

## Thermogravimetric Analysis and Stability Test of Fluoroalkylsilanes Grafted on Alumina Hollow Fibre Membranes

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### ABSTRACT

Alumina hollow fibre membrane surface were modified from hydrophilic to hydrophobic using fluoroalkylsilane (FAS) grafting technique which was found to be effective as shown by the increased contact angle (CA) from less than 90° to more than 100°. The CA increased with respect to the grafting time and leveled off after 24 hours of grafting. The thermogravimetric analysis (TGA) showed that the FAS attached to the membranes were approximately 0.05–0.6% of the original membrane weight depending on the grafting time and the amount of hydroxyl groups present on the membrane substrates. According to the TGA result, the grafted membranes were thermally stable up to 250°C where FAS began to decompose. Then the grafted membranes were used as a contacting media for stripping CO<sub>2</sub> off 2.5 M monoethanolamine (MEA) solution at 80–100°C. The membranes were in contact with hot and corrosive MEA solution for approximately 100 hours without any operational problem. The scanning electron microscopy of the membrane surface showed no difference between the membrane before and after the operation. Also, the CAs of the grafted membranes remained unchanged. These findings suggest that FAS grafted membranes are chemically and thermally stable and can be used in membrane contactors at high temperatures and in chemically harsh conditions.

*Keywords:* Hollow fiber membrane, fluoroalkylsilanes, thermogravimetric analysis, stability test

### 1.0 INTRODUCTION

Although ceramic membranes, e.g. alumina, titania and zirconia membranes, are well known for their excellent thermal and chemical stabilities, they cannot be readily used in a membrane contactor since they are hydrophilic in nature and their pores can get wet very easily when contacting with aqueous solutions. Membrane wetting is a major problem in a membrane contacting process since it increases the mass transfer resistance in the membrane [1]. Thus the surface modification of ceramic membrane surfaces to promote their hydrophobicity has been developed in order to prevent the

membrane wetting problem. Among various modification techniques, silylation, which replaces an acidic hydrogen on the surface with a hydrophobic alkylsilyl group, is one of the most important and has drawn much research interest recently [2–4]

Fluoroalkylsilanes (FAS) is a common silylating agent used for ceramic surface modification and is found to be effective in hydrophobicity enhancement. Several studies on the silylating process and parameters have been conducted. Larbot *et al.* [5] modified tubular membranes made from zirconia and  $\gamma$ -alumina using fluoroalkylsilanes of different chain lengths. Hydrophobic membranes with high contact angles, (CAs > 115°) were obtained and the hydrophobic layers were thermodynamically stable up to 230°C. Ceramic membrane distillation for

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desalination was also demonstrated using the grafted membranes and high salt rejection rates were observed. Akamatsu *et al.* [6] applied the polymerization of FAS on glass to adopt a water-repellent feature and studied the polymerization condition as well as the layer durability.

Picard *et al.* [7] modified their own-made zirconia membranes with trifunctional fluoroalkylsilanes having different lengths of hydrophobic tails ( $C_nF_{2n+1}C_2H_4Si(OR)_3$ , where  $n=1, 6, 8$ ,  $R=OCH_3, OC_2H_5$ ). The modified membrane showed high hydrophobicity as the liquid permeability significantly decreased, compared to the original membranes. Grafting time was found to be the main factor influencing the changes in hydrophobicity. The same authors also applied the FAS-modified zirconia and titania membranes to ozonation in wastewater treatment and obtained a good transfer rate with some advantages over the conventional contacting methods [8].

Krajewski *et al.* [9] studied the conditions of grafting, including the ratio of FAS per zirconia mass, grafting time and temperature. 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane in chloroform was a grafting solution. The result of thermogravimetric analysis (TGA) showed the optimum temperature at 30°C, the ratio of FAS per zirconia at 1.429 mmol/g and the grafting time of 144 hours.

