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Research Article

Modified Silica Incorporating into PDMS Polymeric Membranes for Bioethanol Selection

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In this work, polydimethylsiloxane (PDMS) polymeric membranes were fabricated by incorporating fumed silica nanoparticles which were functionalized with two silane coupling agents—$NH_2(CH_2)_3Si(OC_2H_5)_3$ (APTS) and $NH_2(CH_2)_2NH(CH_2)_3Si(OC_2H_5)_3$ (TSED)—for selective removal of ethanol from aqueous solutions via pervaporation. It was demonstrated that large agglomerates were not observed indicating the uniform distribution of modified silica throughout the PDMS matrices. It is noted that the ethanol diffusivity and the water contact angles were both increased remarkably, being beneficial to the preferential permeation of ethanol through the membranes. The pervaporation results showed that the addition of the two types of modified silica nanoparticles dramatically enhanced both the permeability and selectivity of hybrid membranes. Compared to APTS, silica modified by TSED at the concentration of 4 wt. % resulted in the optimum pervaporation membranes with the maximum separation factor of 12.09 and the corresponding permeation flux of approximately 234.0 $g{\cdot}m^{-2}{\cdot}h^{-1}$ in a binary aqueous mixture at 40°C containing 10 wt. % ethanol. The observation will benefit the choice of coupling agents to improve the compatibility between hydrophilic fillers and hydrophobic polymers in preparing mixed matrix membranes.

1. Introduction

With the aggravation of environmental pollution and the rising of the oil crisis, the clean energy, such as bioethanol, produced by biomass fermentation has got more and more attention [1]. In practice, producing ethanol with traditional fermentation usually produces around 8 wt. % ethanol aqueous solutions since higher ethanol concentration will restrain the reproduction of saccharomyces cerevisiae in fermentation broths, even kill them, and finally stop fermenting [2, 3]. In order to improve the ethanol productivity, an alternative approach is that the ethanol could be continuously and efficiently removed from the fermentation feed. Pervaporation as a membrane separation process is an attractive technique in terms of energy and cost efficiency as compared with broadly utilized separation methods (such as distillation and gas stripping) [4, 5]. This process allows desirable components to preferentially permeate through a membrane impulse driven by a difference in chemical potentials. Apparently, the membrane material is one of the most important key elements in the pervaporation equipment. In the particular application of ethanol recovery, polydimethylsiloxane (PDMS) is the most promising membrane material in terms of its hydrophobicity [6, 7], and its pervaporation membranes have been commercialized, such as PERVAP 4060 manufactured by Sulzer Chemtech and PolyAn produced by PolyAn GmbH [8]. Unfortunately, a drawback is that the ethanol-water selectivity for pure PDMS membranes is generally less than 10.8 [9].

For further improving the ethanol-water separation performances, an alternative approach is that the PDMS matrix has been mixed with various fillers, including zeolites (e.g., silicalite-1[10, 11] and ZSM-5[12]), metal organic frameworks (MOFs) [13, 14], fumed silica [15, 16], polyphosphazene nanotubes [17], and carbon black [18]. Fumed silica is an extremely important inorganic material, which is nontoxic and nonpolluting, possessing porous structure and high specific surface area [19, 20]. However, because of the existence of a broad range of hydroxy groups on its surface, the

