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Original Article

Surface hydrophobic modification of cellulose membranes by plasma-assisted deposition of hydrocarbon films

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Abstract

Surface modification by plasma polymerization is an efficient method to change the surface properties of a membrane. Desirable functionality such as hydrophobicity or hydrophilicity can be obtained, depending on plasma chemistry of gas precursors and discharge conditions. In this work, RF magnetron plasma is produced using acetylene and nitrogen as precursor gases. Variations of RF power, particle flux, deposited time and pressure of the precursor gases have been made to observe coating effects on the cellulose membranes. When appropriated conditions are used, a thin brownish film of hydrocarbon was formed on the membrane, and the water contact angle increased from 35 to 130 degrees.

Keywords: cellulose membrane, reactive plasma, acetylene, RF discharge, Hydrocarbon, Contact angle, Hydrophobic, Hydrophilic

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1. Introduction

Reactive plasmas (Chu *et al.*, 2002; Chaivan *et al.*, 2005; Hodak *et al.*, 2008) formed by discharge of reactive gases such as O_2, N_2, CF_4, SF_6, CH_4 and C_2H_2, are widely used effectively for surface modification of materials with promising applications. Normally, plasmas contain energetic electrons, photons, excited atoms, molecules, radicals, negative and positive ions. The reactive plasmas, therefore, can generate superior conditions, which allow various chemical reactions. Gas precursors and discharge conditions for desirable chemical reactions have been investigated. Polymer materials, such as paper, silk, textiles, rubber, and plastics, have been treated by plasma polymerization in reactive plasmas to enhance their surface properties, such hydrophilicity, hydrophobicity, adhesion, bio-compatibility, and electrical conduction. The reasons, why surface modifications by plasmas are superior compared to wet chemical treatments, are as following:

- particles in the plasmas are very energetic so chemical reactions are fast
- only a few atomic layers on the surface of a polymer are modified by the plasma environment, while the bulk properties remain the same.
- plasmas are environmental friendly, with no toxic

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chemical as by-products.

- high accuracy for operating conditions.
- versatile chemical reactions can be obtained easily by varying discharge conditions.

The demand for flexible packaging materials, which are biodegradable and at low cost, are increasing rapidly in food and pharmaceutical industries (Vaswani, 2005). The materials such as paper and cellulose are suitable for those applications, providing that their surface properties are modified. Fluorocarbon plasma has been used successfully to deposit barrier films on the surface of materials, and the hydrophobicity of the material surface are modified (Vaswani, 2005).

In this work, we investigate the use of RF reactive magnetron plasma to deposit a barrier film on bacterial cellulose membranes. The membrane originally exhibits hydrophilic properties. Acetylene and nitrogen mixing is used as precursor gases. Changes in the membrane surface, due to deposited films, are investigated under different conditions of RF power, particle flux, deposited time and pressure of precursor gases. Contact angle goniometry is used to characterize the hydrophobic properties of hydrocarbon films. The plasma discharge conditions are optimized for film coating, so that cellulose membranes exhibit hydrophobic characters as evidenced by high water contact angles. Water permeate flux is performed to support the type of modification on the membrane surface.

2. Experimental

2.1 Preparation of cellulose membrane

Cellulose membrane was formed by an intertwining of cellulose nanofibres delivered from membrane pores of *A. xylinum*. The bacteria of 1×10^6 cfu.ml^{-1} was cultured in coconut juice media composed of 4.0%(w/v) sucrose, 0.5% (w/v) yeast extract, 0.5%(w/v) peptone, 0.033%(w/v) Na_2HPO_4 and 0.0115%(w/v) citric acid at pH 4. The culture was incubated statically at room temperature (27±2°C) for 3 days. The formed membrane of 50x100 cm area was boiled for 20 min and immersed in 1.5N NaOH for 48 hrs, then washed with tap water until pH reached 7.0. The membrane was dried in a dust free cabinet with 400 W incandescent lights (100W each) at 32±3°C for 4 days.

