

## 폴리디메틸실록산-폴리비닐피롤리돈 빗살 공중합체 합성, 모폴로지 및 투과성질

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### Synthesis, Morphology and Permeation Properties of poly(dimethyl siloxane)-poly(1-vinyl-2-pyrrolidinone) Comb Copolymer

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**요약:** 인위적인 온실 가스 배출로 인한 자연 재해가 증가하고 있으며 이로 인해 기체 분리막의 개발이 촉진되게 되었다. 이산화탄소(CO<sub>2</sub>)는 지구 온난화의 주요 원인이다. 고유의 유연성을 가지는 유기 고분자 막은 기체 분리막의 좋은 후보군 중 하나이며, 이 중 이산화탄소에 대한 높은 확산도를 가지고 있는 폴리디메틸실록산(PDMS)은 유망한 소재이다. 또한, 폴리비닐피롤리돈(PVP)은 이산화탄소에 대한 높은 용해도를 가지고 있는 고분자로 기체 분리막에 활용될 수 있다. 따라서 본 연구에서는 용이한 조건에서 간단한 단일 반응 자유 라디칼 중합에 의하여 다양한 조성의 폴리디메틸실록산-폴리비닐피롤리돈(PDMS-PVP) 빗살 공중합체를 합성하였다. PDMS와 PVP로 합성된 공중합체는 FTIR을 통해 분석하였다. 고분자의 형태학 및 열적 특성은 TEM, TGA 및 DSC를 통하여 분석하였다. PDMS-PVP 빗살 공중합체를 다공성 폴리설폰 지지체 위에 코팅하여 복합막을 제조했으며, 제조한 복합막의 기체 투과 특성을 분석하였다. 그 결과 이산화탄소의 투과도 및 이산화탄소/질소 선택도가 각각 140.6 GPU 및 12.0에 도달하였다.

**Abstract:** The increasing number of natural disasters resulting from anthropogenic greenhouse gas emissions has prompted the development of a gas separation membrane. Carbon dioxide (CO<sub>2</sub>) is the main cause of global warming. Organic polymeric membranes with inherent flexibility are good candidates for use in gas separation membranes and poly(dimethyl siloxane)(PDMS) specifically is a promising material due to its inherently high CO<sub>2</sub> diffusivity. In addition, poly(vinyl pyrrolidone)(PVP) is a polymer with high CO<sub>2</sub> solubility that could be incorporated into a gas separation membrane. In this study, poly(dimethyl siloxane)-poly(vinyl pyrrolidone)(PDMS-PVP) comb copolymers with different compositions were synthesized under mild conditions via a simple one step free radical polymerization. The copolymerization of PDMS and PVP was characterized by FTIR. The morphology and thermal behavior of the produced polymers were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Composite membranes composed of PDMS-PVP on a microporous polysulfone substrate layer were prepared and their CO<sub>2</sub> separation properties were subsequently studied. The CO<sub>2</sub> permeance and CO<sub>2</sub>/N<sub>2</sub> selectivity through the PDMS-PVP composite membrane reached 140.6 GPU and 12.0, respectively.

**Keywords:** comb copolymer, gas separation, composite membrane, permeance, selectivity

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## 1. Introduction

The use of fossil fuels to meet the growing energy demand has led to ever-increasing CO<sub>2</sub> emissions. Although there is growing awareness regarding the negative effects of greenhouse gas emissions and the use of alternative renewable energy resources, the control of CO<sub>2</sub> release into the environment is another strategy to mitigate the impacts of global warming. Gas separation by a polymeric membrane is an important process that has the potential to control the direct release of environmental contaminating gases[1-5].

Poly(dimethyl siloxane) (PDMS) is a useful polymer that can be applied as a gas separation membrane due to its well-known affinity towards CO<sub>2</sub> gas[6-12]. The presence of siloxane bonds in PDMS imbues good thermal stability, lower glass transition properties, and hydrophobicity to the resulting material. A significant advantage of using PDMS-based membranes is its high permeance for many gases, but due to its low mechanical strength and poor selectivity, requires further modification. The polymer backbone has previously been modified and in some cases copolymerized with polyimide, polyamide, polycarbonate, or polyurethane to enhance its gas separation and mechanical properties [13-17]. Poly(vinyl pyrrolidone)(PVP) is another class of polymer which is commonly used in everyday products such as paint, coating, and contact lenses. The presence of lone pairs on the amide group enhances its affinity for CO<sub>2</sub>. Poly(vinyl chloride) can be grafted with PVP to enhance the gas permeation properties of the resulting free standing membrane[18].

