plasma power consumption. Figure 3 clearly shows the surface property of the PP membrane is significantly increased and becomes hydrophilic from the low-pressure H<sub>2</sub>/O<sub>2</sub> plasma modification treatments. However, the increasing RF plasma power level in Figure 3 produced a small surface activation effect in lowering the water contact angles on the PP membrane surface. As seen in Figure 3, an RF plasma power level over 10 W gave a constant water contact angle on the PP membrane



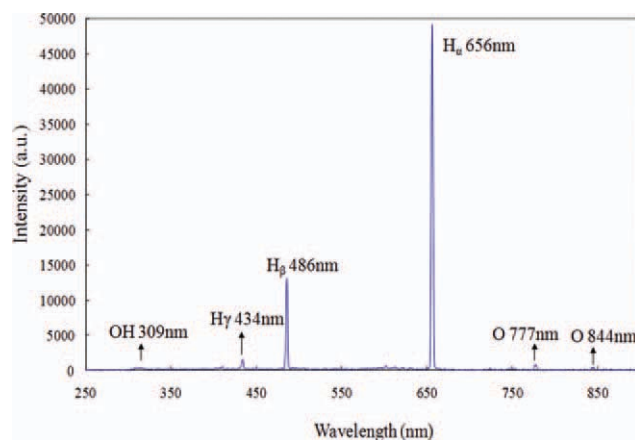
**Figure 3** The average contact angle values of low-pressure H<sub>2</sub>/O<sub>2</sub> plasma modified polypropylene (PP) membrane with different RF plasma power inputs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



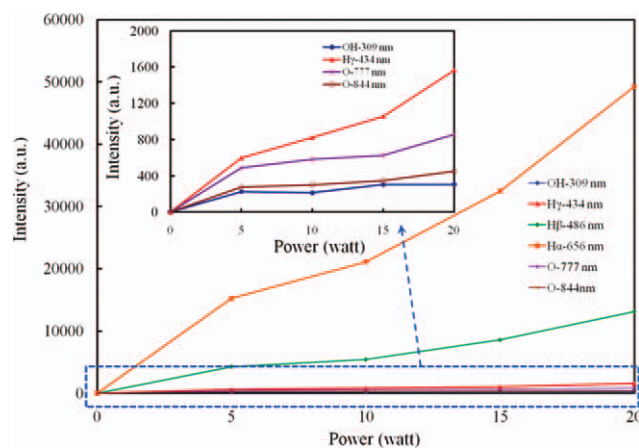
**Figure 4** The average contact angle values of low-pressure H<sub>2</sub>/O<sub>2</sub> plasma modified polypropylene (PP) membrane with different treatment times. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

surface, suggesting an over treatment effect resulted for this operational condition. As discussed by many other researchers,<sup>10</sup> the over treatment effect could be ascribed to the extensive polymer chain scission by bombardment of energetic particles (ions, electrons, excited neutrals, photons) from the plasma, which could degrade the polymer structure integrity of the near-surface region. Further chemical composition analysis from XPS is described in the following section.

Figure 4 shows the water contact-angle change on the low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-modified PP membrane surface with different treatment times. In improving the hydrophilicity of the PP membrane, the longer treatment time was more effective than the shorter treatment time. The experimental results also



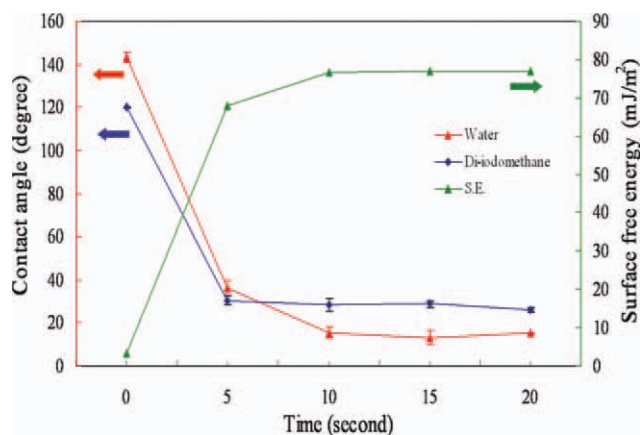
**Figure 5** The optical emission spectrum from low-pressure H<sub>2</sub>/O<sub>2</sub> plasma surface modification process. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6** Optical emission intensity dependence of low-pressure H<sub>2</sub>/O<sub>2</sub> plasma surface modification process. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

