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Enhancement of oxygen permselectivity of polydimethylsiloxane-b-polycarbonate film by the surface modification with fluorine-containing polymer

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Summary

Both oxygen permeability coefficient($^{P}O_2$) and separation factor(α = $^{P}O_2/^{P}N_2$) through polydimethylsiloxane-b-polycarbonate(PDMS/PC) film were improved by the addition of small amounts(1.0 wt%) of the fluorine-containing polymer. This improvement was considered to be caused by the selective solubilization of oxygen in the surface-accumulated fluorine polymer domain.

Introduction

Polydimethylsiloxane(PDMS) based polymers are generally used as oxygen permeable membrane materials. However, the separation factor is not satisfactorily high. In order to improve the low separation factor maintaining the high permeability coefficient, surface modification of the film by the addition of polymers having selective and high oxygen solubility coefficient(high $^{S}O_2$ and $^{S}O_2/^{S}N_2$) seems promising. We reported that both $^{P}O_2$ and α through surface-modified polystyrene(PS) films were noticeably improved by the addition of small amounts of PDMS-g-PS(1).

In this report, we would like to show the improvement of the permselectivity of the mechanically strong and highly permeable PDMS/PC films by the addition of a small amount of fluorine-containing polymer.

Experimental

Syntheses of Monomers

Pentafluorostyrene(Sf): Reaction of acetaldehyde with pentafluorophenyl-magnesium bromide(2) or -lithium(3) gave 1-(pentafluorophenyl)ethanol. Dehydration of the alcohol with phosphorus pentoxide gave pentafluorostyrene in a 48% yield, bp. 53.0°C(34mmHg).

Perfluoroalkyl acrylate(FA:$CH_2=CHCOOCH_2CH_2(CF_2)_nCF(CF_3)_2$): Commercial perfluoroalkyl acrylate was purified by distillation. A fraction which boiled at 80°C at 0.27mmHg was collected. The average n estimated by ^{1}H-NMR was 8.7.

4-Pentamethyldisiloxanylstyrene(S2), and 4-polydimethyl-

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siloxanylstyrene(S20)(degree of polymerization of polydimethylsiloxane is 20): These monomers were synthesized and purified as previously reported(5,6).

Preparation of polymers

Poly(dimethylsiloxane-b-Bisphenol A carbonate) (PDMS/PC): The substrate polymer PDMS/PC was prepared by a method similar to that of a literature(7), except for the use of trichloromethyl chloroformate instead of phosgene. The weight average molecular weight, Mw, of the block copolymer was estimated to be $4.2\text{x}10^4$ by GPC correlating to standard PS. The content and the average chain length of PDMS were 40 wt% and 21, respectively, by ^{1}H-NMR.

Polymers for additives: Polymerizations were carried out in THF using AIBN(0.05 mol% to monomer) as an initiator. In the polymerizations of FA as a monomer, DAIFLON®(1,1,2-trichloro-1,2,2-trifluoroethane)(Daikin Kogyo, Japan) or DAIFLON®/THF was used as the solvent. The polymers were purified by the reprecipitation from the solvent into methanol. All the polymers were solid but they showed poor film forming property.

Preparation of Surface Modified Films and Measurement of Oxygen Permeation Behavior

The procedures were carried out as previously reported(6).

Measurement of Contact Angles

Advancing contact angles toward twice-distilled water on the air-side surface(which has been contact with air in casting) were measured with a goniometer model CA-A(Kyowa Kagaku, Japan).

Results and Discussion

Table 1 shows the contact angles(θa) of the air-side surface of the films of bulk substrate, or additive polymers themselves, and their blends. The θa values of the surface of the blend films increased in the presence of 1.0 wt% fluorine-containing polymer as an additive, and became very close to that of the added fluorine-containing homopolymer itself. The change in the contact angles suggests that the air-side surface of the films have been modified effectively by the surface accumulation of added fluorine-containing polymer. On the other hand, the θa values slightly decreased by the addition of PS or poly(4-vinylpyridine) (PPy). In the case of the additives of PS and PPy, the added polymers are considered to be unable to accumulate at the substrate surface, because they have higher surface free energy than the substrate polymer.