The poor mechanical strength of PDMS can be solved by another method which involves fabricating a composite membrane with a microporous substrate, single layer, or copolymer[19,20]. There are several types of substrates such as cellulose acetate, polyamide, polyacrylonitrile, and polyether sulfone that can support the thin film of PDMS or its copolymers[21,22]. PDMS-b-PI-PDMS triblock copolymers have been linked to functionalized PDMS which is then cast onto

porous polyacrylonitrile substrate[23].

In this work, soft PDMS is copolymerized with hard PVP by a simple one step free radical polymerization to increase the mechanical properties and gas separation performance of the resulting membrane. The PDMS-PVP comb copolymer was characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The PDMS-PVP copolymer is coated onto a microporous polyether sulfone membrane and its gas permeation properties studied.

## 2. Experimental

### 2.1. Materials

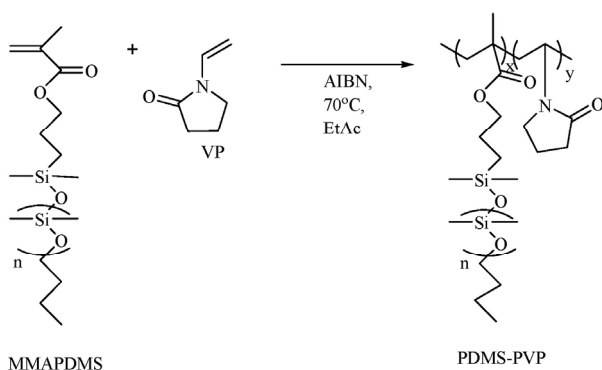
Monomethacryloxypropyl terminated polydimethyl siloxane (MMA PDMS, 120-250 cSt, M<sub>w</sub> = 10,000) was procured from Gelest, Inc. 1-Vinyl-2-pyrrolidinone (VP) and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich. Ethyl acetate and ethanol was obtained from DUCSAN, Korea.

### 2.2. Synthesis of the PDMS-PVP comb copolymer

Different ratios of MMA PDMS and VP were mixed in 100 mL of ethylacetate in the presence of AIBN, a free radical initiator. All the reactants were mixed in a round bottom flask placed on a magnetic stirrer. The mixture was nitrogen purged for approximately 30 min and the temperature of the oil bath was raised to 70°C. The reaction was performed for 24 h and then cooled to room temperature. The product of the reaction was then precipitated in diethyl ether, filtered and the product was dried in an oven. Different copolymers of PDMS-PVP with PDMS : PVP ratios of 1 : 0.5, 1 : 1, 1 : 2, and 1 : 3 were synthesized by changing the amount of constituents added.

### 2.3. Preparation of the PDMS-PVP composite membrane

Solutions of approximately 20 wt% PDMS-PVP comb copolymers in ethanol were prepared. The polymer solution was coated onto a microporous poly-



**Fig. 1.** Synthesis of the PDMS-PVP comb copolymer.

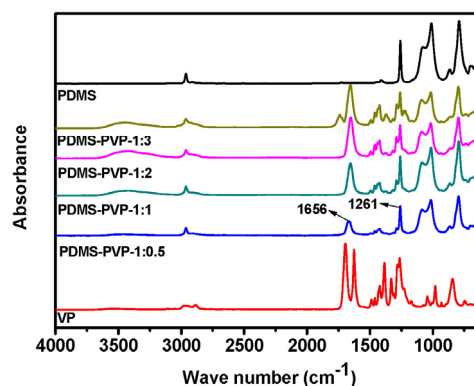
sulfone substrate (average pore size of 0.5  $\mu\text{m}$ , Toray Chemical Inc.) by an RK control coater (Model 101, Control RK Print-Coat Instruments Ltd., UK). The fabricated composite membrane was then dried in a vacuum oven at 80°C for 24 h.

#### 2.4. Gas permeation measurements

Gas permeation measurements were conducted using a gas separation apparatus provided by Airrane Co. Ltd (Korea). The measurements were performed using the constant pressure/variable volume method described in detail in our previous studies[24-26]. The permeance of each pure gas was calculated using the gas permeance and membrane thickness, and the membrane selectivity was defined as the ratio of the permeabilities of the gases.

