Novel Functional Polymers: Poly(dimethylsiloxane)–Polyamide Multiblock Copolymer. IV. Gas Permeability and Thermomechanical Properties of Aramid–Silicone Resins

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SYNOPSIS

Poly(dimethylsiloxane) (PDMS) and aromatic polyamide (aramid) multiblock copolymers (PASs) ranging from 26 wt % to 75 wt % in PDMS content were prepared and cast into transparent, ductile, and elastomeric films from N,N'-dimethylacetamide solutions. The gas permeation properties and dynamic thermomechanical properties of the PAS films were investigated. It was found that the PASs containing < 75 wt % of PDMS had two-phase morphologies due to the great difference between the solubility parameters of the two components, in spite of the relatively low molecular weight of each segment. PASs containing ≥ 35 wt % of PDMS showed the PDMS continuous phase and interfacial mixing occurred clearly between the two phases at the higher PDMS contents. PAS containing ≥ 53 wt % of PDMS showed high enough gas permeability compared with conventional silicone rubbers. The gas permeation properties can be well predicted by the PDMS contribution to the continuous phase rather than by the modulus behaviors alone. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Silicone polymers principally based on poly(dimethylsiloxane) (PDMS) have been widely used in medical fields utilizing their unique properties such as biocompatibility, chemical inertness, low surface energy, lubricity, flexibility, and gas permeability.[1-4] When it comes to applications such as artificial lungs[5] and contact lenses,[6] high gas permeability and good biocompatibility are among the most desired properties of silicone polymers. Such application, however, is sometimes limited by the polymers' poor mechanical properties, especially low tensile strength. To improve the mechanical properties without sacrificing the desired properties of silicone polymers, many investigations have been reported on the synthesis and characterization of block or segmented siloxane copolymers including PDMS as the soft segment.[7-10]

Focusing on the high permeability to many gases and very good biocompatibility, we have been investigating PDMS and aromatic polyamide (aramid) multiblock copolymers, that is aramid–silicone resins (PASs), first synthesized by Kajiyama, Kakimoto, and Imai.[11] In previous papers, we studied the synthesis and characteristics of PAS from a novel biomaterial point of view.[12,13] In that study, PAS exhibited many of the desirable properties of aramid and PDMS for medical applications. We have reported that PAS is moldable into many forms, such as films and hollow fibers.[14] Their surface properties were also investigated in detail[13,15] since the surface properties of copolymers such as PAS—which seem to be strongly influenced by the molding method—play an important role in their functionality, especially in medical applications.

It is expected that the two-phase structures caused by the high degree of incompatibility between the PDMS segment and the aramid segment can provide the copolymer with the characteristics associated with both segments plus some new properties. In this study, for the purpose of clarifying the gas permeation behavior through PAS films, gas permeabilities and thermal properties of PAS were investigated in detail by means of the high-vacuum method and dynamic mechanical measurement, respectively. We discuss the two-phase structures, on which the permeation properties of PAS are highly dependent.

EXPERIMENTAL

PAS Preparation

PAS was prepared by low-temperature solution polycondensation through a two-step procedure according to the literature.[12] Briefly, α,ω-dichloroformyl-terminated aramid oligomers were prepared by the reaction of 3,4'-diaminodiphenylether (DAPE) (Wakayama Seika Industry Co., Wakayama, Japan) with a calculated excess of isophthaloyl chloride (IPC) (Wako Pure Chemical, Osaka, Japan) in a chloroform–triethylamine–hydrochloride system at −15°C for 5 min in the presence of triethylamine as hydrogen chloride acceptor under nitrogen. Next, the preformed aramid oligomers were reacted with PDMS–diamine [number-average molecular weight (M_n) of 1,680; Shin-Etsu Chemical Co., Tokyo, Japan] at −15°C for 1 h. The reaction was then continued at room temperature for 48 h under nitrogen. The polymers were isolated by pouring the reaction mixture into methanol; a low-molecular-weight fraction enriched in PDMS was removed by washing the product three times with n-hexane; and the residue was dried at 60°C for 48 h under vacuum.

