Interfacial Adhesion Between Polymer Separation Layer and Ceramic Support for Composite Membrane

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An in situ characterization method for mechanical and adhesive properties of organic/ceramic composite membranes is built on the basis of nanoindentation technique in this work. The polydimethylsiloxane (PDMS) was used as the separation layer with the support of porous ZrO_2/Al_2O_3 ceramic tubes. The effects of roughness of the ceramic support and the viscosity of PDMS solution on the mechanical properties of the PDMS separation layer and the interfacial adhesion at the interface were investigated in detail. It was found that when the roughness of the ceramic support increased and the viscosity of PDMS solution decreased, the interfacial adhesion strength of PDMS/ceramic composite membrane increased, but these two variables had little effect on the mechanical properties of the PDMS separation layer. Our results indicate that the mechanical interlocking dominates the adhesion between the PDMS separation layer and the porous ceramic support. © 2009 American Institute of Chemical Engineers
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Introduction

Interfacial adhesion plays an important role in soft and flexible film-rigid inorganic support composite systems, because the composite system cannot be effectively used for engineering applications if the soft and flexible film does not bond well to the rigid inorganic support.[1–3] Moreover, the knowledge of mechanical properties such as Young's modulus and hardness (H) at nanolevel could be crucial for the selection, design, and application of membrane materials.[4–6] Therefore, investigation on the mechanical properties, interfacial adhesion, and bonding mechanisms of film/support has attracted a great deal of attention in the past decades. Polymer/ceramic composite membrane is a typical flexible film-rigid support composite system, which shows controllable chemical and physical properties by combining the effects of organic polymers and inorganic supports. There have been numerous studies on the polymer/ceramic composite membrane for pervaporative separation.[7–9] Also, this kind of membrane is potentially suitable for nanofiltration, gas separation, membrane distillation, etc.

It is well known that polymeric films are apt to swelling in many membrane separation processes. The highly swollen polymeric films usually lose their permselectivity and show poor operation stability. If the polymeric film and the underneath support do not swell in a coordinated manner, big shear stress may arise in the interface of the composite structure.[10] Peeling will occur when the interfacial stress surpasses a specific ''critical value.'' Great efforts have been made to improve the structure stability and mechanical properties of composite membrane by means of crosslinking treatment. The structural stability of the composite membranes will be dependent on two aspects: one is the

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crosslinked structure of the separation layer, and another is the interfacial adhesion between the separation layer and the ceramic support.

Commonly, the improved interfacial adhesion between two adjacent layers can also enhance the structural stability of the composite membrane. A variety of surface treatments have been proposed to improve the adhesion between polymer films and support surface.[11,12] The importance of interfacial adhesion has been well recognized, but several works reported only on mechanical and adhesion characterization due to its experimental challenges. The composite structure imposes a tremendous challenge to many existing testing and measuring techniques for experimental studies of their mechanical properties. This motivated us to investigate the variables that dominate the interfacial adhesion property.

In the field of membrane technology, the mechanical properties of polymer composite membranes were commonly studied by tensile strength and elongation measurement. This technique requires that the size of the sample should be large enough to be clamped rigidly by the sample holder without sliding. Therefore, this method is not suitable for composite membranes. The most common method that is routinely applied to estimate the film interfacial adhesion is peeling test. This method has several drawbacks that limit its applicability and effectiveness, such as the repeatability of test is poor and the sample preparation procedure is tedious, and moreover, it is only applicable for flat membrane. Practically, for polymer/ceramic composite membranes, the tubular geometry is obviously dominant for application. Therefore, we focus on the development of an in situ method to characterize the mechanical and adhesive properties of a composite membrane with tubular structure.

Nanoindentation allows us to determine indentation modulus, hardness, residual stresses and fracture toughness of the coating, and the fracture toughness of the coating–substrate interface.[13] As an accessory of nanoindentation, nanoscratch test has been applied for determining the interfacial adhesion strength through film delamination caused by the accumulation of interfacial shear stress during tests. In contrast to the quasi-static loading in most mechanical and adhesion tests, the nanoindentation and nanoscratch tests dynamically use load on the top layer surface. In addition, nanoindentation and nanoscratch techniques allow probing of mechanical and adhesion properties of small-volume samples, which are usually not accessible with other methods.[4]

Silicone elastomeric coatings have many applications because of their surface properties such as low surface energy, nonpolarity, and low modulus. With respect to the separation of alcohol from water, polydimethylsiloxane (PDMS) has been well known as a representative alcohol-permselective membrane material for the alcohol removal from aqueous solution of low alcohol concentration. In our previous work, the PDMS/ceramic pervaporation membranes prepared by dip-coating PDMS solution on the macroporous ceramic supports (pore size, 0.2 μm) have showed exciting high flux for ethanol separation in water/ethanol system.[14] However, the PDMS/ceramic composite membranes cannot be effectively used for engineering applications because the PDMS separation layer does not bond well to the ceramic support. Therefore, investigation on the interfacial adhesion of PDMS/ceramic is an indispensable element for practical application.

Thus, in this work, the mechanical and adhesive properties of tubular PDMS/ceramic composite membranes were investigated by the nanoindentation and nanoscratch tests. The effects of the viscosity of polymer solution and the roughness of ceramic support on the mechanical and adhesive characteristics of tubular PDMS/ceramic composite membranes were investigated in detail. Despite the fact that the samples used in this study cannot represent all kinds of soft and flexible film-rigid inorganic support composite membranes, we believe that the methodology developed in this study would be of wide reference.