Koonaphapdeelert *et al.* suggested that alumina hollow fibre membranes prepared from a single-step fabrication can also be modified by FAS grafting [10]. Such membranes can be

effectively used in membrane contactors for amine stripping at high temperature, the condition in which polymeric membranes cannot withstand [11]. However, the effects of grafting parameters on alumina hollow fibre substrates have never been reported before. Also, the membrane stability in the operation at high temperature has not been reported yet. In this study, the effects of grafting parameters, i.e. grafting time and ceramic substrates, were investigated through thermogravimetry. The thermal and chemical stabilities of the grafted membranes in an amine stripping process at high temperature were also examined.

## 2.0 EXPERIMENTAL

### 2.1 Membrane Preparation

Hollow fibre membranes were prepared from aluminium oxides using a phase inversion / sintering method. The alumina content of a spinning suspension was maintained at 60%w/w while polyethersulfone was used a binder. The membrane precursors were then sintered at different temperatures, ranged from 1200°C to 1500°C. The details of ceramic membrane preparation method can be found elsewhere [10]. Membrane samples of 50 mm length from each batch were rinsed with DI water to remove any surface contaminants, dried in an oven at 100°C overnight and then be ready for surface modification. Some basic properties of the membranes are presented in Table 1.

**Table 1** Basic properties of alumina hollow fibre membranes

Sintering Temp.	Outer $\varnothing$ (mm)	Inner $\varnothing$ (mm)	Bending Strength (MPa)	Effective Porosity* ( $m^{-1}$ )	Mean Pore Radius ( $\mu m$ )	SD of pore radius
1200 °C	1.47	1.02	18.2	14378	0.053	1.47
1300 °C	1.40	0.97	35.5	11032	0.045	1.67
1400 °C	1.28	0.89	80.8	4522	0.039	1.32
1500 °C	1.14	0.78	183.1	1400	0.036	1.31

\*The effective porosity is defined as the ratio between the volumetric porosity of the membrane ( $\epsilon$ ) and the membrane pore length ( $L_p$ ), measured by the method proposed by Kong and Li [12]

## 2.2 Surface Modification

The hollow fibre samples were immersed into the 0.01 mol/litre 1H, 1H, 2H, 2H-perfluorooctylethoxysilane (FAS) (Lancaster synthesis) in n-hexane (Sigma Aldrich) solution in a vertically long glass tube at room temperature. The grafting time was varied from 0.5, 2, 8, 24, 48 and 72 hours to allow the coupling reaction between FAS and the ceramic surfaces to occur. After the immersion, the fibres were rinsed with n-hexane five times to remove any unreacted chemicals from the surfaces and dried at 100°C for 12 hours. Finally, the membranes were stored at room temperature and were ready for characterization.

## 2.3 Membrane Characterization

The membrane hydrophobicity was characterized by contact angle (CA) measurement using deionised (DI) water as testing liquid. The method used in this study was the Wilhemy method which is widely used to test the dynamic contact angles of samples which have different shapes other than flat sheet [13]. A hollow fibre sample was sealed off the opening end with an epoxy resin and hung on the microbalance in a tensiometer (Kruss K100). Then it was gradually immersed into the still testing-liquid. The rate of immersion was controlled at 6 mm/min and all measurement was done at 20°C. Three replicates were used in each measurement.

Thermogravimetric analysis (TA Instruments TGA-2050) was conducted to quantify the amount of FAS grafted onto the membranes. It was also used to determine decomposing temperature of FAS which reflected the membrane thermal stability. In each measurement, a small piece of membrane was placed on a platinum pan hung on a microbalance in an air-filled chamber. Then the temperature was increased at a rate of 10°C/minute to reach the maximum temperature at 600°C. The weight of the sample was recorded on a real-time basis.

The micro-scale images of the membranes were obtained using scanning electron microscopy, SEM (JEOL JSM-5610LV). All samples were sputtered with gold and analyzed with a voltage

of 15 KV. Outer and inner membrane surfaces were examined to reveal membrane structure and morphology.