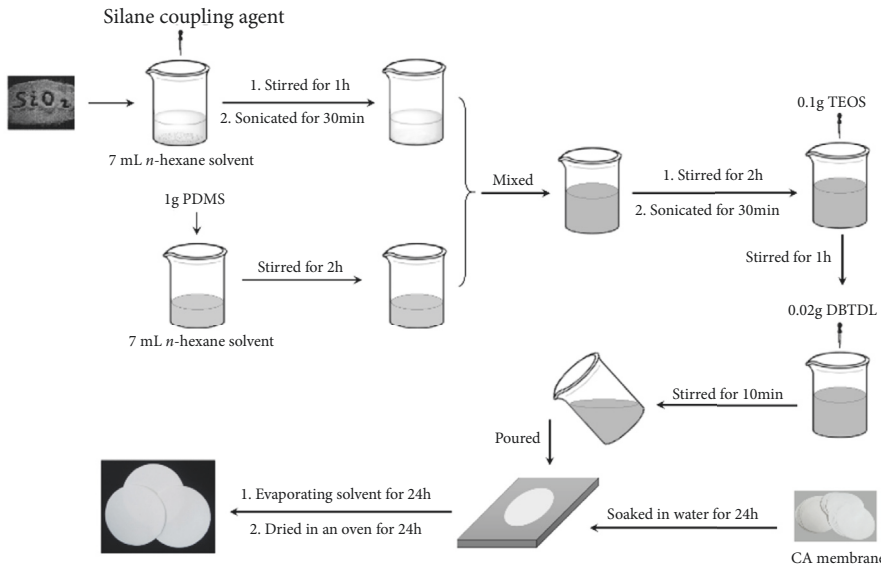


Figure 1: Schematic of preparation of hybrid membranes.

fumed silica nanoparticles in the PDMS matrix would form agglomerations resulting in the uneven distribution. It is therefore of great necessity to treat the surface of silica with chemical methods [21, 22]. Typically, silane coupling agents have been employed to enhance the hydrophobic property of silica in light of their bifunctional groups [15, 23, 24].

In this work, fumed silica nanoparticles after surface treatment by silane coupling agents were dispersed into PDMS matrix to fabricate hybrid membranes layered on cellulose acetate (CA) support membranes for recovering ethanol from water by pervaporation. To illustrate the influence of coupling agents on the separation performances, 3-aminopropyltriethoxysilane ($NH_2(CH_2)_3Si(OC_2H_5)_3$, APTS) and N-(3-triethoxysilylpropyl)ethylenediamine ($NH_2(CH_2)_2NH(CH_2)_3Si(OC_2H_5)_3$, TSED) were employed to modify the silica, and the effects of modified silica on the properties of hybrid membranes were evaluated.

2. Experimental

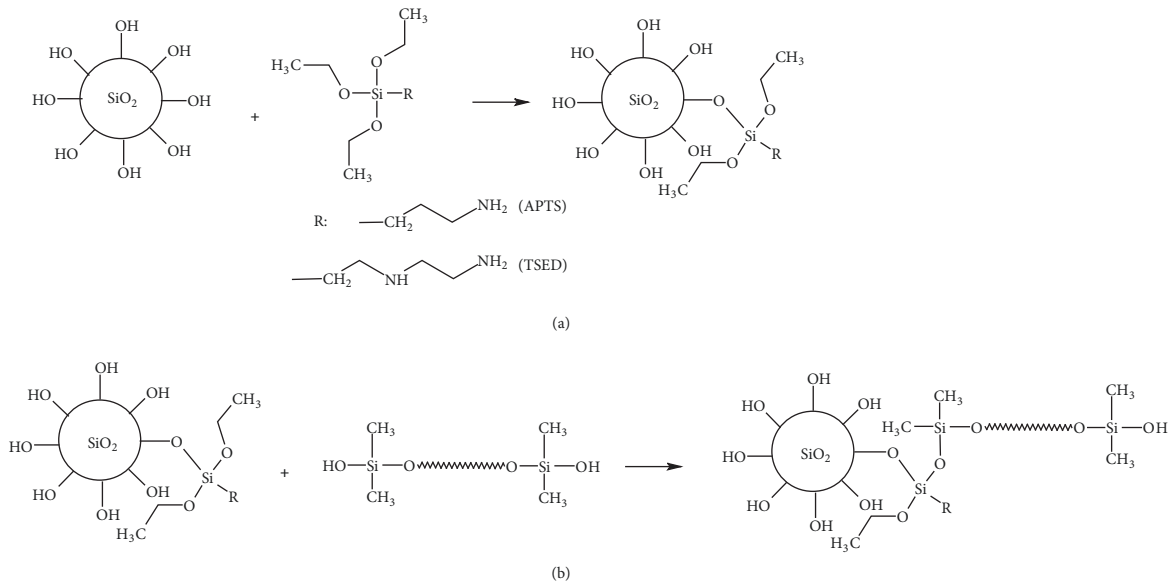
2.1. Materials. PDMS (107#RTV, viscosity 10000 mPa·s) was provided by Chenguang Chemical Institute (Chengdu, China). Fumed silica with a particle size of 12 nm and a specific surface area of 200 $m^2 \cdot g^{-1}$ was obtained from Shenyang Chemical Co., Ltd. (Shenyang, China). APTS and TSED were purchased from Aladdin (Shanghai, China). Tetraethylorthosilicate (TEOS) and dibutyltin dilaurate (DBTDL) were purchased from J&K Chemical Ltd. (Shanghai, China). Ethanol and *n*-hexane were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). CA microfiltration membranes (average pore size 0.45 μm) were procured from Shanghai Xinya Purification Instruments, Ltd. (Shanghai, China).

