Novel Functional Polymers: Poly(dimethylsiloxane)–Polyamide Multiblock Copolymer. III. Synthesis and Surface Properties of Disiloxane–Aromatic Polyamide Multiblock Copolymer*

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SYNOPSIS

Disiloxane–aromatic polyamide (aramid) multiblock copolymers (2SiPASs) were synthesized using 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (BATS) as an analog of aramid–silicone resin consisting of aromatic polyamide and poly(dimethylsiloxane) (PDMS). 2SiPASs afford a transparent and toughened plastic film. The surface properties of 2SiPAS were investigated by X-ray photoelectron spectroscopy (xps) and static contact angle measurement. The results of surface analysis suggested that BATS content of the 2SiPAS surface increased with increasing BATS content in bulk. The interaction between the platelets and the 2SiPAS surface was found to be very weak when the BATS content reached 26 wt % in bulk. © 1996 John Wiley & Sons, Inc.
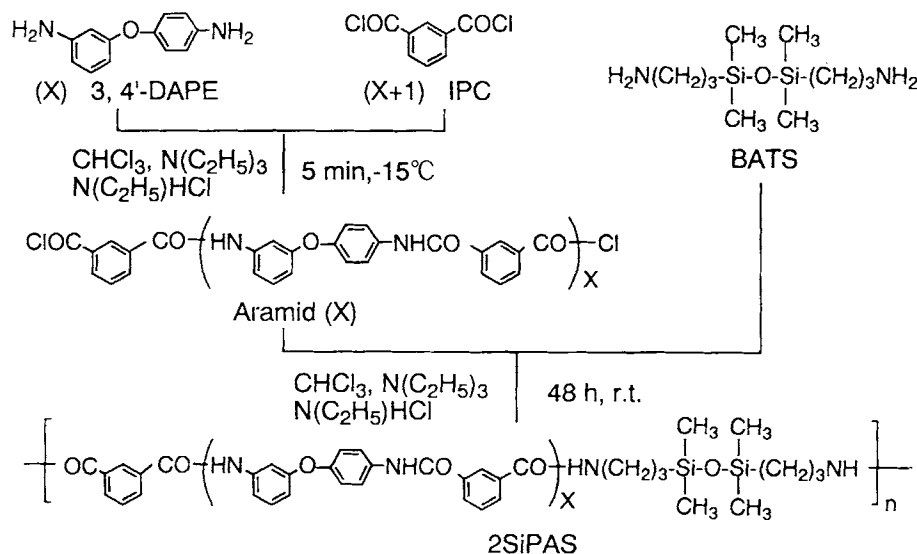
INTRODUCTION

It is well known that multicomponent polymers consisting of different kinds of polymer units often exhibit desirable properties of constituent polymer units or novel properties. In the previous study, we reported the synthesis and properties of poly(dimethylsiloxane) (PDMS)–aromatic polyamide (aramid) multiblock copolymer (PAS).[1-3] The PDMS has excellent properties such as high thermal stability, oxidative stability, water repellency, high gas permeability and bioinertness.[4-7] On the other hand, the aramid is known to have excellent mechanical properties, such as high thermal stability and high modulus of elasticity.[8] Evaluations showed that PAS has good mechanical properties

which are widely variable from tough plastic to rubberlike elastomer. PAS also has high gas permeability and good blood compatibility because of the existence of microphase-separation-like structures in bulk and enrichment of PDMS units at the outermost surface.

PAS has good mechanical properties; however, the tensile strength is drastically lowered when PDMS units are copolymerized. On the other hand, PDMS units tend to be at the surface because of their very low surface free energy. In order to obtain PAS which has the high mechanical properties of aramid with low surface free energy, we synthesized PAS consistent with the low molecular weight of PDMS ($M_n = 900$). The mechanical properties of PAS (PDMS = 900), however, did not improve. For this purpose, it was thought that the PDMS unit must be further altered with a shorter dimethylsiloxane unit. Therefore, novel disiloxane–aramid multiblock copolymers (2SiPASs) consisting of very

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* For Part I, cf. Ref. 1; for Part II, cf. Ref. 3.
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H_2N—◯—O—◯—NH_2
(X) 3, 4'-DAPE

$ClOC$—◯—$COCl$
(X+1) IPC

$H_2N(CH_2)_3$-$\overset{CH_3}{\underset{CH_3}{Si}}$-O-$\overset{CH_3}{\underset{CH_3}{Si}}$-$(CH_2)_3NH_2$
BATS

$CHCl_3$, $N(C_2H_5)_3$
$N(C_2H_5)HCl$ | 5 min,-15°C

$ClOC$—◯—CO—(HN—◯—O—◯—$NHCO$—◯—CO)$_X$—Cl
Aramid (X)

$CHCl_3$, $N(C_2H_5)_3$
$N(C_2H_5)HCl$ | 48 h, r.t.