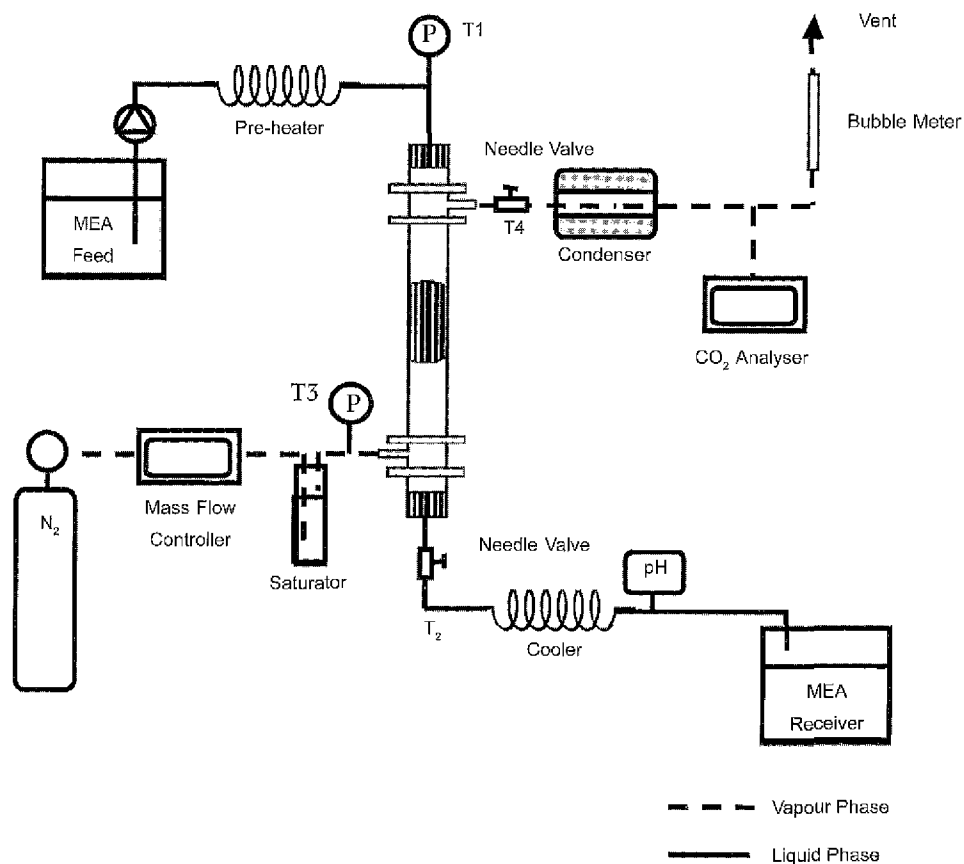
## 2.4 High Temperature Operation

In order to test the chemical and thermal stabilities of the membranes, a number of surface modified membranes were packed into ½"Ø stainless steel modules. The gaps among the fibres at both ends were sealed off using a special solvent-resistant epoxy resin. The modules were then used as packed columns for amine stripping at 80–100 °C. MEA of 2.5 M concentration was employed as the liquid absorbent in this study because it is a typical solvent for CO<sub>2</sub> absorption and is reported to have corrosive effects on polymeric membranes [14–16]. The experimental setup of amine stripping unit is present in Figure 1. The details of each experimental run can be found elsewhere [11]. After approximately 100 hours of operation, the membranes samples were taken from the module and were characterized in order to examine any change occurred to the grafted membranes.

