Reactive and Functional Polymers 98 (2016) 1–8

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react

# Effect of silane coupling agents with different non-hydrolytic groups on tensile modulus of composite PDMS crosslinked membranes

Xing Su, Baoli Shi *

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

ARTICLE INFO

*Article history:*
Received 1 June 2015
Received in revised form 29 October 2015
Accepted 8 November 2015
Available online 11 November 2015

*Keywords:*
Coupling agent
PDMS
Silica
Pervaporation

ABSTRACT

In this paper, four silane coupling agents with different non-hydrolytic groups were used to treat a kind of hydrophilic fumed nanosilica to investigate the influence of different silane coupling agents on the mechanical properties of PDMS composite matrix. The four coupling agents were ethyl triethoxysilane (ETES), octyl triethoxysilane (OTES), phenyl triethoxysilane (PTES), and 3-aminopropyl triethoxysilane (APTES) which exhibited the same hydrolytic groups. For each coupling agent/nanosilica system, six modified nanosilica samples were prepared at different addition contents of the coupling agent; six corresponding PDMS composite crosslinked membranes were also prepared. It was found that compared with pure PDMS membrane, the addition of modified nanosilica to PDMS increased the tensile modulus of the composite membranes. The miscibility strongly influenced the tensile modulus of the composite membranes when the HSP (Hansen solubility parameter) difference $R_a$ was adopted to characterize the miscibility between the non-hydrolytic groups of the four coupling agents and the solvent (*n*-hexane). A better miscibility induced a larger tensile modulus. When the length of the non-hydrolytic groups was larger than the distance between two adjacent hydroxyl groups, the sheltered hydroxyl groups by the non-hydrolytic groups would be prevented to couple with other coupling agent molecules, thereby reducing the available hydroxyl groups. When all of the potentially available hydroxyl groups at the nanosilica surface reacted with the coupling agent molecules, the tensile modulus of the composite membranes would reach a maximum value. In addition, according to the results of equilibrium swelling in ethanol and water, it was found that a membrane with large tensile modulus possessed strong resistant capability to swelling. From the results of ethanol and water pervaporation experiments, connection between ideal ethanol/water permeation selectivity or ideal ethanol/water diffusion selectivity and the tensile modulus was also observed.
© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Pervaporation membrane technology is the most convenient, energy-saving, and economical method to separate ethanol/water mixture efficiently [1–2]. Polydimethysiloxane (PDMS) is a widely investigated material for preparing the separation layer of pervaporation membranes with perm-selective performance to ethanol [3]. To improve the selectivity for separating ethanol/water mixture, various powders such as fumed nanosilica, silicalite-1, zeolite, ZSM-5, and carbon black are added to the PDMS layer to change the PDMS matrix structure [4–8]. The addition of these powders not only changes the separation performances of the composite PDMS membranes, but also enhances the mechanical properties of the composite PDMS layer [9–15].

PDMS is a strong hydrophobic material. The thermodynamic interaction between PDMS and the powders is poor. Therefore, silane coupling agents are often used to treat the powder fillers to increase their surface hydrophobicity, thereby enhancing the stability of the composite membrane [16]. The commonly used silane coupling agents include 3-aminopropyl triethoxysilane (APTES) and vinyldimethyl ethoxysilane (VDMES) [17–20]. The dispersion degree of the powders and the tensile modulus of the PDMS composite membrane increased when the modified powders are added to the PDMS matrix [14–15,19,21].

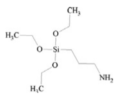
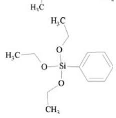
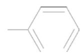
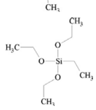
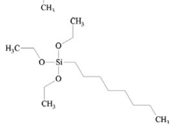
Among the abovementioned powders, fumed nanosilica can be conveniently manufactured by flame hydrolysis of chlorosilanes, and the average size can be controlled accurately [22]. The fumed nanosilica surface contains a specific amount of hydroxyl groups that can react with the hydrolytic groups of silane coupling agents, forming stable modified powders. Thus, fumed nanosilica is one of the important additives to prepare PDMS pervaporation membranes [19,23–24].

The separation layer of the PDMS pervaporation membranes is always swollen by the organic mixture, and the swelling degree of the layer can strongly influence the separation performance. Several factors influence the swelling degree, including the affinity between the organic solvent and PDMS, the crosslinking degree of the PDMS network, and

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

http://dx.doi.org/10.1016/j.reactfunctpolym.2015.11.001
1381-5148/© 2015 Elsevier B.V. All rights reserved.