2.2 Plasma treatment

A magnetron RF plasma source as shown in Figure 1 is used for deposition of the hydrocarbon barrier film on the surface of the cellulose membrane. The RF is an in-house development (Nisoa, 2005). Vacuum chamber and diffusion pump were fabricated by Vacuum Technology and Thin Films Research Laboratory, Faculty of Science, Burapha University, Chonburi, Thailand. The magnetron plasma has been known for its high deposition rate of the polymerized films (Kelly, 2000). The processing chamber is made of cylindrical stainless steel of 20 cm inner diameter and 30 cm height. When rotary and diffusion pumps or only rotary pump are used, the base-pressure is about 2×10^{-5} Torr; 5×10^{-3} Torr can be obtained. The pressures are monitored by Magnetron and Pirani gauges. The magnetron cathode, located inside the cylindrical chamber, is of stainless steel with 4 cm diameter. A needle valve is used to control the flow rate of the C_2H_2 gas inlet, and to vary the working pressure for deposition of the plasma polymerized hydrocarbon film.

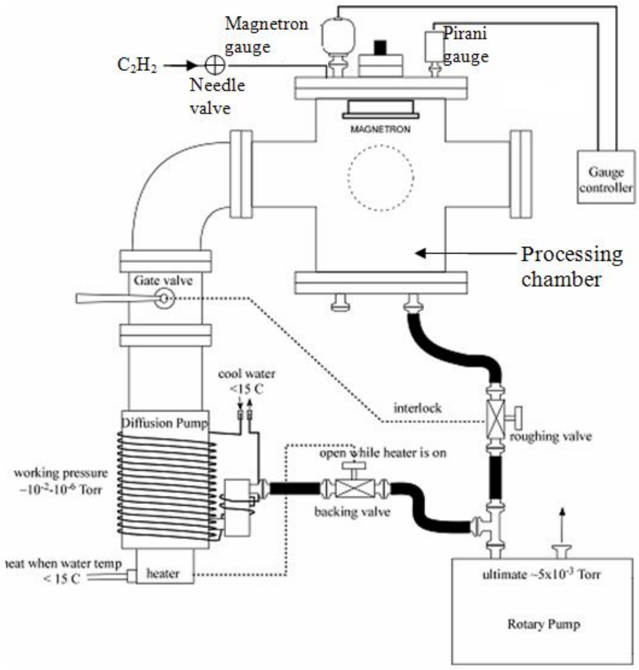


Figure 1. Schematic diagram of the RF magnetron plasma source.

When C_2H_2 is fed into the processing chamber and the RF power source is applied to the magnetron cathode, reactive plasmas are generated. There are two different regions of plasmas, depending on particle flux densities and electron temperature as shown in Figure 2. In the discharge region near the cathode, dense plasmas are produced under a strong RF electric field by energetic electrons. Therefore high-density particle fluxes are obtained. On the other hand, in the remote region outside the discharge region, electrons are cooled down by collisions with background neutral atoms. In this region, there are diffuse plasmas, whereas particle flux density of ions, radical, and excited molecules and atoms are decreased with the distance (*h*) from the cathode. For each discharge condition, a small piece 4×4 cm of cellulose membrane was placed on the glass stage at distance *h* from the cathode as shown in Figure 2. A rotary pump was used to evacuate the processing chamber to the base pressure of about 40 mTorr. After deposition of the plasma polymerized thin hydrocarbon film, the membrane was taken from the processing chamber for measurements of the water contact angle.

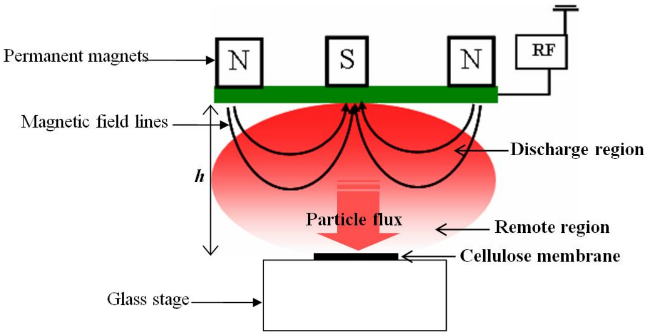


Figure 2. Configuration of plasma polymerized film deposition on the surface of the membrane.