suggested the hydrogen and oxygen-related species significantly affected the surface modification of the PP membrane. The results obtained by the low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-modified PP membrane treatment clearly showed the excited hydrogen and oxygen atoms were very efficient in the hydrophilicity modification of the PP membrane surface. OES was used to monitor the excited plasma reactive species generated by the luminous gas phase of the low-pressure plasma. The photoemitting species are significantly essential in the luminous gas phase, and the location of the luminous gas phase indicates where the chemically reactive species reaction occurs,<sup>11</sup> OES analysis is expected to explicate the reactions of the plasma reactive species that may contribute to low-pressure H<sub>2</sub>/O<sub>2</sub> plasma modification. The typical emission spectrum of low-pressure H<sub>2</sub>/O<sub>2</sub> plasma is shown in Figure 5 from 250 to 950 nm, with no significant emissions outside of this region observed over the 200–1050 nm range of the instrument.

From the OES spectra shown in Figure 5, strong excited hydrogen emission lines are observed at 656 nm, 486 nm, and 434 nm. The minor emission line of the oxygen atom is 777 nm and 844 nm from the oxygen reactive gas. The low intensity of the emission derived from the OH band system (309 nm) was also observed. This supports the assumption of H<sub>2</sub>/O<sub>2</sub> or water vapor-based plasma surface activation owing to the electron-impact-dissociation of gas molecules.<sup>12</sup> From the optical spectra of the low-pressure H<sub>2</sub>/O<sub>2</sub> plasma state, this corresponds to the possible reaction mechanism of the H, O, and OH plasma species. Figure 6 shows the normalized emission intensities of the major emissions as a function of the RF plasma power level. The major emission intensities increased with the increasing RF plasma power level. Figure 6 shows the RF plasma power



**Figure 7** The surface free energy changes of low-pressure  $H_2/O_2$  plasma modified polypropylene (PP) membrane with different treatment times. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

level dependence of the normalized emission intensities of hydrogen lines from excited  $H_2/O_2$  mixture gas. The normalized emission intensities of the hydrogen and oxygen emission lines increased with the increasing RF plasma power level, demonstrating an increase in the density of highly energized electrons. In Figure 6, the normalized emission intensities of minor emission lines are also shown. These stable normalized emission intensities can be considered to correspond to the electron-impact-dissociation in the plasma, and it stabilized with increasing RF plasma power levels.

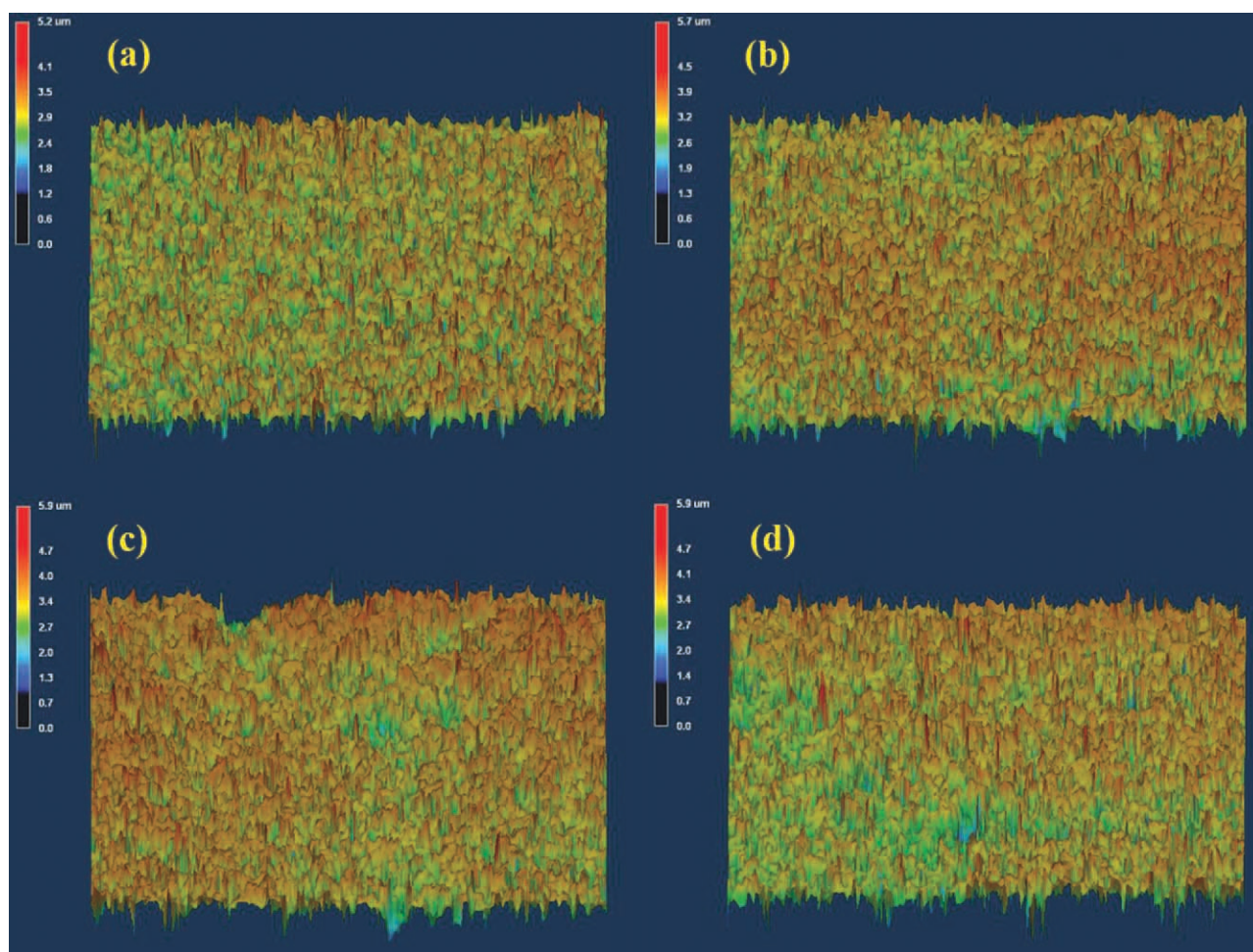
Surface energy is a distinctive feature affecting the material surface properties, such as wetting, permeability, and adhesion.<sup>13,14</sup> Figure 7 shows a plot of surface energy ( $\gamma^s$ ) from the measured contact angles on the low-pressure  $H_2/O_2$  plasma-modified PP membrane surfaces as a function of treatment time. The surface energy of the unmodified PP membrane is 3 mJ/m. The changes in the surface energy of  $H_2/O_2$  plasma-modified PP membrane surfaces significantly increased after a very short treatment time (5 s). The surface energy reached the maximum value for a short treatment time and then leveled