—(OC—◯—CO—(HN—◯—O—◯—$NHCO$—◯—CO)$_X$—$HN(CH_2)_3$-$\overset{CH_3}{\underset{CH_3}{Si}}$-O-$\overset{CH_3}{\underset{CH_3}{Si}}$-$(CH_2)_3NH$)$_n$—
2SiPAS

Scheme 1 Schematic presentation of the synthesis of 2SiPAS.

short dimethylsiloxane units were synthesized; we then investigated their mechanical and surface properties. Recently, Oishi and colleagues reported the synthesis and thermal studies of a disiloxane–aramid multiblock copolymer[9] which has a different structure from 2SiPAS. The surface analysis of the block copolymer, however, has not yet been accomplished.

In this paper, we present the synthesis and the properties of 2SiPAS, especially from the point of view of the surface characterization. We also evaluate the interaction between 2SiPAS and adhered platelets.

EXPERIMENTAL

Materials

1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (BATS) was obtained from Chisso Co. (Tokyo, Japan) and dried at 100°C for 3 h under vacuum (4.5 torr). 3,4'-Diaminodiphenylether (3,4'-DAPE; Wakayama Seika Industry Co., Wakayama, Japan) was purified by distillation. Isophthaloyl chloride (IPC), triethylamine (TEA), and chloroform were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and also purified by distillation. Triethylamine hydrochloride (TEA · HCl; Wako Pure Chemical Industries Ltd., Osaka, Japan) was purified by recrystallization from ethanol. All other solvents and chemicals were purified by distillation.

Synthesis of 2SiPAS

2SiPAS was synthesized by low-temperature solution polycondensation through a two-step procedure (Scheme 1). First, α,ω-dichloroformyl-terminated aramid oligomers were prepared by the reaction of IPC with 3,4'-DAPE in a chloroform–TEA · HCl system at −15°C for 5 min in the presence of TEA as hydrogen chloride acceptor under nitrogen. Next, the preformed aramid oligomers were reacted with BATS at −15°C for 1 h. The reaction was then continued at room temperature for another 48 h under nitrogen. The polymer was isolated with excess amounts of ethanol; a low molecular weight fraction enriched in BATS was removed by washing the product with a good amount of n-hexane three times, then drying it at 60°C for 48 h under vacuum.

The 2SiPAS films for tensile strength measurement, surface analysis, and platelet adhesion experiments were cast from 10 wt % N,N'-dimethylacetamide (DMAc) solution. 2SiPAS solution was slowly evaporated with heat-light at 60°C for 5 days. After that, the film was dried at room temperature for 24 h under vacuum.

Characterization of 2SiPAS

^{1}H-NMR spectra were recorded on a JEOL EX-90 Fourier transform spectrometer (JEOL, Tokyo, Japan). The polymers were dissolved in DMSO-d_6.

Gel permeation chromatographic (GPC) analysis was performed with N,N'-dimethylformamide containing 0.01 mol/L of lithium bromide as an eluent

on a Shimadzu LC-6A system (Kyoto, Japan) equipped with an RI detector (Shodex, SE-51, Tokyo, Japan) using two columns (Shodex AD-80M/S, 8 × 250 mm) at 40°C. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were calculated on the basis of polystyrene calibration.

Inherent viscosity of 2SiPAS was measured using Ostowald's viscometer at a concentration of 0.5 g/dL in DMAc at 30°C.

Tensile Properties Measurement

Tensile properties were determined by the stress–strain curves obtained with a Tensilon UTM-I (Toyo Baldwin Co., Tokyo, Japan) at an elongation rate of 1.0 mm/min. Measurements were performed at room temperature on film specimens (3 mm wide, 15 mm long and 0.1 mm thick); four individual determinations were averaged.

