The Composition and Structure of the Surfaces of Poly(urethane ureas)

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The composition of poly(urethane ureas) modified with and without poly(dimethyl-siloxane) (PDMS) was investigated using Fourier-transform infrared spectroscopy coupled with attenuated total reflectance and X-ray photoelectron spectroscopy. The results indicate that both the air-facing and mold-facing surfaces showed significantly more PDMS and poly(tetramethylene oxide) (PTMO) soft segments than the average concentration in the bulk, and the air-facing surfaces contained more PDMS and PTMO segments than the corresponding mold-facing surfaces. Hydration in water for up to three weeks did not result in any change in the composition of surfaces based on the relative absorbing intensities, neither in hydrogen-bonding structure of the surfaces.

Keywords: Air-facing and mold-facing surfaces; Hydrogen bonds; ATR spectra; Poly(urethane urea); XPS

INTRODUCTION

It has been well known that segmented poly(urethane ureas) are multi-block copolymers composed of alternating hard and soft segments, which are mutually insoluble, resulting in two-phase separation micro-structure of urethane and urea segment domains dispersed in a matrix of polyether,[1] and the composition and structure on the surface of this block copolymer can be greatly different from the bulk. Never-theless, surfaces can also be different in composition and structure, depending on whether the surface was air-facing or mold-facing during

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solution casting. For examples, for two commercial polyurethane and poly(urethane urea), Avcothane® and Biomer® with 10–19% poly-(dimethylsiloxane) (PDMS) and without PDMS, respectively, some researchers reported a greater concentration of polyether and PDMS on the air-facing surfaces than on the mold-facing surfaces,[2,3] other studies indicated the opposite.[4–6] Iwamoto and Ohta[7] studied six balloon pumps made of Avcothane® films. Three of them contained less silicone on the air-facing surface than on the mold-facing surface, whereas the opposite was found for one balloon pump, and the other two had nearly an equal content between the two sides. More interestingly, poly(urethane ureas) may rearrange on the surface region upon immersing in water, which influences their surface morphology as indicated by contact angle.[8]

In this study, we attempt to quantitatively analyze the composition and structure of the surfaces of original and hydrated poly(urethane ureas) with varied soft segments using Fourier-transform infrared spectrometer (FTIR) coupled with attenuated total reflectance (ATR), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

Poly(urethane ureas) were typically synthesized from pre-dried soft segment oligomers, poly(tetramethylene oxide) PTMO, (where needed, modified by PDMS end groups), and 4,4′-diphenylmethane diisocyanate (MDI); a mixture of ethylene diamine and 1,3-cyclohexane diamine was used as chain extenders. Additionally, a copolymer of diisopropyl-aminoethyl methacrylate and decyl methacrylate, as a stabilizing additive,[10,11] was incorporated where needed. The solutions of poly-(urethane ureas) were obtained from the Polymer Technology Group Inc. (Emeryville, CA). Films of polymers were solution cast on pre-cleaned glass plates which were intentionally coated by PDMS on the side in contact with the polymers, followed by evaporating the solvent in a 60°C oven with HEPA filtered air, and then extracted in distilled water for 24 h and dried as 50% relative humidity and 23°C. These films were supplied by Arrow International Inc. (Reading, PA).

Poly(urethane ureas) films used in this study are described as follows:

Poly(urethane urea) type	Soft segment	PDMS (%)
Unstabilized Biospan®	PTMO	No
Biospan®	PTMO	No
Biospan MS/3®	PTMO	3
Biospan S®	PTMO	6
Biospan SC®	Carbonate	6

Methods

FTIR-ATR spectra were obtained using a ZnSe internal reflectance element at an incidence angle of 45° with a Pike horizontal ATR accessory (Pike Technologies, Inc., Madison, WI) which was placed in the sample compartment of Digilab FTS-45 FTIR. Scanning was repeated at least 200 times before the spectra were recorded at a resolution of $2\,cm^{-1}$. The penetration depth (d_p) of sampling is described by the Harrick equation.[12]

$$d_p = \frac{\lambda}{2\pi n_1 (\sin^2 \theta - n_{21}^2)^{1/2}},$$

where θ is the angle of incidence with respect to the surface normal, n_{21} is the ratio of the refractive indexes of the sample (n_2) and the internal reflection element (n_1). The refractive index of ZnSe (n_1) is 2.4, and most organic materials have a refractive index around 1.5, the depths of penetration at some characteristic absorbing peaks can be calculated. After the spectra of these original films were recorded, these poly(urethane urea) films were immersed in deionized water at room temperature for one day or one week, and removed from the hydrating solution and blotted with clean lens paper to remove excess liquid on the surfaces. The films were immediately fixed on the ZnSe flat plate used to collect the FTIR-ATR spectra. At the same time, 20% of the corresponding poly(urethane ureas) were dissolved in dimethyl formide and cast on KBr windows, and placed in a hood for one day,

then dried at 60°C in vacuum oven for one week and scanned in the same FTIR spectrometer to collect the transmittance spectra of the bulk polymer.

XPS was carried out in Kratos Analytical XSAM 800 pci at 700 magnification, 40 eV pass energy, MgK_{α} X-rays. The average composition of the layer within about 50 Å of the surfaces was calculated. The precision of the numbers was roughly ±5% for C, ±10% for Si and O, and ±30% for N.

