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Research Article

Sorption Behaviour of Inorganic Material Filled-PDMS Films in Ethanol, Butanol, Acetone and Water

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Abstract

The pervaporation method in which the transport mechanism through a nonporous membrane is explained by the solution-diffusion model can be used for the separation of water-organic and organic-organic mixtures. The sorption behaviour of a polymeric membrane plays important role in membrane transport, depending on the solvent and polymer properties. Since the membrane itself is the key component in the pervaporation method, as with all other membrane processes, it is necessary to determine suitable membrane material that can selectively separate at least one component from a liquid mixture. Ethanol, butanol and acetone are widely used in many industrial applications. PDMS is one of the polymers that is frequently used in the recovery of organics from organic-water mixtures or the separation of organic-organic mixtures. PDMS gives high chain mobility, low mechanical resistance and low selectivity values. For this reason, its properties need to be improved. In this study, unfilled PDMS, PDMS/TiO_2, PDMS/NaY and PDMS/5A mixed matrix films were prepared, and the sorption behaviours of prepared PDMS films in different chemical substances at temperatures of 30,40 and 50°C were investigated.

Keywords: Polydimethylsiloxane, Membrane, Mixed matrix, Sorption.

İnorganik Malzeme Dolgulu PDMS Filmlerin Etanol, Bütanol, Aseton ve Su İçindeki Sorpsiyon Davranışı

Öz

Gözeneksiz bir membran boyunca taşınım mekanizmasının çözelti-difüzyon modeli ile açıklandığı pervaporasyon yöntemi, su-organik ve organik-organik karışımların ayrılmasında kullanılabilmektedir. Polimerik bir membranın sorpsiyon davranışı, çözücü ve polimer özelliklerine bağlı olarak, membran taşınımında önemli bir rol oynar. Diğer tüm membran proseslerinde olduğu gibi pervaporasyon yönteminde de membran anahtar bileşen olduğundan, sıvı karışımdan en az bir bileşeni seçici olarak ayırabilen uygun membran malzemesinin belirlenmelidir. Etanol, bütanol ve aseton birçok endüstriyel uygulamada yaygın olarak kullanılmaktadır. PDMS, organik-su karışımlarından organiklerin geri kazanılmasında veya organik-organik karışımların ayrılmasında sıklıkla kullanılmaktadır. PDMS, yüksek zincir hareketliliği, düşük mekanik direnç ve düşük seçicilik değerleri verdiğinden özelliklerinin iyileştirilmesi gerekmektedir. Bu çalışmada dolgusuz PDMS, PDMS/TiO_2, PDMS/NaY ve PDMS/5A karışık matris filmler hazırlanmış ve PDMS filmlerin 30,40 ve 50°C sıcaklıklarda farklı kimyasal maddelerdeki sorpsiyon davranışları incelenmiştir.

Anahtar Kelimeler: Polidimetilsiloksan, Membran, Karışık matris, Sorpsiyon.

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1. Introduction

The pervaporation method is widely used as a potential alternative separation process for the removal of water from organic-water mixtures, the recovery of organics from water-organic mixtures and the separation of organic-organic mixtures. Solvent dehydration using hydrophilic polymeric membranes is among the first commercial applications of the pervaporation method.

Pervaporation is an effective membrane separation method in solvent recovery or solvent purification applications. In the pervaporation method, separation is carried out using a non-porous membrane. In this method, which is based on mass transfer across the membrane, the feed mixture is contacted with one side of the membrane and the permeate taken in the vapor phase is condensed on the other side of the membrane (Pereira S.S., 2010; Huang, 1991; Feng, 1997; Lipnizki, 2001). Transport across the membrane can be explained on the base of solution-diffusion model. Therefore, the solubility of different chemical substances in the membrane provides important information regarding transport phenomenon across the membrane (Jyoti, 2015).

In the pervaporation process, polymeric non-porous membranes are used,. The transport across the membrane matrix consists of thermodynamic and kinetic parts. The thermodynamic part indicates the solubility of the component in the membrane material, while the kinetic part refers to its diffusion across the membrane. In addition to the interactions of the components in the mixture with each other, they will also interact with the polymer-based membrane. Therefore, the movement of one component will affect the movement of the other component across the membrane (Jyoti, 2015; Mulder, 1985).