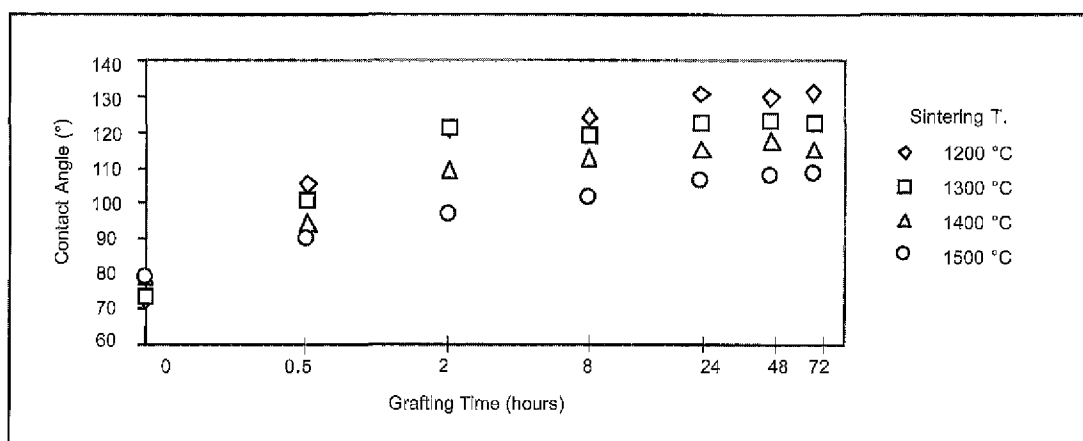
## 3.0 RESULTS AND DISCUSSION

### 3.1 Membrane Hydrophobicity

The CA of DI water on a membrane surface is a typical indicator of surface hydrophobicity. If the CA is less than 90°, the surface is considered hydrophilic. On the other hand, the surface with CA equal to 90° or more is hydrophobic. In this study, the CA of deionised water on the unmodified alumina hollow fibre membranes were in a range of 70°–80°, as shown in Figure 2. After just half an hour of surface grafting, the CA of water on the FAS grafted membranes increased to 90°–110°, indicating the membrane surfaces were changed to hydrophobic. The CAs constantly increased as the grafting proceeded and leveled off after 24 hours of grafting. The maximum CAs, in a range of 110°–130°, was showing fairly high hydrophobicity of the surfaces. The CAs obtained in this study were lower than the values reported in the literature [24–26], which were in a range of 140–150°C, because the membranes in other studies were coated with  $\gamma$ -alumina which has a



**Figure 1** The experimental setup for CO<sub>2</sub> stripping in a hollow fibre module (T = thermocouples, pH = pH meter, and P= pressure gauges)



**Figure 2** The contact angles of DI water on the membranes sintered at different temperatures and grafted for a different number of hours

higher number of hydroxyl groups. However, the membrane preparation method used in this study was relatively simple as both  $\gamma$ - and  $\alpha$ -alumina were mixed and spun at one time, compared to the other works in which the membranes were prepared by multi-step  $\gamma$ -alumina coating techniques. Such preparation simplicity is essential for the cost reduction of ceramic membranes which are often found too expensive in practical uses and commercialization

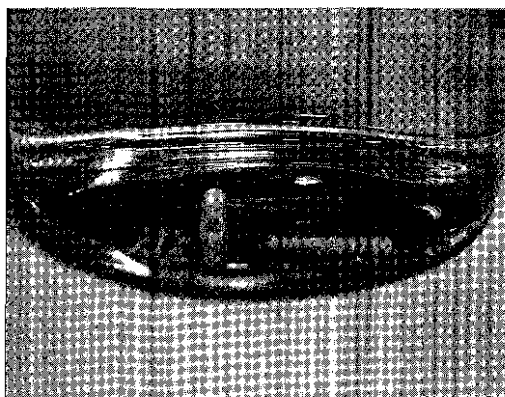
In Figure 2, the membranes sintered at different temperatures variably responded to the surface modification. Those sintered at 1200°C had much higher CAs than those sintered at 1500°C. This can be explained by that membranes sintered at 1200°C had more hydroxyl groups on the surface because alumina had not fully transformed from hydrous forms ( $\gamma$ -alumina) to anhydrous form ( $\alpha$ -alumina).

