

Novel Functional Polymers: Poly(dimethylsiloxane)-Polyamide Multiblock Copolymer. IX. Surface Properties of Blend Film of Aramid–Silicone Resins with Aramid

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ABSTRACT: A blending technique was studied in order to widen the applications of aramid–silicone multiblock copolymer (PAS). A PAS/aramid blend film was prepared and the characterization of the surfaces was investigated. The two-phase nature of poly(dimethylsiloxane) (PDMS) and the aromatic polyamide (aramid) multiblock copolymer (PAS) were clarified in part by evaluating the surface enrichment in PAS/aramid blend films. There were no significant differences among the PASs as additives; however, the PASs were able to alter the aramid surface to that of silicone, even though they were used at low concentration. The atomic force microscopy observation suggested that the mobility of the silicone segment that existed on the surface was restricted by the associated aramid segments. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2198–2205, 2000

Key words: aramid; silicone; blend; surface; atomic force microscopy

INTRODUCTION

Silicone rubber is widely used in medical fields in many forms, such as blocks, tubes, sutures, and films.^{1–4} Generally, the desirable properties of silicone are high thermal stability, oxidative stability, low surface energy, water repellency, good dielectric properties, high gas permeability, and good biocompatibility.^{1–4} The last two characteristics are especially important in the medical field. On the other hand, the mechanical properties of silicone rubber, especially the low tensile strength, sometimes limit its medical application. To solve this problem, we studied a poly(dimeth-

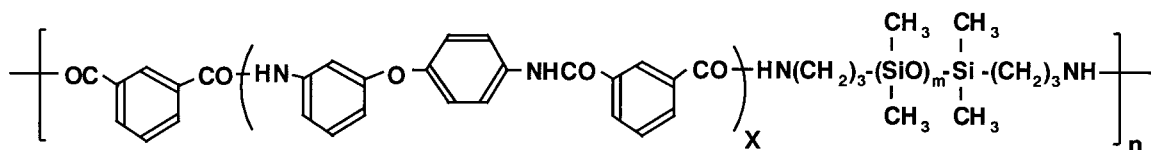
ylsiloxane) (PDMS) and aromatic polyamide (aramid) copolymer (PAS). PAS was first reported by Kakimoto et al.^{5,6} in 1989. Since then we have been investigating its basic properties and applications.

PAS is a multiblock copolymer consisting of a hard segment (aramid) and a soft segment (PDMS). In previous work we studied the synthesis and characteristics of PAS from a novel biomaterial point of view.^{7–9} In those studies the PAS exhibited many of the desirable properties of aramid and PDMS for medical applications. PAS was moldable into many forms, such as films and hollow fibers.¹⁰ Its surface properties were also investigated in detail,^{8,11} because the surface properties of copolymers such as PAS, which seem to be strongly influenced by the molding method, play an important role because of their functionality, especially in medical applications.

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Scheme 1 The structure of PAS.

In order to widen the applications of PAS, we studied a blending technique from the literature.¹² PAS of high silicone content has elasticity and good biocompatibility. If one can alter the surface character of resins that have high mechanical properties to be bioinert, the resins would be very useful as a structural materials for medical use (such as the body of a dialyzer). It is also expected that two-phase structures caused by the high degree of incompatibility of the PDMS segment with the aramid segment can give the characteristics associated with both segments plus some new properties to the copolymer. In this study a PAS/aramid blend film was prepared and the characterization of the surfaces was investigated.

EXPERIMENTAL

Materials

PDMS-diamines of number-average molecular weights of 900, 1680, and 3000 g/mol were obtained from Shin-Etsu Chemical Co. (Tokyo) and dried at 100°C for 3 h under a vacuum. 3,4'-Diaminodiphenylether (3,4'-DAPE, Wakayama Seika Industry Co., Wakayama, Japan), isophthaloyl chloride (IPC), triethylamine (TEA), and chloroform were purchased from Wako Pure Chemicals (Osaka, Japan) and were purified by distillation. TEA hydrochloride (TEA-HCl, Wako Pure Chemicals) was purified by recrystallization from ethanol. All other solvents and chemicals were purified by distillation. Silastic® 500-1 was kindly donated by Dow Corning Corp. (Tokyo).