Measurements

The observed PDMS contents of PAS in bulk were calculated from the $SiCH_3$/aromatic H ratio in the ^{1}H-NMR spectra, measured with a JEOL EX-90 (JEOL, Tokyo, Japan). The oxygen and nitrogen permeabilities of the PAS films ranging in thickness from 50–100 μm, obtained by casting from 10 wt % N,N'-dimethylacetamide (DMAc) solutions of PAS, were determined at 25°C by the routine high-vacuum method.[16] Dynamic thermomechanical analysis was performed with film specimens obtained on a Orientech Rheovibron DDV-3-EP instrument at 11 Hz

in the temperature range of −150°C to 200°C at a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Gas Permeabilities

It is known that PDMS is highly permeable to common gases such as oxygen and nitrogen.[17] This is due to the flexibility of the Si–O linkage, which results in high diffusion coefficients as compared to the C—C backbone of many organic polymers.

To prepare PASs, calculated amounts of IPC and DAPE were used to form aramid dichloride with a desired number-average molecular weight (M_n); the amount of PDMS was exactly the molar equal of the amount of aramid dichloride prepared in $situ$. From the combination of PDMS and five aramid chlorides with M_n ranging from 330 to 2,970, five multiblock copolymers were obtained (Table I). All PASs, ranging from 26 to 75 wt % in PDMS content, were cast into transparent, ductile, and elastomeric films from the DMAc solutions. The oxygen and nitrogen permeabilities of the PAS films are shown in Table II. Both the oxygen and nitrogen permeabilities increased with increasing PDMS content or with a decrease in the aramid block length, but the permeability of PAS with 26 wt % of PDMS was too low to be determined at the same conditions. There was a significant permeability change in accordance with the change in PDMS content from 26 to 35 wt % and also from 46 to 53 wt %. On the other hand, all of the oxygen/nitrogen separation factors of the films ranged from 2.2 to 2.4 independent of the PDMS content. These values are almost the same as that of silicone rubbers based on

Table I Preparation of PAS

| No. | M_n | | PDMS Content (wt %) | |
	PDMS	Aramid[a]	Calculated[b]	Found[c]
1	1680	2970	35	26
2	1680	2310	41	35
3	1680	1650	49	46
4	1680	990	60	53
5	1680	330	78	75

[a] Calculated from the feed ratio of the monomers.
[b] Weight (PDMS)/[weight (PDMS) + weight (aramid)] in the feed.
[c] Calculated from the Si — CH$_3$/aromatic H ratio in the NMR spectrum.[12]

Table II Oxygen and Nitrogen Permeabilities of PAS Films

No.	PDMS Content (wt %)[a]	PO_2[b]	PN_2[b]	PO_2/PN_2
1	26	—	—	—
2	35	40	18	2.2
3	46	41	17	2.4
4	53	171	76	2.3
5	75	224	97	2.3

[a] Calculated from the Si—CH₃/aromatic H ratio in the NMR spectrum.
[b] [(cm³ (STP) cm)/(cm² sec cmHg)] × 10¹⁰.

PDMS.[17] The PASs containing $\geq$ 53 wt % PDMS were highly permeable to the gases and their oxygen permeabilities were high enough compared with the conventional silicon rubbers.

These results, the separation factor behavior, and the oxygen permeability suggest that all of these films have two-phase morphologies and that the continuous phase of the films, which mainly dictate the gas permeation, contains an appreciable amount of PDMS segments, except for PASs with 26 wt % of PDMS.

Dynamic Thermomechanical Properties

For the purpose of investigating the two-phase nature and low-temperature properties of PAS, dynamic thermomechanical spectra were obtained. The dynamic mechanical storage modulus (E') and loss modulus (E'') of PASs are plotted as a function of temperature in Figure 1.