The effect of surface modification can be visually demonstrated in Figure 3. Short sections of grafted and non-grafted ceramic hollow fibres sintered at 1400°C were snapped off and freely dropped on the water surface. As can be seen, the surface-modified fibre was floating on the water surface because its contact angle was so high that water could not penetrate into the pores. As a result, the water surface tension could support the weight of the fibre. On the other hand, the non-grafted fibres immediately sank to the bottom of the beaker because the water broke into the pores right away and filled the voids inside.

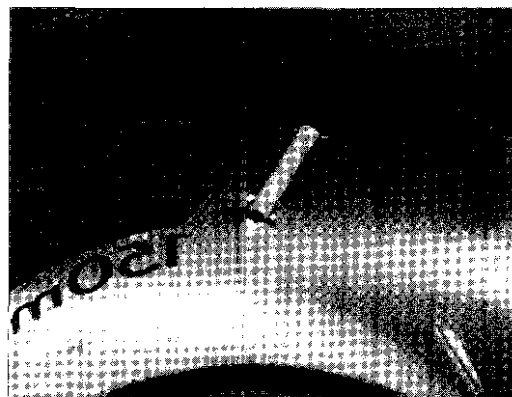
### 3.2 Thermogravimetric Analysis

The CA measurement in Section 3.1 shows that alumina membranes can be effectively modified to be hydrophobic. In this section, TGA was conducted to quantify the amount of FAS grafted on the membrane surface. Figure 4 shows the weight change profiles of membranes sintered at 1200°C and grafted with FAS for 0.5, 2, 8, 24, 48 and 72 hours, respectively. As can be seen, all the weight change profiles were in a reversed-S shape. As the temperature rose from 50°C to 250°C, the membrane samples lost their weight due to the evaporation of moisture and easily-volatile contaminants. Then the samples began to lose their weight rapidly at approximately 250°C at which the silane compounds began to disassociate from the ceramic surfaces and decomposed. The temperature which had the maximum slope ( $T_{max}$ ) was 357°C. This result is in line with the works by Picard *et al.* [7] and McElwee *et al.* [17] which reported the decomposing temperature of FAS at around 250°C. Therefore, the maximum operating temperature of the membrane in any application would be just below 250°C.

Assuming that the FAS was completely burnt out at 600°C, the amount of FAS grafted onto the membranes can be calculated based on the total weight loss of the membrane. Obviously the mass of FAS attached to the membranes depended on the grafting time. The grafted FAS weight gained to approximately 0.2% of the membrane weight