The solution-diffusion model is a widely used to describe the transport mechanism across dense polymer membrane. In this model, the transport of a component in the mixture consists of three consecutive steps (Jyoti, 2015; Mulder, 1985): a) sorption on feed side of the membrane, b) diffusion across the membrane, and c) desorption to the vapor phase on permeate side of the membrane.

Based on solution-diffusion, the separation performance of the membrane can be improved by increasing solubility selectivity and/or diffusion selectivity considering the chemical affinity and interaction of the component to be separated with the polymer-based membrane (Ong, 2016; Mulder M. S., 1986).

The use of hydrophobic membranes is the basic approach for the recovery of organic compounds from water-organic mixtures. High-value products and aroma compounds can be separated by the pervaporation method, which can be used as hybrid processes with traditional membrane separation processes. One of the most used polymeric materials for the separation of organic components is polydimethylsiloxane (PDMS). PDMS is a hydrophobic polymer with a very low glass transition temperature (Tg ≈ -125°), low chemical reactivity, low surface free energy and a flexible chain structure. High permeability values against organic substances can be obtained and it is often preferred for the recovery or removal of organic compounds (Wolf, 2018; Jyoti, 2015; Rezakazemi, 2015). However, PDMS membranes generally give low selectivity values due to their high chain mobility. Therefore, its structural properties need to be improved in order to control adsorption and membrane swelling (Tanaka, 2010). The incorporation of inorganic materials such as zeolite into the polymer matrix can improve membrane performance (Senol, 2021; Kilic, 2021).

In the present study, pristine PDMS, PDMS/TiO_2, PDMS/NaY, and PDMS/5A films were prepared using nano-sized TiO_2, zeolite NaY, and zeolite 5A. Sorption experiments were carried out at 30°C, 40°C, and 50°C to describe the sorption equilibrium behavior in pure water, ethanol, acetone, and butanol (Kilic, 2021).

2. Material and Method

2.1. Material

Zeolite NaY and 5A, and nano-sized TiO_2 used in this study were supplied from Sigma-Aldrich and Nanograf corp., respectively. Tetrahydrofuran was supplied from Merck, while acetone, ethanol, and butanol were supplied from JT Baker. Polydimethylsiloxane and its crosslinker were supplied from Ravago Petrochemicals Inc.

2.2. Preparation of PDMS Films

Zeolite NaY and 5A, and nano-sized TiO_2 were reactivated in a furnace at 300 °C for 4 hours before use. Then, a certain amount of inorganic materials was added to tetrahydrofuran and the mixture obtained was kept in an ultrasonic cleaner to achieve homogenization. The mixture of inorganic materials-solvents was added to PDMS, which was mechanically stirred at a low rate, at 3-minute intervals five times. PDMS and inorganic materials were stirred for 1 hour. The content of inorganic materials in the polymer-based solvent is 10% by weight. After stirring, the cross-linker was added to the solution at a ratio of 10:1 by weight (PDMS: cross-linker), and the mixture was stirred for another 30 minutes. The solution prepared was poured into Petri plates and scraped after being heat-treated in a drying oven at 100°C for 1 hour. Except for pre-treatment of the additive and its addition to the solution, similar steps were performed to prepare pristine PDMS films. The thickness of the films prepared was in the range of 300-400 µm. (Keskin, 2021; Kilic, 2021).

2.3. Sorption Experiments

In the sorption experiments, after weighing the dry weights of the dense PDMS, PDMS/TiO_2, PDMS/NaY and PDMS/5A films, they were immersed in sealed bottles containing pure water, ethanol, acetone and butanol, and kept in an oven at 30°C, 40°C and 50°C. The weights of the films were weighed every day until the sorption equilibrium was reached. The percentage of sorption was calculated using the following equation:

$$Sorption, \% = \frac{w_s - w_d}{w_d} \cdot 100 \qquad (1)$$

where w_s and w_d, is the equilibrium weight of the film and the dry film, respectively.

3. Results and Discussion

3.1. Sorption Results

The sorption behavior of the pristine PDMS, PDMS/ TiO_2, PDMS/NaY, and PDMS/5A films in pure ethanol, acetone, butanol, and water at different temperatures are shown in Figures 1-4.

From sorption results, it is obvious that the sorption values of acetone and butanol were higher for all films. Sorption values indicate that the films sorb the pure chemical substances in the following descending order: acetone > butanol> ethanol > water. With reference to the values of solubility parameters given in Table 1, it can be seen that they are consistent with this order.