2.3 Water contact angle measurement

Water contact angle (Busnaina, 2007) goniometry is used to characterize the surface wettability of the produced cellulose membrane. Depending on the contact angle θ of the water droplet, the surfaces exhibit hydrophilic (water-loving) and hydrophobic (water-fearing) properties when $0 \le \theta \le 90$ and $90 < \theta \le 180$, respectively, as shown in Figure 3.

If θ = 0, the surface is complete wetting or super hydrophilic, water will form a very thin film on the surface. On the other hand, when θ > 150 the surface is super-hydrophobic, a water droplet will rest on the surface without wetting.

In this work, the Tantec Model CAM-MICRO contact angle meter was used to investigate the wetting properties of the hydrocarbon barrier film coated on the surface of the cellulose membrane. The angle ϕ of the water droplet is measured as shown in Figure 4. The readout on the screen is the contact angle θ and $\theta = 2\phi$.

3. Results and Discussion

In this section, the hydrophobic properties of the hydrocarbon barrier films deposited on the cellulose membrane will be investigated for different discharge conditions. The main purpose was to look for the conditions where the deposited films exhibit large hydrophobicity corresponding to a large measured contact angle θ.

3.1 Effect of deposition time

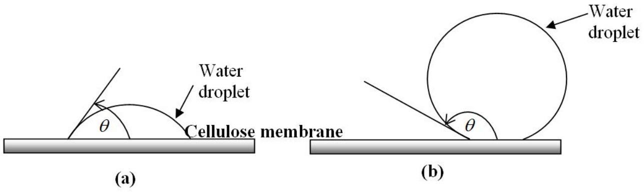


Figure 3. Water contact angle θ for (a) hydrophilic and (b) hydrophobic surfaces.

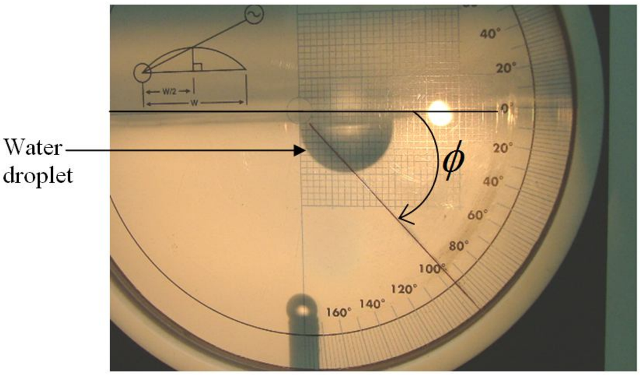


Figure 4. Measurement the contact angle by the Tantec Model CAM-MICRO contact angle meter.

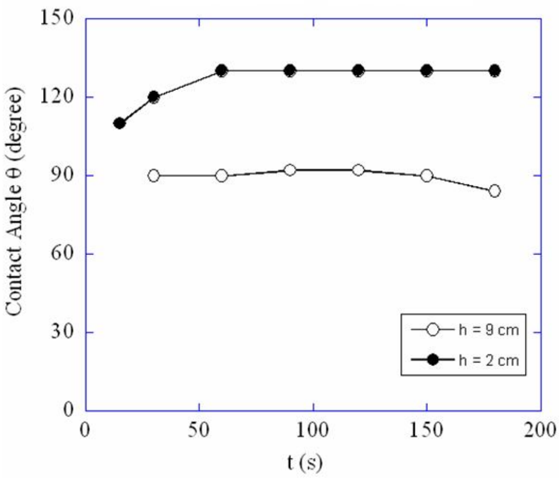


Figure 5. Dependence of contact angle on deposition time for h = 9 (open circles) and 2 (closed circles) cm. Base pressure = 40 mTorr, C_2H_2 pressure = 200 mTorr and P_{rf} = 150 W.