2.2. Preparation of Hybrid Membranes. Hybrid membranes were prepared based on our previously reported method [25]. The procedure is schematically shown in Figure 1. Typically, bare fumed silica was firstly functionalized by silane coupling agents, named as APTS-SiO_2 and TSED-SiO_2, respectively. And the related chemical reaction is presented in Scheme 1(a). After mixed with polymeric solutions, one of the ethoxy groups of APTS-SiO_2 or TSED-SiO_2 was reacted with one of the hydroxyl groups of PDMS, as shown in Scheme 1(b). Then, these grafted PDMS chains were cross-linked with TEOS. Finally, the hybrid membranes were prepared based on casting and solvent evaporation method.

2.3. Morphology Measurement. Surface and cross-section morphologies of hybrid membranes were obtained using an XL30 scanning electron microscopy (SEM, FEI, USA). Membrane samples were fractured in liquid nitrogen for preparing cross-section morphology specimen, and all the samples were gold sputtering before the measurement.

2.4. Contact Angle Test. Membrane wettability was evaluated by contact angle measuring with an OCA20 optical contact angle meter (DataPhysics, Germany). Distilled (DI) water (or anhydrous ethanol) was dropped on the membrane surfaces at room temperature, and the image was taken 10s after the droplet had fallen down the surface. The contact angle was measured with ImageJ.

2.5. Ethanol Diffusivity. Ethanol diffusivity in the separation layers was determined by following Marais' method [26]. Considering the high volatility of ethanol, a reverse procedure was performed. Typically, dry separation layers with 450 μm



Scheme 1: Reaction diagram: (a) fumed silica modification with silane coupling agents, (b) modified fumed silica graft on PDMS.

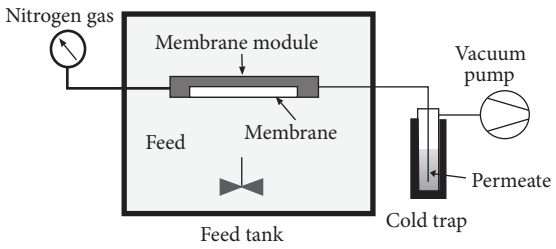


Figure 2: Schematic of the pervaporation setup.

in thickness were soaked in ethanol and left to reach an equilibrium adsorption state in an atmospheric environment. The samples were subsequently taken out, the ethanol was quickly wiped away from their surface, and the saturated adsorption mass m_{eq} as well as the mass m_t was recorded at time t at regular intervals.

2.6. Pervaporation. The experimental pervaporation setup is schematically represented in Figure 2. Membranes sealed in a membrane module were immersed into a feed solution completely. It is worth noting that the concentration polarization was reduced effectively by constantly stirring. The feed concentration was 10 wt. %, and the feed temperature was kept at 40°C using a constant temperature water tank. Permeate vapor was taken out with nitrogen at a stable flow rate at 0.5 L·min^{-1} which was measured with a rotameter. At the same time, a vacuum pump was used on the permeate side, and the downstream pressure on the permeation side was 20 kPa. After stable running, permeate was condensed in a cold trap chilled by liquid nitrogen, subsequently allowed to come to room temperature, and then weighted.