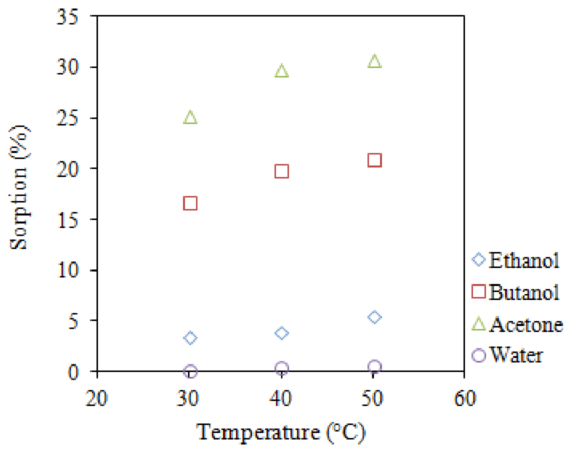

Figure 1. Sorption behavior of pristine PDMS films in pure chemical substances at different temperatures.

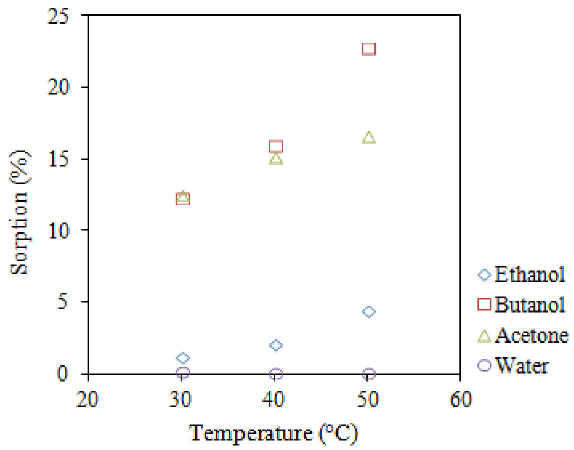

Figure 2. Sorption behavior of PDMS/NaY films in pure chemical substances at different temperatures.

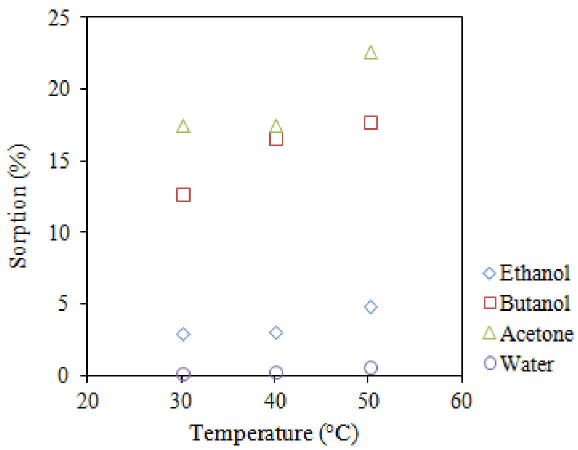

Figure 3. Sorption behavior of PDMS/TiO_2 films in pure chemical substances at different temperatures.

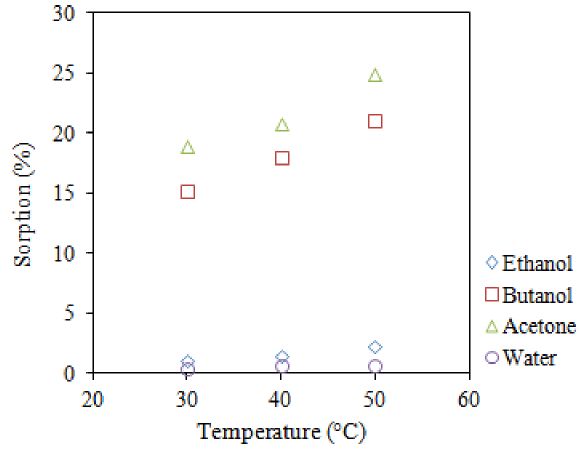

Figure 4. Sorption behavior of PDMS/5A films in pure chemical substances at different temperatures.