Surface Analysis of 2SiPAS Films

Static contact angle measurements against water and methylene iodide were made on a contact angle goniometer (Eruma Type-I; Tokyo, Japan) on 2SiPAS films at 25°C and 65% relative humidity. This procedure was repeated 6 times at various locations on the film's surface in order to ensure the uniformity of structure, and all values reported in this paper represent the average of several readings. Agreement was generally within ± 2°. The surface free energy of the 2SiPAS surface was determined by Young's equation[10] and the component ratio of 2SiPAS surface was calculated by Cassie's equation.[11]

A spectrometer ESCA 1000 (Shimadzu Co., Kyoto, Japan) was used to carry out XPS measurements of 2SiPAS films using a MgKα X-ray source. The Si/C ratios were calculated by the peak area of Si_{2p} and C_{1s} spectra. Typical operating conditions were as follows: X-ray gun, 8 kV, 20 mA; takeoff angle, 90°; pressure in the source chamber, ca. 10^{-8} torr.

Platelet Adhesion Measurement

Platelet rich plasma (PRP) and platelet poor plasma (PPP) were prepared from normal human blood using sodium citrate as an anticoagulant.[12] Platelet suspensions (1.0 mL) with a concentration of 200,000 platelets/mm³ (prepared by mixing the PRP with PPP) were placed on the sample films and glass

plate of 1.8 cm², then incubated at 37°C for 15 min. After being rinsed with phosphate-buffered saline, the sample films were fixed with glutaraldehyde, freeze-dried overnight, and coated with gold. The platelets on the films were then observed with a scanning electron microscope (SEM) (ALPHA-245, Akashi Co., Tokyo, Japan).

RESULTS AND DISCUSSION

Preparation of 2SiPAS

The resulting copolymers' structure was confirmed to be the proposed block copolymers by means of ^{1}H-NMR spectroscopy. The typical NMR spectrum of 2SiPAS in DMSO-d_6 appears in Figure 1. Three remarkable peaks at 0.0, 6.7–8.5, and 10.4 ppm can be assigned to the protons of methyl, phenyl, and amide groups, respectively. The BATS contents of the block copolymers were calculated from the intensity ratio of the protons of the methyl (designated BATS unit) and phenyl groups (designated aramid unit). The results of the preparation of 2SiPAS in this study are summarized in Table I. The BATS content of every 2SiPAS was found to be less than the calculated value, and the yields of the 2SiPASs decreased with increasing the BATS contents. These phenomena were explained as follows: as the reactivity of BATS was relatively low, the 2SiPAS of higher BATS content tends to be lower molecular weight. Though the yields of crude copolymer were almost 100%, a low molecular weight fraction enriched in BATS was removed by n-hexane purification; then the 2SiPASs of relatively high molecular weight and narrow molecular weight distribution
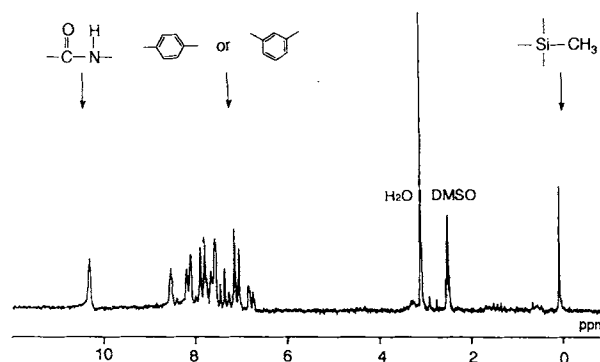
Figure 1 ^{1}H-NMR spectrum of 2SiPAS(IV) in DMSO-d_6. The peaks of protons of methyl, phenyl, and amide groups were given at 0.0, 6.7–8.5, and 10.4 ppm, respectively.

were obtained. Similar results were observed in the case of the preparation of PAS.[1] The inherent viscosities have a good correlation with the M_n determined by GPC. From this result, it becomes clear that the inherent viscosity is useful in estimating the molecular weight of siloxane–polyamide copolymers PAS or 2SiPAS, which have poor solubility in general solvent for GPC.

