

Applications of Polyurethane-Based Membranes in Pervaporation Separations*

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Pervaporation is a new membrane separation technique which enables liquid mixtures to be separated by partial vaporization through a nonporous permselective membrane. The effectiveness of the whole pervaporation process is directly related to the permeation and separation ability of the membrane that is governed by the chemical nature and structure of the membrane material. In this work novel polyurethane- and poly(urethane—urea)-based membrane materials are presented which were designed and synthesized with the aim of separating volatile organic compound/water and organic/organic mixtures. The programming of the polyurethane molecular structure was performed with respect to the particular separation requirements and realized at the synthesis stage by using different reagents in various mole ratios. The obtained polyurethane-based membrane materials were examined in the separation of liquid mixtures of commercial interest, like hydrocarbons mixtures with a high and a low aromatics content, MeOH/MTBE azeotropic mixture, or in the removal of benzene and chloroform from water.

Pervaporation (PV) is a membrane separation process in which a mixture of liquids being separated (feed) is in a direct contact with the surface of a nonporous polymeric membrane. The selectively permeating components of the mixture are collected in a vapour state from the other side of the membrane as a permeate due to the low pressure or a flow of an inert medium applied on the permeate side of a pervaporation cell. The driving force for this process is a difference in a chemical potential corresponding to the concentration gradient between phases on the opposite sides of the interphase barrier.

In PV processes, the transport is described by a sorption-diffusion mechanism in which permeability P of a particular component is a product of its solubility S and diffusivity D ($P = S \cdot D$). S is a thermodynamic parameter describing an amount of the component absorbed into the membrane upon equilibrium conditions and D is a kinetic parameter which determines the mobility of the component molecules in the membrane. The separation effect of the pervaporation process is achieved because of the differences in permeabilities among the components of the separated mixture. Therefore, the intrinsic properties of the membrane material which influence both the S and D are responsible for the effectiveness of the overall separation process [1].

PV techniques can be used for: i) dehydration of

organic solvents, ii) removal of organics from water, and iii) organic/organic separations. Contrary to the solvent dehydration processes which have already been successfully applied in the industrial scale, the industrial applications of other types of the pervaporation separations are still hindered due to the lack of membrane materials with a high pervaporation efficiency. This is mainly due to a poor resistance of the most of polymers in contact with aggressive organic liquid mixtures and/or their low transport parameters values. Moreover, a tailoring of the membrane material for each separation is necessary for both the ii) and iii) types of PV. Therefore, the search for novel membrane-forming materials along with the investigations of their transport properties and structure seem to be the most important stage in the development of PV processes.

In recent years silicone rubber (PDMS) and copolymers thereof, copolymers of styrene, and polyether block amides (PEBA) have been reported in literature as membrane materials for the separation of organics from water [2]. For the separation of organic/organic mixtures, polyethylene, poly(ether imides), PEBA, and poly(methyl acrylate) prepared by plasma graft polymerization have been examined [3] along with some polyurethanes [4].

In this study, we present the series of new polyurethane- and poly(urethane—urea)-based mem-

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brane materials designed and synthesized by us for organic/organic and volatile organic compound (VOC)/water separations. Variations in the polymer structure, responsible for different transport properties of the resulting membranes, were achieved in the synthesis stage by applying different reagents used in various mole ratios. This work is a part of a larger program the goal of which is to correlate a polymer's structure and its transport properties so that membranes with "tailored" pervaporation behaviour could be prepared.

EXPERIMENTAL

Materials

Polyurethanes (PU) and poly(urethane—urea)s (PUU) used as membrane materials were synthesized by a two-step polyaddition method, in DMF solution. In the first step of this method, a prepolymer is created by end-capping of a selected macrodiol with a diisocyanate being in excess in the reaction mixture. This prepolymer is then extended with an appropriate low-molecular mass diol or diamine. The details of the synthesis and the physicochemical characteristics of some of the polyurethanes synthesized are presented elsewhere [5].

Membrane Preparation

Nonporous polyurethane-based membranes of the thickness of about 100–150 μm were prepared by casting a 15 % solution of the polymer in DMF onto a glass plate followed by the solvent evaporation at 333 K for 72 h.

Pervaporation Experiments

Pervaporation experiments were performed at 298 K using a standard pervaporation cell. The downstream pressure was kept below 133.3 Pa and the permeate was collected in a trap cooled by liquid nitrogen. The permeation rate, described as normalized flux F ($\text{kg } \mu\text{m}/(\text{m}^2 \text{ h})$), was determined from the variation in the condensate mass with time and calculated for a standard membrane thickness (1 μm). The composition of the feed and pervaporate were determined by means of refractometry or gas chromatography. The selectivity α was defined as

$$\alpha = \frac{Y(1-X)}{X(1-Y)} \quad (1)$$

where X and Y are the mass fractions of the component which permeates preferentially through the membrane in the feed and permeate, respectively.

