Surface Characterization of Segmented Siloxane–Urethane Block Copolymers

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SYNOPSIS

New siloxane–urethane block copolymers were synthesized and the effect of a siloxane moiety on microphase segregation in soft/hard block copolymers was studied by several analytical methods. Scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) provided topographical and bulk composition information. Electron Spectroscopy for Chemical Analysis (ESCA) provided surface chemical information. Fourier Transform Infrared Spectroscopy (FT-IR) provided chemical bond information for the near-surface region. Thermogravimetric Analysis (TGA) provided information concerning the thermal stability of the polymers. Differential Scanning Calorimetry (DSC) provided information on the soft and hard block segments within the polymer. These studies showed that the block copolymer contained an enhanced silicone-containing surface. For films cast on glass, less silicon was detected in the bulk (exposed by physically removing the surface material), and on the backside (glass) of the polymer film, than on the air-exposed surface. Of particular interest is the fact that data also show that the solvents, from which the polymers were cast, have a significant influence on microphase segregation. The films cast from THF have higher silicone concentrations at the surface as compared to polymers cast from DMAC/CH_2Cl_2 or dioxane. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic polyurethane elastomers, as segmented copolymers, exhibit a heterogeneous microstructure. The heterogeneous microstructure is a result of the thermodynamic incompatibility of the soft and hard block segments. Soft segments are based on polydimethylsiloxanes or polyethers. Hard segments are based on isocyanates (usually dicyclohexylmethane diisocyanate with an aliphatic diol acting as a chain extender).

Segmented polysiloxane polyurethanes, with enhanced silicone-containing surfaces, have interesting properties. The enhanced silicone-containing surface imparts an antithrombogenic character.[1] While references document attempts at producing and characterizing polymers for use as blood compatible products for humans,[2-4] a second important property is an increase in flame retardancy.[5]

An impressive selection of analytical techniques is available to study the surface characteristics of segregated block copolymers. Scanning electron microscopy (SEM) is the most widely used technique for examining surface topology. Energy dispersive spectroscopy (EDS) involves collecting emitted photons, which are generated by the interaction of an incident SEM electron beam, with a sample surface. The spectrum obtained is a plot of the number of emitted photons vs. kinetic energy. Each element has a unique spectrum, and the spectral peaks from a mixture are approximately the sum of the elemental peaks from the individual constituents. Elemental information is derived from both the surface (top few atomic layers) and the bulk film, with an approximate maximum sampling depth of 1 micron at 20 Kev.

A more surface-sensitive analytical method is electron spectroscopy for chemical analysis (ESCA). ESCA involves irradiation of solid materials *in vacuo* with monoenergetic soft X-rays and sorting the emitted electrons by energy. The spectrum obtained

is a plot of the number of emitted electrons vs. kinetic energy. Each element has a unique spectrum, and the spectral peaks from a mixture are approximately the sum of the elemental peaks from the individual constituents.[6] Since the mean free path of the electron is small, the electrons that are detected originate from only the top few atomic layers. Quantitative data can be obtained from the peak heights or peak areas and identification of chemical states often can be made from the exact positions and separations of the peaks.

Another analytical technique, which provides information about the near-surface chemical environment, is infrared spectroscopy (IR) when utilized in a reflectance mode. IR involves the interaction of infrared radiation with the functional groups comprising a sample. A highly complex absorption spectrum is generated, which is uniquely characteristic of the functional groups present.

The literature shows extensive relevant work, a portion of which is cited here. Lee and McCarthy[7] prepared polymers with covalently attached triethoxysilane functionality from the reaction of a polymer film (chlorotrifluoroethylene), containing hydroxy groups and triethoxysilane (3-isocyanato propyl), in the presence of a catalyst. XPS (ESCA) was used to characterize the surface adhesion properties of a modified polymer to glass. Lee and McCarthy concluded that the polymer film had formed a covalent bond with the surface of the glass.

Hearn et al.[8] used XPS and secondary ion mass spectroscopy (SIMS) to analyze the surface of polyurethanes, especially polyether polyurethane block copolymers. An enrichment in polyether at the PEU surface was reported. They presented evidence for small quantities of hard segment component impurities in the polyether surface layer.

Giroux and Cooper[9] utilized additional techniques, including XPS contact angle measurements and FT-IR, to characterize the surfaces of plasma derived polyurethanes. Clark and coworkers[10a-d] published a series of studies based on more than a decade of XPS application to chemical bonding in macromolecules. Millard[11] reviewed the industrial application of surface analysis by XPS for fibers and polymers. Madura[12] studied rubber/metal bond failure by EDS, SIMS, and XPS. He concluded that these analytical tools are highly complementary and are essential for a detailed investigation of rubber/metal bond failure. Yasuda and Marsh[13] employed ESCA to analyze the polymer surfaces treated by a plasma. Another group, headed by Chilkoti et al.,[14] studied plasma-deposited polymeric films by ESCA and SIMS.

Tezuka et al.[15] have characterized polyurethane siloxane block copolymers by ESCA. They reported that the top surface of a cast block copolymer film was completely covered with a polysiloxane component (soft block). They also reported a thickness range of polysiloxane between 20 and 100 angstroms, depending on the block segment length and on the total siloxane content. They reported polysiloxane segment domination on the surface of the block copolymer films, even when the percent siloxane content of the system was less than 10% of the overall weight. Contact angle studies showed the wettability

Table I   Synthesis of Block Copolymers

Polymers	Oligomer	Wt (g) Oligomer	CH_2Cl_2 (mL)	Wt (g) Diisocyanate	Wt (g) HDO	Cosolvent (mL) DMAC	Soft Block (%)
A1	PDMSO(OH)$_2$[a]	1	200	26.9	12.1	15	2.5
A2	PDMSO(OH)$_2$	1	200	13.1	5.9	15	5
A3	PDMSO(OH)$_2$	2	200	19.9	7.7	15	7.5
A4	PDMSO(OH)$_2$	4	200	24.8	11.2	20	10
B1	PDMSO(OH)$_2$[b]	1	200	26.9	12.1	15	2.5
B2	PDMSO(OH)$_2$	1.5	200	19.6	8.9	20	5
B3	PDMSO(OH)$_2$	3	200	25.5	11.5	15	7.5
B4	PDMSO(OH)$_2$	4	200	24.8	11.2	20	10
C	PDMSO(OH)$_2$[c]	42	1200	164	118	120	15

PDMSO(OH)$_2$: Dihydroxy terminated polydimethylsiloxane.
[a] Mol wt 36,000.
[b] Mol wt 18,000.
[c] Mol wt 4200.

behavior of the siloxane polyurethane block copolymer to be similar to pure siloxanes, presumably because siloxane dominated the surface of the polyurethane.

Pascault and Camberlin[16] quantitatively determined that the nearly complete segregation of soft and hard segments in a dimethylsiloxane-based urethane polymer was due to the large difference between the solubility parameters of the two blocks. Shibayama et al.[17] studied the degree of completion of microphase separation for segmented polyurethane-containing block segments of poly(ethylene oxide)-b-poly(dimethylsiloxane)-b-polyethylene oxide by mechanical and thermal analysis, FT-IR, and small angle X-ray scattering (SAXS). From the SAXS analyses, they concluded that the polyure-

thane had formed a microphase structure. A microdomain structure is described as a hard segment, 60 to 70 angstroms in length, embedded in the soft segment matrix.