RESULTS AND DISCUSSION

Composition and Structure of the Surface of Original Poly(urethane ureas)

Figures 1 and 2 illustrate the FTIR-ATR spectra of the air-facing and mold-facing surfaces of these poly(urethane ureas), respectively. Both the air-facing and mold-facing surfaces displayed similar absorbing bands at the same wavenumbers, suggesting that the air-facing surfaces are analogous to the mold-facing surfaces in structure. The major characteristic absorbing peaks are assigned in Table I. Although unstabilized Biospan[R] and Biospan[R] did not contain any PDMS in their backbone chain composition, the absorbing peaks of silicone still can be observed in their FTIR-ATR spectra, implying that the two samples were contaminated from the mold coated by PDMS, as observed in Biomer[R].[12] The peak at $1110 \, cm^{-1}$ was used as an index for soft segment concentration, and the peaks at 1020 and $800 \, cm^{-1}$ indicated the silicone concentration. The $800 \, cm^{-1}$ band of silicone was usually overlapped or sometimes nearly completely hidden by the $820 \, cm^{-1}$ band of the aromatic ring of the poly(urethane ureas),[7] so that the intensity of the absorbing peak at $1020 \, cm^{-1}$ was used as an index for the PDMS concentration. Although there are some arguments about the assignment of the peak at $1593 \, cm^{-1}$ (the aromatic C–C stretching,[13–18] or the aromatic N–H bending[19]), it is still reasonable to employ the absorbing intensity of this peak as the index for the hard segment concentration. Thus, the relative concentration of silicone, soft segment, or hard segment can be judged by the absorbing intensities of these characteristic peaks. These data are summarized in

Table II, which also lists the depth of penetration at some characteristic peaks based on the Harrick equation.[12]

To compare with the average bulk concentration of poly(urethane ureas), the absorbing ratios of the major characteristic peaks of transmittance FTIR spectra were also calculated and shown in Table II. The results indicate that both air-facing and mold-facing surfaces showed significantly higher ratios of A_{1020}/A_{1593} than the bulk. Most of the surfaces exceeding 100% of the relative ratios of the bulk phase,

(a)

wavenumbers (cm⁻¹)

FIGURE 1(a)

(b)

FIGURE 1(b)

FIGURE 1 The FTIR-ATR spectra of air-facing surfaces of as-received poly-(urethane ureas) (a) 2500–3700 cm^{-1}; (b) 600–1800 cm^{-1}.

suggesting that both the air-facing and mold-facing surfaces had greatly more silicone concentration than the average composition.[20] Nevertheless, both the air-facing and mold-facing surfaces contained more PTMO segments than their average composition indicated by the higher ratios of A_{1110}/A_{1593} on the surfaces than their corresponding ratios of the bulk phase. Apparently, the segregation of PDMS and PTMO segments near the surface region occurred. The principal

driving force of this segregation is considered to be the interfacial free energy gap between the initial and the final state of the interfaces. Generally, the surfaces of samples of the block copolymers themselves, as well as mixtures containing them, are substantially enriched in the component of lower surface energy, as described for other block copolymers or blends, such as PS–PEO and PEO–PPO copolymers,[21] and PS–PDMS copolymer.[22] In poly(urethane ureas) with a small amount of PDMS, the PDMS has the lowest surface free energy, around 15–20 dyn/cm (20°C) corresponding to a molecular weight
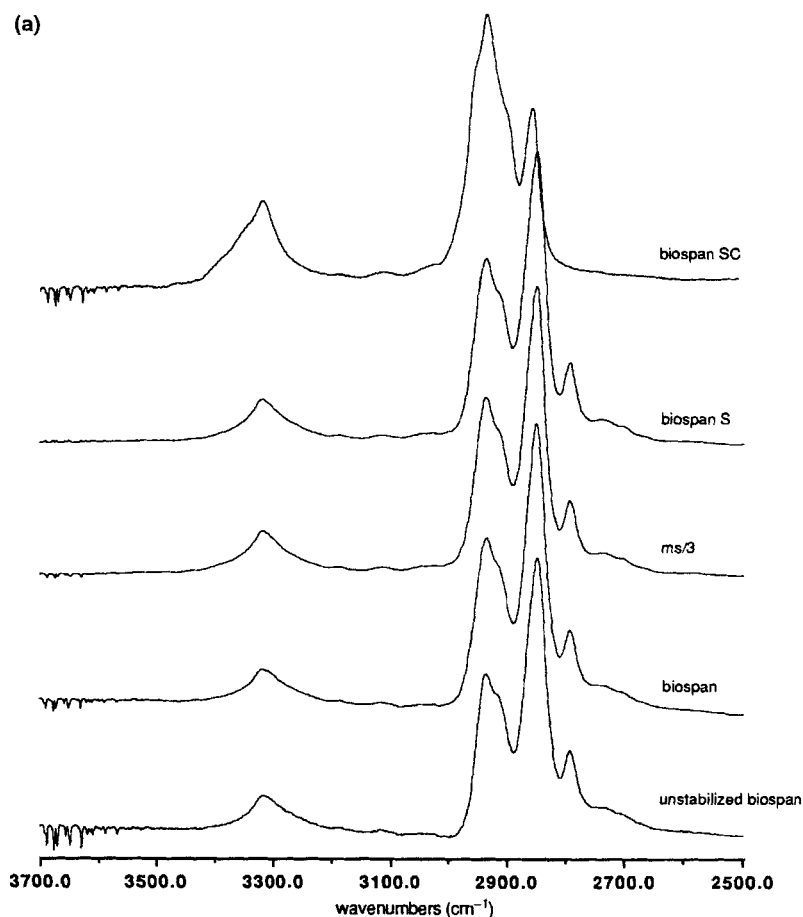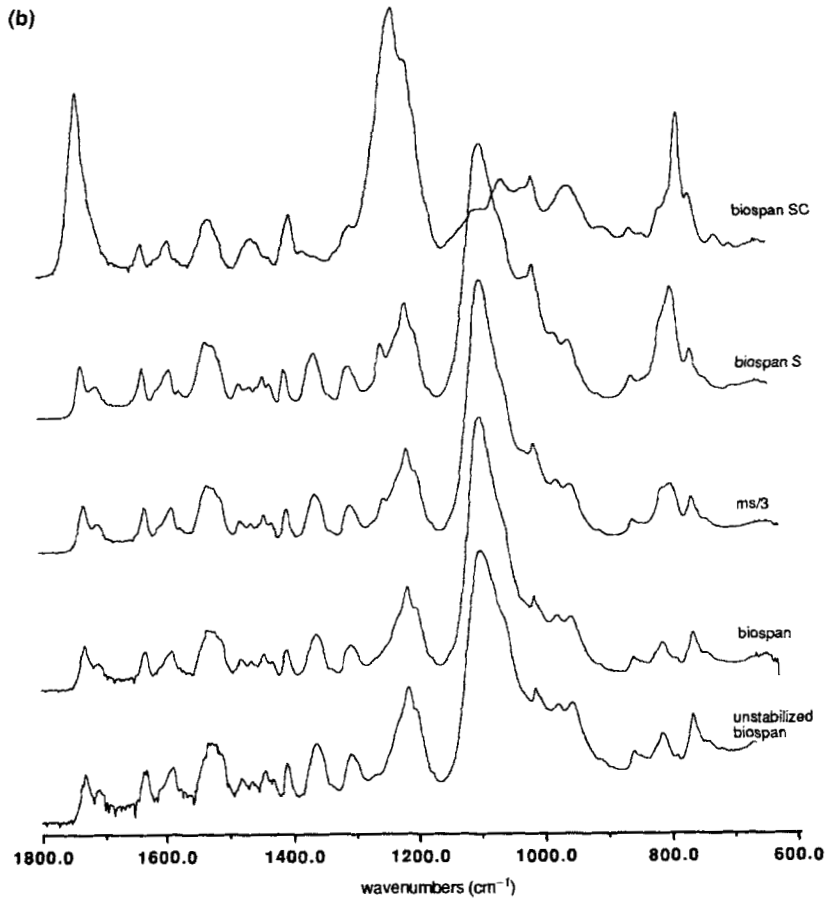
(a)