RESULTS AND DISCUSSION

The reported materials, the schematic structure of which is given in Fig. 1 can be regarded as multi-block copolymers of $(AB)_n$ type. A hard segment (A) of these copolymers is created during the reaction of a diisocyanate with a chain extender and a soft segment (B) is formed from a macrodiol.

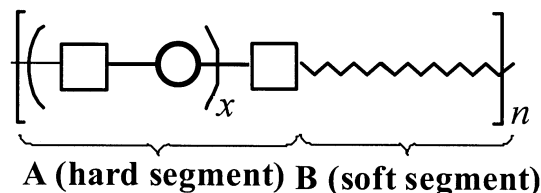


Fig. 1. Schematic representation of a polyurethane structure. \square Diisocyanate; \circ low-molecular-mass diol or diamine (chain extender); $\sim\sim$ polyetherdiol (PEt), polyesterdiol (PEs), polydienediol (PD).

Due to the thermodynamic incompatibility, the blocks undergo microphase separation resulting in a two-phase system composed of permeable, soft-segment rich domains and impermeable hard-segment domains. It has been expected and in some cases already confirmed [5] that the degree of phase separation as well as the domains' structure, size, and distribution resulting from the molecular structure of the polyurethanes can affect the pervaporation characteristics of the membrane materials. Thus, the concept of tailoring transport properties of the membrane materials presented in this work was based on a polyurethane molecular structure design which involved optimization of a chemical nature of each of the segments along with their length and content. The length and content of the hard segments can be programmed by adjusting the mole ratios of the reagents whereas the length of the soft segments can be controlled by a selection of the macrodiol relative molecular mass. In most cases, the changes applied within one segment were combined with subsequent modifications within the second one. The presented method of a membrane material optimization has been performed with regard to the requirements of a particular separation process.

Liquid Hydrocarbons Separations

The separation of close-boiling or azeotropic organic liquids by means of pervaporation requires the membrane materials which exhibit a good mechanical resistance and stability of their physical and transport properties during a long-time contact with separated media.

The refining of a crude oil into fuel involves a series of separation and conversion steps concerning com-

Table 1. Pervaporation Properties of Some PUs and PUUs in the Separations of Benzene/Cyclohexane Mixtures at 298 K

Membrane	40 mass % Benzene		Selectivity α	56 mass % Benzene		Selectivity α
	Flux/(kg $\mu\text{m}/(\text{m}^2 \text{ h})$)			Flux/(kg $\mu\text{m}/(\text{m}^2 \text{ h})$)		
	Total	Benzene		Total	Benzene	
PUU-PEs-1	6.9	5.7	6.9	25.5	22.9	5.8
PUU-PEs-2	9.8	8.0	6.6	25.0	21.7	5.3
PU-PEt-1	—	—	—	81	38.1	2.8

plex mixtures of aromatic and aliphatic hydrocarbons which are chemically different but have similar boiling points and cannot be easily separated by distillation. Depending on the fraction of aromatic compounds in the separated mixtures, the factors that have to be taken into account at the stage of the membrane material design are quite different. The most demanding task is to prepare membranes which could withstand the harmful conditions during the pervaporation of hydrocarbons mixtures with a high aromatics content. The peculiarity of this separation problem is mainly due to the ability of the aromatic hydrocarbons to strongly plasticize the membrane material that in turn causes a strong swelling of the membrane and the loss of its selectivity and durability. As it can be seen from the selectivity data given in Table 1 concerning separations of the feed mixtures varying in the benzene content, only a weak damaging effect of benzene on the pervaporation performance of the investigated membranes was observed. Moreover, polyester-based polyurethanes exhibited an acceptable selectivity and permeability that is illustrated by the pervaporation results obtained for PUU-PEs-1 and PUU-PEs-2 polyurethanes of different hard segment structure. Both the membrane materials also showed an excellent stability in the separation of benzene/cyclohexane azeotropic mixture. It should be noted that the replacement of the polyester macrodiol with the polyether one resulted in a membrane material with a much higher permeability accompanied however by a lower selectivity.