Experimental

Materials

The tubular asymmetric ZrO_2/Al_2O_3 membranes were used as the ceramic supports, with an average pore size of 0.2 μm, which were manufactured commercially by Membrane Science and Technology Research Center in Nanjing University of Technology, China. They were 200 mm in length with an external diameter of 12 mm and an inner diameter of 7.5 mm. PDMS with a weight-average molecular weight of 50,000 was purchased from Shanghai Synthetic Resin Company, China. The polydispersity index of PDMS is characterized to be 1.13, which is obtained by the gel permeation chromatography (Waters, America) using polystyrene standards. Tetraethylorthosilicate (TEOS), *n*-heptane, and dibutyltin dilaurate were supplied by Shanghai Chemical Reagent Company, China.

Preparation of PDMS/ceramic composite membranes

The PDMS/ceramic composite membranes were prepared by the conventional dip-coating method, which was similar to that in our previous study.[15] The PDMS polymer was dissolved in *n*-heptane, and then crosslinking agent TEOS and 0.2 wt % catalyst dibutyltin dilaurate were added into the polymer solution. The polymer solutions were stirred at room temperature for 30 min and became coating precursors by degassing. The outer surface of the ceramic support was polished with 600 mesh sand paper (Riken Corundum Co., Ltd., Japan) and was cleaned several times with deionized water in ultrasonic apparatus and dried in air at room temperature. These supports were sealed with two Teflon caps at both ends, and then the sealed tubes were immersed in the dip-coat solution for 60 s and removed from the solution at the same speed. Subsequently, the membrane was dried overnight at room temperature, and then the membrane was vacuum dried for one more day to remove any remaining solvent from the bulk of the polymer film.

Characterization

The average pore size and pore size distribution of support were characterized by the gas bubble pressure method, which was performed following the American Society for Testing and Materials (ASTM) Publication (F316-80).

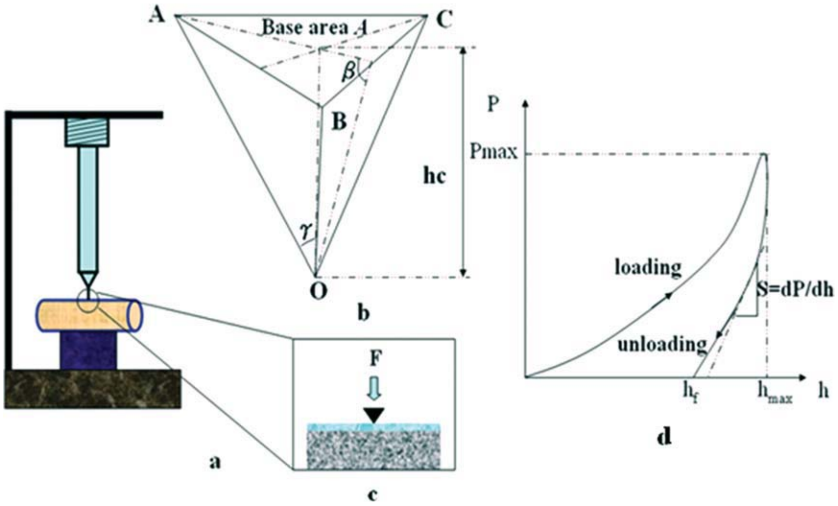

Figure 1. Schematic of a nanoindentation experiment.

(a) Schematically present apparatus; (b) a three-sided pyramid diamond Berkovich indenter ($\beta = 24.7°$, $\gamma = 77.1°$, and $A = 24.56h_c^2$); (c) the dynamic model of the indenter head in contact with a viscoelastic sample; (d) a typical force vs. displacement curve, where h is the indenter displacement; h_f is the final penetration depth; h_{max} is the maximum displacement (i.e., penetration depth of indenter); P is the force applied to indenter; P_{max} is the maximum force applied to indenter; and S is the contact stiffness. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The viscosities of PDMS coating solutions with different prepolymerization times were investigated by using Brookfield viscometer (DV-II+ pro, Brookfield Engineering Laboratories, MA) with spindle RV/HA/HB-4 (27.0 mm of diameter and 140 mm length) at 30 rpm. The determination of viscosity was carried out at 30°C.

Roughness measurement was performed with a handheld surface roughness tester(Time group, TR200). The measurement technique consists of the displacement of a pick-up (diamond stylus), placed in contact with the surface, along a straight line trajectory and at constant velocity. The pick-up copies the surface roughness through vertical displacements, which are converted in an inductive phase-sensitive rectified analog signal. This signal, proportional to the vertical displacement, is then recorded in a plotting device. The measurement range of the apparatus was of 160 μm with a resolution of 0.01–0.04 μm. The stylus was on diamond, with a tip angle and radius of 90° and 5 μm, respectively, with an acting force of 4 mN.

The morphology of membranes was investigated using a scanning electron microscope (SEM; QUANTA-2000). The sample surface was coated with gold powder under vacuum before SEM observation was performed.

Depth-sensing indentation measurement

The mechanical properties (hardness and elastic modulus) and adhesion strength were measured by depth-sensing indentation and scratching techniques. The schematic of the apparatus is shown in Figure 1a. The indentation test was carried out by using the continuous stiffness measurement (CSM) technique; it is one of the measurement techniques for Nanoindenter® XP equipment. CSM is a powerful technique in providing information on mechanical properties such as hardness or elastic modulus of investigated materials. Although there is no safe depth range at which the elastic response of a coated system to indentation is free of substrate influence, the choice of a very low indentation depth minimizes the substrate contribution and provides a reasonable estimate of the coating elastic modulus.

The approach to analyze depth-sensing indentation data has been developed over several decades. So far, the most often used is the Oliver and Pharr method,[16,17] which is based on the research done by Doerner and Nix and SneddEN. The maximum loading point of the curve is used to determine the hardness of the material. The elastic part of the unloading curve provides information about the elastic properties of the tested materials. Hardness, H, is typically defined as the mean pressure under the indenter:

$$H = \frac{P_{max}}{A_c} \tag{1}$$

where P_{max} is the maximum applied force and obtained directly from the force–displacement curve, and A_c is the projected contact area of the indenter tip with the material.