PAS Preparation

The PAS was prepared by low-temperature solution polycondensation through a two-step procedure according to the literature.⁷ Briefly, α,ω -dichloroformyl-terminated aramid oligomers were prepared by the reaction of 3,4'-DAPE with a calculated excess of IPC in a chloroform-TEA-HCl system at -15°C for 5 min in the presence of

TEA as a hydrogen chloride acceptor under nitrogen. Next the preformed aramid oligomers were reacted with PDMS-diamines at -15°C for 1 h. The reaction was then continued at room temperature for another 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 3 times with a large amount of *n*-hexane, and the residue was dried at 60°C for 48 h under a vacuum. PAS and PAS/aramid blend films were cast from 10 wt % *N,N'*-dimethylacetamide (DMAc) solution in stainless steel petri dishes.

Measurements

The observed PDMS contents of PAS in the bulk were calculated from the SiCH₃/aromatic H ratio in the ¹H-NMR spectra measured using a Jeol EX-90 (Jeol, Tokyo). The polymers were dissolved in DMSO-*d*₆ and D₂SO₄. The electron probe microanalysis (EPMA) spectra were obtained with a

Table I Preparation of PAS and Aramid

Sample No.	Aramid Oligomer ^a (X)	PDMS Content ^a (wt %)	η_{inh}^b (dL/g)
Aramid	—	—	1.41
PAS3000-23	30.3	22.9	0.96
PAS3000-61	5.5	60.6	0.33
PAS3000-85	2.8	84.9	—
PAS1680-13	34.9	12.6	0.44
PAS1680-24	15.5	24.2	0.57
PAS1680-39	7.4	39.4	0.65
PAS1680-41	6.8	41.4	0.57
PAS1680-62	2.8	61.8	0.33
PAS1680-77	1.1	77.2	—
PAS900-24	8.5	23.5	0.47
PAS900-33	5.1	33.2	0.41
PAS900-56	1.8	55.8	0.33

^a Calculated from Si CH₃/aromatic H ratio in ¹H-NMR.

^b Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

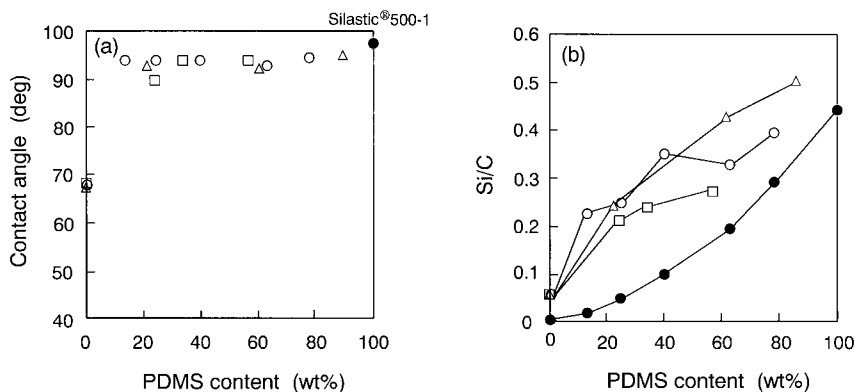


Figure 1 Contact angles and Si/C stoichiometries for PAS films of the (□) PAS900 series, (○) PAS1680 series, and (△) PAS3000 series; (a) water contact angle (at 25°C) and (b) Si/C stoichiometries by XPS; (●) Si/C calculated by $^1\text{H-NMR}$.

Shimadzu EMX-SM (Shimadzu Co., Kyoto, Japan). The EPMA apparatus was operated under an excitation voltage of 15 kV and a sample current of 0.003 mA. An ESCA 1000 spectrometer (Shimadzu) was employed to carry out X-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) images were obtained using a NanoScope III (Digital Equipment) that was operated with a tapping mode in air at an ambient temperature. The contact angles of the PASs were

measured with the sessile drop technique using a goniometer (Erma Co., Tokyo).