Tezuka et al.[18] studied the surface properties of poly(vinyl alcohol)-poly(dimethylsiloxane) graft copolymers by XPS and contact angle. These investigators reported a surface covered with essentially pure polydimethylsiloxane. In addition, they reported the same findings on samples with a 5 mol % siloxane unit content. Again, Tezuka et al.[19] reported a study of surface properties of polyurethane-polysiloxane graft copolymers by XPS and contact angle measurement and found the surface of the copolymers was completely covered with the polysiloxane component.
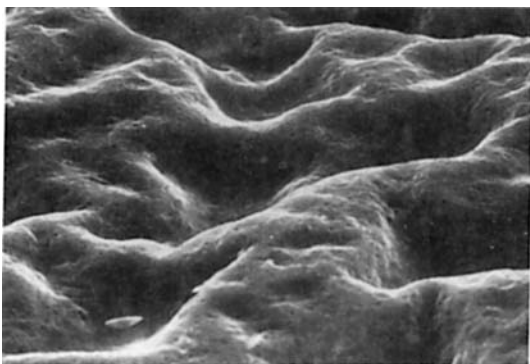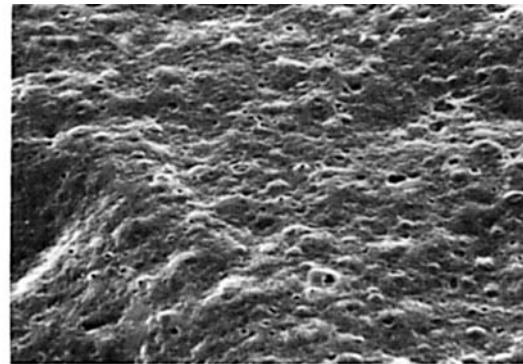

a (510 X)
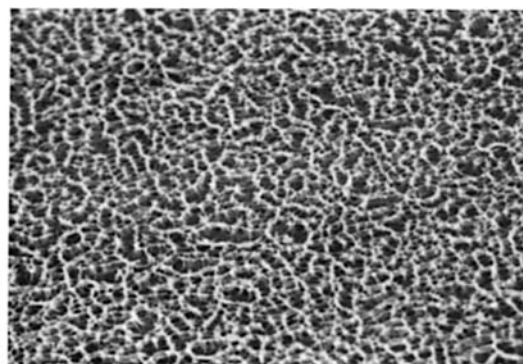
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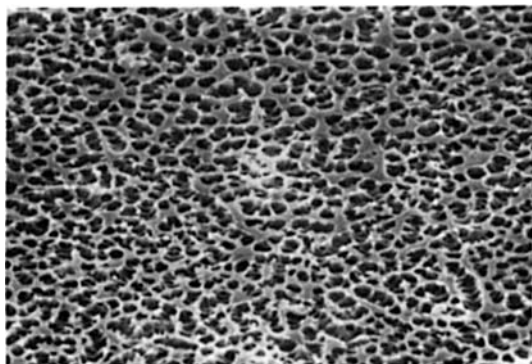
c (510X)

d (510X)

Figure 1 SEMs for block copolymer films with different soft block content. (a) 2.5%, (b) 5%, (c) 7.5%, and (d) 10%.

The purpose of the present work is to analyze the surfaces of segregated polysiloxane–polyurethane films. ESCA, SEM/EDS and FT-IR, TGA, and DSC were employed. Films were cast from DMAC, THF, and 1,4-dioxane as solvents. Solvent dependent differences in microphase segregation of these block copolymers were studied.

EXPERIMENTAL

Materials

Dihydroxy terminated polydimethylsiloxanes (mol wt 4200, 18,000, and 36,000) were purchased from Huls America, or Scientific Polymer Products, Inc.

These materials were degassed in a vacuum oven at 30°C for 48 h. $H_{12}MDI$, MDI, TDI, and Isophrone

were supplied by Miles Corporation and 1,6-hexanediol (HDO) was supplied by Aldrich. Dimethylacetamide (DMAC) was stirred over MgO for one week, then was distilled under vacuum and was kept over a molecular sieve 4 Å, under a nitrogen atmosphere. Methylene chloride was refluxed over CaH_2 and was distilled immediately before use. Tetrahydrofuran (THF) and 1,4-dioxane were distilled from benzophenone ketyl immediately before use.

Synthesis of Block Copolymers

Block copolymers were prepared by a "one shot" technique,[20] from a diol-terminated polysiloxane and corresponding diisocyanate and a chain extender, mixed at room temperature under a dry atmosphere (N_2).
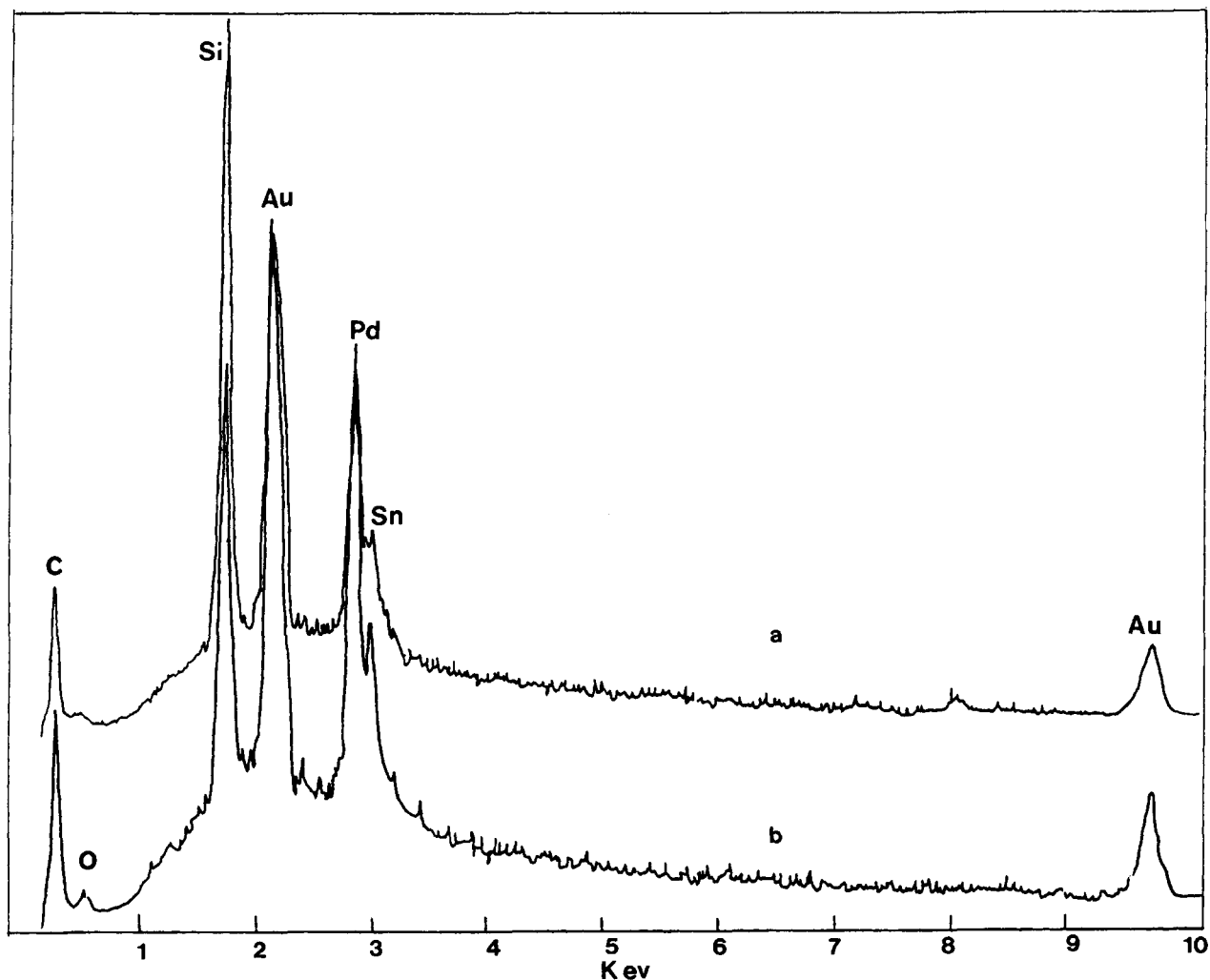

Figure 2   EDS spectra for block copolymer films with (a) 7.5% soft block and (b) 5.0% soft block.

To 4 g of oligomer (dihydroxyterminated poly-dimethylsiloxane, mol wt 36,000) in 100 mL CH_2Cl_2 were added 11.2 g, HDO dissolved in 15 mL DMAC, and 24.8 g bis(4,4'-diisocyanatocyclohexyl)methane (Desmodur W, Miles Corp.) in 100 mL CH_2Cl_2. Several drops of T-12 catalyst solution (dibutyltin dilaurate) were added and the solution was mechanically stirred under nitrogen at room temperature for 120 h. Completion of the reaction was monitored by the disappearance of the isocyanate IR absorption at 2270 cm^{-1}. The solvent was evaporated *in vacuo*, leaving a viscous oil. The polymer was dissolved in 50 mL 1 : 1 CH_2Cl_2/DMAC, THF, or 1,4-dioxane, and the solution was cast into films on glass plates using a 10 mil film applicator. After standing 2 weeks, the films were removed from the glass and were stored for at least 4 weeks before test. For reference, the side of the film, which faces the glass, was considered the backside of the film.