The pervaporation performances of membranes were assessed by the permeation flux (J/g·m^{-2}·h^{-1}) and the separation factor (α) which are defined by (1) and (2) for a binary mixture system:

$$J = \frac{Q}{At} \tag{1}$$

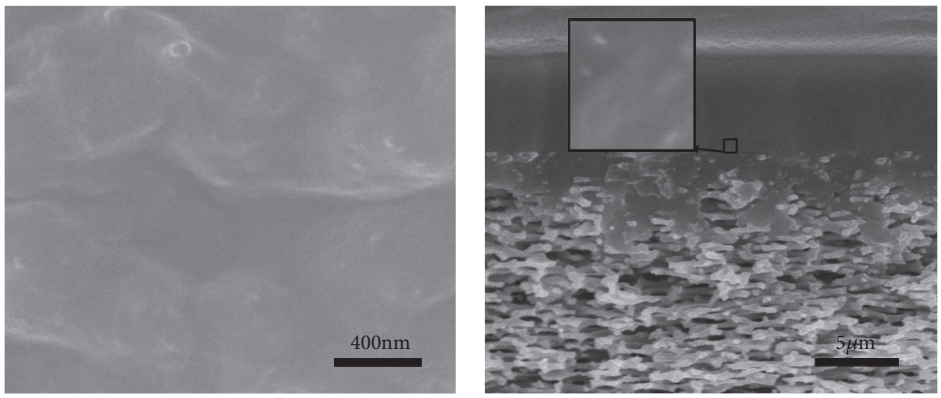
$$\alpha = \frac{y_e/y_w}{x_e/x_w} \tag{2}$$

where Q and t denote the permeate mass and the testing time, respectively. A is the effective area of membranes, and in practice it was 5.03×10^{-3} m^2. y_e and y_w are the ethanol and water mass fractions in the permeate, whereas x_e and x_w are the ethanol and water mass fractions in the feed, respectively. A WAY-2W Abbe refractometer (Jingke, China, accuracy ±0.0002) was employed to measure ethanol concentrations [27]. Furthermore, to separate the influence of driving forces, the permeability (P_i, mol m/m^2 s Pa) of component i (ethanol or water) and the molar selectivity (β) can be described as [28–30]

$$P_i = \frac{J_i}{p_{io} - p_{il}} l = \frac{J_i}{\gamma_{io}\chi_{io}P_{io}^{sat} - p_{il}} l \tag{3}$$

$$\beta = \frac{P_e}{P_w} \tag{4}$$

where l (m) is the thickness of the separation layer, J_i (mol·m^{-2}·s^{-1}) is the molar flux, p_{io} and p_{il} (Pa) represent the partial pressures on the feed and permeate sides, χ_{io} and P_{io}^{sat} (Pa) are the mole fraction and the saturated vapor pressure of pure component i in the feed, whereas γ_{io} is the activity



(a) (b)

Figure 3: SEM images of (a) surface and (b) cross-section of PDMS hybrid membranes filled with 4 wt. % of APTS-SiO_2.

coefficient of component i in the feed, which was calculated with the Aspen Plus software (version 7.2, property method UNIQUAC), and the activity coefficients of ethanol and water are 4.033 and 1.004 for a 10 wt. % ethanol/water mixture at 40°C. P_e and P_w are the permeabilities of ethanol and water, respectively.

At low permeate pressures (the nitrogen flow rate is high), p_{il} could be neglected [31]. Therefore, (3) becomes as follows.

$$P_i = \frac{J_i}{\gamma_{io} x_{io} p_{io}^{sat}} l \quad (5)$$

3. Results and Discussion

3.1. Morphology of Hybrid Membranes. Surface and cross-section morphologies of PDMS hybrid membranes that contain 4 wt. % of APTS-SiO_2 are shown in Figure 3. The thickness of the separation layer was around 10 μm. From Figure 3, it can be seen that the filler particles were not agglomerated together and were homogeneously distributed throughout the PDMS matrix, which was attributed to the formation of chemical bonds between PDMS and SiO_2 through the coupling agent APTS, as schematically shown in Scheme 1. This indicated that dense and defect free hybrid membranes were successfully prepared. It is also worth mentioning that the PDMS chains can also be chemically bonded to the SiO_2 nanoparticles using the coupling agent TSED, and there is no difference on the morphologies between APTS-SiO_2 and TSED-SiO_2 filled PDMS hybrid membranes.