FIGURE 2(a)

(b)
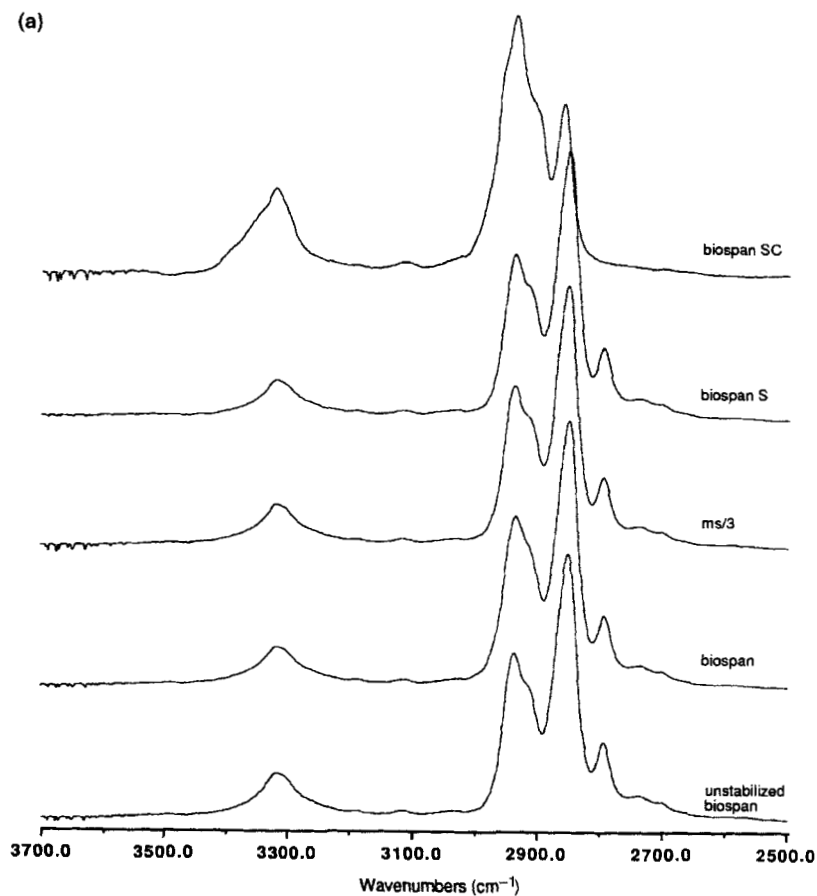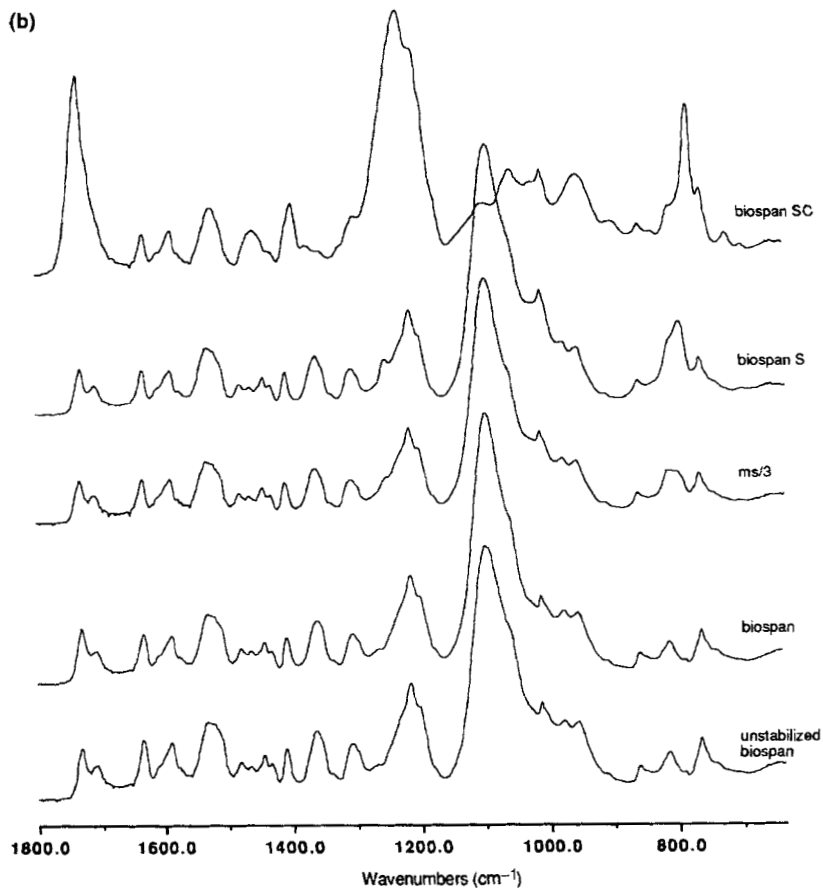
FIGURE 2(b)