For an indenter with a known geometry, the projected contact area is a function of the contact depth. The area of function for a perfect Berkovich indenter (as shown in Figure 1b) is given by

$$A_c = f(h_c) = 24.56h_c^2 \tag{2}$$

where h_c denotes the contact depth.

The initial slope of the unloading curve can be used as a measurement of the elastic properties of the material (as shown in Figure 1d). For a cone indenter, the following expressions are formulated:

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A_c} \tag{3}$$

where S is the contact stiffness, dP/dh is the initial slope of the unloading curve, P is the applied force to the indenter, h is the indenter displacement, and E_r is the reduced modulus of the specimen. The measured displacement includes contribution from both the specimen and the indenter. Therefore, the reduced modulus is given by

$$\frac{1}{E_r} = \frac{1-\upsilon_s^2}{E_s} + \frac{1-\upsilon_i^2}{E_i} \tag{4}$$

where E_s and v_s are Young's modulus and Poisson's ratio for the specimen, respectively, and E_i and v are the same parameters for the indenter. If the indenter is taken as a rigid material, whose Young's modulus goes to infinity, the reduced modulus then can be denoted by

$$\frac{1}{E_r} = \frac{1-\upsilon_s^2}{E_s} \tag{5}$$

The scratching technique involves generating a controlled scratch with a diamond tip on the sample under test. The tip material (commonly diamond) is drawn across the coated surface under constant, incremental, or progressive load. At a certain critical load, the coating will start to fail. The adhesion strength of PDMS separation layers to ceramic supports can be evaluated by comparing force–displacement curves recorded during a scratch test. A characteristic critical load at debond is obtained by noting the discontinuity in the force-displacement curve when a film debonds from a surface. This critical load at the debond is a measure of the adhesive strength of the separation layer.

Results and Discussion

Effect of the roughness of the support

Besides the necessity of providing sufficient mechanical strength, the support should allow the deposition of a thin and defect-free separation layer on its surface. From the interfacial behavior viewpoint, the support roughness also plays an important role in determining the interfacial adhesion of the polymer/ceramic composite membranes.[18,19] In this section, the influences of the ceramic support roughness on the preparation of defect-free membranes and the interfacial adhesion of the PDMS/ceramic composite membranes were discussed.

First, the surface morphologies obtained from the same polymer solution but on two different supports were compared. Figure 2 presents SEM images of the top surface of composite membranes prepared by 7.5 wt % PDMS concentration and 1-min dipping time on the unpolished and the polished ceramic supports, respectively. As shown in Figure 2a, the surface of support was not completely covered with the PDMS layer because the roughness of the ceramic support was too large to cover completely with the PDMS layer. By comparison, Figure 2b showed the surface of PDMS/ceramic composite membranes prepared on the polished support. Apparently, the surface had good morphology, which was continuous and crack free. Based on these observations from SEM, it could be concluded that an appropriate pretreatment on ceramic supports to reduce the roughness is prerequisite to obtain high-quality polymer/ceramic composite membranes.

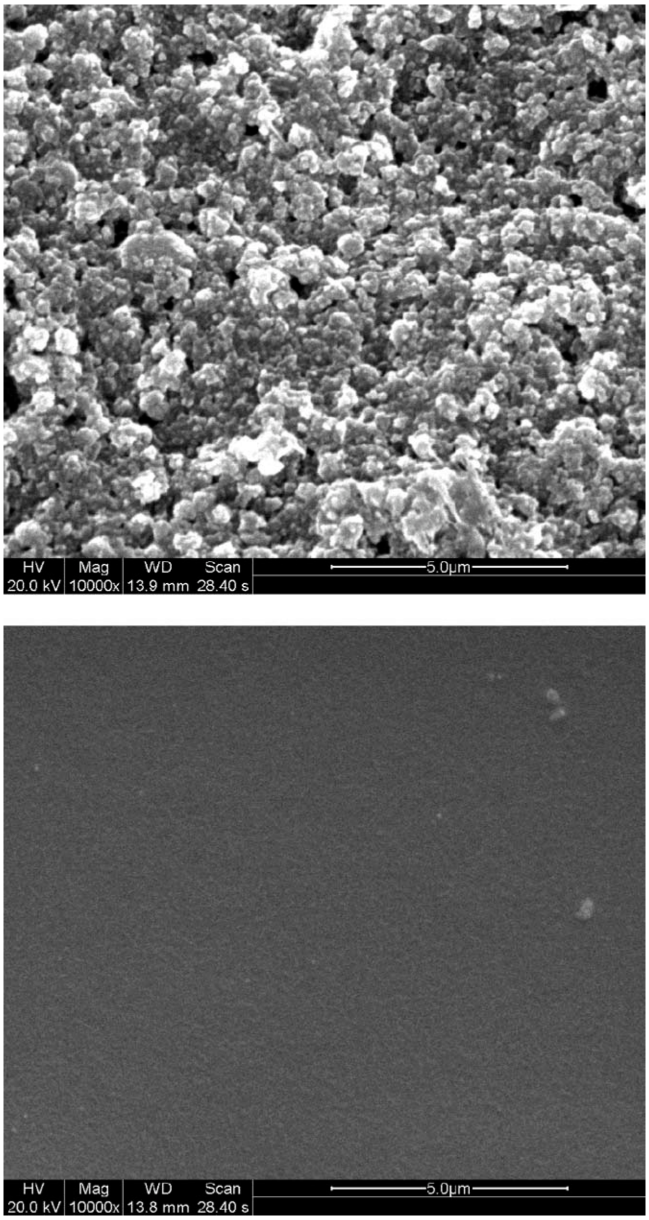

Figure 2. SEM images for the surface of PDMS/ceramic composite membranes with unpolished and polished support.