3.2. Ethanol Diffusivity. The asymptotic mass loss as a function of t for pure PDMS and PDMS hybrid membranes containing fillers at a concentration of 4 wt. % was plotted in Figure 4. It can be seen that the rates of mass loss for the filled PDMS are relatively faster than that of the pure PDMS, and thus it can be concluded that the ethanol diffusivity of both the hybrid membranes improved with the addition of the two modified silica particles as compared to the value of the pristine PDMS membrane. Notably, the effect of TSED

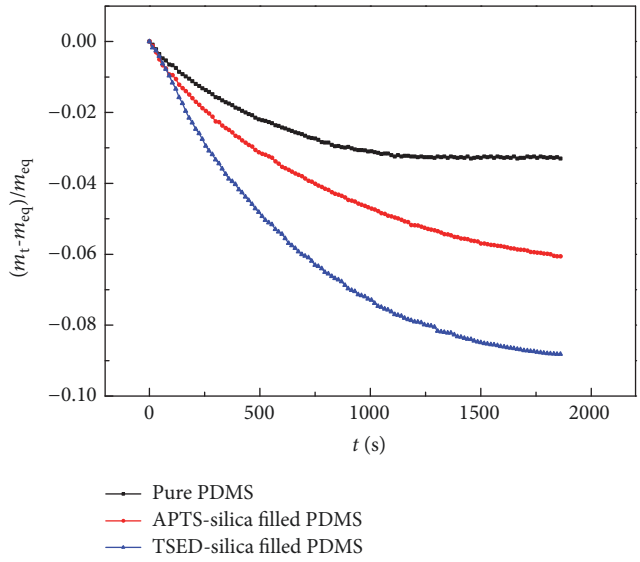


Figure 4: Mass loss as a function of t for the filled and unfilled PDMS separation layers.

on ethanol diffusivity in modified membranes was more obvious than APTS. This is ascribed to the fact that the hydrophobicity of TSED is higher than that of APTS. It should be noted that the amino is protonated with abundant hydrogen ions under acidic condition, resulting, therefore, in hydrophilicity; conversely, in other cases (neutral or alkaline condition), it exhibits hydrophobicity. Apparently, in this experiment, both APTS and TSED are hydrophobic, and the latter hydrophobicity is higher than the former according to their chemical structures.

3.3. Contact Angle. To assess the hydrophobic nature of PDMS hybrid membranes filled with silica modified by different coupling agents, water contact angles were performed, and the obtained data are gathered in Figure 5. According

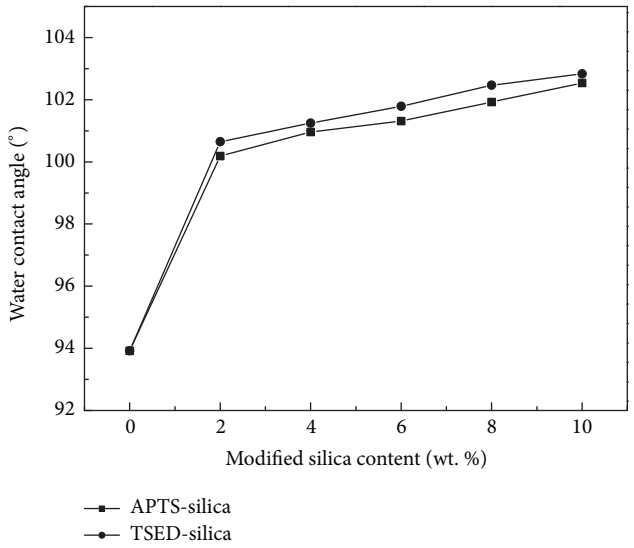


Figure 5: Contact angle of water at the surface of modified PDMS membranes.