All polymers and films were made using the same general procedure, the variations in reaction parameters are reported in Table I.

All samples intended for surface analysis were exposed to an additional 4 days in a vacuum oven at 25–30°C. The samples deployed for TGA and DSC were dried in a vacuum oven at 65–70°C for 14 days. The polydimethylsiloxane is the soft block and the polyurethane part is the hard block.

INSTRUMENTATION

An Olympus Stereo model X-TR microscope was used to examine the surface of the polymer films. The inspections were performed at 50× magnification.

SEM and EDS analysis was performed on a model S-2700 Hitachi scanning electron microscope with an attached Kevex light element detector. Electron beam energies were 20 Kev. Data were collected from a scanned region of approximately 100 × 100 square micrometers. The X-ray detector was operated in the thin window mode at less than 20% dead time. A Denton Desk II Sputter coater, with a Pd/Au target, was employed for coating SEM samples to reduce surface charging affects.

Electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS) data were obtained with a Phi model 15-255G cylindrical mirror analyzer (CMA), attached to the Phi model 590 scanning auger microprobe. The spectra were generated with Mg K-alpha X-rays, at a power of 400 watts. The analysis area covered about 1 mm^2. The pass energy was set at 50

EV for multiplexed data and 200 EV for survey scans. Peak heights were expanded on survey scans to fit the tallest peaks to full scale. The total peak intensity of individual elements were adjusted on multiplex data by the sensitivity factor, stored in the software for each element. The results were reported as atomic percent. The samples were positioned at a 60° tilt angle, relative to the CMA. The photoelectron signal was maximized at approximately 30 K counts per sec.

a (1000 X)
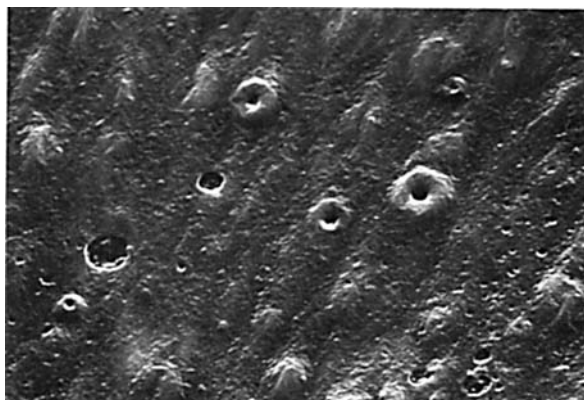
b (1000 X)

Figure 3   SEMs for two sides of film (2.5% soft block), (a) front surface and (b) back side of the film.

FT-IR spectra were recorded on a Nicolet model 5DXB FT-IR spectrometer, using a Spectra-Tech, Inc. model 500 specular reflectance attachment. Set-up included 150 scans with a resolution of 8 cm^{-1} and a detector gain of 4.

Thermogravimetric analysis was performed on a DuPont model 951 TGA attached to a DuPont model 9900 analyzer. Version 2.2 analysis software was utilized to calculate the percent residue. The samples were analyzed in a tared aluminum pan placed in a platinum basket. The purge rate was set at 50–60 mL/min for N_2 or air and the heating rate was set for a 20°C/min increase from ambient temperature to 630°C.

Differential scanning calorimetry (DSC) experiments were performed on a DuPont model 910 DSC attached to a DuPont model 9900 analyzer, using version 2.2 DSC software to analyze some of the transitions. Samples were analyzed in a crimped aluminum pan with a lid. An empty aluminum pan with a lid served as a reference. The purge rate was 34 mL/min N_2 and the heating rate was 10°C/min, from −75 to 150°C.

RESULTS AND DISCUSSION

SEM and EDS

Block copolymer films with different soft block contents (2.5, 5, 7.5, and 10%) have dissimilar surface topography. Figures 1(a) through 1(d), taken at 520X magnification, show distinct topographical differences. EDS spectra in Figure 2 illustrate higher
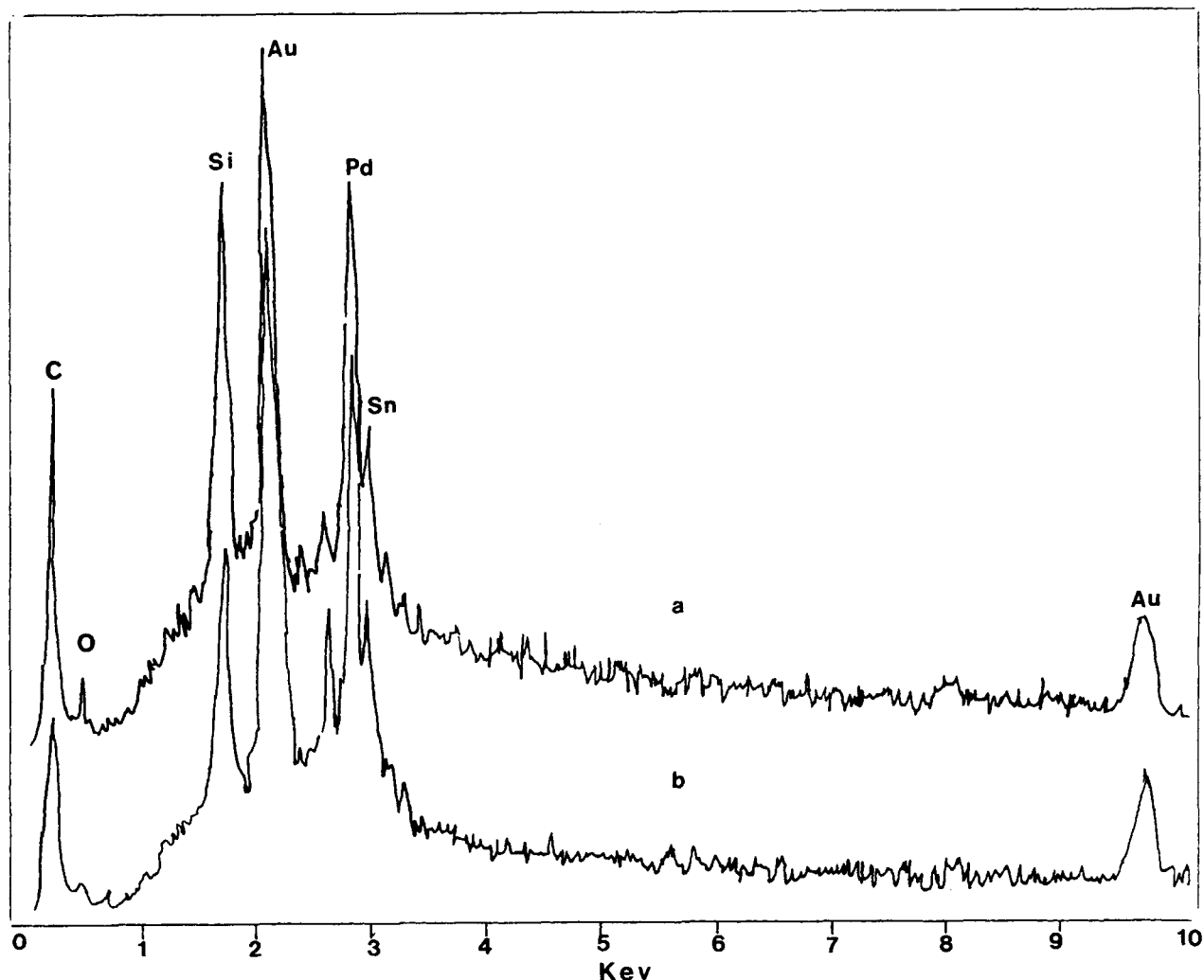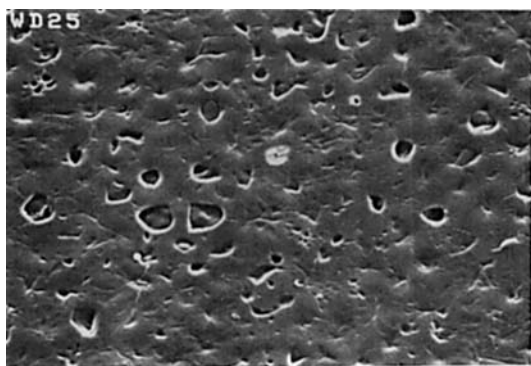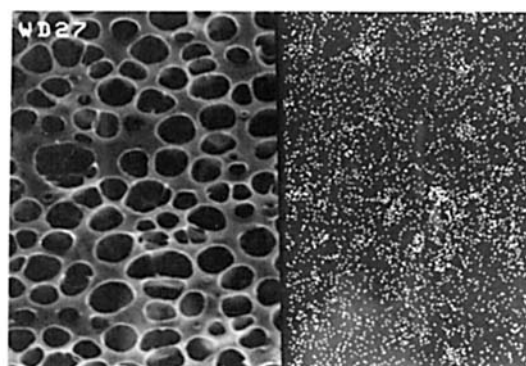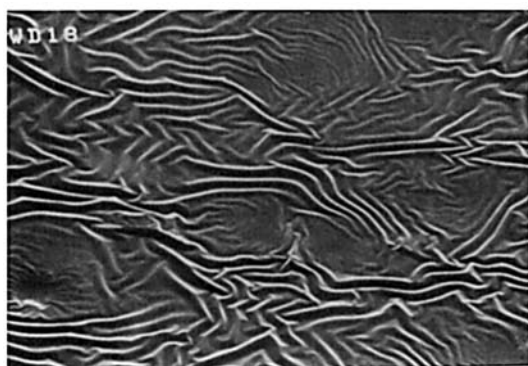