(a) PDMS coating on bare support; (b) PDMS coating on polished support with roughness 0.937 μm.

In this work, the surface roughness of the ceramic support was modulated by polishing with 600 mesh sand paper. Figure 3 shows the typical SEM images of the surfaces and the cross section of the polished and unpolished ceramic supports. Furthermore, SEM results (not shown here) suggested that the PDMS/ceramic membranes prepared with the polished ceramic supports showed high reproducibility without any defect on their surface. Because polishing reduces the number of the ceramic surface flaws, it improves the integrity of the polymer/ceramic composite membrane. A method based on the bubble pressure and gas transport was used to measure a pore size distribution of membrane under wet condition. In this work, we found that the pore size of

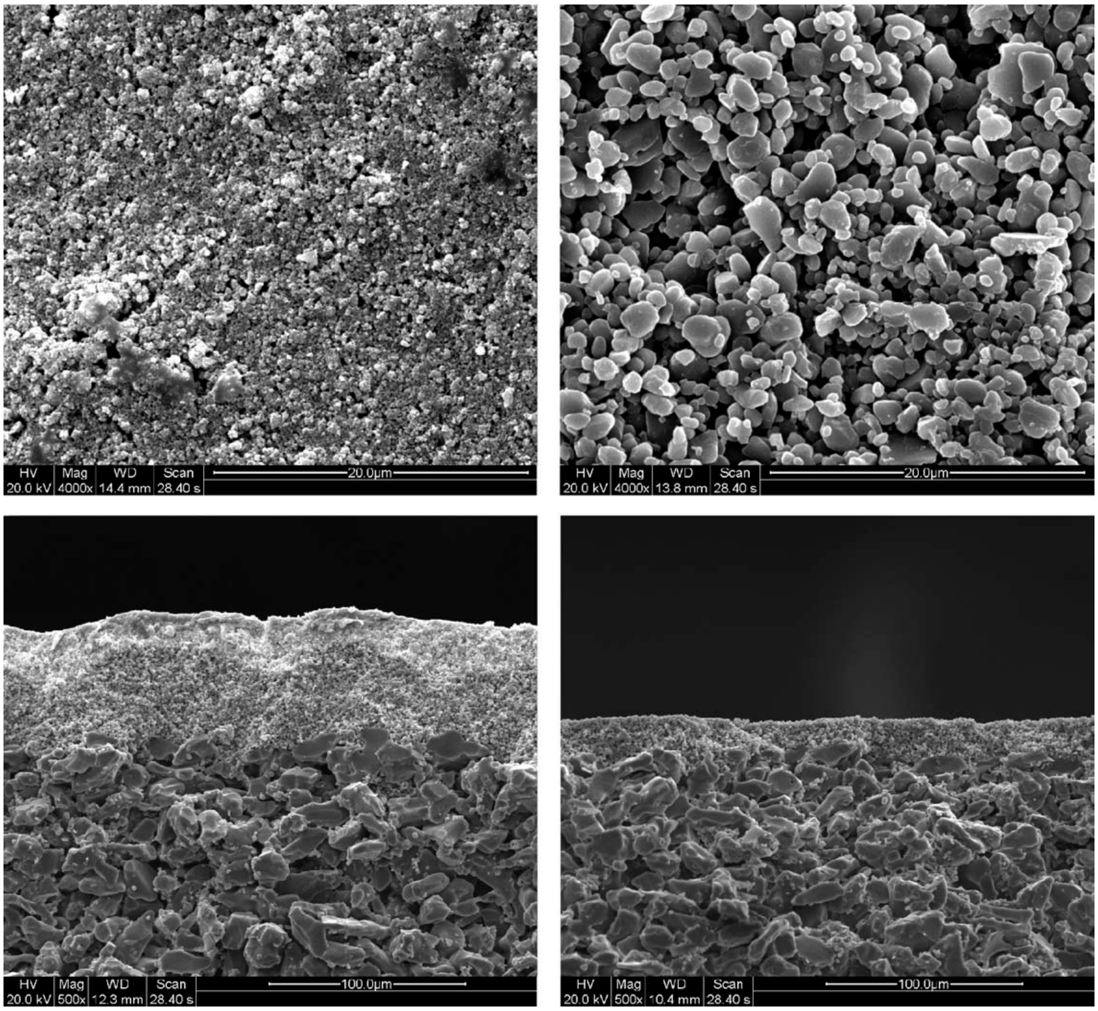

Figure 3. SEM images of surfaces and cross sections of the ceramic supports.

(a) Unpolished support surface; (b) polished support surface with roughness 0.440 μm; (c) unpolished support cross section; (d) polished support cross section.

the ceramic support increased from 0.2 μm before polishing to 0.43 μm after polishing.