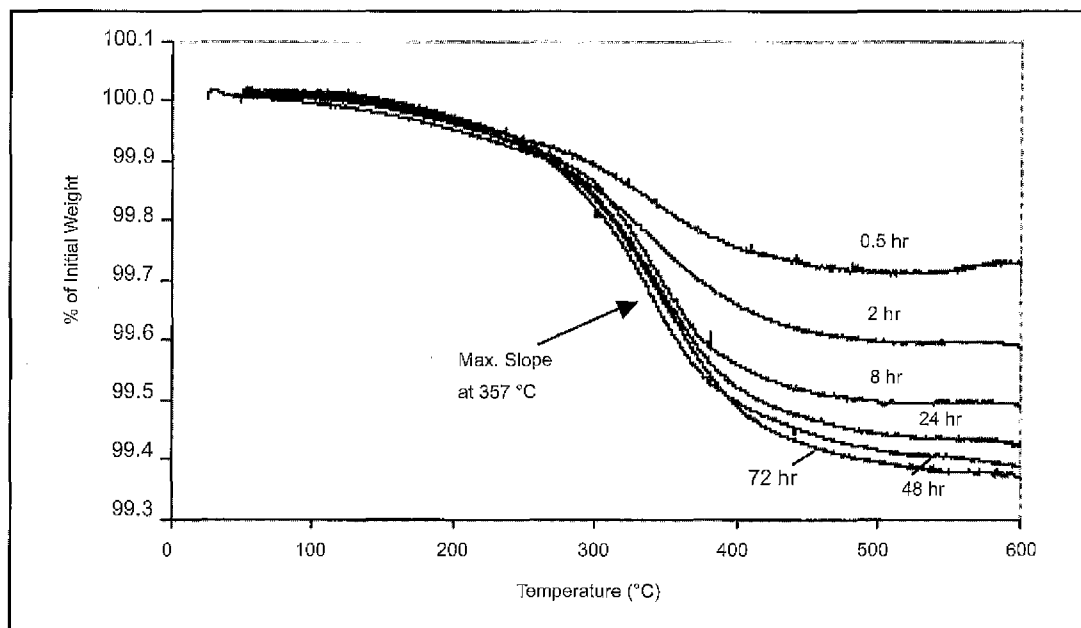


Grafted fibre



Non-grafted fibres

**Figure 3** A short section of grafted fibre was floating on water whereas the original fibre sank



**Figure 4** The weight change profiles of the membranes sintered at 1200 °C and grafted with FAS for different periods of time

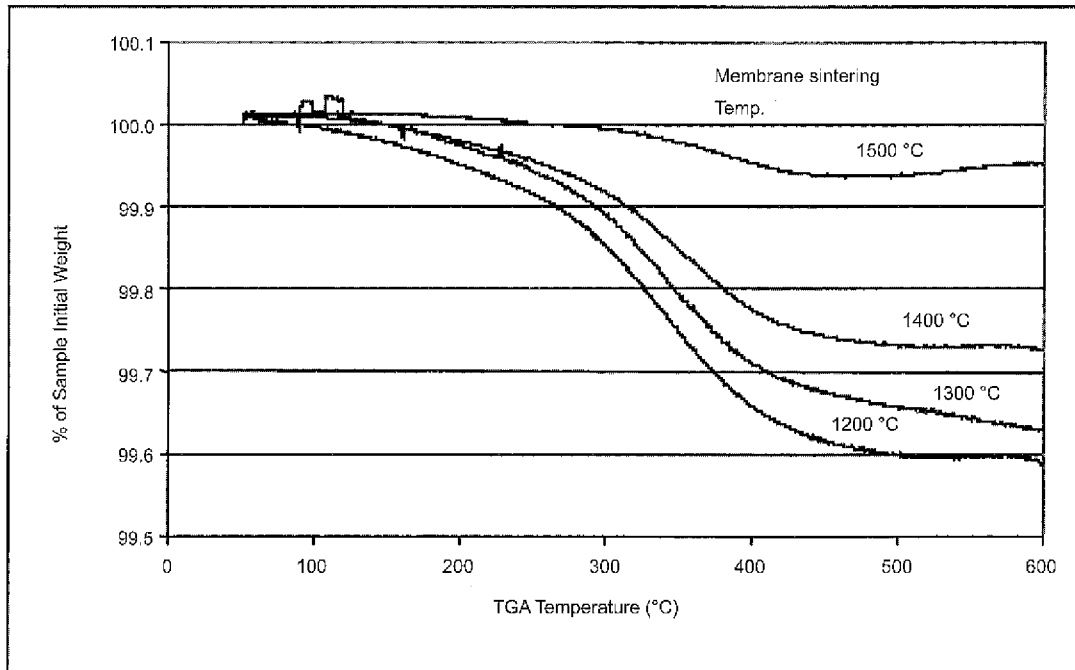
after just 0.5 hour of grafting time. The grafted FAS weight reached 0.4%, 0.5% and 0.6% after 2, 8 and 24 hours of grafting, respectively. However, the grafting rate was slower as time passed since there were less hydroxyl sites available for the reaction. After 24 hours, the grafting was going on at a very slow rate as the weight gain was less than 0.1% even 72 hours had passed. At this point, almost all hydroxyl groups were expected to be occupied and the weight gain was a result of FAS polymerization.