Figure 4   EDS spectra for two sides of block copolymer film with 2.5% soft block, (a) front surface and (b) back side of the film.
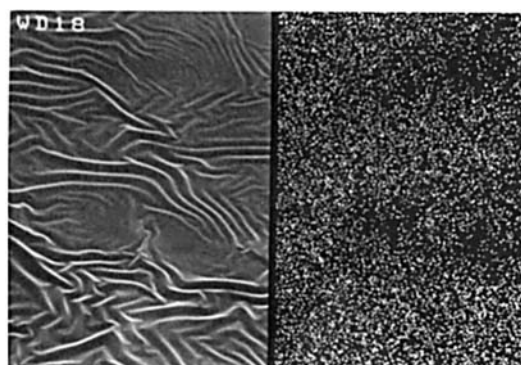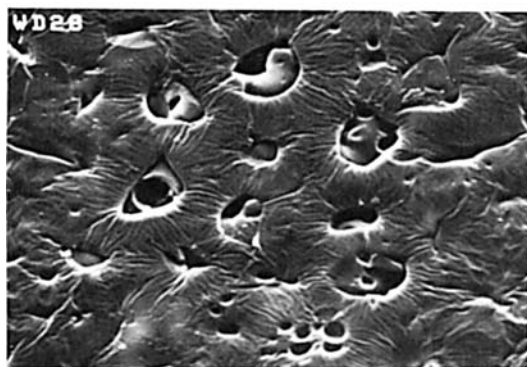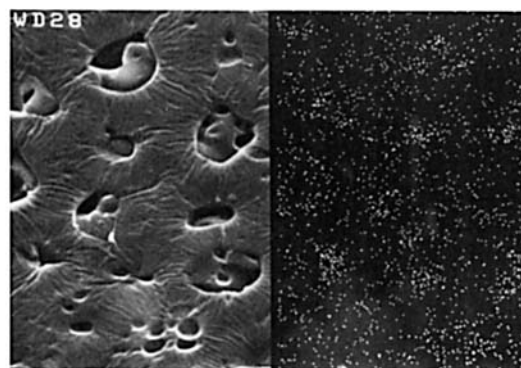
a (400X)

a (1000X)

b (900X)

b (900X)

c (900X)

c (900X)

Figure 5 SEMs of films cast from block copolymer (class B, 7.5% soft block content) in (a) DMAC/CH₂Cl₂, (b) THF, and (c) 1,4-Dioxane.

Figure 6 SEMs with secondary image for silicon for films cast from block copolymer (class B, 7.5%), (a) DMAC/CH₂Cl₂, (b) THF, and (c) 1,4-Dioxane.

silicon detection on films consisting of higher soft block content. Data taken from the top surface of the films were compared with data taken from the backside of the films. Figure 3 demonstrates the difference in surface topography of the front and backside on a film with 2.5% soft block content. EDS spectra for these two surfaces are shown in Figure 4. Higher silicon is indicated on the front surface of the film. SEM micrographs of films cast in three different solvents (DMAC/CH_2Cl_2, THF, and 1,4-Dioxane) are presented in Figures 5(a–c). The block copolymers show microphase segregation of soft and hard block components. The SEM and EDS results for films cast from DMAC/CH_2Cl_2, THF and 1,4-dioxane show that these films have different surface topography and different levels of segregation. The results from films cast in THF show a higher silicon concentration on the surface and a more uniform

distribution of soft block segments. These data indicate better microphase separation. Therefore, segregation of hard and soft block components, and the uniformity of the polymer surface, relate to the solvent casting system employed (Fig. 6).

Optical micrographs show that the surface of the film cast in DMAC/CH_2Cl_2 was generally smooth. The surface of the 1,4-dioxane film is covered with large openings. The THF film has some openings, which are spread across the surface. However, most areas on the film cast in DMAC/CH_2Cl_2 are not as smooth as the one cast in THF. Figure 6(a–c) shows split screen images of each of the three films. The left side is a secondary electron image of a specified region of the sample and the right side is the corresponding EDS elemental map for silicon (Si). When compared to the other two films, the film cast in THF has a better distribution of silicon across
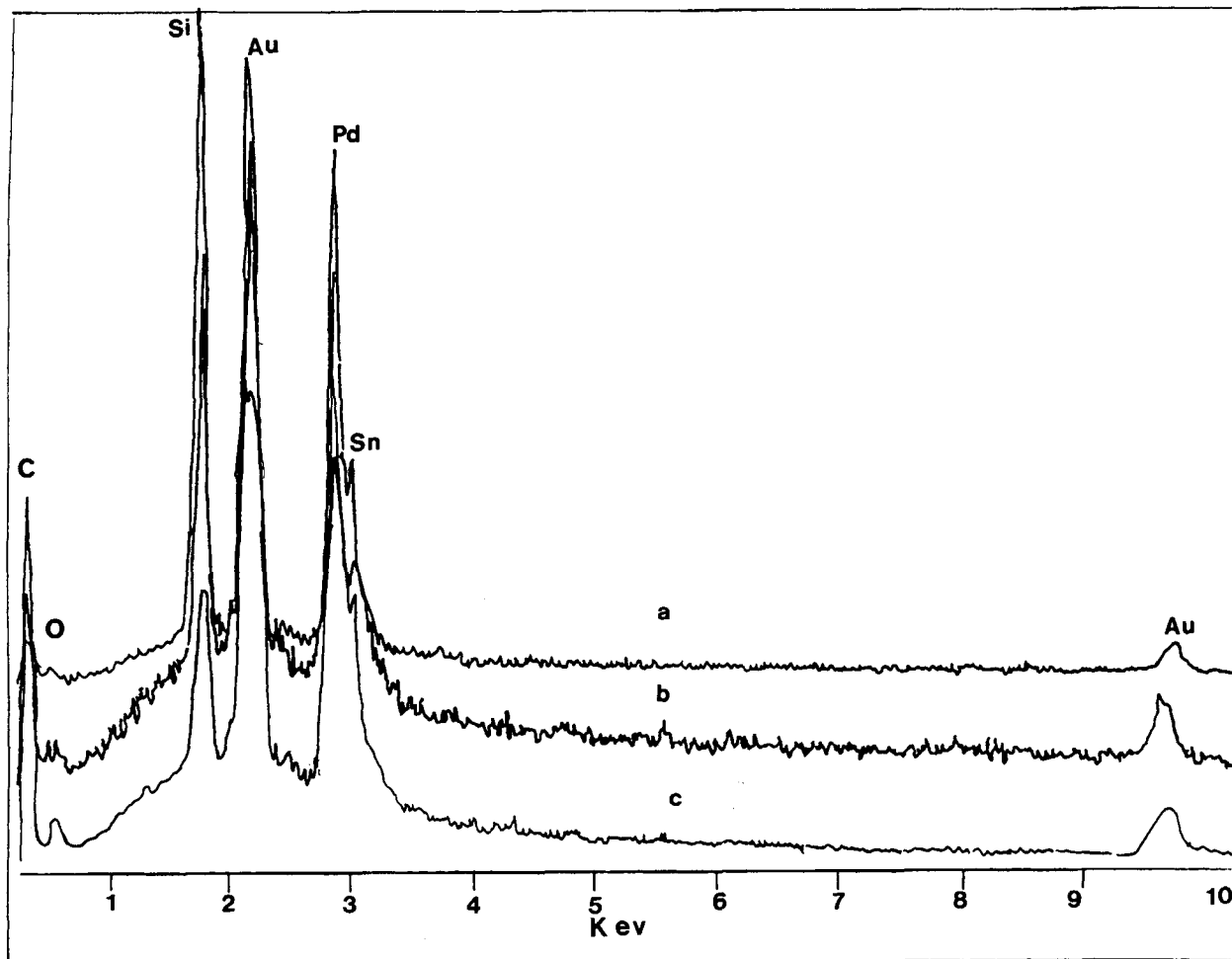

Figure 7 EDS spectra for mapped area for silicon (Fig. 7) for block copolymer cast in (a) THF, (b) DMAC/CH_2Cl_2, and (b) 1,4-dioxane.

the surface. This directly correlates to a more uniform surface structure. "Hot spots" of silicon were detected on films with less uniform surfaces. EDS spectra were collected from the surface of the three films (Fig. 7). A greater peak intensity for silicon was recorded for the THF sample.