FIGURE 2 The FTIR-ATR spectra of mold-facing surfaces of as-received poly-
(urethane ureas) (a) 2500–3700 cm^{-1}; (b) 600–1800 cm^{-1}.

from 162 to 7500; PTMO (2500) is 32 dyn/cm, when compared to the
typical MDI-ethylene diamine hard segment, with a value of 49 dyn/
cm.[23] Thus, during the process of fabricating and drying these poly-
(urethane urea) films, PDMS and PTMO segments migrated towards
the near surface layer and spread over the surfaces to minimize the inter-
facial free energy. Especially for the PDMS segment, these segments
tended to occupy the topmost layer since it has the lowest surface free

TABLE 1   The assignment of characteristic peaks of poly(urethane ureas)

Absorption bands (cm^{-1})	Assignment
3500	Stretching of free NH
3320	Stretching of H-bonded NH
2972	CH_2 stretching (asymmetric)
2856	CH_2 stretching (symmetric)
1741	Stretching of free urethane C=O
1712	Stretching of H-bonded urethane C=O
1638	Stretching of H-bonded urea C=O
1593	Vibration of aromatic ring
1415	Stretching of aromatic C–C
1365	Bending of CH_2 of polyether
1264	Bending of Si–CH_3
1110	Stretching of C–O–C
1020	Stretching of Si–O
820	Vibration of aromatic C–H
800	Stretching of Si–C
767	Bending of C–C=O

TABLE II   Quantitative results of ATR-FTIR and transimittance FTIR of poly-(urethane ureas)

	A_{1020}/A_{1593}			A_{1110}/A_{1593}		
	Bulk	Air-side	Mold-side	Bulk	Air-side	Mold-side
Unstablized Biospan®	0.71	1.96	1.54	2.34	5.0	4.49
Biospan®	0.76	2.22	1.68	4.19	7.38	5.91
MS/3®	1.04	2.27	1.91	4.08	6.16	5.61
Biospan S®	1.31	3.09	2.62	4.06	6.09	5.50
BiospanSC®	1.36	2.61	2.09			
d_p (µm)	1.63 ($1020\,cm^{-1}$)		1.49 ($1110\,cm^{-1}$)	1.04 ($1593\,cm^{-1}$)		

energy, accompanying with more –Si–O and –O–CH_2–CH_2–CH_2–CH_2– on the surfaces than in the bulk.[24]

Comparing the composition between the air-facing side and mold-facing side is interesting. Recall that these glass plates, as molds, were intentionally coated by PDMS on the sides contacted with poly-(urethane ureas), which was suppose to lead to more silicone on the mold-facing surfaces than on the air-facing surfaces. But the results showed less silicone on the mold-facing surfaces than on the air-facing surfaces.[2,3] Obviously, PDMS segments preferentially moved into the air/polymer interfaces than into the inorganic/polymer interfaces,

TABLE III   XPS results of the mold-facing surfaces of some poly(urethane ureas)

	C (%)	N (%)	O (%)	Si (%)	O/C	N/C	Si/C
Unstabilized Biospan[®]	72	3	20	5	0.278	0.042	0.069
Biospan[®]	75	5	17	4	0.227	0.067	0.053
MS/3[®]	62	2	22	14	0.35	0.032	0.226
Biospan S[®]	62	4	21	13	0.339	0.064	0.21
Biospan SC[®]	64	2	24	10	0.375	0.031	0.156

indicating that the former was more beneficial than the latter to reduce interfacial free energy of the final state. Similarly, the air-facing surfaces contained more PTMO segments than their corresponding mold-facing surfaces.