PASs with PDMS contents ranging from 35 to 53 wt % clearly show the upper and lower two transitions corresponding to hard aramid segments and soft PDMS segments, respectively. Between two transitions there exist the rubbery plateaus which have somewhat constant E' values. The thermomechanical spectrum showed that the nature and extent of the rubbery plateaus were affected by varying the PDMS content. It can be seen that as the soft segment content increases the value of modulus corresponding to the rubbery plateau decreases, and the PAS with 75 wt % of PDMS showed very sharp drop in modulus. This drop in modulus at $-50°C$ is assumed to be associated with the crystalline melting point of PDMS.[7] The almost complete absence of a drop in modulus due to the aramid segment in the PAS with 75 wt % of PDMS indicates that the aramid segment is dispersed in the PDMS matrix phase and, therefore, does not contribute

significantly to the mechanical properties of PAS other than acting as a pseudo-crosslink for PDMS. It also can be said that the phase separation becomes less complete as the PDMS content increases and some interfacial mixing probably occurred in the copolymer with 75 wt % of PDMS. These results also strongly implied the presence of the microphase separated structure between the PDMS and aramid phases in PAS.

Glass Transition Temperatures (T_gs)

The T_gs of the soft PDMS segment and the hard aramid segment for each PAS were obtained from the temperatures at the lower and upper two tan δ peaks, shown in Table III. It is evident that T_g values of the soft PDMS segment lowered with decreasing PDMS content or with an increase in the aramid block length. This T_g behavior of PDMS segments suggested that the PDMS–aramid multiblock copolymers having lower PDMS content or composed of longer aramid block length exhibited a higher degree of microphase separation structure than the block copolymers with higher PDMS content, in which somewhat interfacial phase mixing probably occurred. This interfacial phase mixing, however,
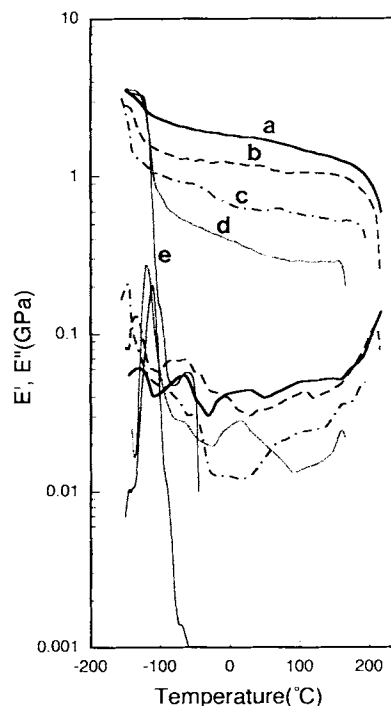

Figure 1 Temperature dependence of the dynamic modulus E' and the loss modulus E'' measured at 11 Hz of PAS films. PDMS contents are (a) 26 wt %, (b) 35 wt %, (c) 46 wt %, (d) 53 wt %, and (e) 75 wt %.

did not significantly affect the gas permeation properties such as the oxygen/nitrogen separation factors.

At a constant PDMS M_n of 1,680, the T_g of the aramid block was quite dependent upon molecular weight, ranging from 158°C at 4 repeat units to 217°C at 14 repeat units. This effect was said to be analogous to the dependence of T_g on molecular weight in homopolymers.[18] The results of transition temperature for the PDMS segment did not show a reciprocal behavior with the molecular weight of aramid. In other words, as the soft PDMS segment of 1,680 M_n has a high degree of mobility, the end restriction due to the hard aramid segment coupling did not increase the T_g value of the soft segment.

The extensive phase separation displayed by these systems at such low block molecular weight levels (i.e., both segments $= \sim 1,500\ M_n$) seems to be unusual.[19] This phenomenon, however, is interpreted as resulting from the high degree of incompatibility of the nonpolar PDMS segment and the polar aramid segment. The solubility parameters of the PDMS and aramid segments are calculated to be 7.4 and 13.3, respectively, by using group contribution calculations.[20] In contrast to this, much higher segment M_n ($\geq 5,000$) is required in PDMS–polysulfone block copolymers where much closer solubility parameters (7.3 and 10.6, respectively) were obtained.[19]

The values of lower tan δ peak due to the PDMS segment are shown in Table III. The height of the peak appears to be quantitatively associated with the PDMS content.