SEM images and EDS elemental maps for silicon on class C copolymers (15% soft block content) are combined in Figure 8(a–c) for the front surface, backside, and peeled surface (bulk). The distribution of silicon, as indicated by the EDS maps, parallels the topography of the samples. When the sample surface is smooth and uniform, the silicon detected at that surface is found to be equally uniform. Corresponding EDS spectra for the class C copolymer film front surface, backside, and peeled surface (bulk) are shown in Figure 9.

ESCA

ESCA studies, for films obtained from polymers with different soft block contents, show the film with a higher soft block composition resulted in a higher surface concentration of silicon. Figures 10 and 11 display ESCA results from films of block copolymer concentrations of 2.5, 5, 7.5, and 10% soft block content, cast from $DMAC/CH_2Cl_2$ and THF. The elemental percentages for the surfaces of films cast from $DMAC/CH_2Cl_2$ and THF solution are shown in Table II. Despite a low silicon content in the block copolymers (0.95 to 3.79%), the results show a high concentration (up to 28%) of silicon on the surface. The silicon concentration on the surface is increased by raising the percentage of soft block content of the copolymer. Lower siloxane content films show some scatter enrichment of silicon on the surface, however, these films had lower overall silicon content across the surface when compared to films containing higher siloxane content. Figures 12 and 13 show increasing silicon on films with higher soft block content. Films, cast from THF, show a higher concentration of silicon as compared with films cast from $DMAC/CH_2Cl_2$. Data indicate that silicon enrichment on the surface can be linked to the increased solubility of the soft block in THF. Nitrogen is an element of the hard block. In the case of THF, a range of 0.5 to 1.1% nitrogen was detected on the surface. A range of 1.6 to 3.9% nitrogen was detected on films cast from $DMAC/CH_2Cl_2$. This again suggests a predominantly silicone soft block surface and an insignificant presence of hard block. ESCA results from the front surface, backside, and peeled surfaces for polymers with 15% soft block content
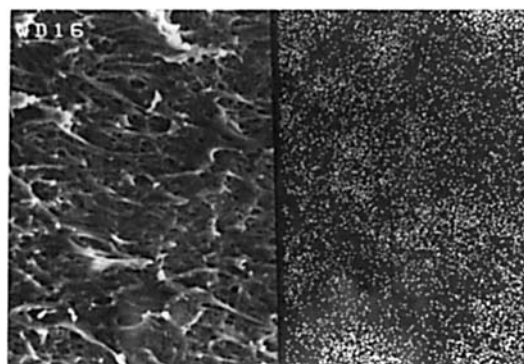
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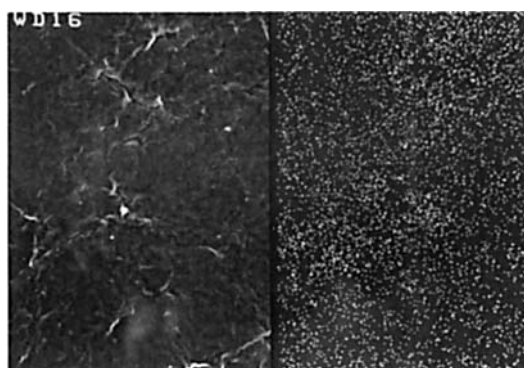
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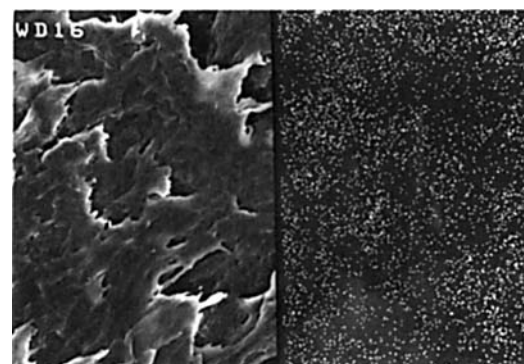
c (1000 X)

Figure 8   SEMs for films of block copolymer (class C, 15% soft block content) for (a) front surface, (b) back of the film, and (c) peeled surface (bulk).
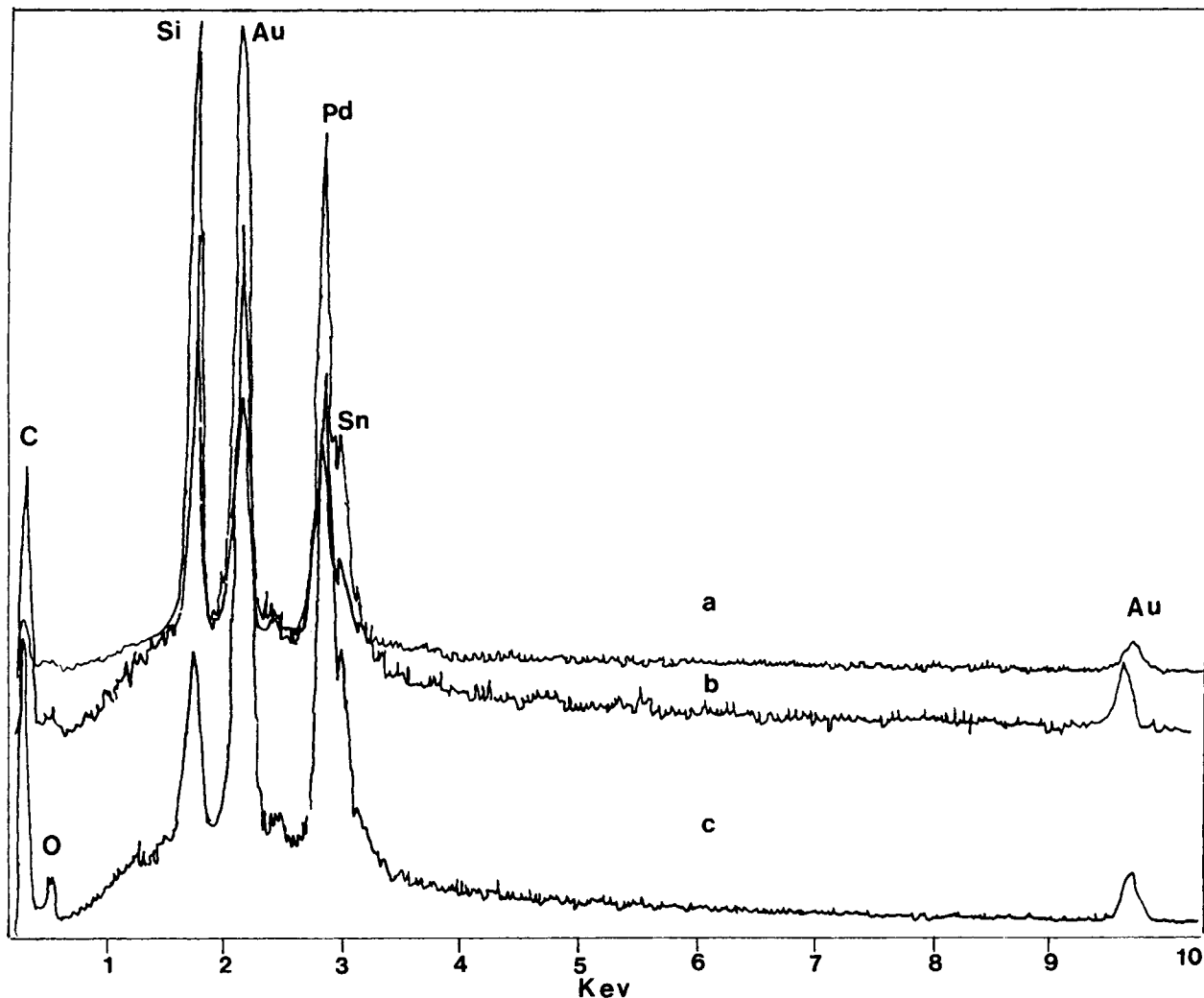
Figure 9 EDS spectra for films of block copolymer (class C, 15% soft block content), (a) front surface, (b) back of the film, and (c) peeled surface (bulk).

are shown in Figure 14. The front surface again shows a higher silicon concentration when compared to the other regions. Note that in the spectrum taken of a skinned surface (bulk), the $N(1s)$ peak, which relates directly to the hard block segment, is more intense when compared to the other two spectra.