The requirements concerning membrane durability and stability can be much easier fulfilled when the membrane is designed for the separation of hydrocarbons mixture with a low aromatics content. Pervaporation performances of some of the polyurethane-based membranes selected for this kind of separation are given in Table 2. In this case, the feed of commercial interest is simulated by the model benzene/cyclohexane mixture containing 5 mass % of benzene. Table 2 shows that a transport properties modification can be achieved within a wide range of the flux and selectivity values by programming the molecular structure of the polyurethane, *i.e.* by changing M_r of a macrodiol (PET-1 < PET-3) or the length of the hard segments (PET-1 > PET-2). However, the increase in the flux value is generally accompanied by the loss of

Table 2. Pervaporation Properties of Some PUs and PUUs in the Separation of the Benzene/Cyclohexane Mixture at 298 K

Membrane	5 mass % Benzene		Selectivity α
	Flux/(kg $\mu\text{m}/(\text{m}^2 \text{ h})$)		
	Total	Benzene	
PU-PEt-1	0.3	0.25	17.4
PUU-PEt-2	10.2	2.1	5.0
PUU-PEt-3	40.3	5.8	3.2

Table 3. Pervaporation Properties of Some PUs in the Separation of the MTBE/MeOH Mixture at 298 K

Membrane	15 mass % MeOH	
	Flux/(kg $\mu\text{m}/(\text{m}^2 \text{ h})$)	Content of MeOH in permeate/mass %
	Total	
PU-PEt	0.4	100
PU-PEs	1.7	90

the membrane selectivity. The more detailed discussion on the correlation between the poly(urethane—urea)s molecular structure and their transport properties is given in [5].

Alcohol/Ether Separations

For the production of *tert*-butyl ethers (MTBE, ETBE), which can be used as fuel additives effectively enhancing its octane value, removal of alcohol from its mixture with ether by pervaporation could be an interesting alternative to the existing separation processes provided that high-performance membranes can be manufactured.

Table 3 shows the pervaporation characteristics of some of the tailor-made polyurethane-based membranes in the separation of MTBE/MeOH model mixture containing 15 mass % of MeOH. These polymers were designed by carefully choosing the macrodiol component of the reaction mixture and by ad-

Table 4. Pervaporation Properties of Some PUs in the Removal of VOC from Water at 298 K

Membrane	Benzene/Water (0.065 mass %)			Chloroform/Water (0.065 mass %)		
	Flux	Benzene in permeate	Selectivity	Flux	Chloroform in permeate	Selectivity
	kg $\mu\text{m}/(\text{m}^2 \text{ h})$	mass %	α	kg $\mu\text{m}/(\text{m}^2 \text{ h})$	mass %	α
PU PD-1	2.0 ÷ 1.4	76 ÷ 70	5300 ÷ 3900	–	–	–
PU-PD-2	2.2	59	2400	1.4	47	1360
PU-PET-1	4.0	37	1000	3.7	29	630

justing the kind and concentration of the other components. The obtained membranes were preferentially permeable to MeOH over MTBE, however, their transport properties were strongly dependent on the kind of the macrodiol used. The data given in Table 3 show that an excellent separation ability (100 % of MeOH in permeate) is exhibited by PU-PET membrane prepared from polyether-based polyurethane. On the other hand, the replacement of the polyether in a polyurethane soft segment by the polyester resulted in the more permeable membrane with slightly lower separation ability. The so far obtained pervaporation results along with the details of the polymer molecular structure give some promises for the further membrane properties optimization.

Removal of VOCs from Water

Separation of VOCs from liquid streams by pervaporation is considered to be an alternative to conventional treatment methods in water pollution reduction, groundwater cleanup or for organic recovery and reuse from industrial wastewater streams. The low energy consumption and efficiency of the membrane separation process is due to the fact that VOCs, present in small quantities in large flow streams, form nonideal solutions with water, they have a low vapour pressure and they preferentially permeate the membrane material.

The experimental data presented in Table 4 show the performance of some of the polyurethane-based membranes in the removal of benzene and chloroform

from water. Based on the results obtained so far, the polydieneurethanes (PU-PD) can be regarded as the most effective membrane materials for VOC/water separations. They exhibit excellent selectivity, especially PU-PD-1 polyurethanes with longer hard segments, which is accompanied by an acceptable permeability. The structural modifications concerning the application of the polyether instead of the polydiene macrodiol (PU-PET-1 *vs.* PU-PD-2) led to some improvement of the membrane permeability, however, at the expense of its selectivity.

The results discussed in this work indicate that polyurethanes might constitute new membrane-making materials the transport properties of which can be modified to a great extent during the synthesis to obtain the membranes with the desired transport properties.

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