



Influence of molecular weight of polydimethylsiloxane precursors and crosslinking content on degree of ethanol swelling of crosslinked networks



Wanqiu Zhang^a, Xing Su^a, Baoli Shi^{a,b,*}, Lili Wang^a, Qingwen Wang^b, Shujun Li^b

^a Polymer Membrane Laboratory, College of Science, Northeast Forestry University, Harbin, Heilongjiang 150040, China

^b Key Laboratory of Bio-Based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin, Heilongjiang 150040, China

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ABSTRACT

Using PDMS (polydimethylsiloxane) as a basic polymeric matrix to the preparation of ethanol-permselective pervaporation membranes is a vibrant field of research. In this paper, a detailed study of the effects of the molecular weight of PDMS precursors and the content of the TEOS (tetraethyl orthosilicate) crosslinker on the degree of swelling in ethanol and ethanol contact angle is reported. Five PDMS precursors with molecular weights of 26.6 K, 35.5 K, 50.2 K, 71.7 K, and 110.4 K, and five crosslinking contents (1 wt%, 2 wt%, 5 wt%, 10 wt%, and 15 wt%) were chosen to prepare twenty-five PDMS networks. Considering only the maximum tensile strength of the networks, the optimum molecular weight of the precursor was found to be 35.5 K and the optimum crosslinker content was 5 wt%. The average Young's modulus of the PDMS network prepared under these conditions reached 0.63 MPa after using toluene to extract the network. Some uncrosslinked precursors always occur in the networks, and have some influence on the molecular weight of the precursors and the crosslinker content that is used. It was found that the content of the uncrosslinked precursors has direct effect on the contact angle of ethanol sessile drops at the surface of the extracted PDMS networks, and higher extraction corresponded to a smaller ethanol contact angle. A combined parameter (S), defined as the quotient of the extraction amount (A_E) and the tensile elastic modulus (E_Y), gives a good linear relationship with the increase in weight of networks swelled in ethanol. This means that the degree of equilibrium swelling of the networks is simultaneously strongly influenced by the tensile modulus and the content of the uncrosslinked precursors.

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1. Introduction

Using lignocellulose biomass to make biofuels is an attractive field. In fermentation technology to produce bioethanol, a key problem is how to separate ethanol from the aqueous solution [1]. Pervaporation technology can offer considerable savings in energy for evaporation, so many researchers believe that using a pervaporation membrane with high ethanol-permselectivity and permeation flux could replace the traditional distillation process for ethanol separation [2].

Although many materials have been considered for the preparation of an ethanol-permselective pervaporation membrane, PDMS (polydimethylsiloxane) still receives more attention than other

* Corresponding author at: Polymer Membrane Laboratory, College of Science, Northeast Forestry University, Harbin, Heilongjiang 150040, China. Tel./fax: +86 451 8219 2327.

E-mail address: shi_baoli@yahoo.com (B. Shi).

polymer materials. Hundreds of pervaporation studies have been published since the 1980s, and most of these are based on this PDMS silicone rubber matrix. Many commercial PDMS pervaporation membranes are also available [3,4]. Published research can be assigned to two classes, according to the source of the membrane used: either commercial PDMS pervaporation membranes [5–9] or PDMS pervaporation membranes prepared by the researchers themselves [10–24]. The latter is the main research approach for ethanol pervaporation separations.

To obtain a stable separation, the PDMS linear precursors must be crosslinked to form networks. Generally, hydroxyl-terminated linear PDMS precursors are chosen to prepare ethanol-permselective membranes, and TEOS (tetraethyl orthosilicate), a four-functionality liquid, is used as the crosslinker. According to rubber elasticity theories, the chain length between the junction points of PDMS networks determines the mechanical properties and the swelled performances of PDMS networks [25]. It is widely known that ethanol has a greater swelling capacity than water when contacted with

PDMS pervaporation membranes. For a solvent, its swelling capacity to PDMS networks depends strongly on the difference in their cohesive energy densities (CED). Because the CED difference between ethanol and PDMS is smaller than its between water and PDMS, the swelling degree in ethanol is always larger than in water [26,27].

After carefully studying all the published PDMS pervaporation papers, we found that many researchers did not give detailed information concerning their PDMS materials, and that even basic information was often neglected, such as the molecular weight or viscosity of precursors [10,13,15–18,20,21,24]. For work which did contain specific information about the PDMS precursors, we found that the molecular weights of the PDMS precursors had a very wide distribution range [11,12,14,19,22,23], with the exception of papers from one research group [13,15]. Lack of such critical detail undoubtedly limit the development of PDMS pervaporation technology.