off. This may be due to the lack of oxygen content incorporated into the PP membrane surface, as the exposure time increased. Finally, the surface energy was reached at 77 mJ/m. A similar trend is observed for the polar component. This is mainly a result of the incorporation of polar groups such as CO, COO, OH, etc.<sup>15</sup> Figure 7 clearly shows the polar component of the surface energy of the PP membrane is significantly increased and becomes hydrophilic from the  $H_2/O_2$  plasma surface modification. Table I also summarized the static contact angle values of two suitable liquids (D.I water and diiodomethane) and the surface-free energies of untreated and  $H_2/O_2$  plasma-treated PP membrane surfaces. This result confirmed the plasma treatment made the material surface more hydrophilic at a certain level, depending on the operational conditions.

In general, the surface property treated by plasma surface activation/modification greatly relies on the chemical characteristics and surface morphology. Besides the possible etching/bombardment of the plasma surface, activation/modification sensitively affects the change in the surface morphology and roughness.<sup>16,17</sup> CLSM was used to detect the change in the surface morphology and roughness with respect to the low-pressure  $H_2/O_2$  plasma-modified PP membrane surfaces. Figure 8 shows the three-dimensional surface of the differently treated films. Figure 8(a) presents the surface of the unmodified PP membrane surfaces showing the porous structure of the natural shape of the PP membrane. Figure 8(b–d) shows the CLSM images of low-pressure  $H_2/O_2$  plasma-modified PP membrane as a function of treatment time. Figure 8(a) shows the surface of the unmodified PP membrane is comparatively smooth. The surface roughness of the PP membrane increased after the plasma treatment, even for a shorter exposure time (5–20 s). Etching of the PP membrane surface is more rapid, resulting in protrudes which can be seen in the CLSM pictures [Fig. 8(b–d)]. For longer treatment times, protruding spikes that are flattened due to continued etching can go deeper into the membrane causing higher roughness [Fig. 8(b–d)]. The CLSM analysis reveals

**TABLE I**  
Static Contact Angle Values of Two Suitable Liquids for the Measurement of Surface Energy Before and After Plasma Treatment

Plasma treatment time (second)	Average contact angle (°)		Surface energy (mJ/m <sup>2</sup> )		
	H <sub>2</sub> O	Di-iodomethane	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$
untreated	143°	120°	3	3	0
5	36°	31°	68	44	24
10	16°	29°	77	45	32
15	13°	29°	77	45	32
20	15°	26°	77	46	31