RESULTS AND DISCUSSION

Table I summarizes the results of the preparation of the PAS used in this study. It was clear that a wide variety of PASs could be obtained. The observed PDMS contents of the PASs, calculated

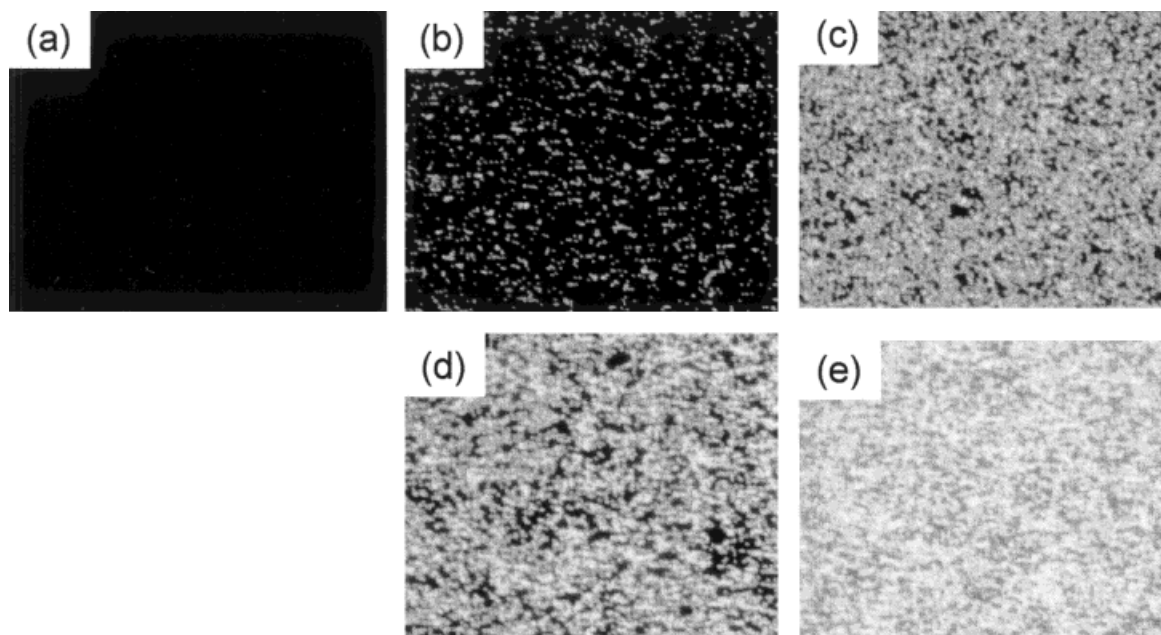


Figure 2 Surface analysis of PAS films by EPMA. The white areas are the silicon component: (a) aramid (PDMS content = 0 wt %), (b) PAS1680-24 (PDMS content = 24.2 wt %), (c) PAS1680-41 (PDMS content = 41.4 wt %), (d) PAS1680-62 (PDMS content = 61.8 wt %), and (e) PAS1680-77 (PDMS content = 77.2 wt %).