Mechanical Properties

The tensile properties of 2SiPASs are shown in Figure 2. The tensile strength could be drastically improved (40 to 80 MPa) for all 2SiPASs, though the tensile strength of PAS (PDMS = 1,680) whose PDMS content was 25 wt % (6 mol %) indicated 12 MPa.[1] A comparison of the curves shows significant decrease in tensile strength and decrease in elongation at break with increasing BATS content. In the former study, different results were observed for PAS. In the case of PAS which had a longer dimethylsiloxane chain (PDMS; M_n = 1,680), the elongation at break of the films decreased with decreasing PDMS content.[1] The high elongation of 2SiPAS having low BATS content can be explained by the necking phenomenon during the tensile experiment. By simple calculation, the molar ratios of the BATS units to aramid units were determined to be 1 : 6 for 2SiPAS(III) and 1 : 4 for 2SiPAS(II). The critical value for the necking phenomenon seemed exist around these molecular ratios. This result shows that a certain aramid-unit chain length is necessary for the necking phenomenon to occur, and that the BATS in 2SiPAS of lower BATS content must be mixed with aramid at molecular uni-
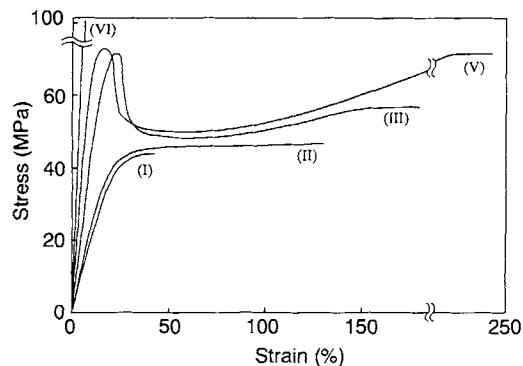

Figure 2 Stress–strain curves for 2SiPAS. BATS contents in bulk are shown in Table 1.

formity (not phase separated). The same results were reported in our previous paper[1] and in the study of Oishi and coworkers.[9] To confirm this speculation, the DSC study of 2SiPAS is now in progress.

Surface Composition of 2SiPAS

Figure 3 shows Si/C stoichiometries of the 2SiPAS films by X-ray photoelectron spectroscopy (XPS). It is apparent that the Si/C ratio increases with increasing BATS content in the 2SiPAS films. The surface Si/C ratio calculated from XPS spectra increased logarithmically with increasing BATS content, whereas the bulk Si/C ratio calculated from ^{1}H-NMR spectra increased exponentially. From this difference between the XPS data and the ^{1}H-NMR data, it seemed that a significant excess of BATS units in the near surface region can be observed for all the 2SiPASs, as expected from the much lower surface tension of siloxane relative to that of aramid

Table I Preparation of 2SiPAS

No.	Aramid Oligomer in Feed (X)	BATS Content (wt %)		Yield (%)	Inherent Viscosity[c] (dL/g)	$M_n{}^d \times 10^{-4}$	$M_w/M_n{}^d$
		Calcd[a]	Found[b]				
I	1	35	26	75	0.48	7.8	1.4
II	2	25	17	80	0.55	7.6	1.6
III	4	15	11	89	0.65	9.8	1.5
IV	6	10	7	90	0.42	6.3	1.5
V	8	8	5	95	0.67	9.9	1.6
VI	—	0	0	100	1.42	18.3	1.6

[a] Weight (BATS)/[weight (BATS) + weight (aramid)] in feed.
[b] Calculated from the SiCH$_3$/aromatic H ratio.
[c] Measured at a concentration of 0.5 g/dL in DMAc at 30°C.
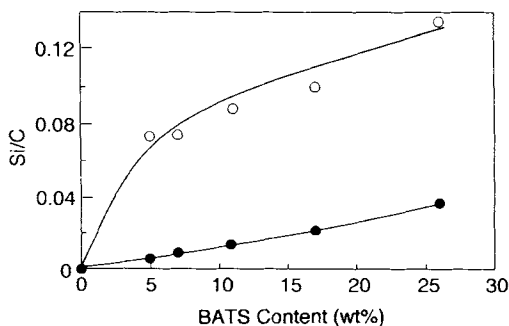[d] Determined by GPC on the basis of polystyrene calibration.

