論文の要旨
題目

Morphology and gas permeation properties of thermoplastic elastomer/polyolefin polymer blend: thin film and composite hollow-fiber membrane with a three-layered structure （熱可塑性エラストマーとポリオレフィンから成る、ポリマーブレンドのモルフォロジーとガス透過特性：薄膜フィルム、三層複合中空糸膜）

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In this thesis, 1) morphology and gas permeation properties of a polymer alloy film consisted of thermoplastic elastomer and polyolefin, 2) morphology and gas permeation properties of the thin dense layer from the polymer alloy in a composite hollow-fiber membrane with a three-layered structure, and 3) degassing applications of the composite hollow-fiber membrane for liquid chemicals (IPA and developer solution in semiconductor industry) were studied in detail.

To prepare a degassing membrane, melt-spinning and stretching process is preferable and solvent process is not preferable because residual solvent leads contamination to the liquid chemicals. Thermoplastic elastomers and polyolefins are candidate thermoplastic polymer materials because of their good resistance to the liquid chemicals.

When the thermoplastic elastomer is hot-stretched to thin thickness and the film is cooled to room temperature, elastic recovery occurs and the thickness returns to its original thickness. So, restriction of the elastic recovery in thermoplastic elastomer is very important. On the other hand, when polyolefin is stretched, the polyolefin can crystallized during the stretching, which leads the lower gas permeability.

We proposed the formation of a thin dense membrane by morphology control of a polymer blend consisting of both thermoplastic elastomer and polyolefin, allowing the shortcomings of each to be mutually overcome. For this purpose, desired phase separation structure would be a bi-continuous structure (3D-network structure) of the thermoplastic elastomer and the polyolefin, in which if both components would form 3D-network structure in melt state and after cooling of the melt, the solidification of the polyolefin component would occur and the elastic recovery would be constrained.

In this study, MK-polymer material, which is a polymer blend of polystyrene-block-poly(ethylene butylene)-block-polystyrene triblock copolymer (SEBS) as a thermoplastic elastomer with polyolefins (Ethylene-ethylacrylate random copolymer (EEA) and Ethylene-propylene random copolymer (EPP)), was used as the membrane material. Phase separation structure of this material was not well known. During the stretching, the changes in both the phase separation structure and the gas permeation behavior were also not known. So the morphology and the viscoelastic behavior of the MK-polymer film were investigated in Chapter 2.

In Chapter 2, MK-2F polymer (SEBS 50wt%, EEA 30wt%, EPP 20wt%) was selected as an experimental material. After the blow-molding of MK-2F at 190 ˚C and annealing at 115 ˚C, as-blown annealed film was obtained. When the as-blown annealed film was stretched at 120 ˚C, thin thickness film could be obtained. While both ends of the hot-stretched film were cramped, the film was cooled to room temperature and released from the stretching machine. The stretched and cooled film did not show the elastic recovery and thin thickness film could be obtained. TEM observation of the stretched films showed that 3D-network structure of SEBS phase and (EEA+EPP) phase, in which both the SEBS and the (EEA+EPP) were co-continuous. By this 3D-network structure, the morphology control concept of the polymer alloy in Chapter 1 was verified.

Viscoelastic measurement results of the stretched films suggested that

1. The viscoelastic properties of the stretched films were governed by that of SEBS matrix phase.
2. The viscoelastic properties of the stretched films were mainly determined by the molecular mobility of the ethylene/butylene (EB) rubber chain.
3. The molecular mobility of the EB rubber chain was decreased in MD (machine direction) by the uniaxial stretching. But, the mobility was increased along the direction to ND (normal direction to the film) and TD (transverse direction to both MD and ND) by the uniaxial stretching. The change in molecular mobility of the EB rubber was anisotropic during the stretching.
4. This anisotropic molecular mobility of the EB rubber chain was remained during the stretching because of the 3D-network structure.

To explain these anisotropic behaviors of the EB rubber chain in SEBS matrix, deformation model of the SEBS matrix was proposed.

In Chapter 3, gas permeation behavior of the stretched films was investigated during the uniaxial stretching process and the results were explained by the deformation model of the SEBS matrix. Gas permeability of the as-blown annealed film was $P_{O2} = 9.2\times10^{-10}$ $cm^3(25\ ^\circ C)\ cm\ cm^{-2}\ s^{-1}\ cmHg^{-1}$ and $P_{N2} = 2.7\times10^{-10}$ $cm^3(25\ ^\circ C)\ cm\ cm^{-2}\ s^{-1}\ cmHg^{-1}$, $P_{O2}/P_{N2} = 3.4$.

When the as-blown annealed film was subjected to uniaxial stretching in the MD, each f_{O2} and f_{N2} of the stretched film linearly increased and each P_{O2} and P_{N2} of the stretched film reached to almost constant value with the increase of the stretching ratio K. The gas permeability of the stretched film was larger than that of the as-blown annealed film. In addition, f_{O2}/f_{N2} decreased gradually with K and reached to a constant value of 2.95–3.0 at around $K = 4.5$.