Different roughness levels of ceramic support surface have been obtained by controlling polishing times, which were quantified by surface roughness tester. The arithmetical mean roughness R_a values for each surface treated by various polishing degree are presented in Figure 4. The results showed that the polishing time determines the roughness of the ceramic supports. As we know, good adhesion between the ceramic support layer and the polymer is attributed not only to the mechanical interlocking but also to the interfacial chemical bonds. The hydrogen-bonding force between the —OH in the ceramic support and oxygen atom in the PDMS is formed at the PDMS separation layer/ceramic support interface during heat-treatment crosslinking process.[20] Moreover, it is well known that the strength of the short-range intermolecular forces strongly depends on the surface topography of the ceramic support. Two competitive quantities have to be considered while studying the adhesion of an elastic body to a rough support[18,19]: (i) the attractive

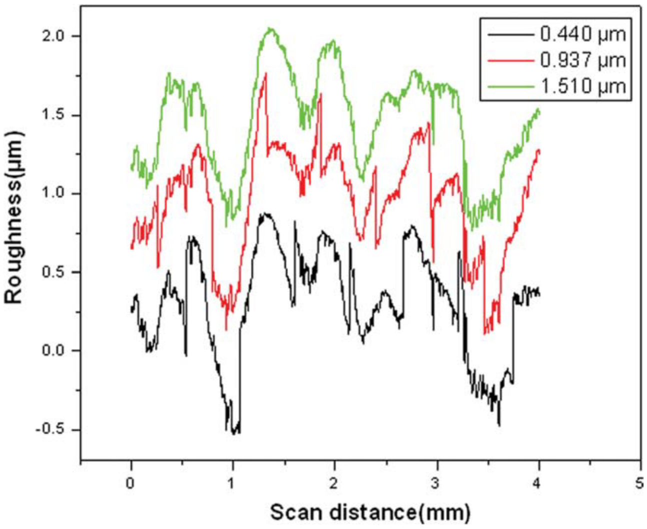

Figure 4. Roughness test results of the three selected polished ceramic supports.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 1. Critical Load of Interfacial Failure as a Function of the Ceramic Support Surface Roughness

R_a (μm)	Critical Load (mN)	Penetration Depth at Critical Load (nm)
0.440	27.6 ± 3.3	6753.3 ± 27
0.937	35.5 ± 4.7	5845.2 ± 19
1.510	50.7 ± 5.1	6922.8 ± 23

interaction and (ii) the repulsive interaction. Therefore, the surface roughness significantly influence the level of the interfacial adhesion.

In the scratch test, a diamond tip was drawn over the film surface under progressively increasing normal load until the film was detached from the substrate. Scratch behavior is a complex phenomenon, which is related to several intrinsic and extrinsic factors. The intrinsic factors are related to the testing conditions such as loading rate, scratching speed, and indenter shape, and the extrinsic parameters are connected to film-support system such as material properties, friction coefficient, and physical dimensions.[21] For better analysis of the critical load results for the PDMS/ceramic composite membranes, the composite membranes with various ceramic support roughness were prepared when the intrinsic factors related to the testing conditions were kept constant during all tests.

Table 1 shows the critical load of interfacial failure as a function of ceramic support surface roughness. As the roughness of ceramic support increases from 0.440 to 1.510 μm, the interfacial adhesion of PDMS/ceramic composite membranes increases from 27.6 to 50.7 mN. This result can be explained by the following reasons. According to the Wenzel model,[22] which characterizes the influence of surface roughness on wettability of a solid, hydrophilicity is strengthened with the increasing roughness. This results in an increased gradient in chemical potential between the PDMS coating solution and the ceramic support, and hence provides a positive effect on the adhesion of wet PDMS film on the ceramic support. It is shown that a high polar component with a simultaneously high overall surface energy of the substrate can lead to a better adhesion strength.[23,24]

In the studied range, the mechanical interlocking between the rough ceramic support and the PDMS separation layer plays an important role, because the additional contact area between the rough ceramic support and the PDMS separation layer gives rise to higher interfacial adhesion. However, with the increase in roughness, separation layer thickness should be increased accordingly to avoid the formation of defects in separation layer. If the thickness of the PDMS layer is smaller than the roughness of the ceramic support, the PDMS layer cannot cover the ceramic support surface completely, thus a great number of defects would appear on the surface of the PDMS layer. As a consequence, the interfacial adhesion reaches its peak when the roughness of the ceramic support approaches 1.5 μm. Beyond this peak content, it can be reasonable that the selectivity will drop down with the decreasing of the permeate flux.

Influence of viscosity of PDMS coating solution

A comprehensive understanding of the separation layer formation process is not easily achieved, mainly because many factors influence on the resulting separation layer. Recent investigations have shown that the viscosity of coating solution has a direct influence on the final properties of the coated films.[25] Moreover, the viscosity of coating solution also affects the intrusion of polymer solution into porous support layer during immersing the ceramic support into the coating solution.[26,27] In this work, the other parameters were kept constant, the solution viscosity as the main parameter was taken into account. To investigate the effect of viscosity of the PDMS solution on the membrane morphology, PDMS/ceramic composite membranes were prepared using 7.5 wt % PDMS dip-coating solutions with various prepolymerization times.

Figure 5 shows the viscosity of the PDMS solution with various prepolymerization times. Solution viscosity increases with the increase of prepolymerization time. In particular, the viscosity increased significantly after 8 h prepolymerization. The viscosity of a polymer solution reflects the intermolecular interactions between polymer chains, and therefore can affect the integrity of the surface of the composite membranes during the separation layer formation process.

Figure 6 shows the SEM images of the surfaces of PDMS/ceramic composite membranes prepared by PDMS coating solutions with various viscosities. The changes in the membrane morphology with increasing prepolymerization time can be related to the coating solution properties. It was found that the nonintegrity of the surface of the composite membranes could form when the viscosities of PDMS solutions were low. At the low viscosity, the polymer solution predominately penetrates into the pores of the ceramic support. As shown in Figures 6c–e, with increasing viscosity of the PDMS coating solution, the surface of the PDMS separation layer gradually became very smooth. These results indicate that the viscosity of the PDMS coating solution can prominently affect the integrity of the PDMS/ceramic composite membranes.

