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Permselectivity for VOC with Fluoroalkyl Methacrylate-Grafted PDMS Membrane

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ABSTRACT

The purification of ground water, which is contaminated with chlorinated organic compound such as trichloroethylene (TCE), have been extensively studied for pervaporation applications with membranes that permeate chlorinated organic compound preferentially. It is desirable to enhance the selectivity of a polydimethylsiloxane (PDMS) membrane for chlorinated hydrocarbons. In this study, the PDMS membranes were improved by graft polymerization of 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA), which has the effect of increasing the selectivity for chlorinated VOCs. The PDMS membranes were by a ^{60}Co or plasma. The grafted membranes by a ^{60}Co had a microphase-separated structure, i.e., a separated structure of PDMS and grafted HDFNMA. The degree of grafting on the inside and reverse side of the plasma-grafted PDMS membranes were lower than on the surface. The solubility of VOCs for the grafted PDMS membrane was high when compared with the solubility for the PDMS membrane. The grafted PDMS membrane that had the high VOC concentrations of sorbed solution showed an excellent separation performance.

Key words: VOC, pervaporation, PDMS membrane, 1H,1H,9H-hexadecafluorononyl methacrylate, graft polymerization.

1. INTRODUCTION

The purification of ground water, which is contaminated with chlorinated organic compound such as trichloroethylene (TCE), have been extensively studied for pervaporation applications with membranes that permeate chlorinated organic compound preferentially [1-6]. Polydimethylsiloxane (PDMS) has been well known as an excellent polymer membrane material [7] by its high permeability (diffusivity) to gases and liquids.

Fluorinated polymers has also been studied as an organic aqueous mixture separation membrane application [8, 9] expected an excellent affinity to the organic compounds by its hydrophobicity [10] based on the low surface energy. In this study, we modified the PDMS membrane with fluorinated alkylmethacrylates followed ^{60}Co or plasma by irradiation in order to maintain high diffusivity and increase a chlorinated hydrocarbon partition coefficient into the membrane.

2. EXPERIMENT

2.1 Graft polymerization of HDFNMA by a ^{60}Co source

PDMS membranes of 7 × 7cm and HDFNMA solution in ampoules were degassed and sealed under vacuum simultaneously. The ampoules were then irradiated at dose rates of 0.1 Mrad/h for 5h from a ^{60}Co source at 25°C.

2.2 Graft polymerization of HDFNMA by plasma

The membrane was treated by 13.56MHz plasma at 10 W for 180s under vacuum. The membranes were then contacted with HDFNMA in the liquid phase at 60°C. After the polymerization stopped, the membranes were rinsed in acetone overnight to remove the homopolymers and any nonreacted monomers, then dried for 48 hours in an evacuated vessel.

The degree of grafting was calculated as

$$\text{Degree of grafting}(\%)=(W_1-W_0)/W_0\times 100 \quad (1)$$

where W_0 and W_1 denote the weight of the PDMS membrane and the grafted PDMS membrane, respectively.

2.3 Characterization of the grafted Membrane

The grafted PDMS membranes were characterized by X-ray photoelectron spectroscopy (XPS).

2.4 Pervaporation Experiment

Chlorinated hydrocarbon aqueous feed solutions were prepared by mixing the chlorinated hydrocarbon with pure water at a concentration below the saturation of chlorinated hydrocarbon solubility. In pervaporation measurement, the permeation side of the cell was kept below 10 mmHg, at 25 °C.

3. RESULTS AND DISCUSSION

3.1 Characterization of the grafted Membrane

The surface morphologies of the grafted membranes were analyzed by XPS spectra, and characterized in Table I. The ratio of fluorine, oxygen, carbon, and silicon atoms were analyzed and calculated for a few nm beneath the surface of membrane at 30° and 90° photoelectron emission angle. In this spectrum, the composition of atoms are determined up to 4.5 and 9 nm deep from the surface at the photoelectron emission angle of 30° and 90°, respectively [11].

Gamma-grafted PDMS membrane:

The ratio of the fluorine atom at 30° was almost the same to that at 90° on the surface of the membrane. The ratio of the fluorine atom by XPS spectra corresponded to that calculated by the degree of grafting. For the structure of the grafted PDMS membrane, the layer of poly(HDFNMA) was not formed on the surface of the PDMS membrane. The poly(HDFNMA) domains were dispersed into the entire PDMS membrane homogeneously by irradiation. The domains of poly(HDFNMA) in the grafted PDMS membranes had a particle size which scattered natural light, and the domains were dispersed homogeneously as expected.