Figure 5 shows the weight change profiles of the membranes sintered at different temperatures and grafted for 2 hours. As can be seen, the weight loss of the grafted membranes sintered at 1200 °C was approximately 0.6% of initial weight. The weight losses of the membranes sintered at higher temperatures, i.e. 1300, 1400 and 1500 °C, were decreased. This result can be explained by that there is a smaller number of hydroxyl groups available for the reaction on the membranes sintered at higher temperatures. The result also agrees with the result of CA measurement in Section 3.1.

The amount of FAS grafted on the membrane sintered at 1500 °C was merely <0.05% of the total membrane weight, indicating that the grafting was not very effective. As the result, the CA of water on such membrane was just above 100°, near the border line of hydrophobicity at 90°. Therefore, membranes sintered at 1500 °C were not appropriate for membrane contactors as their hydrophobicity was too low. Only the membranes sintered at 1200 °C, 1300 °C and 1400 °C were used in the membrane stability test.

### 3.3 Membrane Stability

The thermal and chemical stabilities of the grafted membranes were investigated by testing them in a CO<sub>2</sub> stripping experiment at high temperature. The hollow fibre membranes acted as contacting media that provided contacting area between hot gas and liquid. It was found that the membranes sintered at 1200 °C and 1300 °C were unable to survive in the course of experiment because they were broken after a few hours of operation. Only the membranes sintered at 1400 °C could withstand the



**Figure 5** The weight change profiles of R10 membranes sintered at different temperatures and grafted for 2 hours

mechanical stress caused by material expansion at high temperature. Thus the membrane mechanical strength is very crucial for practical membrane application. The bending strength of the membrane sintered at 1400°C was 80.8 MPa which can be regarded as the minimum strength required for this application.