The oxygen permeation constants through the individual bulk and the blend polymer films are also shown in Table 1. By adding PS or PPy, α increased but P_{O_2} decreased. Such

Table 1. Contact angles and oxygen permeation behavior of bulk and blend polymer films.

No	Blend Polymer$^{1-2)}$		θa	P_{O_2} 3)	D_{O_2} 4)	S_{O_2} 5)	α	D_{O_2}/D_{N_2}	S_{O_2}/S_{N_2}
	Bulk Polymer	Additive$^{6)}$							
1	PDMS/PC	-	98.5	2.60	2.08	1.25	2.30	1.24	1.86
2	PSf	-	99.5	0.53	0.089	5.87	2.46	1.5	1.64
3	PFA	-	104.2	0.40	0.06	6.0	2.4	1.2	2.0
4	PS	-	91.7	0.12	0.06	2.2	5.5	3.0	1.8
5	PPy	-	90.0	0.2	0.1	2.2	-	-	-
6	PDMS/PC	PSf	99.8	2.87	1.67	1.71	2.49	1.40	1.68
7		P(Sf/S2)	98.8	3.71	1.63	2.28	2.54	1.23	2.07
8		P(Sf/S20)	98.5	2.74	1.62	1.68	2.63	1.44	1.83
9		PFA	104.0	2.96	1.12	3.32	2.49	1.29	2.06
10		P(FA/S2)	102.6	3.34	0.94	3.54	2.55	1.09	2.34
11		P(FA/S20)	100.9	2.70	0.86	3.13	2.43	1.25	1.95
12		PS	95.3	2.06	0.99	1.86	2.54	1.41	1.97
13		PPy	97.0	2.20	1.11	1.87	2.64	1.63	1.74

1) For the abbreviations, see text.
2) Blend of the substrate PDMS/PC with the 1.0 wt% additive polymer based on fluorine component(run number 6-11), PS(run number 12), or PPy(run number 13).
3-5) Expressed in 10^{-9}cc(STP)•cm•cm^{-2}•sec^{-1}•cmHg^{-1}, 10^{-6}cm^{2}•sec^{-1}, 10^{-3}cc(STP)cm^{-3}•cmHg^{-1}, respectively.
6) contains 1.0 wt% fluorine component to the substrate.

Table 2. Analysis of permeability coefficient of the PDMS/PC based blend films containing PS or PPy by serial model.[1)]

No	Additive(1.0 wt%)	$P^{2)}$	L(%)
1	None	2.60(=P_1)	-
12	PS	2.06	1.27$^{3)}$
13	PPy	2.20	1.52$^{4)}$

1) Calculated by $L= P_2(P-P_1)/P(P_2-P_1)$.
P, P_1, P_2 : oxygen permeability constants of the blend, the bulk substrate polymer, and bulk additive polymer films, respectively.
2) Expressed in 10^{-9} cc(STP)•cm•cm^{-2}•sec^{-1}•cmHg^{-1}.
3) P_2=0.12.
4) P_2=0.2.

change in P_{O_2} can be analyzed nicely by a serial model(Table 2)(1). Namely, the P_{O_2} values of the blend films are the concentration-averaged values of those of the two component polymers in the blend.

On the other hand, both α and P_{O_2} increased in the surface-modified films with a fluorine-containing polymer as the additive. If the P_{O_2} change of the blend polymer film was also fit in a serial model, the $^{P}O_2$ should be lower than that of the substrate polymer film itself, because the $^{P}O_2$ of a fluorine-containing polymer was lower than that of the substrate polymer. This increase in $^{P}O_2$ suggested the specific influence of the surface-modifying fluorine-containing polymers on $^{P}O_2$.