Figure 3 Elemental analysis of 2SiPAS surface by XPS. (O) Si/C calculated by XPS; (●) Si/C calculated by ^{1}H-NMR.

Figure 4   Contact angle of 2SiPAS surface. (O) Against water; (●) against methylene iodide.

(the critical surface tension of wetting for PDMS is 22 dyn/cm,[13] versus 46 dyn/cm for aramid).

The 2SiPAS surfaces' static contact angles against water and methylene iodide appear in Figure 4. Evidently, the contact angles against both water and methylene iodide give increasing linear plots.

The surface free energy and the proportion of BATS content in 2SiPAS surface versus BATS content in bulk are shown in Figure 5. The surface free energy was lineally decreased, and finally reaching 25 dyn/cm. Because the critical surface tension of wetting for PDMS is 22 dyn/cm, it is thought that the contribution of the aramid component remains on the surface. XPS measurement confirms this speculation. BATS content of the surface, calculated by Cassie's equation, was lineally increased with increasing BATS content in bulk. Especially for 2SiPAS(I), the BATS units occupied about 80 mol % of the outermost surface, although the chain length of the dimethylsiloxane was very short. On the contrary, in the case of PAS whose PDMS component had M_n of 1,680, the introduction of PDMS into the copolymer also caused PDMS-unit condensation at the outermost surface; and the PAS surface was fully covered by PDMS, with PDMS content of less than 1 wt %.[1]

Platelet Adhesion to 2SiPAS

It is thought that the surface of 2SiPAS with 26 wt % BATS content may possess blood compatibility similar to PAS, from the fact that the surface free energy is very low (25 dyn/cm). Figure 6 shows the SEM micrograph of platelets adhering to the surfaces of 2SiPAS, aramid, and glass. On the surface of 2SiPAS(I), platelets were scarcely adhered. It might be concluded that the surfaces of 2SiPASs whose BATS contents were 26 wt % in bulk had in
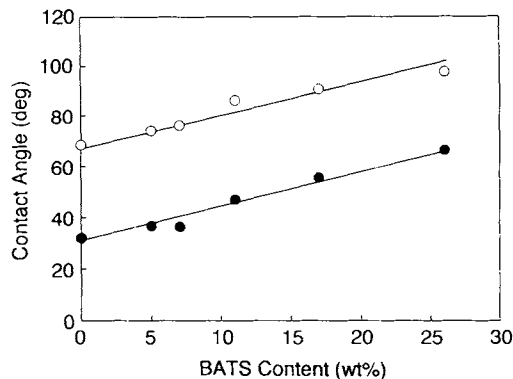
vitro bioinertness, which must be caused by the enrichment of BATS units at the outermost surface.