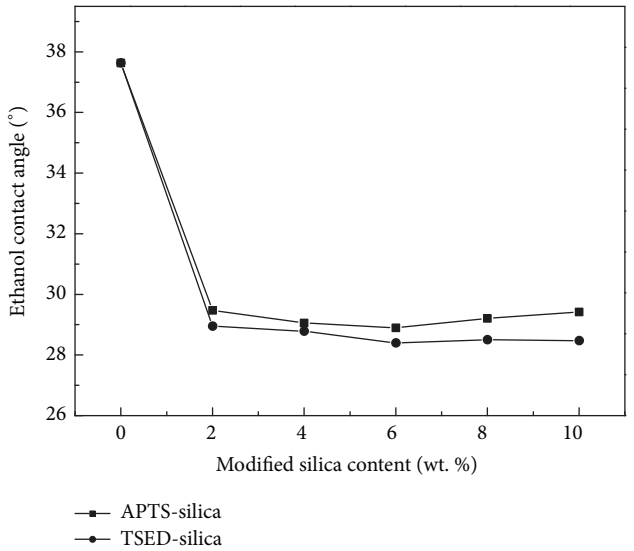


Figure 6: Contact angle of ethanol at the surface of modified PDMS membranes.

to two sets of experimental data, it is clear that the water contact angles of the two types of hybrid membranes are both larger than that of the pristine membrane. Furthermore, it is noted that they both tend to increase with the increment of the modified silica content. The main reason is that the surface of the silica particles was changed from hydrophilic to hydrophobic by the silane coupling agents. Consequently, the hydrophobicity of the hybrid membranes was improved remarkably when they were introduced into PDMS matrices. It is noteworthy that the higher values of water contact angles of TSED-SiO_2 filled PDMS membranes are in accordance with the higher hydrophobicity of TSED as expected.

Figure 6 shows the ethanol contact angles at the surface of two hybrid membranes. It is found that with the increment of the modified silica content, the ethanol contact angles decrease significantly and then maintain almost constant for both APTS and TSED modified membranes, but with lower values for TSED. As noted above, it could be concluded that the addition of the modified silica increases the affinity of PDMS membranes for ethanol which is conducive to preferential permeation over water.

3.4. Pervaporation. Figure 7 shows the effects of silica coupled with APTS and TSED on the permeation flux of PDMS hybrid membranes in aqueous solutions at 40°C containing 10 wt. % of ethanol. It is observed that ethanol fluxes of two hybrid membranes both considerably increase first and then decrease, while water fluxes both increase and then remain almost constant apart from those with 4 wt. % modified silica content. As a result, the total fluxes both significantly increase with the increment of the modified silica content and then remain at an almost constant level. According to the literature [32, 33], the incorporation of nanofillers into a polymeric matrix can effectively disrupt the packing of polymer segments and, as a result, increase in free volume, therefore leading to the improvement of the permeation flux. From the total fluxes of two hybrid membranes, it is also inferred that the effect of the silane coupling agents on the total and ethanol fluxes is as follows: TSED>APTS. This is mainly attributed to the difference in molecular volumes of the two silane coupling agents, as illustrated in Scheme 1. Due to the larger molecular volume of TSED, the TSED-SiO_2 possesses the larger molecular size. Consequently, the effect of silica modified with TSED is more remarkable for the disruption of chain packing and the subsequent increase in the free volume than that of APTS, which leads the total and ethanol flux of the corresponding hybrid membrane to be much higher.

The obtained separation factors are gathered in Figure 8. It is obvious that they first increase and then decrease for both two PDMS hybrid membranes as the modified silica loading increases. To sum up, their separation factors present a similar trend with a maximum at a concentration of 4 wt. %. As mentioned above, the PDMS chain packing was probably disrupted and thus the free volume of the hybrid membrane may be improved as a consequence of the addition of modified silica particles. This could lead to the increase in the diffusivity of ethanol which was responsible for the observed increasing trend. It is worth mentioning that this effect is more remarkable for TSED, as demonstrating in Figure 4. Therefore, it can be observed that the separation factors of the TSED modified hybrid membranes are higher than those of hybrid membranes modified by APTS. However, more filler nanoparticles would probably inhabit free volume cavities, resulting in the reduction in ethanol flux, as shown in Figure 7(b). Consequently, the separation factors subsequently decreased.