#### 2.5. Membrane characterization

Intermolecular interactions were investigated using an Excalibur series FT-IR instrument (Digilab Co., Hannover, Germany) in the frequency range of 4000-500  $\text{cm}^{-1}$ . For the FT-IR measurements, the PEDOT-PSS solution was cast onto a glass dish and dried in a vacuum oven overnight. The dried PEDOT-PSS film was scraped from the glass dish and used for the measurements. The morphology of the membranes was examined using a field-emission scanning electron microscope (FE-SEM, SUPAR55VP, Carl Zeiss, Germany). TEM images were obtained using a Zeiss Libra120 operating at 120 kV. To prepare the TEM samples, polymeric solutions were drop-cast onto a standard copper



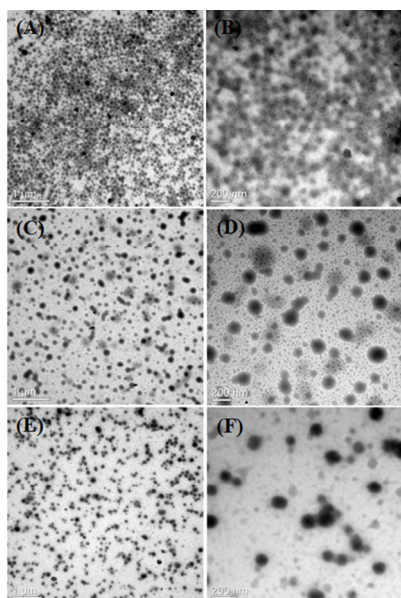
**Fig. 2.** FT-IR spectra of neat PDMS, VP, and PDMS-PVP comb copolymers with various ratios.

grid and measured without staining. DSC measurements (DSC8000, Perkin Elmer, USA) were performed to analyze the structure and thermal properties of the polymers at a heating rate of 10  $^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. The thermal stability of the copolymer was investigated by thermogravimetric analysis (TGA, Q50, TA Instruments), at a heating rate 10  $^\circ\text{C}/\text{min}$  under nitrogen from 50 to 700°C.

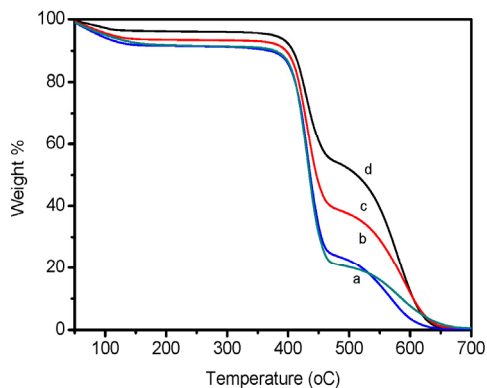
### 3. Results and Discussion

PDMS-PVP was synthesized by a one step free radical polymerization process under mild conditions in ethyl acetate, as presented in Fig. 1. The chemical linking between PDMS and PVP was characterized by FT-IR and presented in Fig. 2. The carbonyl band from the amide group in PVP gives rise to the peak at 1656  $\text{cm}^{-1}$ . The binary band in the vinyl pyridine is merged into one band after the formation of the PDMS-PVP copolymer. The Si-CH<sub>3</sub> peak of PDMS is observed at 1261  $\text{cm}^{-1}$  which clearly indicates the formation of the PDMS-PVP comb copolymer.

Fig. 3 shows the results of the morphological studies of the PDMS-PVP comb copolymer by TEM. Clear microphase separation morphology can be seen with the dark phase corresponding to the PDMS domain and the bright phase corresponding to the PVP[27,28]. The image contrast is because the electron density of the silicon atoms present in PDMS is higher than its PVP



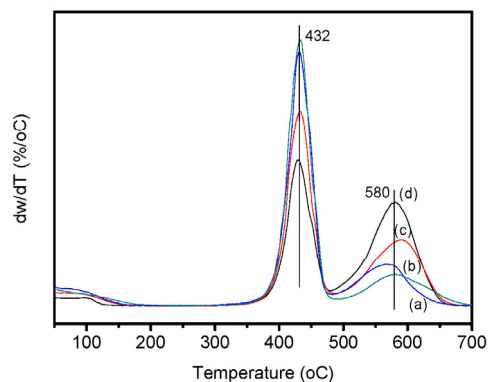
**Fig. 3.** TEM images of (a, b) PDMS-PVP (1 : 0.5), (c, d) PDMS-PVP (1 : 1) and (e, f) PDMS-PVP (1 : 2) comb copolymers.