Furthermore, EDX line scanning analysis was carried out across the ceramic support to investigate the intrusion of the PDMS in the ceramic support. The Si signal coming from

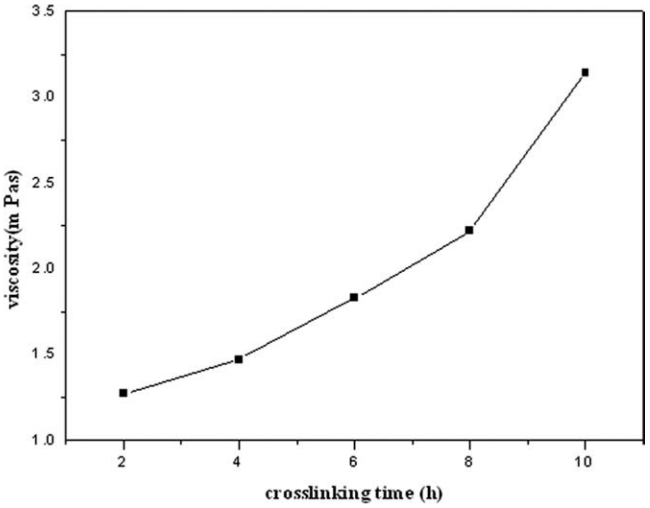

Figure 5. Viscosity of PDMS solution as a function of the prepolymerization time.

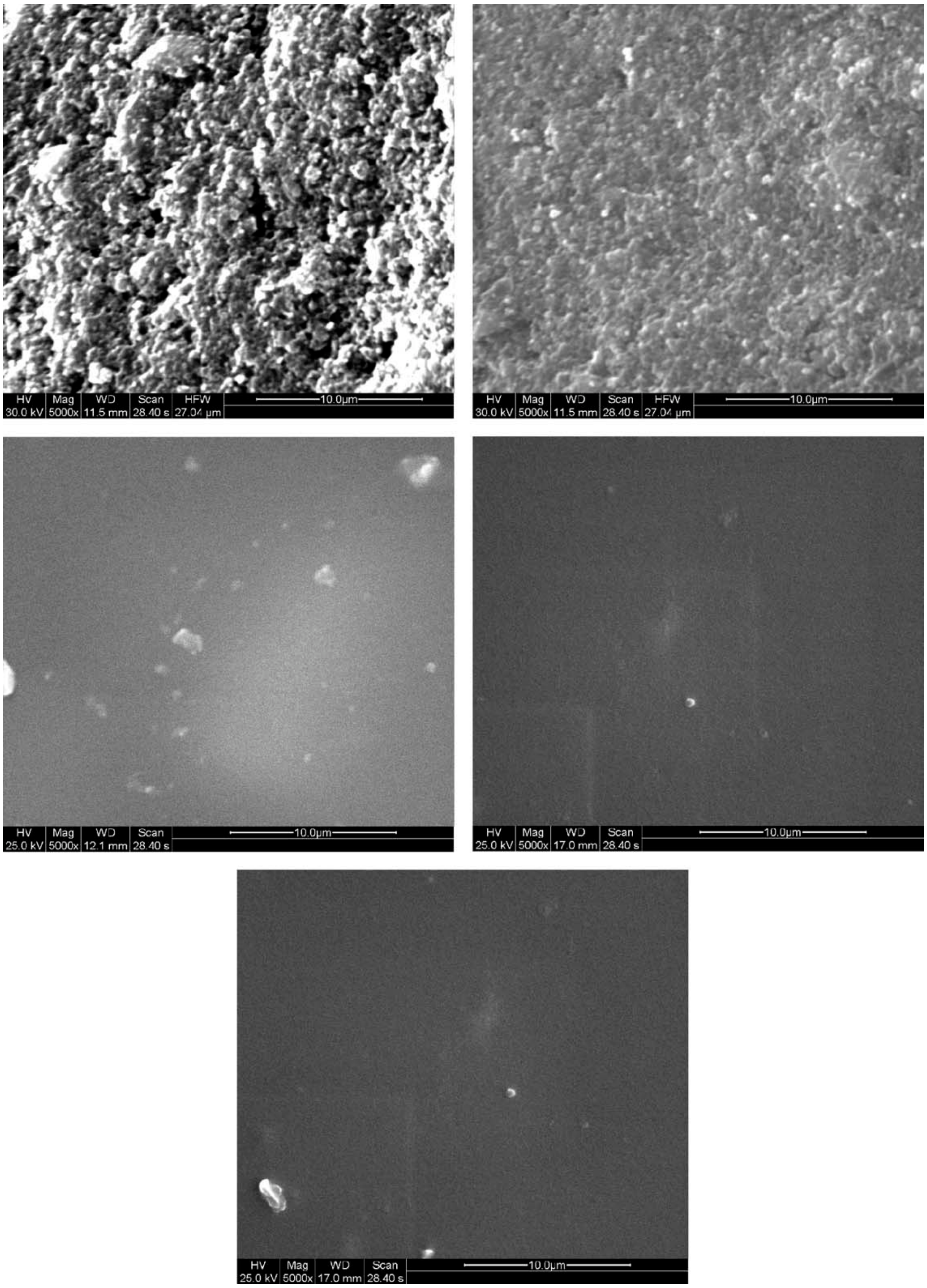

Figure 6. SEM images of the top view of the PDMS/ceramic composite membranes obtained by various solution with viscosity.