Table III lists the average composition of the mold-facing surfaces of some poly(urethane ureas) by XPS. Assuming that poly(urethane urea) (for instance, Biospan S[®]) are composed of 20% soft segment and 80% hard segment with a mixture of ethylene diamine and 1,3-cyclohexane diamine (50% : 50% wt ratio) as extenders and PDMS of 6% of the backbone polymer by weight percent, then the mole ratios of the repeat units of the soft segment, ethylene diamine based hard segment, cyclohexane diamine based hard segment and PDMS are roughly 3.22 : 1.67 : 1.40 : 1. Thus the average atomic composition of C, N, O and Si of poly(urethane urea) bulk is 75.5%, 12.8%, 10.8% and 1%, respectively. However, the average content of O and Si is significantly lower than those of the mold-facing surfaces of these selected poly(urethane ureas) 21% and 13%, respectively as shown in Table III. Obviously, these higher values came from poly(tetramethyl oxide) containing 25% atomic O, and PDMS containing 25% O and 25% Si, which means that the topmost layer is mostly covered by PDMS with small amount of poly(tetramethyl oxide). Similarly, the other poly(urethane ureas) also showed greatly more (PDMS) on the surfaces than in the bulk, confirming that the components with lower surface free energy segregated near the surface region, leaving components with high surface free energy in the bulk phase.

Composition of the Surface of Hydrated Poly(urethane ureas)

PDMS has very good biocompatibility and blood-compatibility, high thermal and oxidative stability, UV resistance, low surface energy and

an extremely low glass-transition temperature ($-123°C$). Its low surface free energy is expected to lead to spreading over the surface of the block copolymer when in air or in vacuum, accompanying with dominantly more PDMS on the surfaces than in the bulk. However, PDMS is not always preferentially on the surface when facing different environments. It was found[8,24] that at the block copolymer–water interface, more hard segments were observed on the surface indicated by the contact-angle of the block copolymer approaching that of pure urethane, not PDMS or PTMO. The surface of polyurethane or poly(urethane urea) reoriented and became more hydrophilic upon hydration.

Recent XPS investigation on the surface of PDMS-modified poly-(urethane urea) block copolymer indicated that although both urethane (NCOO) and urea (N_2CO) groups in hard segments are more hydrophilic, they did not move towards the surface during immersing in water.[25] The surface rearrangement likely happened by switching the positions of the Si–O–Si backbone (with CH_3 groups) and $-O-CH_2-CH_2-CH_2-CH_2-O-$ groups upon immersion in water. In the present study we attempted to investigate the composition and structure of the surfaces of hydrated poly(urethane ureas) using FTIR-ATR spectrometer.

Poly(urethane ureas) were immersed in deionized water at room temperature for a period of three weeks. During this period, these films were taken out of the water and blotted by lens papers, and then immediately placed on the flat plate out of the ATR accessory already located in the sample compartment of FTIR spectrometer to record FTIR-ATR spectra, followed by replacing the films into the deionized water as soon as the FTIR-ATR spectra were recorded. The mold-facing surface of poly(urethane urea) was studied since this surface is usually contacted with blood serum when used as artificial heart. Figures 3 and 4 display the FTIR-ATR spectra of one day- and three week-immersion, respectively. Compared to the original films (see Figure 2(a)), the spectra of hydrated poly(urethane ureas) display a wide shoulder near $3500\,cm^{-1}$, implying that hydration probably resulted in freeing some hydrogen-bonding NH groups. (Further discussion is presented in the next section.) Table IV summarize the relative absorbtion intensities of some characteristic peaks. It is surprising that the ratios of A_{1020}/A_{1593} and A_{1110}/A_{1593} are changed little, suggesting that

the surface molecules might not reorient to maximize polar group interaction with water, or become more hydrophilic upon immersion in water, as expected. Since the CH_3 groups of PDMS takes several hours to move back to the surface layer after poly(urethane urea) is taken out of water[25] and half an hour is needed to take the FTIR-ATR spectrum of one film, surface restructing during scanning is negligible. Therefore, the results reported in Table IV indicate that the average composition of a depth of 1 μm did not vary in responding to the medium, even though the surface rearrangement did occur on the topmost layer up to 100 Å thickness[24,25] as indicated by XPS and

(a)

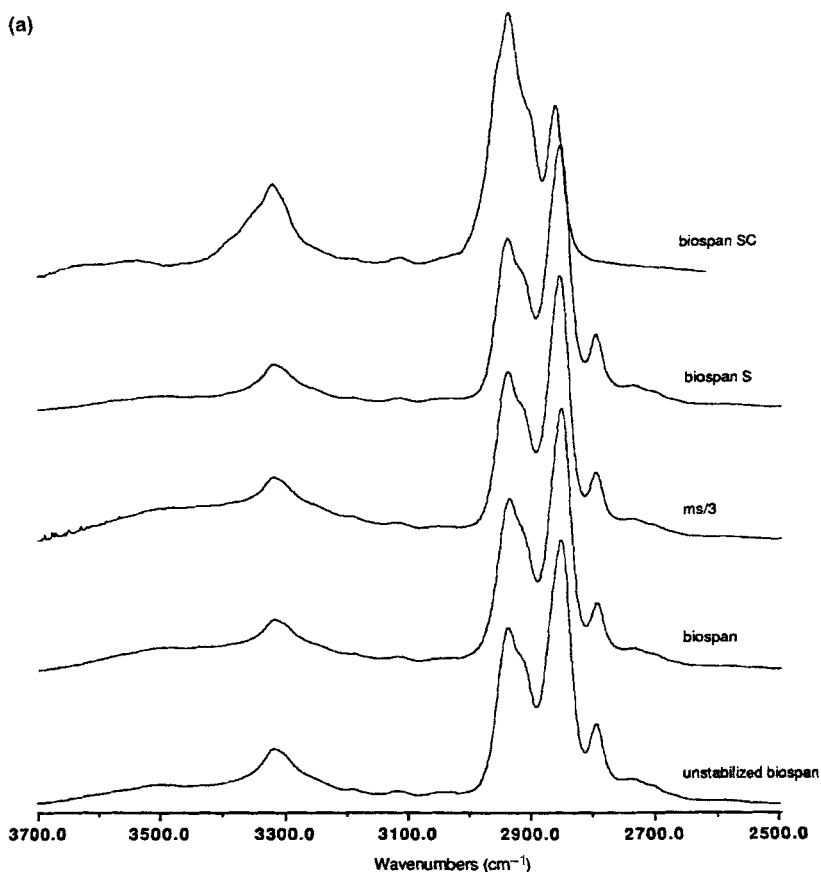FIGURE 3(a)

