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Surface hydrophilic modifications on polypropylene membranes by remote methane/oxygen mixture plasma discharges

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ABSTRACT

The aim of this study was to evaluate the remote effect of low-pressure 13.56 MHz radio-frequency (RF) methane (CH_4)/oxygen (O_2) mixture plasma on surface modification and its correlation with photoemission of plasma species. We also conducted surface analysis of microporous polypropylene (PP) membranes modified with RF CH_4/O_2 mixture plasmas. We applied Fourier transform infrared spectroscopy, confocal laser scanning microscopy, and scanning electron microscopy to determine correlations between changes in surface properties and the luminous effect. We showed that the CH_4/O_2 mixture plasma treatment effectively enhances the surface hydrophilicity and surface free energy of PP membranes in the remote plasma region.

1. Introduction

In recent years, polymer materials have been widely used in a variety of industrial fabrications [1]. Low-pressure plasma surface modification is a promising technique that can improve surface properties of the polymers without changing their bulk properties. Low-pressure plasma modification is environmentally friendly and is an inventive alternative technology to conventional methods [2,3]. It is often used to enhance the quality of the polymers through cleaning (removal of surface contaminants) and activation (formation of new surface chemical groups) processes, increasing the adhesion and wettability of the polymers [4,5]. Surface modification of polymer membranes by plasma processing can be applied to tailor the membrane surface properties. Polypropylene (PP) is a versatile polymer because of its low cost, easy processing, and good mechanical properties [3–5]; it is used in many applications such as membranes, fibers, slit tape, containers, closures, and automotive interior trim [6,7]. The singular structure of PP is responsible for its chemical inactivity; for this reason, PP is strongly hydrophobic and poses difficulties for surface modification [8,9].

To control the surface modification effect in a predictive manner, a fundamental understanding of the reactions during plasma modification processes is critical. When a polymer surface is exposed to the plasma, consisting of electrons, ions, and radicals, these plasma species react on the polymer surface resulting in: (1) introduction of functional groups and (2) etching of polymer chains [10,11]. The former reaction contributes to surface modification, but the latter one degrades these same desired surface modifications. To eliminate the etching/degradation effects inherent to plasma surface modification, the method has to be further modified through remote/afterglow treatment. Optimization of the process opens up enormous opportunities for designing and developing modification methods by tailoring the sample position within the plasma treatment. Because of this aspect, understanding behavior in the glow region and the remote region in plasma surface modification is essential for effective polymer surface treatment.

The use of a mixture of an organic monomer (CH_4) and a highly reactive gas (O_2) has good potential to induce functionalization and enhance durability. Depending on the type of input gas used for creating the plasma and its process parameters, such a modification process can be used to tailor surface properties of the polymer membranes. The monomer molecules are activated in the plasma phase, affect the membrane surface, and promote the dissociation of bonds at the topmost layers and chemical reaction between the active surface and reactive species in the plasma [12,13]. From this aspect, the mixture of an organic monomer and a reactive gas can be recognized as a prospective input gas source for plasma

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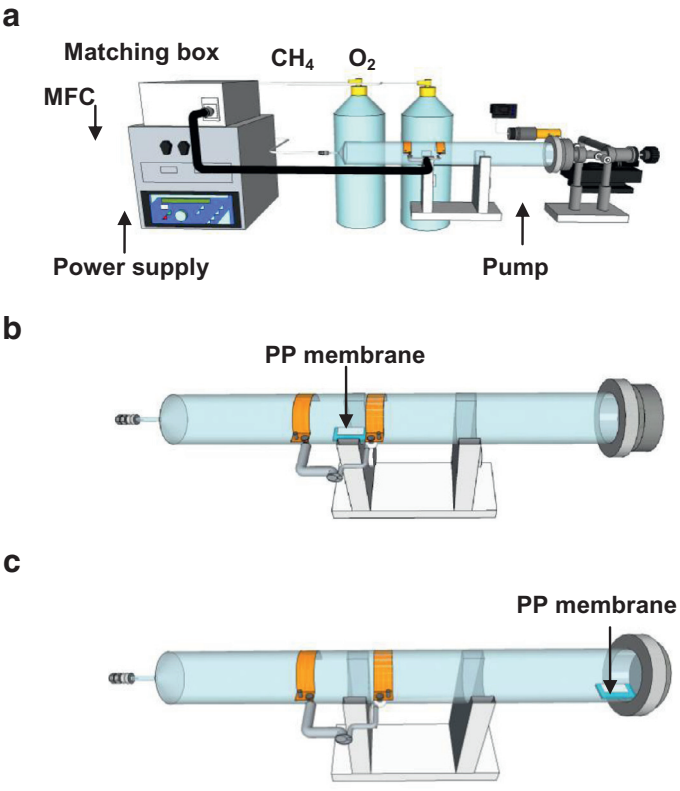

Fig. 1. Schematic diagrams of (a) experiment instrument, (b) glow/direct sample position, and (c) remote sample position.

surface modification. However, in spite of extensive use of the plasma modification process, surface modification by the CH_4/O_2 mixture plasma process has not been systematically studied.