(a) 1.27 mPa·s; (b) 1.47 mPa·s; (c) 1.83 mPa·s; (d) 2.22 mPa·s; and (e) 3.14 mPa·s.

the support layer could indicate the intrusion of PDMS in the supports. Figure 7 shows the EDX line scanning spectra obtained along a line drawn in the cross section corresponding to the Figures 6c–e. We found that with the increasing viscosity of the PDMS coating, the penetrated content in the ceramic support decreased. A slight pore penetration can

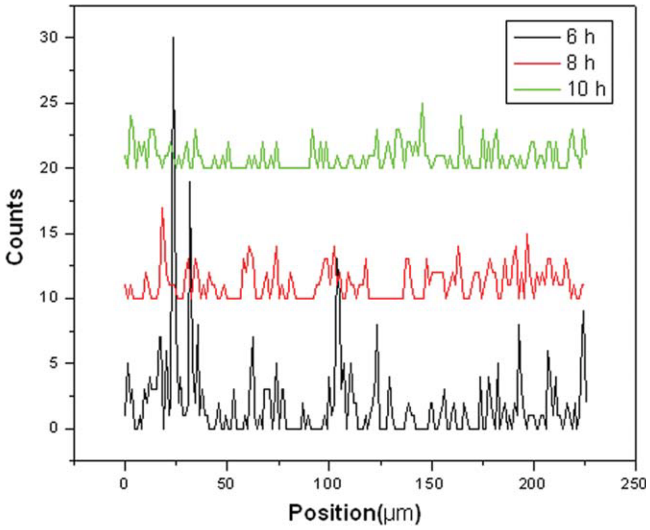

Figure 7. EDX line scan of the cross section with intensities of the Si element of the PDMS/ceramic composite membranes prepared with various prepolymerization times.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

enhance the adhesion between separation layer and support layer. However, the mass transfer resistance remarkably increases due to pore penetration, and the permeation flux through composite membrane decreases. So, we can modulate the pore penetration of interfacial region by varying the viscosity of PDMS solution.

Figure 8 illustrates the typical load–displacement curve according to various prepolymerization conditions. It was found that, although the viscosity of PDMS solution varied, the elastic modulus of the PDMS separation layers basically remained at the level of about 90 MPa because the elastic modulus was an intrinsic property of these materials. Table 2 gives the elastic modulus and hardness calculated from indentation data according to Oliver and Pharr method, including their corresponding standard deviation values. The standard deviations indicate that the effect of PDMS viscosity on the mechanical properties is not significant. As shown in Figure 8 and Table 2, both the calculated Young's modulus and indentation hardness of PDMS separation layer were almost unchanged as the viscosity of PDMS solution increased. It indicates that the stiffness sites are dominated by the hard inorganic silica clusters components, whereas the softness ones are dominated by the organic polymer chains.

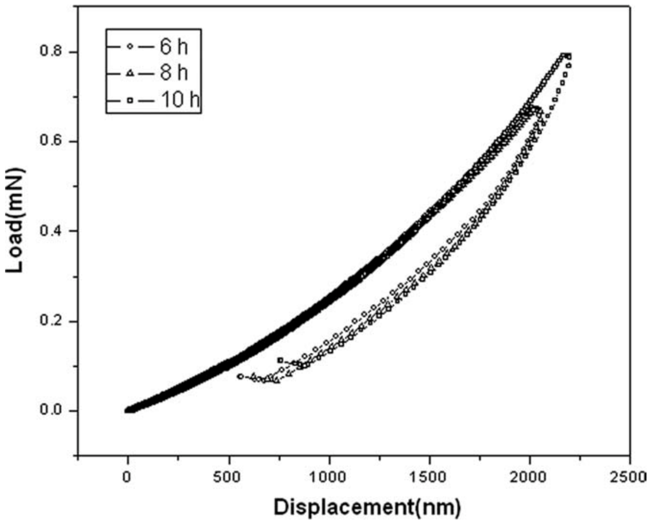

Figure 8. Load–displacement curves for PDMS separation layer with various prepolymerization times on the ceramic support.

Table 2. Modulus and Hardness of PDMS Separation Layers as a Function of the Viscosity of PDMS Solution

Viscosity (mPa·s)	Elastic Modulus (MPa)	Hardness (MPa)
1.28	86 ± 10	15 ± 2.9
1.48	91 ± 8	13 ± 2.1
2.22	98 ± 11	13 ± 1.9

Bonding mechanisms of PDMS separation layer on ceramic support

Five adhesion mechanisms are generally used for intrinsic adhesion, including mechanical interlocking, diffusion theory, chemical bonding, electronic and adsorption theories.[28,29] Several adhesion mechanisms might simultaneously contribute to the intrinsic adhesion, so it is difficult to discern the respective contribution of each mechanism. Mechanical interlocking, adsorption theory, and chemical bonding are commonly accepted for the adhesion mechanisms on polymer/ceramic interface. Because of the identical chemical bonding and adsorption for the interfaces, the contributions from mechanical interlocking could be different for the samples with different surface roughness.

The investigation of the effect of surface roughness on the adhesion of PDMS selective layer clearly showed that adhesion of the selective layer deposited by dip-coating method mainly depends on the surface roughness. Therefore, the increase in the adhesion strength was attributed to the stronger mechanical interlocking, which were developed at the separation layer-support interface during dip-coating process. As PDMS solution fills a rough interface, the interface that can sustain tensile forces increases dramatically and the associated capillary forces can dominate the work of adhesion between the polymer layer and the ceramic support. The rougher surface provides more contact area for PDMS–ceramic interface. Because the PDMS coating solution fills the rough interface, the area that can sustain tensile forces between the separation layer and porous ceramic support increases dramatically.

Conclusions

In this work, an in situ mechanical and adhesive property characterization method based on nanoindentation technique was proposed for PDMS/ceramic composite membranes. The investigation revealed that it was possible to modulate the interfacial adhesion property of binding region by varying the roughness of ceramic support and the viscosity of PDMS solution. As the roughness of ceramic support increases from 0.440 to 1.510 μm, the interfacial adhesion force for PDMS/ceramic composite membrane increases from 27.6 to 50.7 mN. The roughness of ceramic support as well as the viscosity of PDMS solution had little effect on the mechanical properties of the PDMS separation layer. The mechanism for the interfacial adhesion is considered to be the mechanical interlocking between the PDMS separation layer and the porous ceramic support.