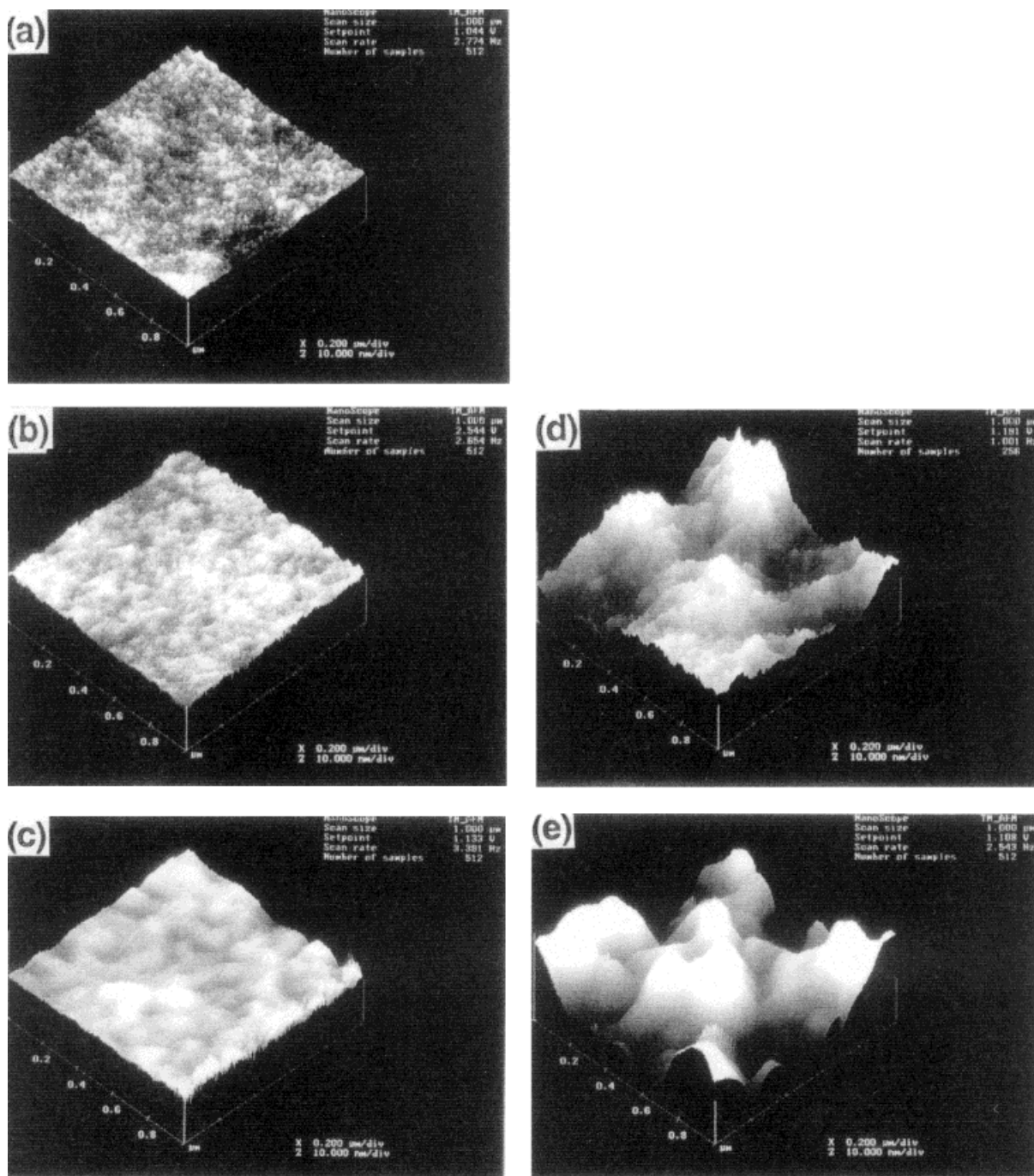


Figure 3 Atomic force micrographs of the surface of PAS films of (a) aramid (PDMS content = 0 wt %), (b) PAS1680-24 (PDMS content = 24.2 wt %), (c) PAS1680-41 (PDMS content = 41.4 wt %), (d) PAS1680-62 (PDMS content = 61.8 wt %), and (e) PAS1680-77 (PDMS content = 77.2 wt %).

from the $\text{SiCH}_3/\text{aromatic H}$ ratio on the $^1\text{H-NMR}$ spectra, were in good agreement with the PDMS contents calculated from the reactant in the feed. GPC measurements were attempted for the molecular weight determination of the PASs; how-

ever, it was impossible to obtain reliable results for the molecular weight of the PASs because of the poor solubility of the PDMS unit of the PAS with DMF as the eluent. Kajiyama et al. also reported the abnormal solubility of PAS in the

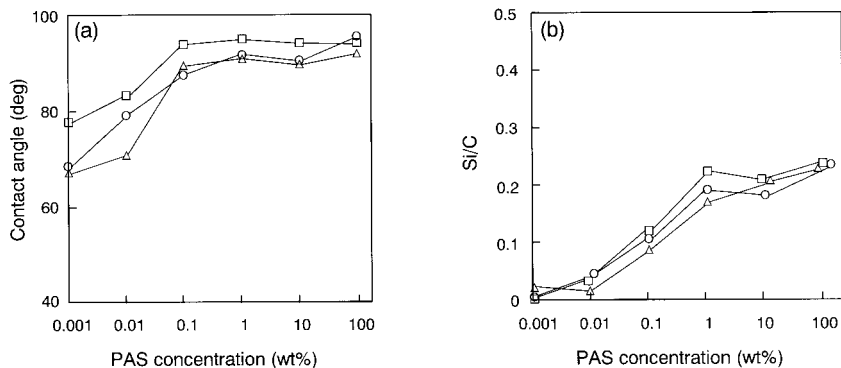


Figure 4 Contact angles and Si/C stoichiometries for PAS/aramid blend films of the (□) PAS900-24 series, (○) PAS1680-24 series, and (△) PAS3000-24 series; (a) water contact angle (at 25°C) and (b) Si/C stoichiometries by XPS.

viscosity measurements of the PAS/DMAc solution.⁵ From the results of the mechanical properties discussed elsewhere,^{13,14} we confirm that the PASs synthesized in this study have equally high molecular weights.

