

**UV/Ozone처리된 폴리이미드실록산과
폴리우레탄우레아실록산 막소재의 기체 투과특성**

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**Gas Permeation Properties of UV/Ozone Treated
Poly(imide siloxane) and Poly(urethane urea siloxane)
Membrane Materials**

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New types of composite polymeric membranes are being pursued using UV modification technique. The development is part of a growing interest in surface modification methods where membrane enhancements are achieved through some post treatment of a membrane structure.

In many phase-separated copolymeric systems, the thermodynamic driving force for minimizing the total free energy of the system, as well as the bulk composition, block length, processing conditions, and block sequence distribution, results in preferential surface segregation of the lower surface energy constituent [1-3]. In particular, polysiloxanes are generally used as a surface modifier through blending or copolymerization with other polymers, because of the free rotatability and polarizability of the Si-O bond. Consequently, the Si-O-Si chain is able to align itself accordingly, resulting in a rich in-depth distribution of the surface in copolymers and blends. Thus, some of the most interesting and unique features of siloxane containing copolymers are associated with their surface morphology and the resultant surface properties.

Poly(dimethylsiloxane) (PDMS) has extremely low surface tension and surface energies because of its very large molar volume combined with its very low cohesive energy density and high flexibility. For linear PDMS, the surface tension is from 12 to 15 dyn/cm [4]. This is at least 10 dyn/cm lower than the surface tensions of many other polymeric systems. As a result, the air-polymer surfaces of siloxane-containing copolymers as well as their blends with other polymers are substantially enriched in the lower surface energy siloxane. To achieve the desired surface modification, only a small amount of siloxane content (1-2 wt%) is usually needed. For these reasons, poly(imide siloxane) (PIS) and poly(urethane urea siloxane) (PUUS) used in this study have an asymmetric structure consisting of a siloxane-rich top surface and an imide-rich or a urethane urea-rich bulk.

In this study, we focused on the characteristic properties of the siloxane-based copolymers and assumed a SiO_x -rich top surface in the present membranes after UV/ozone treatment. To examine this assumption regarding the surface layer of the present UV/ozone treated PIS and PUUS membranes, electron spectroscopy for chemical analysis (ESCA) was used. From ESCA, the UV/ozone treated surface layer of the membranes contains a mixture of original copolymers and silicon bonded to three or four oxygen atoms. In addition, the UV/ozone treated PIS and PUUS membranes were characterized by FT-IR spectroscopy, X-ray diffraction, and AFM.

Gas permeation measurements were also conducted using the high vacuum time-lag method at a feed pressure of 760 Torr and a feed temperature of 25°C using small molecules (He , O_2 , N_2 , and CO_2) having sizes from 2.6 to 3.64 Å. Generally, the decrease in PIS and PUUS permeability with UV treatment is largely attributed to the formation of an oxidized surface (SiO_x -rich) layer. This layer has been observed to be less than 100 nm in thickness. The cause for the variability in gas pair selectivity is less certain but it can likely be attributed to the differences in the conditions of the UV treatments, the inhomogeneous nature of the surface layer modification, and possible defects formed.

References

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