(b)

FIGURE 3(b)

FIGURE 3 The FTIR-ATR spectra of mold-facing surfaces of poly(urethane ureas) hydrated for one day (a) 2500–3700 cm^{-1}; (b) 600–1800 cm^{-1}.

contacting-angle. In fact, in the XPS study on the surfaces of PDMS-modified poly(urethane ureas), Wen et al.[25] investigated the surface composition as a function of hydration time with variable takeoff angle (normally 15°, 30°, 45°, and 90°) corresponding to a depth from 25 to 100 Å, respectively. Although the Si/C ratio drops fast for the first few hours at small takeoff angles, this trend became less and less obvious as the takeoff angle increased. At a takeoff angle of 90°,

or around a depth of $100\,\text{Å}$, the Si/C does not vary very much even after being hydrated for almost several weeks. Thus, it is not difficult to imagine that the composition over the average depth of $1\,\mu\text{m}$ does not vary upon hydration in water. However, although the PDMS on the surfaces of Biospan® and unstabilized Biospan® came from PDMS-coated glass plates, which means that these PDMS are physically, not chemically interacting with poly(urethane ureas), they were not removed during immersing in water and still populated the surfaces.

(a)

FIGURE 4(a)

(b)

Labels on spectra (top to bottom): biospan SC; biospan S; ms/3; biospan; unstabilized biospan
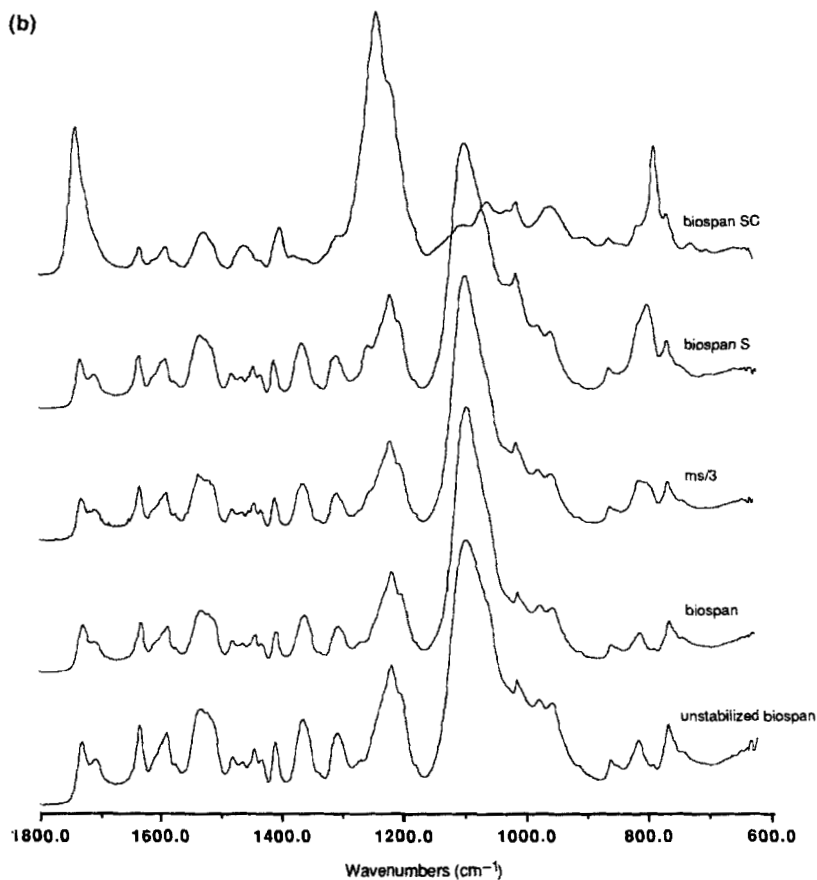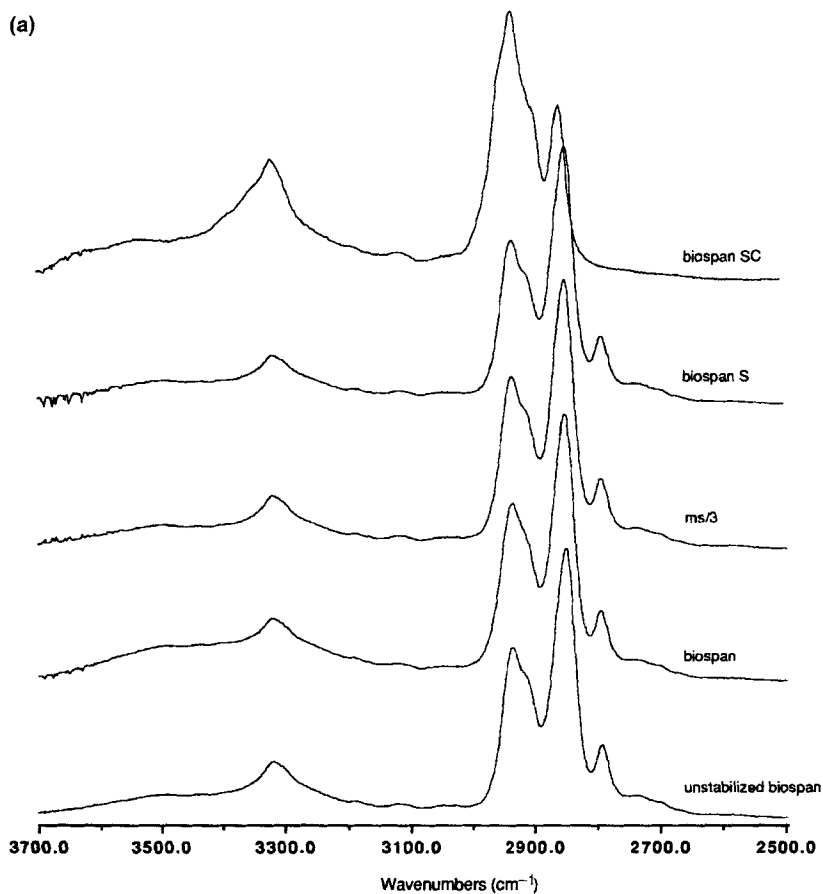