In order to clarify the specific influence of the fluorine-containing polymers on the $^{P}O_2$ at the surface of the film, the permeability coefficient was considered in two factors of diffusion($^{D}O_2$) and solubility($^{S}O_2$) coefficients by the following equation.

$$^{P}O_2 = {}^{D}O_2 \times {}^{S}O_2$$

Since the fluorine-containing polymers(run number 6-11 in Table 1) have higher $^{S}O_2$ but lower $^{D}O_2$ than the substrate polymer(PDMS/PC), the surface-modified films by the fluorine-containing polymers should show higher $^{S}O_2$ and lower $^{D}O_2$ than the substrate polymer itself. The analysis of the changes in $^{D}O_2$ by a serial model(Table 3) indicated that the change in $^{D}O_2$ fits in a serial model fairly well. The normal decrease in $^{D}O_2$ suggests that the diffusion process is not influenced so much by the fluorine-containing polymer in the blend. These results suggest the relatively large increase in $^{S}O_2$ than the decrease in $^{D}O_2$ seems to be the reason of the over all increase in $^{P}O_2$. Such enhancement of $^{S}O_2$ may be ascribed to the effective surface modification by the fluorine-containing polymer.

Table 3. Analysis of the diffusion coefficient through surface modified PDMS/PC films with fluorine-containing polymer by a serial model.

No	Additive(1.0 wt%)$^{1)}$	$D^{2)}$	L_D(%)$^{3)}$
1	None	2.08(=D_1)	-
6	PSf	1.67	1.0
9	PFA	1.12	2.5

1) For the abbreviations, see text.
2) Expressed in 10^{-6} $cm^2 \cdot sec^{-1}$.
3) $L_D = D_2(D-D_1)/D(D_2-D_1)$, where D, D_1, D_2 are oxygen diffusion coefficients of the blend, bulk substrate polymer, and the additive polymer films, respectively.

Although the $^{S}O_2$ and $^{D}O_2$ values of bulk polyFA(PFA) film are almost the same as those of polySf(PSf), the changes in $^{S}O_2$ and $^{D}O_2$ of the surface-modified films by PFA were higher than those by PSf. The reason is not clear right now, but there may be some differences in the morphology of the blend films between these two polymers. For instance, it is conceivable that PFA, which has lower surface energy than PSf, covers the blend film surface more effectively than PSf and contributes more effectively to increase the solubility coefficient by the surface-lying fluorine domain, but such surface-covering domain will lower the diffusibility of the gases.

The increase in θa and ${}^{S}O_2$ values of the surface modified film by homopolymers(PFA or PSf) were larger than those by the graft copolymers(P(FA/S20) or P(Sf/S20)). Lower surface free energy of the homopolymers and their lower compatibility with the substrate polymer seem to make the homopolymers accumulate more effectively at the surface, and results in the large ${}^{S}O_2$ increase. While the graft copolymers will be distributed even inside of the film because of their higher compatibility with the substrate polymer due to PDMS component. Such thick PDMS domain modified by fluorine component may lower the diffusibility of gases.

The ${}^{S}O_2$ values of the surface-modified films by the random copolymers(P(FA/S2), P(Sf/S2)) were larger than those by the other type fluorine containing polymers. The random and homogeneous distribution of perfluoroalkyl and pentamethyl disiloxanyl groups along the polymer backbone without phase separation might have changed the packing of the polymers in the membrane, thus affecting the solubility and diffusion coefficients. Further research is needed to clarify the exact reason.

In order to discuss the change of the separation factor (α), it was divided into the ratios solubility and diffusion coefficients by the following equation(Table 1).

$$\alpha = {}^{P}O_2/{}^{P}N_2 = ({}^{D}O_2/{}^{D}N_2) \times ({}^{S}O_2/{}^{S}N_2)$$

The values of ${}^{D}O_2/{}^{D}N_2$ and ${}^{S}O_2/{}^{S}N_2$ of the surface modified film by the fluorine-containing homopolymers and graft copolymers are between those of substrate and added polymer. But the change in ${}^{S}O_2/{}^{S}N_2$ is larger than expected. This may be due to the fact that ${}^{S}O_2/{}^{S}N_2$ of the blend film is controlled largely by that of the surface accumulated polymer, whereas the change in ${}^{D}O_2/{}^{D}N_2$ of the surface modified films is relatively small. The higher ${}^{S}O_2/{}^{S}N_2$ of the surface modified film may contribute to the higher separation factor.

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