In this work, microporous PP membranes were modified in a 13.56 MHz RF glow discharge of methane (CH_4)/oxygen (O_2) mixture plasma glow discharge in the glow/remote regions, with the aim of improving intrinsic surface properties and exploring the luminous gas effect. The changes in hydrophilicity of plasma-modified PP membranes were characterized by measuring the contact angle and surface free energy. Optical emission spectroscopy (OES) and Fourier transform infrared spectroscopy (FTIR) were used to assess whether various chemical species cause plasma surface modification. Finally, we applied scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM) to study surface topography of the PP membranes.

2. Materials and methods

2.1. Materials and device

In this study, the microporous PP membrane used was manufactured by GE Water & Process Technologies. The average porous size of this membrane was 0.45 μm, and the diameter was 90 mm. Before the experiments, the membrane was cut to a 2- × 2-cm square, and then the membrane was cleaned in an ultrasonic cleaner with ethanol and deionized water in order for 10 and 15 min, respectively. Methane (CH_4) and oxygen (O_2) gases used to generate the gas mixture plasma were both industrial grade with 99.997% purity. The plasma reactor system used in this work was a Pyrex-glass tubular reactor (60.5 mm o.d., 53 mm i.d., and 730 mm length), as shown in Fig. 1. Copper coils were used to generate the capacitively coupled mode electrical plasma power. They are each 30 mm in width and distance of 100 mm between the two copper coils. The plasma power was applied at 13.56 MHz radio-frequency with a required match network unit (PFG-300RF generator Huttinger Elektronik Inc., Freiburg, Germany). The tubular plasma reactor was evacuated using an ULVAC Model GLD-210B rotary vacuum pump; the pump can achieve close to 10^{-3} Torr vacuum pressure in the plasma reactor. In this study, the plasma power, plasma treatment time, and sample position were adjusted to examine the differences of surface properties on the PP membrane.

2.2. Characterization and analysis of the membrane surface

The static contact angle of the plasma-treated PP membrane was measured by projecting an image of an automatic sessile droplet resting on the membrane surface with a Magic Droplet Model 100SB Video Contact Angle System (Sindatek Instruments Inc., Taipei, Taiwan). To understand the nature of the surface changes of the PP membrane, the dispersion and polar interaction contributions to the surface energy of the materials were calculated using the Owens–Wendt model [14]. The surface energy of a solid (γ_S) has two components, namely, a polar component and a dispersive component. Both components contribute to the total surface energy. The liquids used for calculating surface energies of the untreated and plasma-treated PP membranes were water and diiodomethane with known γ^p (polar component) and γ^d (dispersive component). The polar and dispersive components are responsible for the hydrophilic and hydrophobic properties [14].

$$\gamma_{LV}(1+\cos\theta) = 2\left(\gamma_L^d \cdot \gamma_S^d\right)^{1/2} + 2\left(\gamma_L^p \cdot \gamma_S^p\right)^{1/2} \quad (1)$$

The major plasma diagnostic apparatus for the CH_4/O_2 mixture plasma is the optical emission spectroscopy (OES). This equipment consists of instrumentation and spectrum analysis software supplied by Hong-Ming Technology, Inc. (Taiwan). The observable spectral range was 250–950 nm with a resolution of 2 nm, which was carried out using a Perkin Elmer Spectrum 100. For each sample, 256 scans were co-added over the wavelength range from 450 to 4000 cm^{-1} and analyzed. SEM analysis was performed with a JEOL model JSM-5600 scanning electron spectroscope and a JEOL model JSM 6701f field-emission scanning electron microscope. A tungsten filament was used as the electron source. A 5-keV accelerator voltage was used for scanning the sample surfaces.

Surface morphology and roughness of the plasma-treated membranes were investigated by confocal laser scanning microscopy (CLSM) (VK9700, Keyence Co., Japan) with a computer-controlled laser scanning assembly attached to the microscope. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Scientific Microlab 310F system, using non-monochromatic Mg Kα-radiation ($h\nu = 1253.6$ eV) and Al Kα-radiation ($h\nu = 1486.6$ eV) operated at 25 kV. Spectra were acquired with the incidence angle of the emitted photoelectrons onto the PP membrane surface equal to the take-off analysis angle of 70°.

3. Results and discussion

3.1. Characteristics of the plasma

The luminous gas phase of plasma treatment in different membrane sample positions is shown in Fig. 2. In a plasma glow discharge, the location of the luminous glow represents the electron energy level therein. Because of this, the glow characteristics in RF CH_4/O_2 mixture plasma polymerization have important implications for understanding the creation mechanisms of chemically reactive species in plasma deposition. Herein, the PP samples referred to as glow region PP are those placed in the plasma generation region (the electrode area), while those samples placed a sufficient distance from the plasma generation region are defined