Figure 5 shows the dependence of contact angle on deposition time when the membrane was placed at two different distances h. At h = 2 cm, the measured contact angles are larger compared to those of h = 9 cm. This might be caused by polymerization of higher densities of particle fluxes at the discharge region of h = 2 cm. At h = 2 cm, the contact angle increased with increasing deposition time when $0 < t < 50$ s, then saturated at about 130 degrees when $t > 50$ s. This result implied that there was a minimum thickness of the deposited hydrocarbon film which enhanced the surface of the cellulose membrane to have maximum hydrophobicity. By using FTIR and XPS analysis, Du *et al.* (2007) have reported that the hydrophobic layer on the solid surface, deposited by acetylene plasma, was composed of hydrocarbon.

3.2 Effect of C_2H_2 pressure

Figure 6 shows the dependence of the contact angle on the C_2H_2 pressure for h = 2 and 9 cm, where the deposition

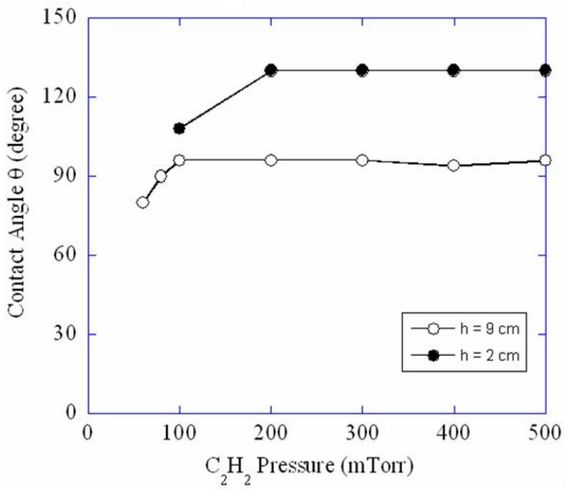


Figure 6. Dependence of contact angle on C_2H_2 pressure for h = 9 (open circles) and 2 (closed circles) cm. Base pressure = 40 mTorr, t = 120 s and P_{rf} = 150 W

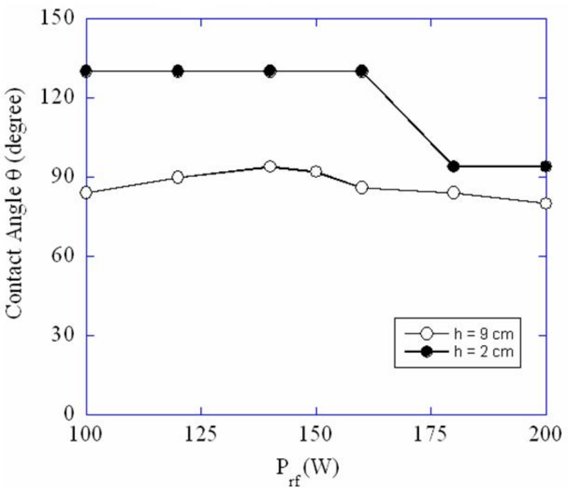


Figure 7. Dependence of contact angle on RF power P_{rf} for h = 9 (open circles) and 2 (closed circles) cm. Base pressure = 40 mTorr, t = 120 s and C_2H_2 pressure = 200 mTorr