Superstructure

Figure 2 shows how the oxygen permeability varies as a function of the volume fraction of PDMS, calculated by using the group contributions to molar volume.[20] The oxygen permeability was dependent
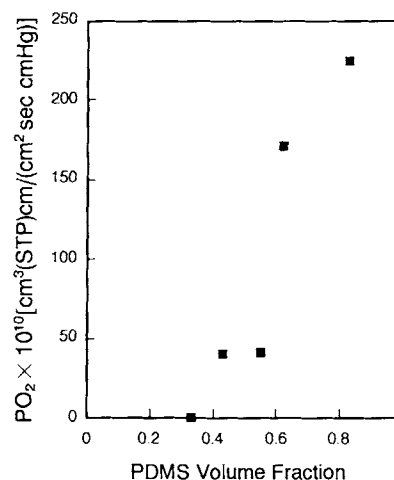

Figure 2 Oxygen permeation coefficient (PO_2) versus PDMS volume fraction.

on the PDMS content, which takes the form of an S-curve expected for two-phase systems.[7]

As the aramid phase is less permeable compared with the PDMS phase, the continuous PDMS phase can be obtained in the copolymer containing ≥ 0.43 volume fraction of PDMS. It is most probable that in the PASs ranging from 0.43 to 0.61 in PDMS volume fraction, both the PDMS and aramid phases seem to exist in co-continuous phases with lamellar structures that are also indicated by the modulus behaviors. On the other hand, in the PAS with 75 wt % of PDMS the PDMS phase exists as the continuous phase with the aramid phase present as discrete domains, judging from the dynamic thermomechanical results.

The rapid decrease in permeability at 0.55 volume fraction is somewhat attributable to the partial formation of the discrete PDMS domain, which makes the PDMS contribution to the continuous phase less than expected from the volume fraction. There was no significant change in the oxygen permeability between 0.43 and 0.55 volume fraction. Almost the

Table III Glass Transition Temperatures (T_gs) of PASs

No.	M_n		T_g (°C)		Tan δ
	PDMS	Aramid (x)[a]	PDMS	Aramid	PDMS
1	1680	4650 (14.1)	−124	217	0.025
2	1680	2988 (9.1)	−134	215	0.068
3	1680	1840 (5.6)	−145	195	0.097
4	1680	1358 (4.1)	−117	158	0.161
5	1680	428 (1.3)	−103		0.350

[a] Calculated from the Si—CH₃/aromatic H ratio in the NMR spectrum.

same permeability, 2.8×10^{-8} [(cm³ (STP) cm)/ (cm² sec cmHg)], was determined for the PDMS by extrapolation of 0.61 and 0.81 volume fraction PDMS samples, assuming total PDMS continuity, and was 3 to 4 times the values determined by 0.43 and 0.55 volume fractions.

When the PDMS phase became major, the modulus changed significantly between 0.61 and 0.81 volume fractions. But a change in permeability was as small as expected from a change in the volume fractions of the PDMS segment. The permeation properties of the block copolymers seem to be highly dependent on their superstructure, especially on phase continuity.

CONCLUSIONS

The two-phase nature of poly(dimethylsiloxane) (PDMS) and aromatic polyamide (aramid) multiblock copolymer (PAS) were clarified in part by evaluating the gas permeation and dynamic thermomechanical properties. Although somewhat interfacial mixing occurred between the two phases, PAS containing $\geq$ 53 wt % of PDMS showed high gas permeability compared with conventional silicone rubbers. The gas permeation properties can be well predicted by the PDMS contribution to the continuous phase rather than by the modulus behaviors alone.

It has been well accepted that the morphology of segmented copolymers is affected by hard and soft segment type, respective volume fraction of the two segments, intermolecular bonding, molecular weight distribution, and the length of the segment.[21] It is, however, still desirable to investigate these issues systematically, as biocompatibility as well as the gas permeation properties are highly dependent on the superstructure of polymer surfaces.

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