In general, these results are consistent with the ESCA, SIMS, and contact angle measurements reported by other investigators.[16-18] They reported enhanced silicone-containing surfaces for silicone-containing copolymers.

FT-IR

FT-IR resulted in less quantitative data than did EDS and ESCA. The FT-IR penetration was deeper into the film. EDS and ESCA penetration was lim-

ited to the near surface portion of the samples. Qualitative results were obtained and surface spectra showed peaks relating to polydimethysiloxane. Data points (1263, 1108, and 1059 cm^{-1}) were compared to the literature[21] (1260, 1130–1000, and 1090–1020 cm^{-1}). FT-IR spectra for two films with different silicone soft block content of 2.5 and 10% are shown in Figure 15. The 10% soft block film shows enhancement of appropriate peaks.

Thermal Analysis: TGA and DSC

Thermogravimetric analysis studies showed a correlation of an increased percentage of silicone soft block with increased thermal stability in both nitrogen and air (Table III).
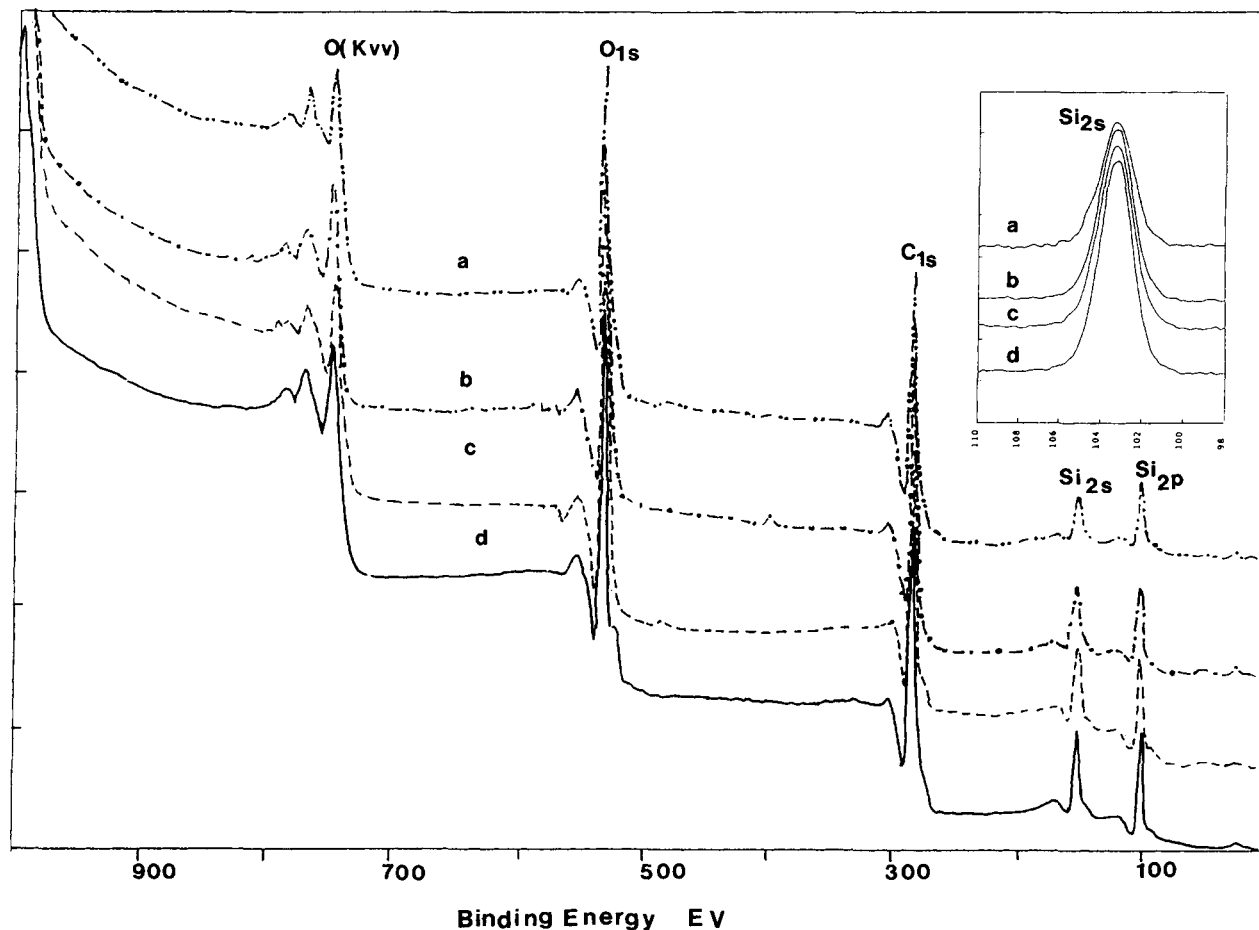
Figure 10   ESCA spectra for block copolymer films [class B, with (a) 2.5%, (b) 5%, (c) 7.5%, and (d) 10% soft block content cast from THF].

Table II   Comparison of ESCA Results for Polymer Films Cast in DMAC/CH₂Cl₂ and in THF[a]

Polymer	Soft Block Content (%) (Si %)	O (%)	Si (%)	N (%)	C (%)
A1	2.5 (0.95)	18.1 (22.3)	19.7 (23.6)	3.9 (1.1)	58.4 (52.9)
A1	2.5 (0.95)	— (21.8)	— (24)	— (1.3)	— (52.9)
A2	5.0 (1.9)	20.6 (22.8)	20.9 (26.8)	1.6 (0.5)	57.0 (49.9)
A2[b]	5.0 (1.9)	— (25.5)	— (25.5)	— (0.5)	— (51.0)
A3	7.5 (2.8)	18.9 (22.3)	16.5 (25.1)	3.4 (0.6)	57.0 (49.9)
A4	10 (3.7)	19.9 (22.3)	19.4 (28)	2.5 (0.5)	48.3 (49.2)
B1	2.5 (0.9)	19.2 (24.0)	18.5 (20.2)	2.7 (1.4)	59.6 (54.4)
B2	5.0 (1.8)	19.8 (21.8)	18.5 (22.2)	2.4 (1.7)	59.2 (54.3)
B3	7.5 (2.8)	20.6 (22.7)	20 (27.6)	1.9 (0.4)	56.8 (49.3)
B4	10 (3.7)	21.1 (22.1)	18.9 (26.1)	2.4 (0.1)	57.5 (50.8)
C1 Surface	15 (4.9)	22.6	28.9	0.5	48
C1[b] Surface	15 (4.9)	22.6	28.6	0.5	48.3
C1 Peeled	15 (4.9)	21.4	22.4	1.8	54.4
C1 Back	15 (4.9)	22.0	22.0	1.7	54.3