Table 1. Solubility parameters of chemical substances and PDMS (Nijhius, 1993; Mulder, M.S., 1986; Barton, 1975)

	Solubility parameter, cal$^{1/2}$cm$^{-3/2}$			
Component	**δ**	**δ_d**	**δ_p**	**δ_h**
Ethanol	12.7	7.7	4.3	9.5
Butanol	11.4	7.8	2.8	7.7
Acetone	9.9	7.6	5.1	3.4
Water	23.4	7.6	7.8	20.7
PDMS	8.1	7.8	0.05	2.3

Sorption values of pure PDMS, PDMS/ TiO_2, PDMS/NaY, and PDMS/5A films at 30°C, 40°C, and 50°C are given in Figures 5-7, respectively. It can be evidently seen from Figures that the sorption values increase with the increase in temperature due to increase in thermal motion of the polymer chain, and that the prepared PDMS films are selective to butanol and acetone. Sorption results are in agreement with the solubility parameter values given in Table 1.

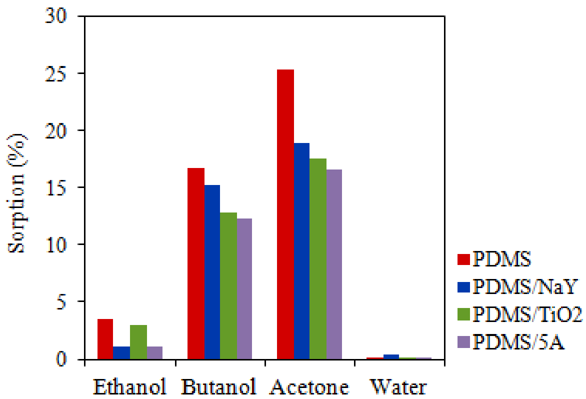

Figure 5. Comparison of sorption behavior of PDMS films in different pure chemical subtances at 30°C

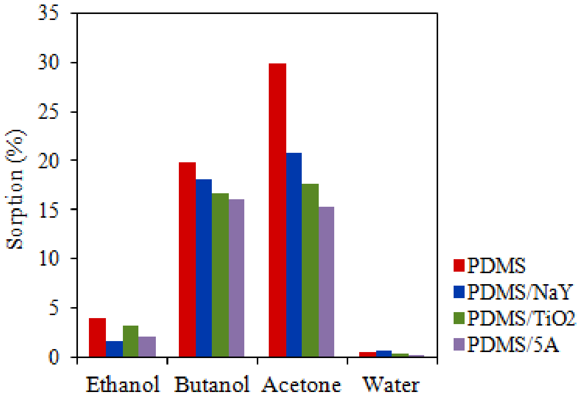

Figure 6. Comparison of sorption behavior of PDMS films in different pure chemical subtances at 40°C

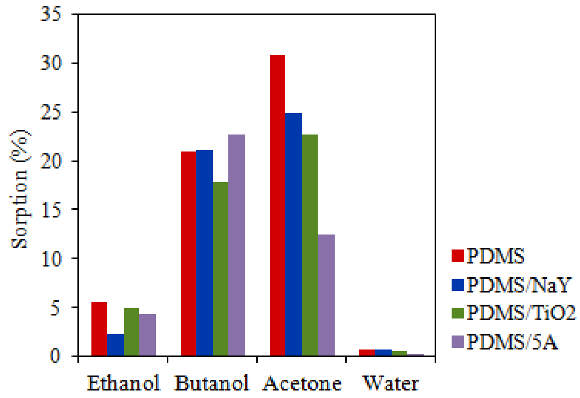

Figure 7. Comparison of sorption behavior of PDMS films in different pure chemical subtances at 50°C

4. Conclusions and Recommendations

Polydimethylsiloxane is an important polymer used in many engineering areas from electronics, sensor, and adhesive applications to membrane and biomedical applications. However, as PDMS has a high chain mobility resulting from its flexible structure, it gives low values of membrane selectivity (Senol, 2021; Kilic, 2021). For this reason, filled PDMS films were prepared using zeolite NaY, zeolite 5A and nanosized TiO_2 to combine the properties of different inorganic materials and polymer. Since the transport phenomenon in the pervaporation method is mainly explained on the base of solution-diffusion model, the sorption behavior of the prepared PDMS films in pure ethanol, butanol, acetone, and water was investigated. Sorption results show that the prepared filled-PDMS films are promising for the separation of acetone and butanol from different binary mixtures.

5. Acknowledge

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