다중상으로 구성된 폴리우레탄과 폴리우레탄우레아막의 증기 및 기체분리특성

하재웅, 박호범, 이영무
한양대 응용화학공학부

Vapor or Gas Transport through Polyurethane and Polyurethaneurea Membranes with Multi Phase

Jae Woong Ha, Ho Bum Park, Young Moo Lee
School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea

1. Introduction

Polyurethanes and polyurethane ureas possess excellent mechanical and physical properties, high combustion resistance, wear resistance with a broad temperature range for use, good blood and tissue compatibility. These polymers are usaually composed of multi-phase segments. Theses alternating hard and soft segment structures are suitable for many applications by imparting various properties. Particulary, segmented polyurethanes (PU) and Polyurethane ureas (PUU) are a class of thermoplastic elastomers that form multiphase structures due to the thermodynamic incompatibility between the hard and soft segments. The hard segment usually consists of an aromatic diisocyanate such as 4,4-diphenlymethane diisocyanate (MDI) extended by either a low molecular weight diol, such as 1,4-butandiol (BD), or a low molecular weight diamine. The soft segment usually consists of either a polyether or a polyester with molecular weight between 500 and 2000 Da. The hard segments, which act as fillers and crosslinks, are in a crystalline state or an amorphous glassy state; the soft segments are in a rubbery state that gives the flexibility and the elasticity. The combination of hard and soft segments provides this class of materials very peculiar properties which can be changed by controlling the chemical structure of the polymers and, equally significantly, by adjusting the multiphase structure and morphology of

the polymers during processing and other polymerization methods.

The aim of this study is to investigate the effect of mixed soft segment and/or the number of segment block in the polyurethane urea matrix on the vapor or gas permeation property and to study on the vapor or gas permeation properties of poly(dimethyl siloxane)(PDMS) based polyurethane urea. Generally, PDMS-based polyurethane shows a high degree of phase separation due to decreased compatibility of the soft and hard segment. The effect of the phase separation on the vapor or gas permeation property will be considered here. This paper will describe the synthsis of segmented polyurethane and polyurethane urea membranes with single or multi block consisiting of various soft segments and the evaluation of their transport properties such a s permeability (P), diffusivity (D), and solubility (S) of various gases.

2. Experimental

2.1. Materials

The chemicals used in this study were 4,4-diphenlymethane diisocyanate (MDI) (Aldrich Chemical Co., Milwaukee, WI, USA), amine terminated polydimethylsiloxane (PDMS) (the number average molecular weight (Mn): 900 and 1600, Shinetsu Co., Japan), hydroxyl terminated polytetramethylene oxide (PTMO) (Mn: 1000, BASF, Germany), hydroxyl terminated polyethylene oxide (PEO) (Mn: 1000, Aldrich Chemical Co., Milwaukee, WI, USA), hydroxyl terminated polypropylene oxide (PPO) (Mn: 1000, Aldrich Chemical Co., Milwaukee, WI, USA) and hydroxyl terminated propylene oxide-ethylene oxide triblock copolymer (PEO-PPO-PEO, Pluronic L-31) (Mn: 1100 and 1900, Aldrich Chemical Co., USA). 1,4-butanediol (BD) as a chain extender and dibutyltin dilaurate (DBTDL) as a catalyst were used without further purification. N,N-dimethyl formamide (DMF), tetrahydrofuran (THF) and N,N-dimethyl acetamide (DMAc) were dried over calcium hydride and then conducted fractional distillation under vacuum.

2.2. Synthesis of polyurethane and polyurethane urea

The polymers prepared in this study are classified into two categories. The one is single-block segmented copolymers having only

single soft segment denoted as S-series and the other is mixed soft segmented copolymers having two soft segments denoted as M-series. S-series are polyurethanes (S-1, S-5, S-6, S-7, S-8) and polyurethane ureas (S-2, S-3, S-4), which were synthesized in order to compare with mixed soft-segmented copolymers, and all the M-series are polyurethane ureas containing amine-terminated PDMS. Owing to the low reactivity of hydroxyl-terminated PDMS because of the solubility difference between PDMS and hard segment (-MDI-BD-), amine-terminated PDMS was used in this study instead of hydroxyl-terminated PDMS.

3. Results and discussion

3.1. Gas permeation properties

Figure 1 shows the effect of siloxane content on the permeability of N_2, O_2 and CO_2, and the selectivity of O_2/N_2 and CO_2/N_2 of PUU membranes. Permeability of all the gases increased with siloxane content in PUU membranes. The O_2/N_2 and CO_2/N_2 selectivity of PDMS containing membranes slightly decreased with increasing the PDMS content in the membrane.

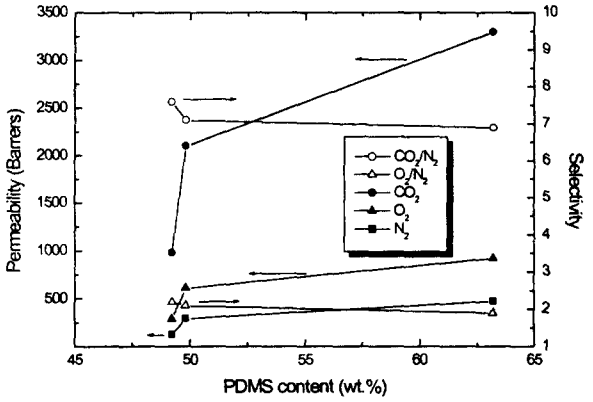

Figure 1. The effect of siloxane content on gas permeability and selectivity of PUU membranes.

3.2. Vapor permeation properties

Figure 2 shows experimentally measured steady-state pressure-normalized permeabilities of toluene vapor and N2 vs. the toluene feed concentration in the range between 0.5 and 2.5vol.% for both PTMO/PDMS based PUU membranes. The permeabilities of toluene vapor and nitrogen through PUU membranes containing mixed soft segment (PTMO/PDMS) increased with feed toluene concentration. Furthermore, the toluene vapor permeabilities of PUU membranes increased with an increase of PDMS segment in the mambrane matrix rather than with an increase of PTMO segment.

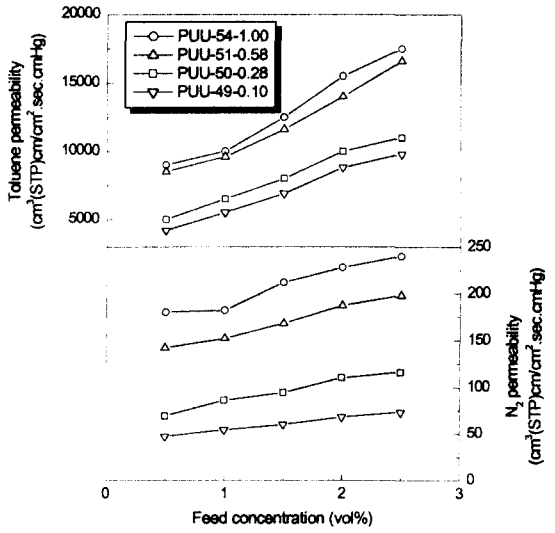

Figure 2. Feed concentration *vs.* steady-state pressure-normalized permeabilities of toluene vapor and nitrogen through PTMO/PDMS based polyurethane urea membranes.

4. Reference

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