X-axis: Wavenumbers (cm^{-1}), from 1800.0 to 600.0
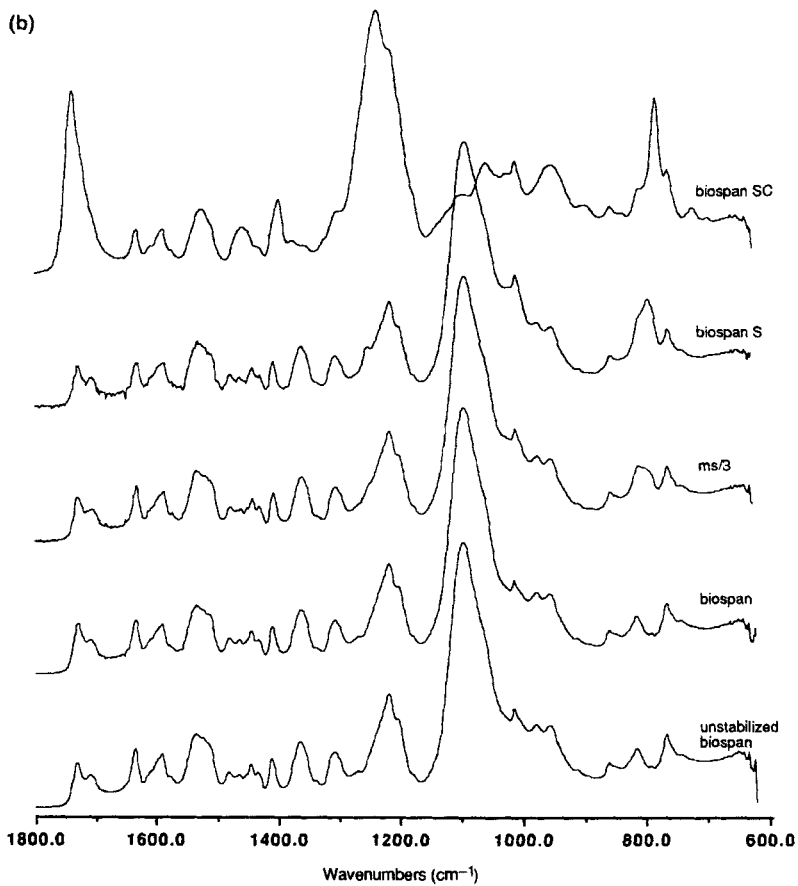
FIGURE 4(b)

FIGURE 4   The FTIR-ATR spectra of mold-facing surfaces of poly(urethane ureas) hydrated for three weeks (a) 2500–3700 cm^{-1}; (b) 600–1800 cm^{-1}.

TABLE IV   Quantitative results of ATR-FTIR spectra of the mold-facing surfaces of poly(urethane ureas)

	A_{1020}/A_{1593}			A_{1110}/A_{1593}		
	One day immerse	*One week immerse*	*Three week immerse*	*One day immerse*	*One week immerse*	*Three week immerse*
Unstablized Biospan®	1.58	1.52	1.55	3.72	4.28	5.23
Biospan®	1.59	1.47	1.52	5.84	5.52	5.37
MS/3®	1.95	1.90	1.99	5.95	5.54	5.76
Biospan S®	2.55	2.60	2.77	5.40	5.40	5.76
Biospan SC®	2.27	2.46	2.37			

The Hydrogen-Bonding Structure of the Surface of Poly(urethane urea)

The immiscibility between the hard segment and the soft segment usually results in microphase separation of polyurethane or poly(urethane ureas), accompanying with a hard segment-domain, soft-segment matrix, where some hard-segments are dissolved in the soft-segment matrix phase. The extent of microphase separation and the domain formation is strongly dependent upon the intermolecular interaction of hydrogen-bonding between the hard–hard segments of urethane and/or urea linkages, which is also shown to be related to blood compatibility.