Driving force normalized performances in terms of permeability and molar selectivity with the same PV

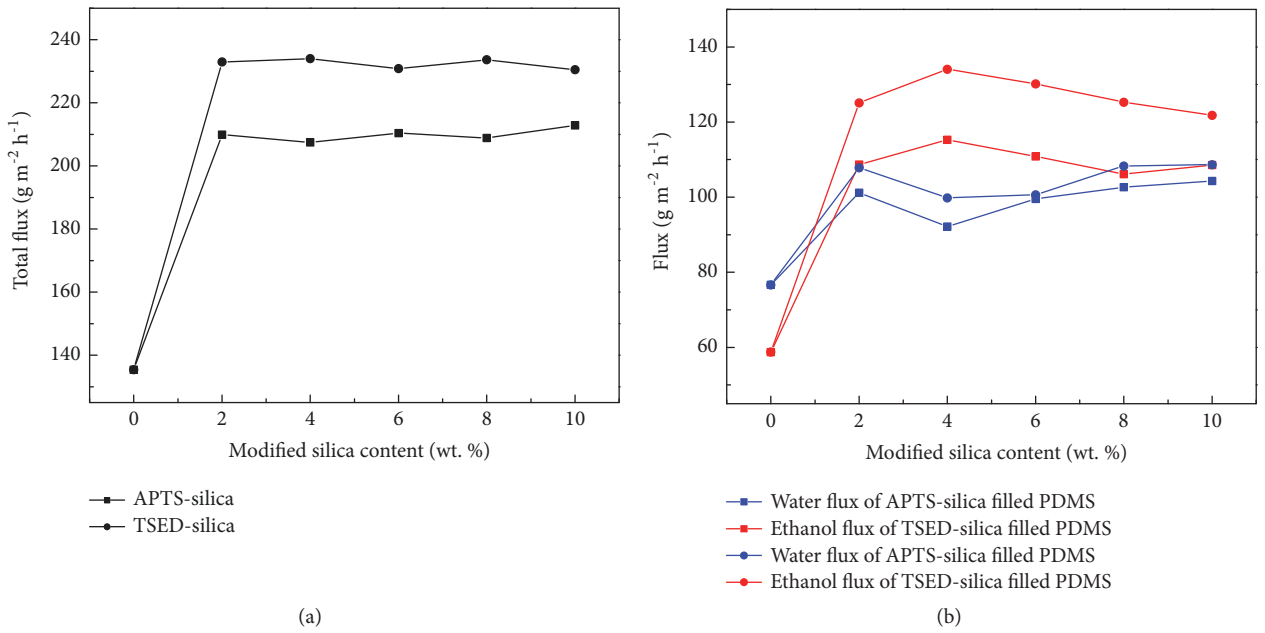


Figure 7: Effect of modified fumed silica content on permeation flux: (a) total flux, (b) ethanol and water fluxes.

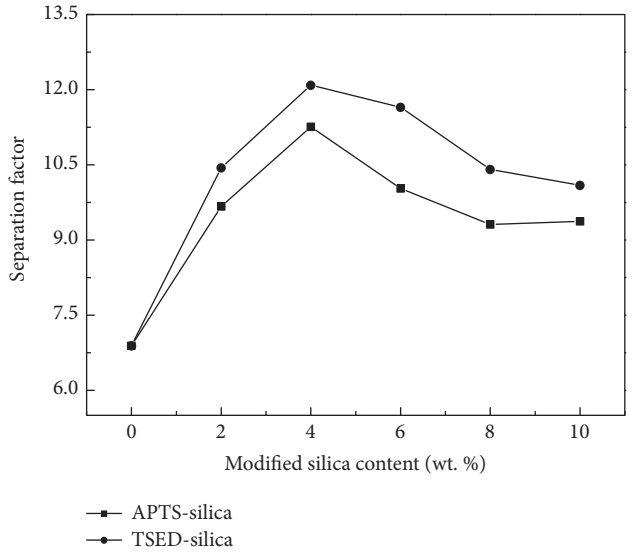


Figure 8: Effect of modified fumed silica content on separation factor.

performance data of TSED-SiO_2 filled PDMS membranes are replotted in Figure 9. It can be found that the ethanol permeability, water permeability, and molar selectivity show the same trends with ethanol flux, water flux, and separation factor, respectively. For the membrane containing 4 wt% of TSED-SiO_2 the molar selectivity increases up to 1.240 from 0.7075 for the pure PDMS membrane which is almost double, indicating an improved ethanol permselectivity.