**Figure 8** CLSM images of untreated and low-pressure H<sub>2</sub>/O<sub>2</sub> plasma modified polypropylene (PP) membrane with different treatment times. (a) Untreated PP membrane; (b) 5 s, H<sub>2</sub>/O<sub>2</sub> plasma-treated PP membrane; (c) 10 s, H<sub>2</sub>/O<sub>2</sub> plasma-treated PP membrane; and (d) 20 s, H<sub>2</sub>/O<sub>2</sub> plasma-treated PP membrane. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

surface roughness increases with treatment time, and this indicated possible plasma etching was simultaneously occurring. As a result, CLSM analysis determines the smooth surface in the H<sub>2</sub>/O<sub>2</sub> plasma plasma-treated PP membrane originated from the high crosslinking reaction and etching. In the case of the H<sub>2</sub>/O<sub>2</sub> plasma, relatively small amounts of free radicals were generated in the activated gas species because of the scavenging effect of the oxygen species.

XPS analysis was used to correlate the results obtained by contact angle measurement, suggesting a significant activation/oxidation at the surface of the low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-modified PP membranes. A quantitative evaluation of the changes in the atomic concentration in the PP membrane surfaces as a function of plasma treatment time is summarized in Table II. The quantitative data confirm the oxygen contents increase and the carbon content decreases. It shows the ratio of O1s/C1s increased after H<sub>2</sub>/O<sub>2</sub> plasma surface modification. This could

be attributed to the increase in the newly formed functional groups by the low-pressure H<sub>2</sub>/O<sub>2</sub> plasma treatment, as will be discussed from the XPS spectra of unmodified and H<sub>2</sub>/O<sub>2</sub> plasma-modified PP membranes. To study the major functional groups introduced into the PP membrane surfaces by low-pressure H<sub>2</sub>/O<sub>2</sub> plasma surface modification, XPS deconvolution analysis of the C1s peaks was performed. As shown in Figure 9(a), the C1s spectrum of untreated PP membrane contained two well-separated peaks at 284.5 and 285 eV, corresponding to C—C and C—H groups, respectively.<sup>18</sup> The spectra of H<sub>2</sub>/O<sub>2</sub> plasma-modified PP membranes with different treatment times [Fig. 9(b,c)] also showed peaks for C—C at 284.5 eV and C—H groups at 285 eV, at the same time, additional peaks at 286.5, 287.4, and 288.8 eV also appear and rise which could be attributable to the —C—O, C=O, and O—C=O groups.<sup>19</sup> The percentage contribution of the C1s components of low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-treated PP membranes, calculated from the C1s spectra, is

**TABLE II**  
**Element Composition/Ratio (%) of C1s and O1s in the Polypropylene (PP) Membrane with Binding Energy Change Before and After Plasma Treatment: Untreated PP Membrane and 20 s H<sub>2</sub>/O<sub>2</sub> Plasma Treated PP Membrane**

Sample	Elemental composition (%)		Elemental ratio (%)
	C1s	O1s	O/C
(a)	100	0	0
(b)	81.35	18.65	22.93

Contribution of C1s components (%)					
Sample	C—C 284.5 eV	C—H 285 eV	C—O 286 eV	C=O 287.4 eV	O—C=O 288.8 eV
(a)	61.01	38.99	0	0	0
(b)	28.64	30.22	26.43	4.86	9.85