The hydrogen-bonding structure of desiccated polyurethanes or poly(urethane ureas) has been extensively studied.[26–31] It is generally believed that NH groups of urethane and urea are the proton donors, whereas carbonyl groups of urethane and urea are proton acceptors. The hydrogen-bonding of NH to O=C is a measure of microphase separation and domain formation. The presence of three-dimensional hydrogen-bonding between the hard segments, where each urea carbonyl is bonded to two NH groups, greatly increases the extent of microphase separation and domain formation;[27,28] all of the urea carbonyl groups are hydrogen-bonded, and no free urea carbonyls can be observed.[31,32] However, the NH groups can also form hard–soft segments by hydrogen-bonding with the ether oxygen, which represents the extent of phase mixing between hard and soft segments. However, relative to the investigation of the hydrogen-bonding structure of the desiccated polyurethanes or poly(urethane ureas) the hydrogen-bonding of these surfaces, especially the surface of the hydrated polyurethane or poly(urethane urea) has not been studied extensively.

Here we investigated the hydrogen-bonding structure of the mold-facing surface of poly(urethane ureas) hydrated for a period of time up to three weeks. Table V lists the relative absorbtion intensities of these hydrogen-bonding peaks: H-bonded urethane C=O ($1713\,\mathrm{cm^{-1}}$), H-bonded urea C=O ($1638\,\mathrm{cm^{-1}}$) and H-bonded NH ($3320\,\mathrm{cm^{-1}}$) groups; the free urethane C=O was measured using the peak at $1415\,\mathrm{cm^{-1}}$ of the aromatic C–C stretching as the nonchanging reference peak since there is no unanimous conclusion about the assignment of the absorbing peak at $1593\,\mathrm{cm^{-1}}$.[19] The results indicate that a

TABLE V Quantitative analysis of H-bondings of surfaces of poly(urethane ureas)

	A_{1735}/A_{1415}				A_{1713}/A_{1415}				A_{1638}/A_{1415}				A_{3320}/A_{1415}			
	Mold-side	One day	One week	Three week	Mold-side	One day	One week	Three week	Mold-side	One day	One week	Three week	Mold-side	One day	One week	Three week
Unstabilize Biospan®	1.15	1.16	1.13	1.17	0.76	0.82	0.80	0.80	1.3	1.42	1.48	1.47	0.40	0.45	0.47	0.41
Biospan®	1.37	1.35	1.33	1.36	0.79	0.82	0.81	0.87	1.17	1.35	1.28	1.36	0.34	0.43	0.43	0.44
MS/3®	1.18	1.14	1.16	1.22	0.77	0.82	0.82	0.84	1.18	1.48	1.39	1.42	0.38	0.56	0.59	0.37
Biospan S®	1.25	1.20	1.20	1.23	0.75	0.80	0.80	0.84	1.17	1.27	1.25	1.23	0.36	0.41	0.46	0.35

majority of the urethane carbonyl groups were not hydrogen bonded for the desiccated and hydrated poly(urethane ureas). Hydration in water did not lead to an increase in urethane carbonyl groups although Bummer and Knutson[9] reported more hydrogen-bonded urethane carbonyl groups upon three week immersion in water. Free (not hydrogen bonded) urea carbonyl stretching bands absorbing near $1695\,cm^{-1}$ were not present in any desiccated or hydrated polymer spectra, suggesting that urea carbonyl groups were all hydrogen bonded,[9,25] and interurea hydrogen-bonding could not be disrupted upon hydration. For the desiccated polymer film, a single symmetrical band was observed near $3320\,cm^{-1}$ corresponding to the stretching vibration hydrogen-bonded NH. Stretching absorbing bands of free NH groups near $3500\,cm^{-1}$ were not present, which means that almost all of the NH groups were hydrogen bonded on the surface of the desiccated polymer film.[34] As mentioned above, hydration in water presents a wide shoulder near $3500\,cm^{-1}$. Bummer and Knutson[9] indicated that this shoulder was caused by freeing of hydrogen-bonded NH groups after three weeks of water hydration, and these free NH groups were generated in the interfacial regions by breaking the NH of urethane bonded to the oxygen of polyether bonds, since interurethane hydrogen bonds are much stronger than those between urethane and polyether oxygens.[35,36] However, in this study, since nothing is changed in the hydrogen-bonded urethane, urea carbonyl groups, and NH groups, we believe that this shoulder is the OH stretching band vibration of water.[33] However, comparing the hydrogen-bonding of different poly(urethane ureas) demonstrates that the incorporation of PDMS into poly(urethane ureas) does not disturb the hydrogen-bonding structure of the surfaces.

CONCLUSION

The analyses on the surface of poly(urethane urea) films show that the surfaces contained extremely higher PDMS and PTMO segments than the bulk, suggesting that these segments with low surface free energy moved towards the surface layer to minimize the free energy of the final state. Moreover, the air-facing surfaces contained more PDMS and PTMO segments than their corresponding mold-facing surfaces.

Hydration in water did not result in any obvious increase or decrease in PDMS and PTMO on the surfaces, which means that the structure and average composition over the depth of penetration of ATR did not change by subjecting the films to a water environment. Furthermore, hydration caused no change in the hydrogen-bonding structure in the interfacial regions.

Acknowledgment

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