In general, when an amorphous polymer material is stretched, the degree of orientation of the polymer chains increases, which results in lower molecular mobility for the chains. Therefore, the diffusion coefficient of gas molecules decreases, leading to a reduced gas permeability coefficient. It has also been reported that if a semi-crystalline polymer material is stretched, both the crystallinity and degree of crystal orientation increase, which leads to a decline in the diffusion coefficient of gas molecules and the gas permeability coefficient.

However, the gas permeability of the MK-2F stretched films increased with the stretching. This was very interesting. The reason for this unique gas permeation behavior was that molecular mobility of the poly(ethylene butylene) chains in the direction normal to the film increases and reached an equilibrium state at around $K = 4.5$. This change in gas permeation behavior of the stretched film could be explained using the deformation model of the SEBS phase described in Chapter 2.

In Chapter 4, gas-permeable composite hollow-fiber membrane with a three-layered structure composed of a high-density polyethylene (HDPE) porous layer, a MK-2F thin dense layer, and a HDPE porous layer has been successfully developed by melt-spinning and cold/hot stretching process. When the stretching ratio increased, oxygen permeance, f_{O2}, and nitrogen permeance, f_{N2}, linearly increased, while f_{O2}/f_{N2} was almost constant at 2.95–3.0. The no-pinhole thin layer with a thickness of 2–5 μm could be achieved and its f_{O2} was 4.0–8.5×10^{-6} cm^3(25 °C) cm^{-2} s^{-1} $cmHg^{-1}$.

TEM structural analysis of the MK-2F thin layer indicated that the thinnest thickness was 2 μm, which agreed with the thickness calculated from the gas permeation results. TEM photos also showed that the SEBS phase and the (EEA+EPP) phase formed a 3D-network structure. The gas permeance ratio of f_{O2}/f_{N2} for the thin MK-2F layer (2–5 μm) was 2.95–3.0, which was the same as that of stretched films (27–52 μm) in Chapter 3. This result showed that the EB rubber chain in the MK-2F thin layer (2–5 μm) was sufficiently relaxed and the chain mobility was in a saturated state. The elastic recovery of the SEBS matrix was restricted by the (EEA+EPP) phase, which maintained the saturated state for the EB rubber chain.

Results in Chapters 2–4 suggested that the 3D-network structure restrains the elastic recovery of SEBS phase and the deformation model of SEBS matrix describes the gas permeation behavior of the MK-2F thin membrane.

In Chapter 5, the membrane module was prepared from the composite hollow-fiber membrane with a thin thickness of 2 μm, in which f_{O2} = 8.5×10^{-6} cm^3(25 °C) cm^{-2} s^{-1} $cmHg^{-1}$ and f_{N2} = 2.7×10^{-6} cm^3(25 °C) cm^{-2} s^{-1} $cmHg^{-1}$, and the effective surface area was 1m^2. The liquid chemicals (IPA and developer solution) were supplied to the inner side of the hollow-fiber membranes with a single path flow and the outer side of the hollow-fiber membranes was vacuumed to 3.2 kPa, and then the degassing efficiency of the dissolved gas in the liquids was measured. The results were as follows:

1. In the developer solution, the degassing efficiency of the dissolved O_2 was achieved to 90–95% and that of the dissolved N_2 was achieved to 80–90% at 50–500 mL/min,
2. In IPA, the degassing efficiency of the dissolved oxygen was achieved to 85–95% and that of he dissolved N_2 was achieved to 80–95% at 50–100 mL/min.

These degassing efficiencies data were superior to that in PTFE tube. The reason for the superior results was high gas permeance of the MK-2F thin layer.

To measure the vapor permeation rate (g m^{-2} h^{-1}) of the MK-2F thin layer, the chemical liquid was circulated at 23°C between the tank and the membrane module with a chemical pump and the permeated vapor through the membrane was cold-trapped with liquid nitrogen under a downstream pressure of 1 kPa and the weight of the permeated vapor was measured. The H_2O vapor permeation rate of the MK-2F thin layer was about 1/4 that of Poly(dimethylsilicone) (PDMS), and the IPA permeation rate was about 1/12 that of PDMS even though the oxygen permeance of the MK-2F thin layer was almost the same as that of PDMS. These results of MK-2F were due to the low swelling to IPA for both the SEBS matrix phase and the polyolefin phase. On the other hand, the swelling to IPA for PDMS was larger than that of MK-2F. The larger vapor permeation rate of H_2O for PDMS was due to its larger molecular mobility at 23 °C compared with that of the EB rubber chain since PDMS has a lower T_g (T_g : about –120 °C for PDMS, –55 °C for the EB rubber chain).

Therefore, when the MK-2F thin layer is used in a degassing membrane, vapor loss from the liquid chemicals would be reduced.

We have successfully developed a gas permeable composite hollow-fiber membrane with a thin dense layer of SEBS/polyolefin polymer alloy. The composite hollow-fiber membrane showed a high degassing efficiency for IPA and water at a high flow rate. The thin thickness (2 μm) of the polymer alloy layer was achieved with a new morphology concept, which was a bi-continuous structure of SEBS and polyolefin. The unique gas permeation behavior of the polymer alloy could be explained by the deformation model of the SEBS matrix phase.