We therefore intend to undertake detailed research into the effects of the molecular weight of PDMS precursors and degree of crosslinking on some basic aspects of performance that are related to the interaction between ethanol and PDMS networks. As the first step, in this paper, we concentrate only on the relationship between PDMS network parameters and the degree of ethanol swelling and ethanol affinity. Five PDMS precursors and five crosslinking contents were chosen to prepare twenty-five PDMS networks. We found that there is a strong correlation between ethanol contact angle and unreacted (uncrosslinked) amount of the PDMS precursor, and that there also is a strong correlation between the degree of ethanol swelling and the amount of unreacted (uncrosslinked) PDMS precursor and the Young's modulus of the PDMS networks. In the next work, the effects of PDMS precursors and crosslinking factors on the micro-structure and pervaporation performance of the PDMS networks will be further researched.

2. Experimental

2.1. Materials

Five α,ω -dihydroxy-terminated PDMS precursors with molecular weights (M_n) of 26.6 K, 35.5 K, 50.2 K, 71.7 K, and 110.4 K were purchased from Sigma–Aldrich. TEOS was used as the crosslinker, dibutyltin dilaurate (DBTOL) as the catalyst, and *n*-hexane as the solvent. All chemicals were purchased from Sigma–Aldrich.

2.2. Preparation of PDMS networks

PDMS, TEOS, and *n*-hexane were added to a beaker at room temperature. The mass ratio of PDMS to *n*-hexane was 1:5. The mass ratios of the crosslinker (TEOS) to PDMS were 1 wt%, 2 wt%, 5 wt%, 10 wt%, and 15 wt%. The polymer solution was stirred by a magnetic mixer for several hours, then the catalyst (DBTOL) was added. The mass of DBTOL added was ten times the theoretical amount of the crosslinker. Table 1 lists the mass content of each component. The polymer solution was stirred continuously with the magnetic mixer until the viscosity of the polymer gelation

solution reached twice that of the initial polymer solution. The viscosity was measured with a digital rotational viscometer, NDJ-5S (Shanghai Jingtian Electronic Instrument Co. Ltd., China). The viscous polymer solution was then poured onto a polytetrafluoroethylene (PTFE) sheet and the sheet was placed in a self-made ventilation oven at room temperature for one day to vaporize the solvent. A homogeneous crosslinked PDMS network was obtained with a thickness between 100 μ m and 200 μ m. All operations were performed at room temperature.

2.3. Measurement of uncrosslinked PDMS content

The PDMS precursors did not crosslink totally during network formation. Because ethanol could dissolve the uncrosslinked PDMS slowly, disturbing the calculation of swelling degree, to obtain stable PDMS networks, the uncrosslinked PDMS was extracted with toluene as an extractant at room temperature and the uncrosslinked PDMS content was also measured. The PDMS networks of known weight were swelled in toluene for one day and the uncrosslinked PDMS precursors were dissolved. The PDMS networks were then removed from the toluene and dried naturally for one day. Finally, the content of the extracted PDMS precursors was recorded. At least five samples were measured for each PDMS network and the average value obtained.

2.4. Measurement of tensile strength

Young's moduli of the PDMS networks (before and after extraction in toluene) were measured on a self-made film mechanical testing instrument at room temperature. At least five samples with a size of 5 mm \times 40 mm were measured for each PDMS network. The tensile rate was 3 mm/min and the maximum elongation rate was controlled at less than 10%. The average Young's modulus was calculated when the standard deviation (SD) value was less than 5%.

2.5. Measurement of equilibrium swelling degree in ethanol

The increase in weight of the extracted PDMS networks swelled in ethanol was measured at room temperature. For each PDMS network, at least three samples of known mass were swelled by soaking in ethanol for 24 h. The increase in weight following contact with ethanol was recorded and the average value calculated.

2.6. Measurement of ethanol contact angle

The contact angle of ethanol sessile drops at the surface the PDMS networks extracted in toluene was measured on a self-made contact angle apparatus with ADSA (Axisymmetric Drop Shape Analysis) functionality at room temperature. The volume of the ethanol drop was 5 μ L for each test. At least five measurements were performed for each PDMS network and the average value calculated.

Table 1

Mass amount (or mass ratio to PDMS precursor) of each component for preparation of PDMS networks.

M_n of PDMS precursors	26.6 K	35.5 K	50.2 K	71.7 K	110.4 K
$\log M_n$	4.43	4.55	4.70	4.86	5.04
Theoretical amount of crosslinker (wt%) required to form a perfect crosslinked network f (functionality) = 4	0.39	0.29	0.20	0.15	0.09
Actual amount of crosslinker used (wt%)	1, 2, 5, 10, 15	1, 2, 5, 10, 15	1, 2, 5, 10, 15	1, 2, 5, 10, 15	1, 2, 5, 10, 15
Actual amount of catalyst used (wt%) (10 times the theoretical amount of crosslinker)	3.9	2.9	2.0	1.5	0.9

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