**Table 1**
Structure and molecular weight of coupling agents.

| Name | Chemical structure | Molecular weight | Non-hydrolytic group |
|---|---|---|---|
| APTES |  | 221.37 | $CH_2CH_2CH_2NH_2$ |
| PTES |  | 240.37 |  |
| ETES |  | 192.33 | $CH_2CH_3$ |
| OTES |  | 276.49 | $CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ |

the mechanical properties of the PDMS network [25–26]. Compared with other parameters, the mechanical properties are also important for membrane life. Membrane with a strong mechanical strength will possess a good resistant capability to solvents and a long life. In addition, according to rubber elasticity theories, the mechanical property has strong connection with the micro-structure of chains and junction points [27]. Therefore, researching the mechanical properties is a significant work, either for membrane application or for theoretical research. Various silane coupling agents can be used to treat fumed nanosilica. However, whether different silane coupling agents induce change in the mechanical properties of the PDMS/modified nanosilica membrane remains unknown.

In this work, four silane coupling agents with different non-hydrolytic groups were used to treat a kind of hydrophilic fumed nanosilica with an average size of 12 nm to investigate the influence of different silane coupling agents on the mechanical properties of the PDMS composite matrix. The four silane coupling agents were ethyl triethoxysilane (ETES), octyl triethoxysilane (OTES), phenyl triethoxysilane (PTES), and 3-aminopropyl triethoxysilane (APTES) which exhibited the same hydrolytic groups. For each silane coupling agent/nanosilica system, six modified nanosilica samples were prepared at different addition contents of the silane coupling agent; six corresponding PDMS composite crosslinked membranes were also prepared. The tensile modulus of the PDMS composite membranes was measured. The change trend of the tensile modulus with the addition content of silane coupling agent was explained by the preventive action of the non-hydrolytic groups on the hydroxyl groups. The difference in the tensile modulus was elucidated by Hansen solubility parameter (HSP) theory.

## 2. Experimental

### 2.1. Materials

Dihydroxy-terminated PDMS precursor with $M_n$ of 35,500 was purchased from Sigma-Aldrich Co., Ltd., USA. Fumed nanosilica (Aerosil 200) with specific surface area of 200 $m^2/g$ was purchased from Evonic Industries Co., Ltd., Germany. The average particle size was 12 nm and the hydroxy density was 4.4–4.6/$nm^2$. Tetraethylorthosilicate (TEOS), dibutyltin dilaurate (DBTOL), APTES, ETES, OTES and PTES were purchased from Sigma-Aldrich Co., Ltd., USA. *n*-Hexane (AR) was purchased from Tianjin Chemical Reagent Co., Ltd., China. Table 1 lists the chemical structure and molecular weight of the four coupling agents.

### 2.2. Preparation of composite membranes

Fig. 1 shows the schematic of the preparation of the modified nanosilica/PDMS composite membranes. Fig. 2 presents the reaction diagram. In step 1, a hydroxyl group at the nanosilica surface reacts with one $CH_3CH_2O$– group of silane coupling agent, forming modified nanosilica (M–$SiO_2$). In step 2, another $CH_3CH_2O$– group of the silane coupling agent reacts with a hydroxyl group at one end of PDMS precursor. In step 3, after the crosslinking agent (TEOS) is added, the left hydroxyl group at the other end of the PDMS chain reacts with one $CH_3CH_2O$– group of TEOS.

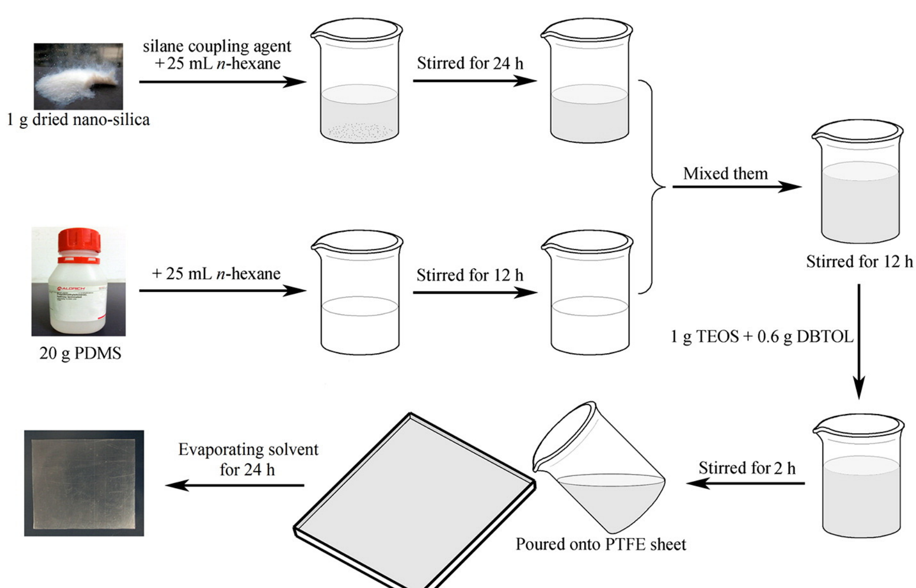



**Fig. 1.** Schematic for the preparation of modified nanosilica/PDMS composite membrane.

Download English Version:

https://daneshyari.com/en/article/5209695

Download Persian Version:

https://daneshyari.com/article/5209695

Daneshyari.com