CHAIN SCISSION OF CHITOSAN MEMBRANE BY ARGON PLASMA

Tanitporn NARKKUN[1], Wirach TAWEEPREDA[1,2], Akitoshi OKINO[3], Pikul WANICHAPICHART[1,4]*

[1]*NANOTEC Center of Excellence at Prince of Songkla University, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand*
[2]*Membrane Science and Technology Research Center, Department of Material Science and Technology, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand*
[3]*Department of Energy Sciences, Tokyo Institute of Technology, Nagatsuta 4259 J2-35, Midori-ku, Yokohama 226-8502 Japan*
[4]*ThEP Center, CHE, 328 Si Ayutthaya Road, Bangkok 10400, Thailand*
**Corresponding author: Tel.6674-288749, Fax: 6674-288754, E-mail address: pikul.v@psu.ac.th*

Abstract:

Degradation of chitosan by argon plasma was investigated under variation of oxygen content in argon gas and the effect of chain scission on the chitosan membrane was demonstrated by means of water flux and membrane MWCO. Chain scission effect was only found in 760K g/mol chitosan, based on the increased water flux and MWCO. The chitosan membrane of 400K g/mol showed similar contact angle but opposite results in water flux and the MWCO, after the treatment.

Introduction:

Chitosan is a nontoxic, biocompatible and biodegradable polymer, and has been utilized in many applications including membrane separation. Membrane modification allows cross-linking of polymer chains or chain scissioning, and changing membrane hydrophilicity - essential factors for proliferation and filtration performance. With plasma technique, surface modification is fast and chemical free – a promising method to meet industrial need.

This study compared the effect of Ar plasma treatment on chitosan membrane of 400K and 760K MW under variation of O_2 flow rate.

Membrane Preparation and plasma treatment:

Chitosan membranes were prepared by solvent evaporation method. The 335 mm atmospheric damage-free linear plasma source (PCT-DFL1335, Plasma Concept Tokyo Inc., Tokyo, Japan) was used for argon plasma with an oxygen additional gas. A 27.12 MHz of RF power was fed to the electrodes through a matching circuit. Front electrode acted as a remote plasma source, having a 335 mm long x 1 mm wide slit for plasma blowing through. The electrode was grounded and gas temperature was as low as 400 K, to assure risk-free condition.

Result and discussion:

Table 1 Contact angle of chitosan membrane after treated with Ar plasma under variation of O_2 flow rate.

Plasma condition	Contact angle (degree)	
	CH400K	CH760K
Control	91.24±0.70	97.32±0.84
0 mL/min	73.53±4.05	80.83±3.17
15 mL/min	74.89±3.30	81.08±5.68
30 mL/min	93.16±1.48	86.00±3.93

The contact angle was decreased after the membranes was treated with Ar plasma and the results seemed to be independent of O_2 flow rate, as show in table 1.

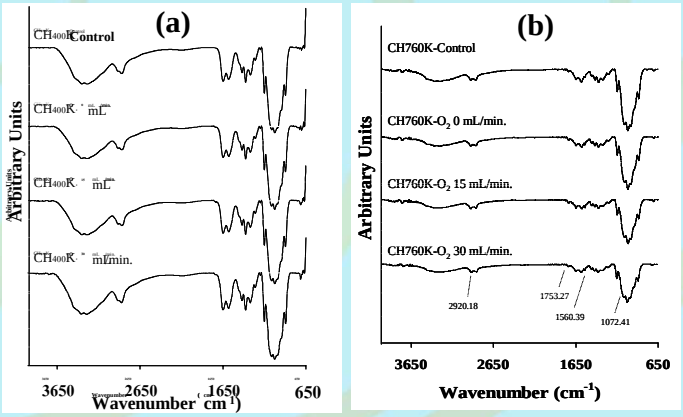

Figure 2. A comparison of FTIR-ATR spectra of chitosan membranes after treated with Ar plasma under variation of O_2 flow rate. (a) CH400K and (b) CH760K

FTIR spectrum of chitosan-400000 membranes had no obvious difference after treated with Ar plasma. The peaks at 3371 cm-1 (O-H stretch), 2880 cm^{-1} (C-H stretch), 1655 cm^{-1} (C=H stretch of carbonyl group), 1380 cm^{-1} (C-H of methyl group) and the peaks assigned to the saccharide structure were at 1155 cm^{-1} (bridge-O-stretch), and 1072 cm^{-1} (C-O stretch) as shown in Fig1(a). But the spectrum of chitosan-760000 membranes as shown in Fig1(b) had a little difference between each of membrane treatment system. Shoulders at 1560 and 1753 cm^{-1} (indicated in spectra with arrows) due to ethylenic and free-aldehydic bonds, respectively.

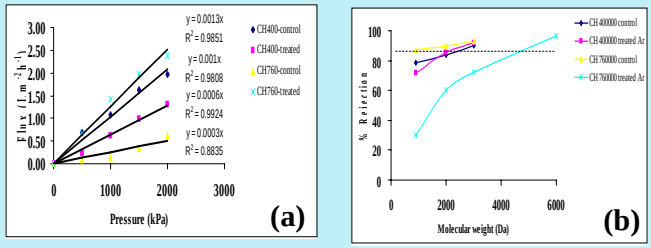

Figure 2 Effects of Ar plasma on chitosan membranes (a) changing water flux and (b) decreasing molecular weight cut off, after plasma treatment at 15 mL/min O_2 flow rate .

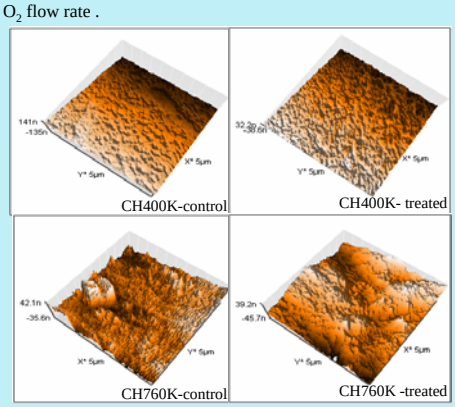

Figure 3 AFM images of chitosan membranes before (control) and after treated with Ar plasma of 15 mL/min O_2 flow rate.

Water flux in Fig2(a) of treated CH400K membrane was reduced, while the reverse was true for CH760K membrane. The result corresponded with MWCO as shown in Fig.2(b). The increased water flux was explained as due to larger MWCO after plasma treatment on CH760K membrane.

The surface of both CH400K and CH760K membranes, shown as AFM images (Fig.3), was more homogeneous and smoothness after the plasma treatment.

Conclusion:

After plasma treatment, chitosan membrane increased in surface wettability and possessed a smoother surface. Plasma reduced effective pore area and MWCO of CH400K membrane, but the effects were reversed in CH760K membrane. This implied that plasma caused chain scissoring in higher molecular weight membrane. It is possible that high chain density increased more chance of interaction between plasma and polymer chains and the interaction occurred throughout the membrane thickness.

References:

1. Boyan, B.D. et al., Biomaterial. 17, p.137-146*(1996)*
2. Kumar, M.N.V.R., Reach Funct. Polym, 46, p.1-27 (2000)
3. R. Sasaki,et al., IEEJ.FM, Vol.129, No.12, pp.903-908 (2009). (in Japanese)

Acknowledgement : **This work was partially supported by the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its program of Center of excellence network. We also thanks Prof.Eiki Hotta, Department of Energy Sciences, Tokyo Institute of Technology, Japan with assistance in Plasma operation. Grant was obtained from Thailand Excellent Center in Physics.**