Acknowledgments

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Notation

H = hardness, MPa
$P_{\max}$ = maximum applied force, mN
A_c = projected contact area, nm^2
h = indenter displacement, nm
h_c = contact depth, nm
S = contact stiffness, MPa
P = applied force, mN
E = Young's modulus, MPa
v = Poisson's ratio
R_a = arithmetical mean roughness, μm

Literature Cited

1. Kim BR, Ko MJ. The assessment of the fracture behavior in spin-on organosilicates by nanoindentation and nanoscratch tests. *Thin Solid Film*. 2009;517:3216–3221.
2. Zhang X, Hu L, Sun D. Nanoindentation and nanoscratch profiles of hybrid films based on (γ-methacrylpropyl)trimethoxysilane and tetraethoxysilane. *Acta Mater*. 2006;54:5469–5475.
3. Oláh A, Julius Vancso G. Characterization of adhesion at solid surfaces: development of an adhesion-testing device. *Eur Polym J*. 2005;41:2803–2823.
4. Fischer-Cripps AC. Critical review of analysis and interpretation of nanoindentation test data. *Surf Coat Technol*. 2006;200:4153–4165.
5. Saha R, Nix WD. Effects of the substrate on the determination of thin film mechanical properties by nanoindentation. *Acta Mater*. 2002;50:23–38.
6. Pelletier H, Mendibide C, Riche A. Mechanical characterization of polymeric films using depth-sensing instrument: correlation between viscoelastic-plastic properties and scratch resistance. *Prog Org Coat*. 2008;62:162–178.
7. Rezac MZ, Koros WJ. Preparation of polymer-ceramic composite membranes with thin defect-free separating layers. *J Appl Polym Sci*. 1992;46:1927–1938.
8. Song KM, Hong WH. Dehydration of ethanol and isopropanol using tubular type cellulose acetate membrane with ceramic support in pervaporation process. *J Membr Sci*. 1997;123:27–33.
9. Yoshida W, Cohen Y. Ceramic-supported polymer membranes for pervaporation of binary organic/organic mixtures. *J Membr Sci*. 2003;213:145–157.
10. Shao P, Huang RYM, Feng X, Anderson W, Pal R, Burns CM. Composite membranes with an integrated skin layer: preparation, structural characteristics and pervaporation performance. *J Membr Sci*. 2005;254:1–11.
11. Ahn D, Shull KR. Effects of substrate modification on the interfacial adhesion of acrylic elastomers. *Langmuir*. 1998;14:3646–3654.
12. Millare B, Thomas M, Ferreira A, Xu H, Holesinger M, Vullev VI. Dependence of the quality of adhesion between poly(dimethylsiloxane) and glass surfaces on the conditions of treatment with oxygen plasma. *Langmuir*. 2008;24:13218–13224.
13. Fischer-Cripps AC. *Nanoindentation*. New York: Springer-Verlag, 2004.
14. Xiangli FJ, Chen YW, Jin WQ, Xu NP. PDMS/ceramic composite membrane with high flux for pervaporation of ethanol–water mixtures. *Ind Eng Chem Res*. 2007;46:2224–2230.
15. Xiangli FJ, Wei W, Chen YW, Jin WQ, Xu NP. Optimization of preparation conditions for polydimethylsiloxane (PDMS)/ceramic composite pervaporation membranes using response surface methodology. *J Membr Sci*. 2008;311:23–33.
16. Oliver WC, Pharr GM. Improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J Mater Res*. 1992;7:1564–1580.
17. Oliver WC, Pharr GM. Measurement of hardness and elastic modulus by instrumented indentation: advances in understanding and refinements to methodology. *J Mater Res*. 2004;19:3–19.
18. Packham DE. Surface energy, surface topography and adhesion. *Int J Adhes Adhesives*. 2003;23:437–448.
19. Clarke A. Coating on a rough surface. *AIChE J*. 2004;48:2149–2156.
20. Choi GY, Kang JF, Ulman A, Zurawsky W, Fleischer C. Acid-base interaction in the adhesion between two solid surfaces. *Langmuir*. 1999;15:8783–8786.
21. Steinmann PA, Tardy Y, Hintermann HE. Adhesion testing by the scratch test method: the influence of intrinsic and extrinsic parameters on the critical load. *Thin Solid Film*. 1987;154:333–349.
22. Wenzel RN. Resistance of solid surfaces to wetting by water. *Ind Eng Chem*. 1936;28:988–994.
23. Mirabedini SM, Rahimi H, Hamedifar S, Mohseni SM. Microwave irradiation of polypropylene surface: a study on wettability and adhesion. *Int J Adhes Adhesives*. 2004;24:163–170.
24. Lugscheider E, Bobzin K. The influence on surface free energy of PVD-coatings. *Surf Coat Technol*. 2001;142–144: 755–760.
25. Hijón N, Manzano M, Salinas AJ, Vallet-Regí M. Bioactive CaO-SiO_2-PDMS coatings on Ti_6Al_4V substrates. *Chem Mater*. 2005;17:1591–1596.
26. Vankelecom IFJ, Moermans B, Verschueren G, Jacobs PA. Intrusion of PDMS top layers in porous supports. *J Membr Sci*. 1999;158:289–297.
27. Kim HJ, Nah SS, Min BR. A new technique for preparation of PDMS pervaporation membrane for VOC removal. *Adv Environ Res*. 2002;6:255–64.
28. Mittal KL. *Adhesion Measurements of Films and Coatings*. Utrecht, The Netherlands: V.S.P. International Science, 2001.
29. Kinloch AJ. *Adhesion and Adhesives: Science and Technology*. London, New York: Chapman and Hall, 1987.

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