In conclusion, a novel disiloxane–aromatic polyamide multiblock copolymer (2SiPAS) was obtained in a high yield, thereby giving good transparent and tensile properties. Specifically, we found that the BATS contribution to the 2SiPAS surface increased lineally when BATS content was increased in bulk, as there was a wide difference of surface free energy between aramid and siloxane. Because of its unique properties, the novel functional polymer 2SiPAS is expected to have application for not only a biomaterial but also a tough and easy surface alternating material.
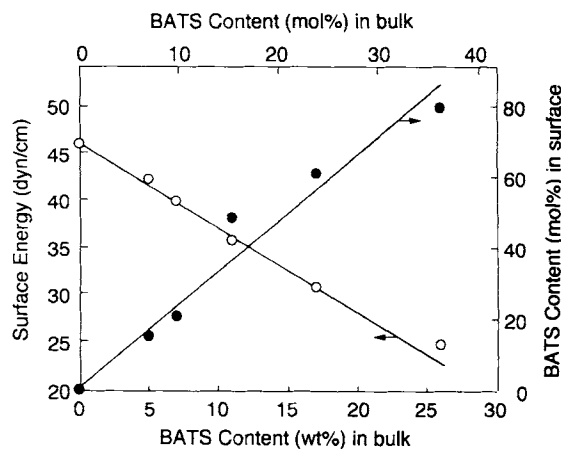
Figure 5   Surface characterization of 2SiPAS films by static contact angle. (O) Surface free energy; (●) BATS content calculated by Cassie's equation (in surface).
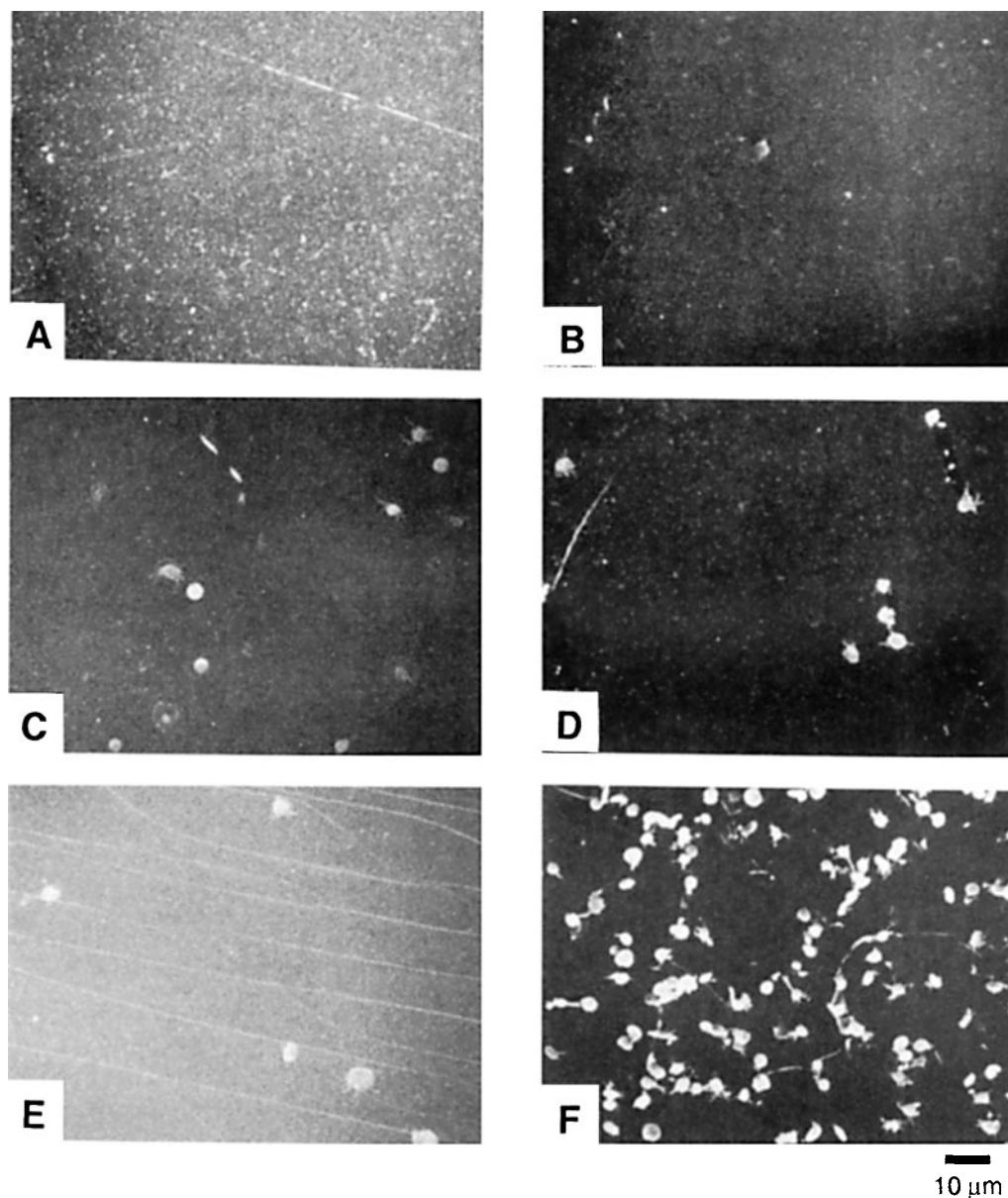
10 µm

Figure 6   Scanning electron micrographs of adhered platelets on 2SiPAS films (original magnification ×1,000). (A) 2SiPAS(I), (B) 2SiPAS(II), (C) 2SiPAS(III), (D) 2SiPAS(V), (E) 2SiPAS(VI) (aramid film), and (F) glass plate.

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