실록산-우레탄 우레아 공중합체막을 통한 증기 및 기체의 투과거동 및 모폴로지 특성

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Vapor or Gas Transport through Siloxane-Urethane Urea Copolymer Membranes and Their Morphological Properties

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The most desirable properties of polyurethanes (PUs) and poly(urethane urea)s (PUUs) are tailor-made and thus many PUs and PUUs with different chemical characteristics and microstructures make possible to be easily prepared. Particularly, PUs and PUUs are multiblock copolymers consisting of hard segments and soft segments. The hard segments, which act as fillers and physical crosslinks, are in a crystalline state or an amorphous glassy state while the soft segments are in a rubbery state that leads to the flexibility and the elasticity. These polymers exhibit very interesting mechanical and thermal properties due to both their chemical structure and the extent of phase separation between hard and soft blocks.

Siloxane-based elastomers are high performance materials that have good oxidative and thermal stability, good gas permeability and biocompatibility. However, they exhibit very poor mechanical properties. To overcome this disadvantages, block copolymers were prepared with hard segments based on PUs, polyamides or polycarbonate-PUs, and as soft segments polybutadiene, polyisobutylene or poly(dimethylsiloxane) (PDMS)[1]. Particularly, PU block copolymers based on PDMS soft segments exhibit improved environmental stability characteristics

compared with conventional polyether or polyester soft segments. These features include improved hydrolytic stability, low moisture permeability, a wide service temperature range due to the low glass transition temperature of PDMS (-123°C), and good thermal and oxidative stability. Furthermore, PDMS-based PUs provide very hydrophobic surfaces and are of low toxicity, making these copolymers candidates for potential biomedical applications[2].

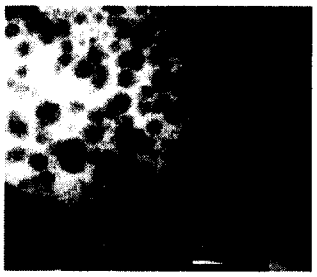
The study on the transport properties of fluids through PU and PUU membranes is especially interesting because the molecular structure of the polymer chain can be easily changed in a wide range by varying the reagents, which are generally polyisocyanates and polyhydroxyl or amino-terminated compounds. In PU and PUU membranes, the factors determining the trends in gas permeation behavior will be summarized as follows. (1) An increase in the aromatic content (hard segment) results in a decrease in the permeability coefficient. The gas permeation rate of PU membrane could be varied by controlling the ratio of hard domain to soft domain[3, 4]. (2) The gas permeation property of PU membranes is dependent on the polyols and different chain extenders [5]. Beside these factors, the most significant factors in gas permeation were the molecular weight and the kind of soft segment. The effect of chemical composition on the gas permeability might be due to the degree of phase separation and to the nature of chain packing [6]. Particularly, many studies on the polyether or polyester-based PU and PUU membranes have exhibited the above relationship between the structure and gas property of PU membranes[7-9]. However, there were a few studies on the gas permeation of PDMS-based[10] or mixed soft segment-based PU and PUU membranes.

Generally, it was known that PDMS-based PUUs show a high degree of phase separation due to low compatibility of the soft and hard segments, which caused the synthesis of PDMS-based PUs very difficult[11]. Moreover, although an increased degree of phase separation is generally thought to improve mechanical properties, PDMS-based PUs generally exhibit inferior tensile strength, extensibility, and toughness compared to conventional PUs, as reviewed[12]. The inferior mechanical properties have been attributed to an inability of the soft

segments to crystallize under strain and to poor interfacial adhesion between the hard and soft microdomains.

Therefore, in this study we intend to elucidate the structure-gas and vapor permeation property of PDMS-based PU or PUU membranes having well-phase separated structures. Particularly, the primary objective of this study was to synthesize the PDMS/polyether mixed soft segment PUUs and to investigate the gas permeation behavior through these polyphasic PUU membranes as well as the structure-property relations. In this paper, we will compare the gas and vapor permeation properties of mixed soft segment PUU membranes with those of PU and PUU membranes with various single soft segments. Also, the gas and vapor permeation properties such as diffusivity, permeability and selectivity will be discussed together with morphologic aspects.

(a) MDI/PDMS/BD



(b) MDI/PTMO/PDMS/BD

Figure 1. Transmission electron micrographs of copolymers; (a) PUU(PDMS), and (b) PUU(PDMS/PTMO) (scale bar indicates 500nm)

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