Figure 1 shows the contact angles and the Si/C stoichiometries measured by XPS for the PAS films. It is clear that the contact angles of all PASs did not change, regardless of the PDMS content. This result indicates that the outermost surface of the PAS film in all ranges of PDMS content is almost fully covered with the silicone unit. These results are acceptable because PDMS has low surface energy and it seemed that the PDMS unit migrated to the surface during the casting of the PAS film. The Si/C ratio increases with the PDMS content in the PAS films. The Si/C ratio is approximated to 0.44, when the surface of the film is fully covered with PDMS units. The Si/C ratio in the bulk phase was calculated from the $\text{SiCH}_3/\text{aromatic H}$ ratio from the $^1\text{H-NMR}$ spectra. The Si/C ratio calculated from the XPS spectra increased logarithmically with the PDMS content whereas the Si/C of the bulk phase increased exponentially. From the difference between the surface and bulk composition, it becomes clear that the silicone block was condensed at the surface for all PASs.

Figure 2 shows EPMA scanning electron micrographs of the silicon distribution on PAS films. The silicon units are indicated as white areas. It was obvious that the white areas increased with increasing PDMS content in the PAS. From this result it seemed that the silicone and aramid blocks underwent microphase separation. Figure 3 shows the AFM images of PAS films. It was clear that the surface roughness and the size of

the mound increased with increasing PDMS content. From the force curve of the surface, it was anticipated that the mound was soft. Considering the data of the contact angle, XPS, and EPMA together, the mound seemed to consist of silicone segments of PAS. From these results it became clear that the outermost surface of the PAS homopolymer was covered or condensed by silicone segments.

Figures 4 and 5 represent the contact angles and the Si/C stoichiometries measured by XPS of the PAS/aramid blend films, which were prepared using a PAS series of different silicone chain lengths (Fig. 4) and using a PAS series of different silicone contents (Fig. 5). For both results it was obvious that the contact angles and Si/C ratios of the aramid films were increased when the PASs were blended. The blended PAS affected the contact angle at a very low concentration (0.01 wt %). This result suggested that PAS was concentrated at the outermost surface, even at a low concentration. The contact angle increase leveled off at 0.1%. On the other hand, the Si/C stoichiometries were dependent on the PAS concentration. This difference seemed to be due to the difference of the sampling depth between the contact angle measurement (outermost surface) and the XPS (about 100 Å deep). There were no differences of contact angles and Si/C ratios among the PAS series used. This result suggests that the silicone and the aramid segment are liable to separate, even though the concentration of the silicone was extremely low. There were wide gaps of surface tension between the aramid and the silicone.

Figure 6 shows EPMA images of the silicon distribution on PAS/aramid blend films. The white areas increased with increasing PAS con-

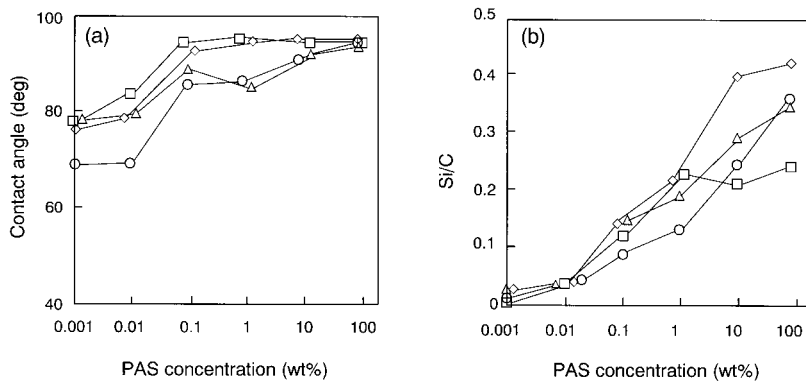


Figure 5 Contact angles and Si/C stoichiometries for PAS films of the (□) PAS1680-24 series, (○) PAS1680-41 series, (△) PAS1680-62 series, and (◇) PAS1680-77 series; (a) water contact angle (at 25°C) and (b) Si/C stoichiometries by XPS.