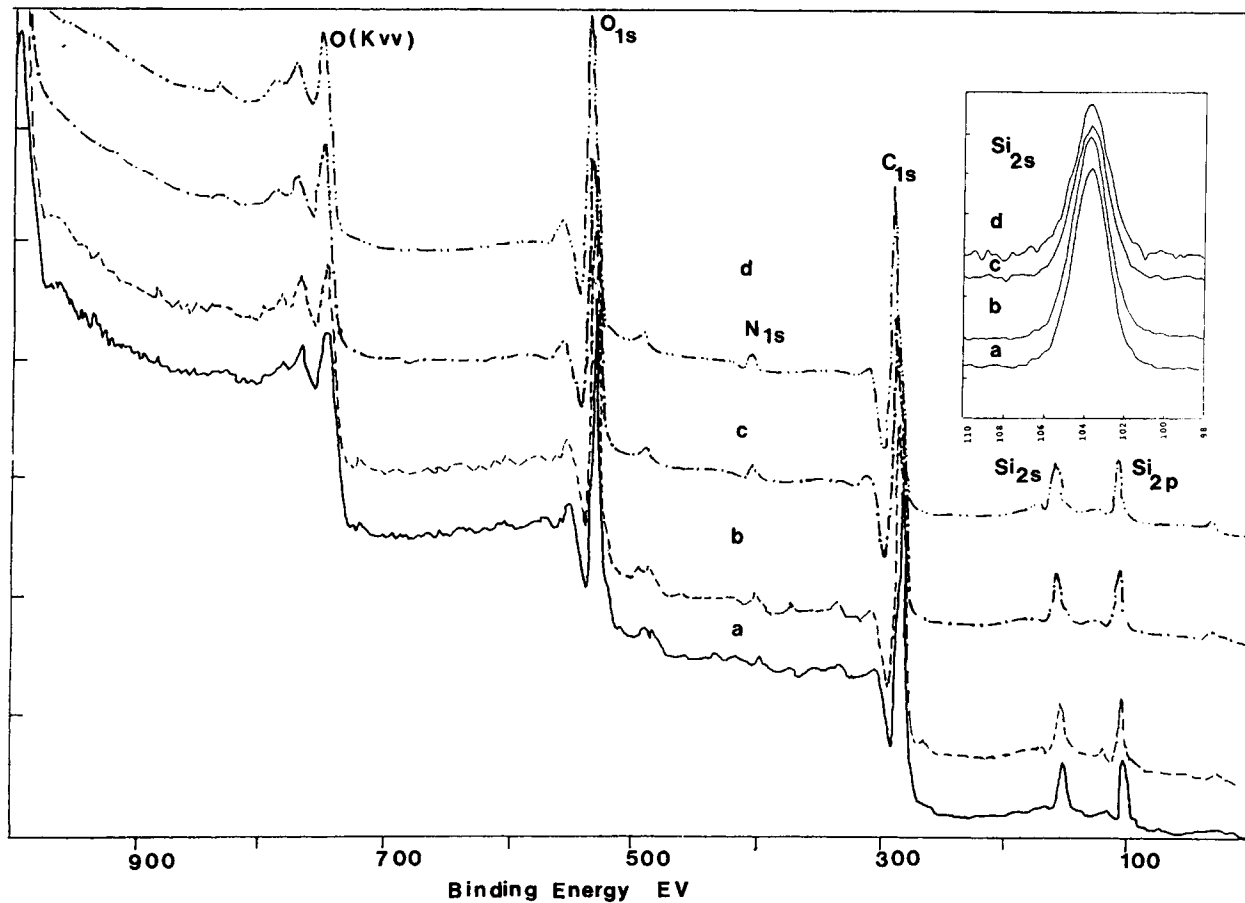[a] The values in parentheses are for films cast in THF.
[b] Repeated Results

Figure 11 ESCA spectra for block copolymer films [class B, with (a) 2.5%, (b) 5%, (c) 7.5%, and (d) 10% soft block content cast from DMAC/CH$_2$Cl$_2$].

Figure 12 Si found (ESCA) on the surface of block copolymer films with different soft block content (class A, 2.5; 5; 7.5; and 10%) and cast from THF ($\triangle$), and DMAC/-CH$_2$Cl$_2$ ($*$).
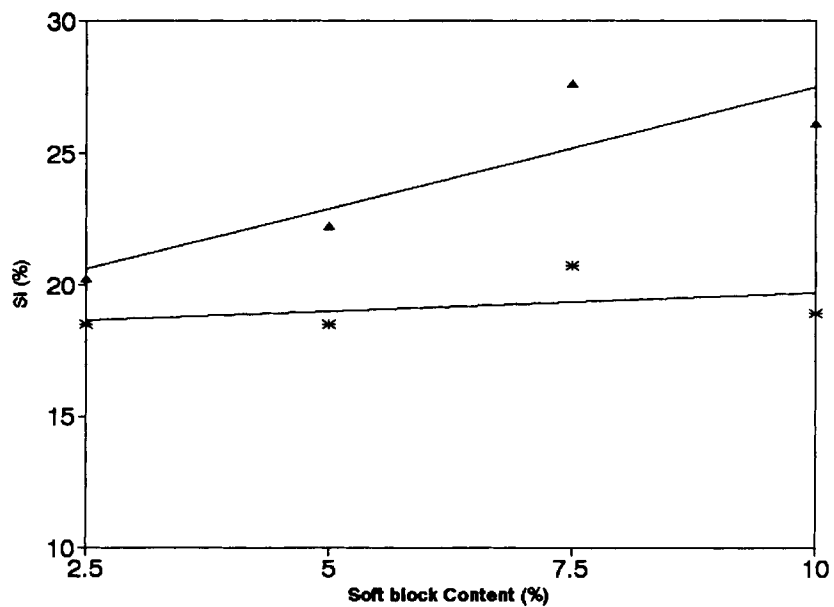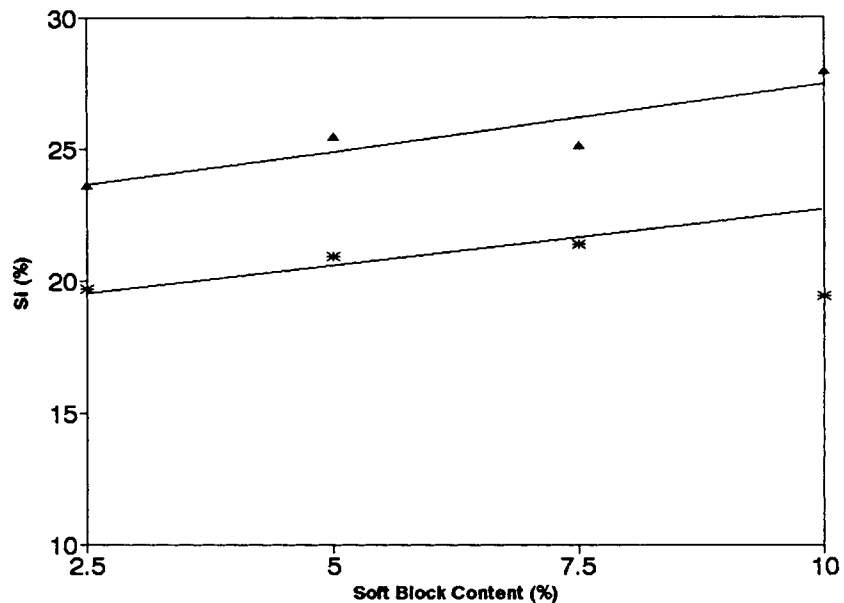
Figure 13 Si found (ESCA) on the surface of block copolymer films with different soft block content (class B, 2.5; 5; 7.5; and 10%), and cast from THF ($\triangle$), and DMAC/-CH_2Cl_2 ($*$).
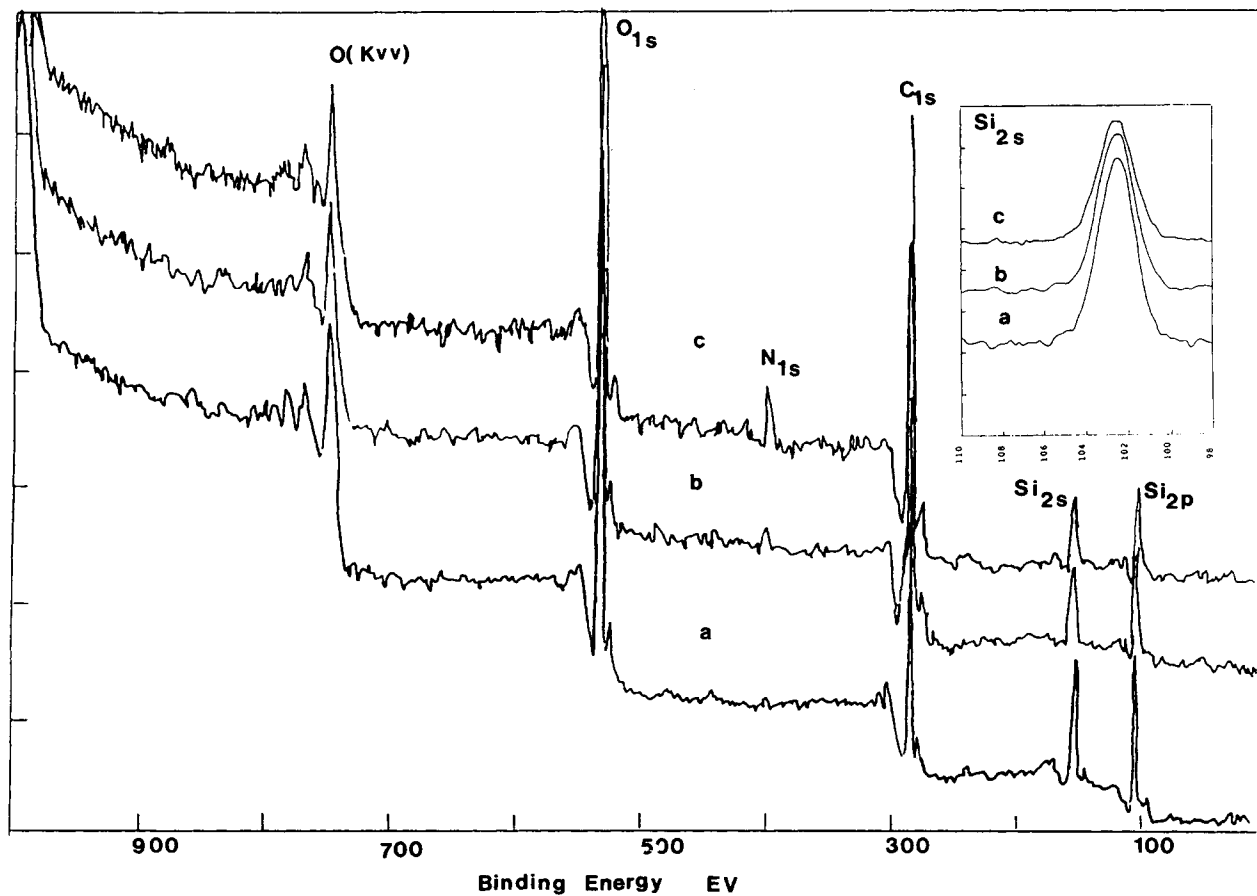