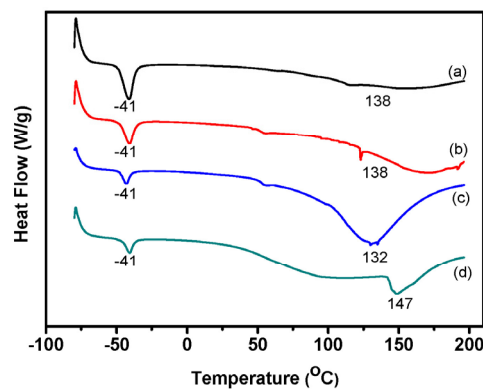
**Fig. 4.** TGA curves of (a) PDMS-PVP (1 : 0.5), (b) PDMS-PVP (1 : 1), (c) PDMS-PVP (1 : 2) and (d) PDMS-PVP (1 : 3).

counterpart. The density of the dark phase is highest for PDMS-PVP (1 : 0.5), indicating that the ratio of PDMS was the highest of the three prepared copolymers. The size of the dark phase is smallest for the PDMS-PVP comb copolymers with higher PDMS ratios along with smaller micellar size.

Fig. 4 shows the TGA analysis of the PDMS-PVP comb copolymers. The thermal stability of the copolymer increases when the proportion of the hard PVP domain is higher in the copolymer. PDMS-PVP (1 :



**Fig. 5.** DTA curves of (a) PDMS-PVP (1 : 0.5), (b) PDMS-PVP (1 : 1), (c) PDMS-PVP (1 : 2) and (d) PDMS-PVP (1 : 3).



**Fig. 6.** DSC curves of (a) PDMS-PVP (1 : 0.5), (b) PDMS-PVP (1 : 1), (c) PDMS-PVP (1 : 2) and (d) PDMS-PVP (1 : 3).

0.5) has the lowest and PDMS-PVP (1 : 3) has the highest stability. The degradation of the polymer starts at approximately 400°C and peaks at 430°C. The presence of the two domains in the PDMS-PVP comb copolymer is clearly visible from the two different degradation profiles. The second degradation starts at approximately 500°C and peaks at 580°C which is likely due to the PVP hard domain.

Fig. 5 shows the differential thermal analysis (DTA) of the PDMS-PVP copolymers. It clearly indicates two peak degradation temperatures of PDMS and PVP at 432 and 580°C, respectively, due to the different thermal stability of the domains. Fig. 6 shows the results of the differential scanning calorimetry (DSC) characterization of the PDMS-PVP copolymers. The presence

**Table 1.** Gas Permeance and Ideal Selectivity of Selectivity (CO<sub>2</sub>/N<sub>2</sub>) through the PDMS-PVP Comb Copolymer Membranes

Membrane	N <sub>2</sub> Permeance (GPU)	CO <sub>2</sub> Permeance (GPU)	Selectivity (CO <sub>2</sub> /N <sub>2</sub> )
PDMS-PVP (1 : 05)	11.7	140.6	12.0
PDMS-PVP (1 : 1)	5.2	34.9	6.7

of two glass transition temperatures ( $T_g$ s) indicates microphase-separated structure of the PDMS-PVP copolymers, which is consistent with the above TEM analysis. The increase in the hard PVP domain content in the copolymer might increase the chain stiffness. This value is correlated with the gas separation properties of the copolymer, which is discussed in the next section.

The gas separation properties of the PDMS-PVP comb copolymer are shown in Table 1. The PDMS-PVP (1 : 0.5) comb copolymer shows the highest CO<sub>2</sub> permeance of 140.6 with a CO<sub>2</sub>/N<sub>2</sub> selectivity of 12. The CO<sub>2</sub> permeance decreased by a factor of 4 and the selectivity was halved when the PVP concentration was doubled in the PDMS-PVP comb copolymer. It has been reported that when the proportion of the hard urethane segment increases in the PDMS/poly(propylene oxide) urethane membrane, the gas permeance and selectivity decreased[29]. The increase in the PVP content with a higher  $T_g$  is another factor that explains the decrease in the permeance of the copolymer.

#### 4. Conclusion

A series of PDMS-PVP comb copolymers were synthesized by one-pot free radical polymerization. The copolymerization of PDMS and PVP was characterized by FTIR spectroscopy. The thermal stability and glass transition temperature of the PDMS-PVP copolymer increased with higher percentages of the PVP domains in the comb copolymer. The soft PDMS domain and the hard PVP domain showed two distinct degradation profiles, showing a clear difference in their thermal stability. The increase in the proportion of PVP domains in the copolymer could be determined from their phase separation properties. The PDMS-PVP (1 : 0.5) comb copolymer with the least amount of hard PVP

chains showed the best CO<sub>2</sub> permeance and CO<sub>2</sub>/N<sub>2</sub> selectivity.

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