Plasma-grafted PDMS membrane:

On the surface of the PDMS membrane exposed to the air after irradiation, the O/Si and C/Si ratios increased. The surface of the membrane was oxidized by oxygen or water vapor in the air. The F/Si and C/Si ratios on the surface of the grafted PDMS membrane increased due to the graft polymerization of HDFNMA by the plasma. The F/Si, O/Si and C/Si ratios on the reverse side of grafted PDMS membranes were lower than on the grafted surface. After the irradiation, the degassed HDFNMA was placed in the reactor, and the PDMS membranes were soaked and grafted. The graft polymerization was promoted in the grafted PDMS membrane. The quantity of the radicals on the inside and reverse side of the grafted PDMS membrane was lower than that on the surface. Hence, the degree of grafting on the inside and reverse side of the grafted PDMS membrane was lower than that on the surface.

Table I. Fluorine to silicon, oxygen to silicon, and carbon to silicon atomic ratios for surface of PDMS and grafted PDMS membranes by XPS analysis.

Grafted membranes	Electron emission angle	Atomic ratio F / Si	O / Si	C / Si	F / Si calculated by degree of grafting
Gamma-grafted PDMS membrane	30°	5.54	1.41	3.61	3.39
(modified face)	90°	5.62	1.83	4.07	
Plasma-grafted PDMS membrane	30°	0.110	1.80	3.34	-
(modified face)	90°	0.101	2.15	4.82	
(reverse side)	30°	0.0288	1.29	1.83	
	90°	0.0268	1.36	1.80	
PDMS	90°	-	1.44	1.87	-

F / Si: Fluorine atomic ratio (%) / Silicon atomic ratio (%).

O / Si: Oxygen atomic ratio (%) / Silicon atomic ratio (%).

C / Si: Carbon atomic ratio (%) / Silicon atomic ratio (%).

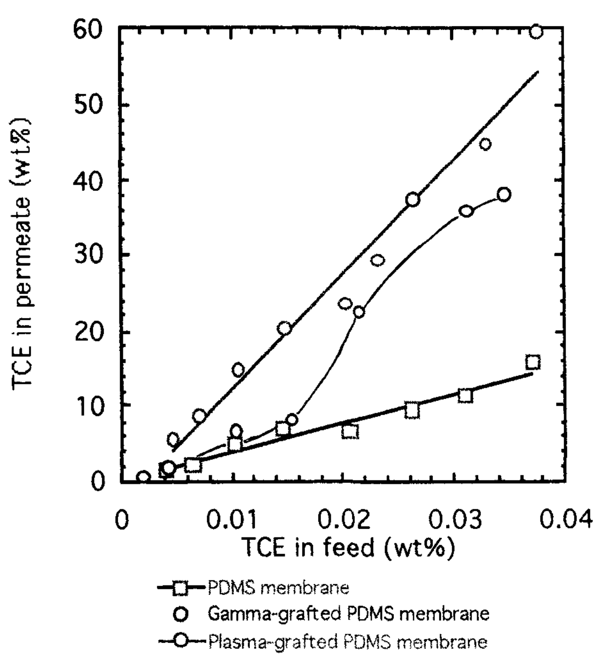

Fig. Pervaporation of TCE/Water mixtures through PDMS membrane and grafted PDMS membranes.

3.2 Pervaporation Experiment

Gamma-grafted PDMS membrane:

For the grafted PDMS membrane, especially that irradiated in 100wt% HDFNMA for 5h, the water flux was further decreased with increasing feed concentration. The TCE flux was increased with increasing feed concentration and especially for the membrane irradiated in 100wt% HDFNMA for 5h, the tendency was significant. The relationships between the TCE concentration in the feed and permeate are shown in Fig. for the grafted PDMS membranes. The TCE concentration in the permeate was increased with increasing in the feed concentration, and especially when the membranes was irradiated in 100wt% HDFNMA for 5h, the increase was significant. In the grafted PDMS membrane, the best separation performance was shown, due to the introduction of the hydrophobic polymer, poly(HDFNMA).

Plasma-grafted PDMS membrane:

For the PDMS and the grafted PDMS membranes, the water flux decreased with increasing feed TCE concentration. The TCE flux increased with increasing feed concentration. For the grafted PDMS membranes, this tendency was significant. The total flux consisted of TCE and water for the grafted PDMS membrane increased with increasing feed concentration while the total flux for PDMS membrane decreased with increasing feed concentration. The PDMS membranes that grafted with HDFNMA and simultaneously oxidized by plasma-graft polymerization, had a high selectivity for TCE. The relationships between the TCE concentration in the feed and permeate are shown in Fig. for the grafted PDMS membranes. For all the membranes, the TCE concentration in the permeate increased with increasing feed concentration, and for the grafted PDMS membranes, the tendency was significant. The relationship between the feed concentration and the permeate concentration was observed to be linear. In the grafted PDMS membrane, the best separation performance was, due to introducing the hydrophobic polymer, poly(HDFNMA).

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