Figure 14 ESCA spectra for block copolymer films [class C, 15% soft block content] (a) front surface, (b) back of the film, and (c) peeled surface.
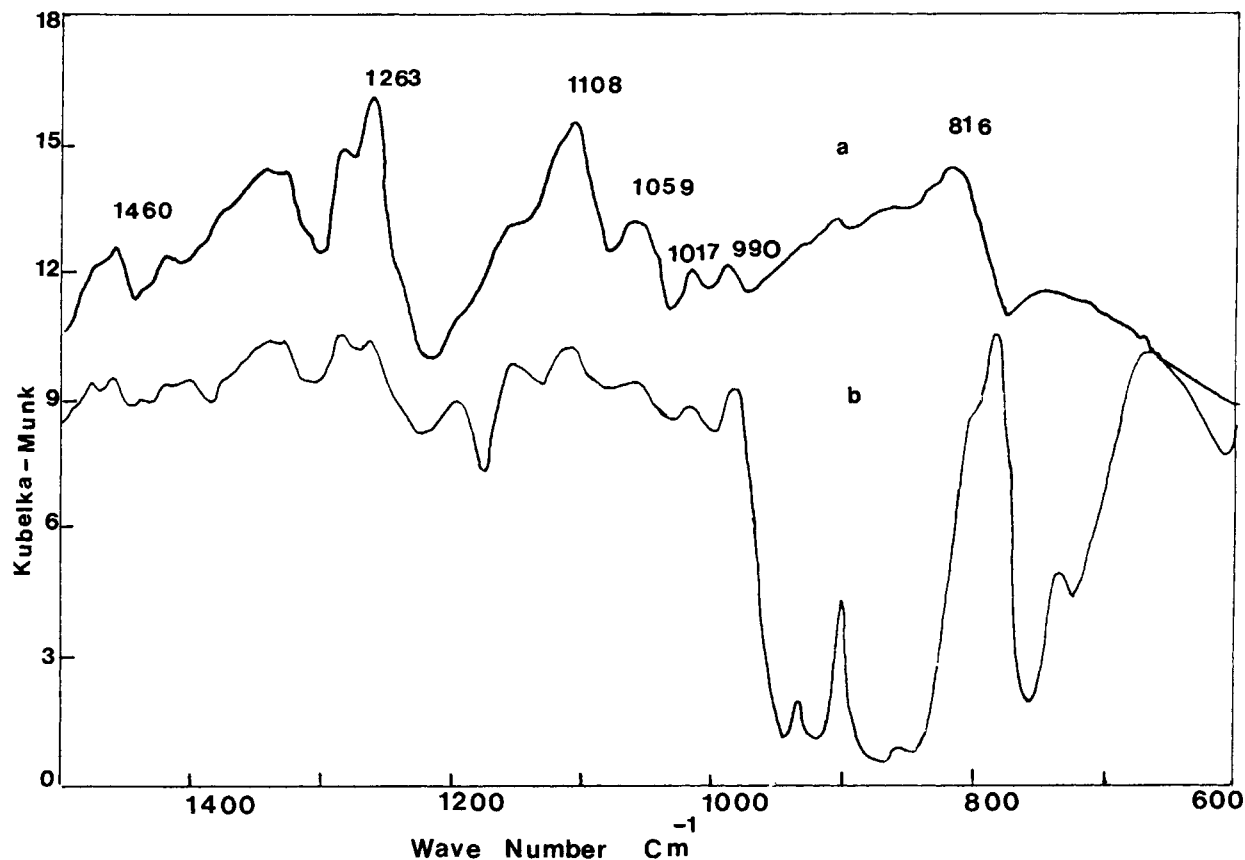
Figure 15 IR spectra for films surface of block copolymer [class B, with (a) 10% soft block, and (b) 2.5 soft block content].

Differential scanning calorimetry was also performed on these films (Table IV). Polymers with higher silicone content (> 5%) showed two glass transitions, one at −45 to −35°C and another above room temperature, and a melting point (T_m) for the hard block segment above 100°C. Low and high temperature T_gs are for the soft and hard segments of the block copolymers, respectively. For films with

a silicone content lower than 7.5%, the first transition is barely detectable. For a polymer with 25% soft block, when the sample is cooled after the first run and the DSC is repeated, the second run is consistent with the first.

CONCLUSIONS

The surface characteristics of segmented siloxane urethane block copolymer films, cast from different

Table III   Thermogravimetric Analysis of Class B Block Copolymers in N$_2$[a]

Polymer	Soft Block Content (%)	T °C at 10% Weight Loss	T °C at 50% Weight Loss
B1	2.5	261 (252)	353 (359)
B2	5.0	267 (273)	353 (365)
B3	7.5	297 (298)	356 (370)
B4	10	314 (316)	374 (370)
B5	25	335 (336)	389 (386)

[a] The values in parentheses are for TGA in air.

Table IV   Thermal Transition Temperatures of Selected Block Copolyurethanes, Class B

Polymer	Soft Block Content (%)	T_g 1	T_g 2	MP
B1	2.5	—	53	93
B2	5	−45	31	—
B3	7.5	−47	51	120
B4	10	−47	47	93
B5	25	−47	54	119

solvent systems, were studied by a variety of analytical techniques. EDS and ESCA both show silicon dominated polymer surfaces (an indication of a highly siliconated soft block at the surface). A higher percentage of soft block component in the polymer results in an increased silicon concentration at the surface.

These materials show two glass transitions. The first of these transitions is nearly nonexistent in polymers with a low soft block content. The films exhibit good thermooxidative stability. Their stability is dependent upon the amount of silicone soft block in the block copolymer, for example, the thermal stability of the film increases as more silicone is inserted into the structure of the block copolymers.

Of particular interest is the fact that microphase segregation of the block copolymers is dependent upon the solvents used to cast the polymers. Smooth polymers, cast in THF, showed the most soft block segregation on the surface of the polymer, leading to a uniform distribution of silicon across the surface.

A polymer film or sample can be designed with surface properties of the soft block and the mechanical properties of the hard block. Design freedom includes specific chemical identity and block length. The extent of segregation and surface enhancement of the soft block can be further controlled by using different solvent systems or processing conditions.

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