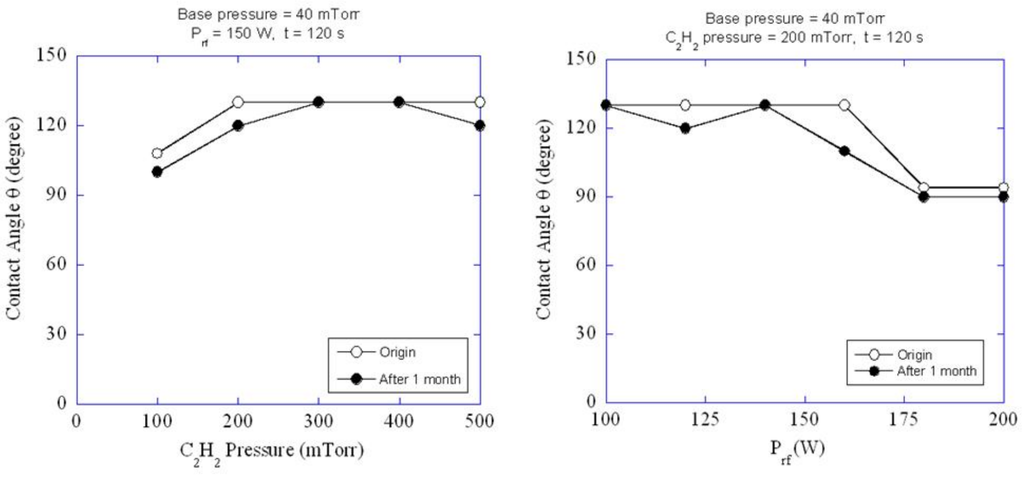
time t and RF power P_{rf} were fixed at 120 s and 150 watts, respectively. The graphs are similar to those in Figure 5, whereas the contact angle increased with increasing C_2H_2 pressure, when the pressure were between zero and 100 mTorr for h = 9 cm, or between zero and 200 mTorr for h = 2 cm. Then the angles saturated at about 100 degrees (for h = 9 cm) and 130 degrees (for h = 2 cm) when the pressure were greater than 100 and 200 mTorr, respectively. The angles were increased when increasing the C_2H_2 pressure because higher densities of radicals were produced in the plasmas. Therefore, the surfaces of cellulose membrane were enhanced to become more hydrophobe.

3.3 Effect of RF power

Figure 7 shows the RF power influence on the contact angles for h = 2 and 9 cm, where the deposition time t and C_2H_2 pressure were fixed at 120 s and 200 mTorr, respectively. The graphs have the same variation for h = 2 and 9 cm. There are differences only in the magnitudes of the contact angles, whereas the contact angles for h = 2 cm are greater than those for h = 9 cm at all values of P_{rf}. The angles are almost constant when $100 \leq P_{rf} \leq 150$ watts, then when $P_{rf} > 150$ watts they are decreased with increasing P_{rf}. These results show that when $P_{rf} > 150$ watts, there are strong effects of degradation on the deposition of the polymerized film, caused by the bombardment of energetic particles. Therefore the hydrophobicity of the barrier films was reduced.

3.4 Ageing behavior

In order to investigate the stability of the hydrophibicity of the plasma polymerized film, deposited on the



(a) **(b)**

Figure 8. Dependence of contact angle on (a) C_2H_2 pressure and (b) P_{rf}. Open and closed circles are the contact angles of the initial original barrier films and the films that were exposed to ambient air for 1 month, respectively.

cellulose membrane, the film had been exposed to ambient air for one month. It has been known that ageing of plasma polymerized film can be induced by physical and chemical processes (Hwang, 2003). Figure 8 shows the dependence of the contact angles on the C_2H_2 pressure and P_{rf}, respectively, comparing between the initial films and the films that had been exposed to ambient air for 1 month. It is found that there are no apparent changes in the contact angles after exposure to ambient air for one month.

4. Conclusions

C_2H_2 plasmas have been used successfully to deposit hydrophobic barrier films on bacterial cellulose membranes. C_2H_2 were used in this work instead of CH_4 or SF_6, because C_2H_2 is cheaper and is available at the local market. Therefore, it has the potential for local industrial applications, such as food packaging and bio-material processing. The maximum contact angle of about 130 degrees can be obtained by the appropriate conditions of deposition time (t), distance between cathode and the membrane (h), C_2H_2 pressure, and RF power (P_{rf}). The ageing tests by exposure to ambient air show that the hydrophobic barrier hydrocarbon films have quite a good stability.

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