centration in the PAS/aramid blend films. At 10 wt % the silicone segments were segregated to form a domain. The reason for this phenomenon is still unclear. One possible reason seemed to be the poor solubility of the silicone segment in DMAc. Figure 7 shows the AFM images of the PAS/aramid blend films. Contrary to the results of Figure 3, it was clear that the surface roughness did not change, in spite of the PAS concentration. The size of the mound was slightly increased with increasing PAS concentration. The

silicone mounds were soft for all the samples, but the reproducibility was fairly good. This means that the mound of the silicone segment was tightly immobilized to the film surface. Figure 8 shows the effect of heat treatment (160°C, 2 h in dry air) on the Si/C ratio of the PAS/aramid blend film (PAS1680-41, 0.1 wt %). There was no effect on the heat treatment. This means that the PDMS segment was condensed at the outermost surface during casting; however, once the surface of the film formed, the rotation or the replacement of the molecules hardly occurred. This was due to the strong intermolecular force of the aramid segment. Therefore, the silicone segment that existed on the surface was very stable. In other words, the mobility of the silicone chain may be restricted.

This finding can explain the cell adhesion result reported in previous work.^{15,16} In that study PAS showed lower cell adhesivity than silicone film. It is well known that cell adhesion is reduced when the surface-free energy becomes low. PAS has the same surface-free energy as silicone; however, the number of cell adhesions was markedly reduced compared to that of silicone. One difference between the surface of PAS and silicone is the restricted mobility of silicone chains. Another piece of evidence came from the TEM observation. The thickness of the silicone layer of the surface of PAS, which had the best biocompatibility (i.e., cell nonadhesivity), was very thin. There are no reports on the mobility of surface molecules and cell or protein interaction; the result obtained here suggested important findings for understanding the biocompatibility of polymers.

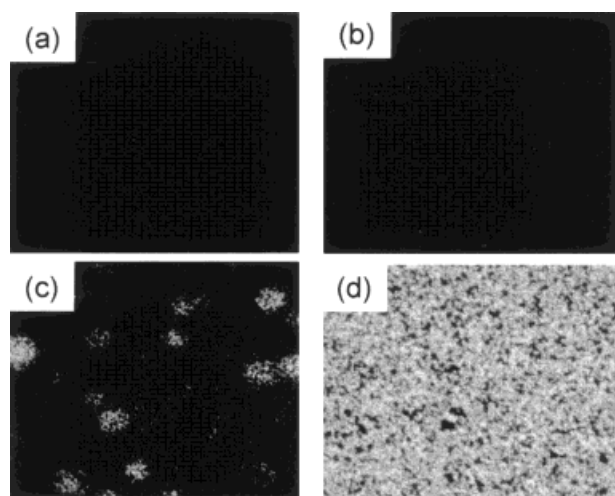


Figure 6 Surface analysis of PAS/aramid blend films by EPMA. The white areas are the silicon component. (a) Aramid original (PDMS content = 0 wt %), (b) PAS1681-41/aramid = 1.0 wt % (PDMS content = 0.41 wt %), (c) PAS1681-41/aramid = 10.0 wt % (PDMS content = 4.14 wt %), and (d) PAS1680-41 original (PDMS content = 4.14 wt %).