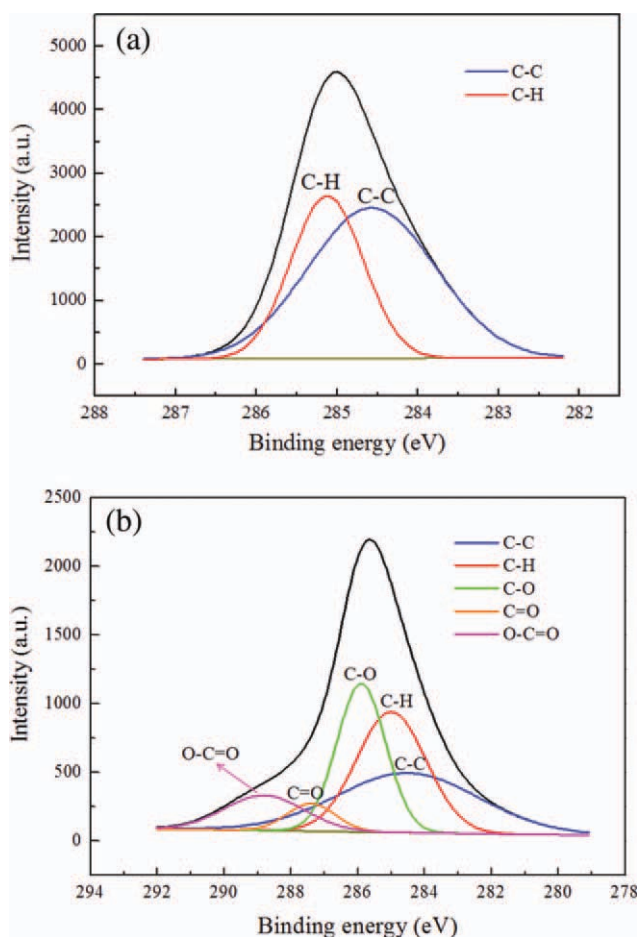
  

Contribution of O1s components (%)		
Sample	C=O* 532.4 eV	O*—C=O 533.4 eV
(a)	0	0
(b)	21.29	78.71

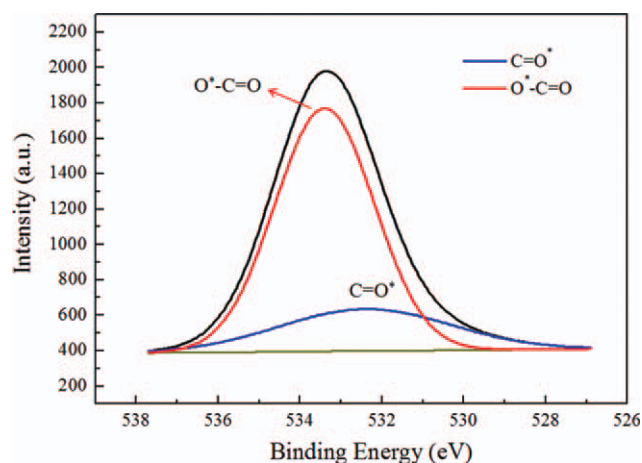
shown in Table II. Table II show, following H<sub>2</sub>/O<sub>2</sub> plasma treatment, the C—C and C—H groups decrease, and —C—O, C=O, and O—C=O groups increases with respect to treatment time. These results suggested that air plasma treatment cleave the C—C and C—H bonds and introduces oxygen-containing functional groups into the molecular chain of the PP membrane surface.<sup>20</sup> These polar groups help increase the surface hydrophilicity of the PP membranes. The polar contribution of the surface-free energy and the intensity of the XPS O1s peaks both increase with O<sub>2</sub> content in H<sub>2</sub>/O<sub>2</sub> plasma-modified PP membranes in Figure 10. This suggests the activated species can easily form reactive oxygen-containing functional groups on the surface. The activation of the surface and the chemical etching process can occur simultaneously using these reactive species.

### CONCLUSIONS

This investigation demonstrated the rapid surface modification capability of low-pressure H<sub>2</sub>/O<sub>2</sub> mixture gas plasma processing. The static contact angle measurement results indicated the H<sub>2</sub>/O<sub>2</sub> mixture gas plasma rapidly improves the hydrophilicity and surface energy of the microporous PP membranes. OES determined the plasma reactive species from H<sub>2</sub>/O<sub>2</sub> mixture gas plasma, contributing to the surface modification/activation of the PP membranes. The interaction of hydrogen and oxygen-based plasma species in the plasma with the PP membrane surface can be recognized as the enhancement of surface modification from OES analysis. The polar functional groups generated due to plasma



**Figure 9** The C1s spectra of XPS analysis of (a) untreated PP membrane and (b) low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-treated PP membrane. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]



**Figure 10** The O1s spectrum of XPS analysis of low-pressure H<sub>2</sub>/O<sub>2</sub> plasma-treated PP membrane. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

treatment on the surface of the PP membranes causes decreased contact angles and increased surface energy. The XPS results showed the carbon content decreased and the oxygen content increased on the surface of the H<sub>2</sub>/O<sub>2</sub> mixture gas plasma treated microporous PP membranes. The CLSM analysis indicated the increased roughness of PP membranes by the impact of plasma species for removing the top monolayer of the PP membrane surface. The chemical and surface morphological changes made on the surface of the PP membranes lead to increased hydrophilic properties. The plasma modification capability demonstrated through this study indicates the tremendous potential of this H<sub>2</sub>/O<sub>2</sub> mixture gas plasma as a promising membrane surface modification/activation technique.

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