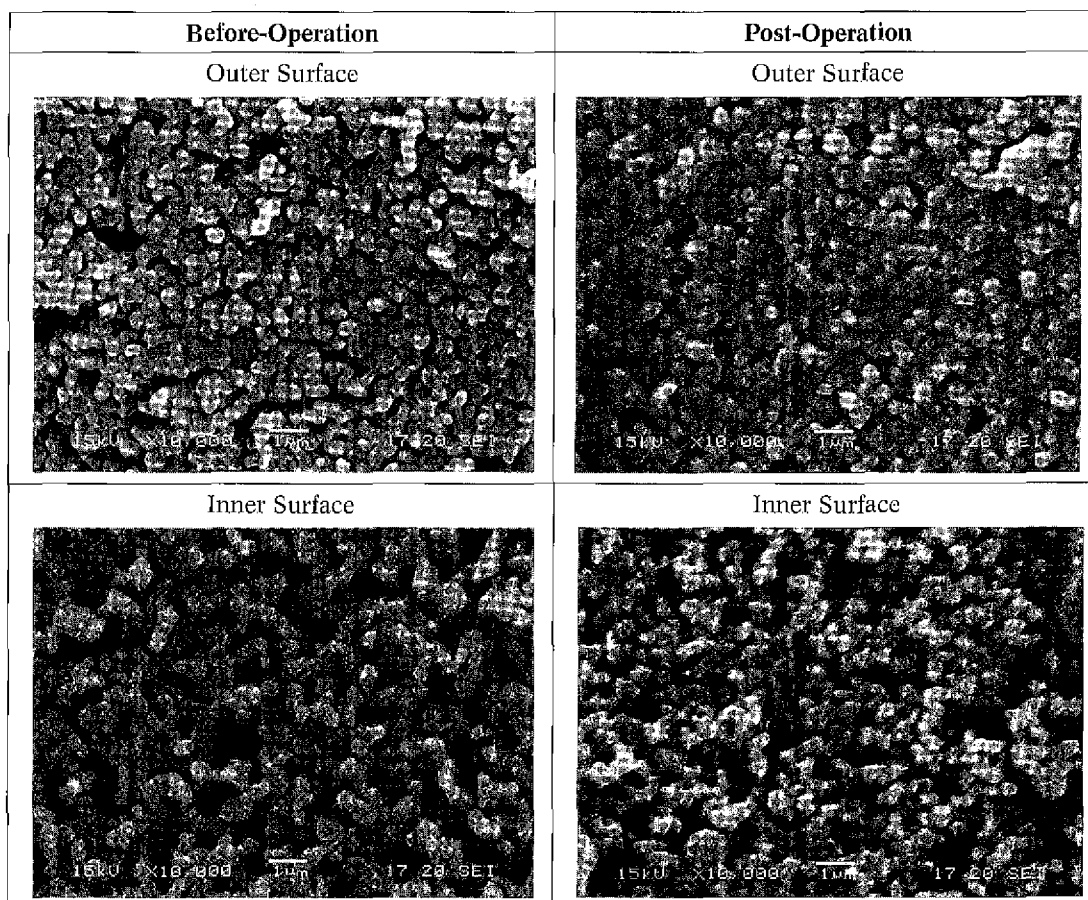
After approximately 100 hours of operation, the membrane modules were disassembled and the membranes were taken out for inspection. Each sample was washed by deionised water and dried in an oven overnight. CA measurement was then performed on the samples. Table 2 shows the CA of the membranes with DI water. As can be seen, the CAs of the membranes after operation were slightly different but still within the standard deviation, indicating that the degree of hydrophobicity of the membranes remained unchanged after being exposed to high temperature MEA solution. Figure 6 shows the SEM micrographs of the membrane surfaces before and after amine stripping experiment. As can be seen, their surface morphology was

**Table 2** The contact angles of the membranes before and after operation

Membranes	Contact Angles with Water (degrees)	
	Before Operation	After Operation
Module 1	115.1 ± 2.8	116.3 ± 3.1
Module 2	118.3 ± 0.7	116.9 ± 1.9
Module 3	115.1 ± 2.8	114.2 ± 2.4

hardly changed. Thus it can be concluded that the modified membranes were fairly stable under the harsh operating condition.

The membranes sintered at low temperatures, i.e. 1200°C and 1300°C, were good substrates for surface grafting as they had more hydroxyl groups available for the reaction than those sintered at high temperature. However, they had relatively low bending strength which was inadequate for practical applications. There is a trade-off between



**Figure 6** The SEM micrographs of membrane surfaces before and after amine stripping operation

the membrane hydrophobicity and mechanical strength that needs a good balance on them. In this study, only the membranes sintered at 1400°C could provide good hydrophobicity and sufficient strength to withstand the condition in an amine stripping column. The mechanical strength is considered to be a weakness that needs to be overcome. The mechanical strength of membranes can be enhanced by several methods. For instance, the elimination of finger-like layers and macrovoids and the promotion of a sponge-like layer in the membrane wall can improve the strength. Another way is the addition of some zirconia particles into alumina spinning suspension to produce a co-ceramic product, known as zirconia-toughened alumina which is reported to have 30–40% higher bending strength than pure alumina [18].

#### 4.0 CONCLUSION

Surface modification of ceramic membranes can effectively change ceramic membranes from hydrophilic to hydrophobic. The degree of hydrophobicity mainly depends on the reaction between the hydroxyl group on the membrane surface and the FAS molecules. Such coupling reaction is considerably fast that hydrophobic membranes could be prepared within just half an hour of grafting. It was found that the most appropriate grafting period was about 24 hours when most of the hydroxyl groups had been occupied. Beyond this period, the coupling rate was much slower and less efficient.



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