4. Conclusions

In this study, in order to enhance the ethanol separation performance and improve the compatibility between the PDMS matrix and nano-fumed silica particles, the fumed silica was functionalized with two silane coupling agents for comparison. The effects of the modified silica on the properties of hybrid membranes were tested. The SEM images showed that the silica nanoparticles were compatible with the PDMS. According to the experimental results, it was demonstrated that the ethanol diffusivity and the water contact angles were elevated significantly, and the pervaporation performances of the hybrid membranes both remarkably improved with the addition of two modified silica nanoparticles. Nevertheless, the effect of TSED was better than that of APTS owing to the hydrophobicity as well as the molecular volume. When the addition of TSED-silica was 4 wt. %, the separation factor had the maximum of 12.09 along with the permeation flux of 234.0 g·m^{-2}·h^{-1} in an aqueous solution at 40°C containing 10 wt. % ethanol. In summary, this work might provide some references in choosing coupling agents for the modification of fillers before introduction into polymeric matrices in the application of the separation of organic components over water by pervaporation.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

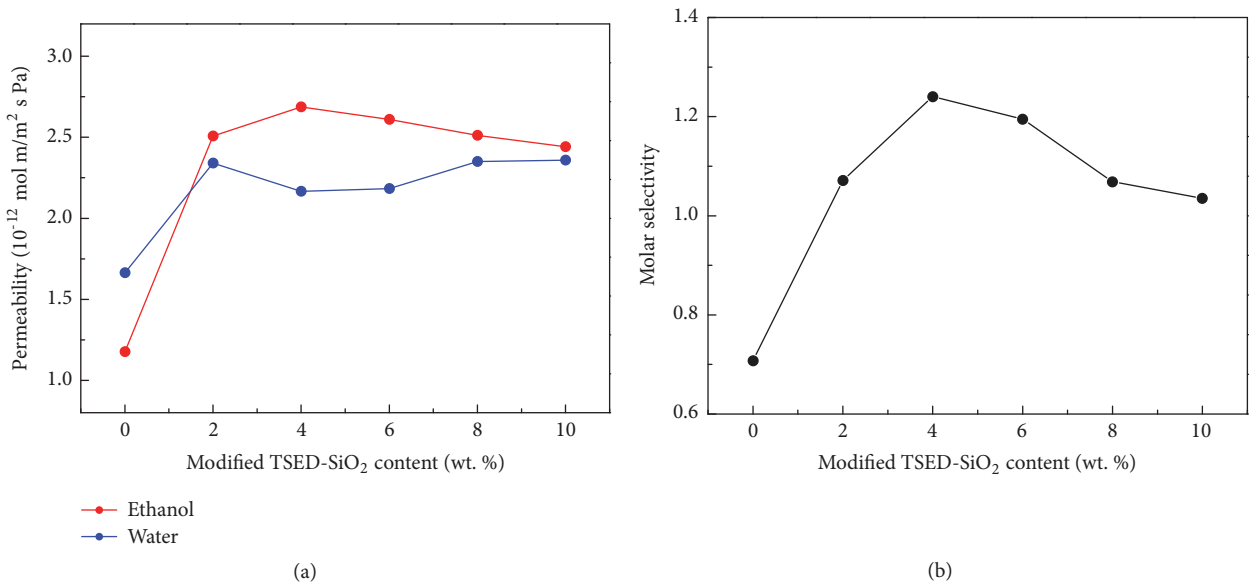


FIGURE 9: Effect of modified TSED-SiO$_2$ content on (a) ethanol permeability and water permeability and (b) molar selectivity.

Acknowledgments

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