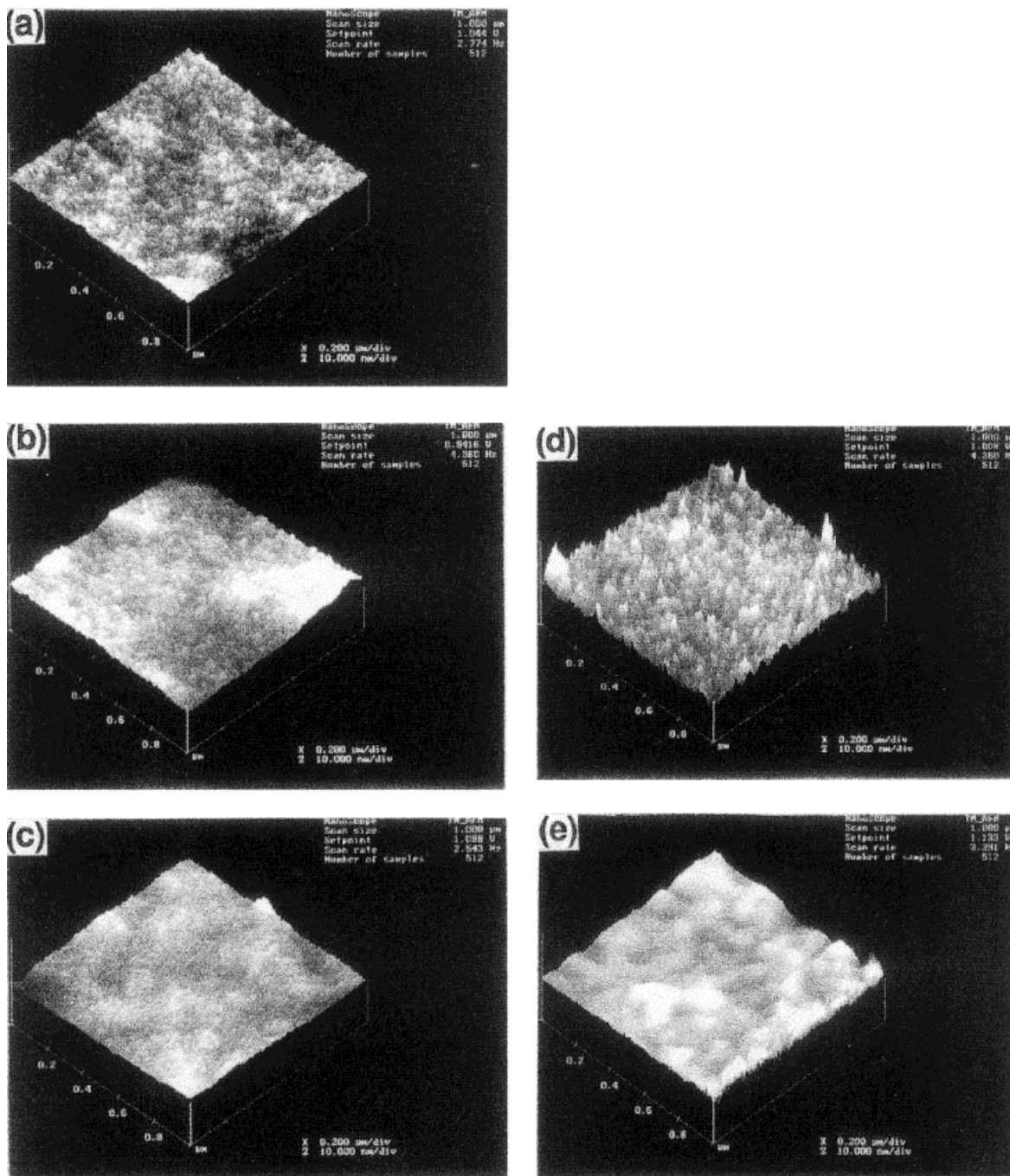


Figure 7 Atomic force micrographs of the PAS/aramid blend film surface of the (a) aramid original (PDMS content = 0 wt %), (b) PAS1681-41/aramid = 0.001 wt % (PDMS content = 4.1×10^{-4} wt %), (c) PAS1681-41/aramid = 0.1 wt % (PDMS content = 4.1×10^{-2} wt %), (b) PAS1681-41/aramid = 10.0 wt % (PDMS content = 4.14 wt %), and (d) PAS1680-41 original (PDMS content = 41.4 wt %).

CONCLUSIONS

The two-phase nature of PDMS and PAS was clarified in part by evaluating the surface enrich-

ment in PAS/aramid blend films. Although there were no significant differences among the PASs as additives, all the PASs proved to be useful to alter the aramid surface to bioinert. The AFM

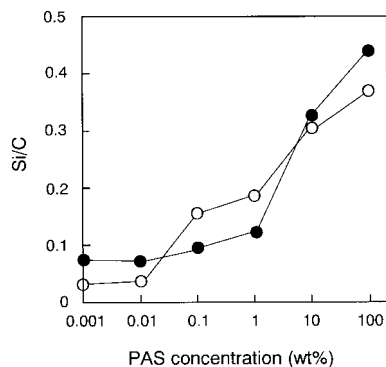


Figure 8 The effect of heat treatment on the Si/C stoichiometries of PAS/aramid blend films (○) as cast and (●) heat treated.

observation suggested that the mobility of surface molecules could be a key to the biocompatibility of polymeric materials. This is the next goal of our study.

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