Surface Composition of Biopolymer Blends Biospan-SP/Phenoxy and Biospan-F/Phenoxy Observed with SFG, XPS, and Contact Angle Goniometry

Zhan Chen,[†,‡] **Robert Ward,**[§] **Yuan Tian,**[§] **Aaron S. Eppler,**[†,‡] **Y. R. Shen,**[‡,∥] **and Gabor A. Somorjai***[,†,‡]

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720,
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720,
The Polymer Technology Group Inc., Berkeley, California 94710, and Department of Physics,
University of California at Berkeley, Berkeley, California 94720

The surface compositions of two biopolymer blends, Biospan-SP/Phenoxy (BSP/PHE) and Biospan-F/Phenoxy (BF/PHE), have been studied using sum frequency generation (SFG), X-ray photoemission spectroscopy (XPS), and contact angle goniometry. BSP and BF are polyurethanes capped with poly(dimethylsiloxane) (PDMS) and fluoroalkyl $(-(-CF_2-)_n-)$ as end groups, respectively. With contact angle goniometry, the surface tensions of pure BSP, BF, and PHE were found to be 26, 16, and 45 dyne/cm. For each of the blends, the polymer component with a lower surface tension (BSP or BF, not PHE) tends to segregate to the surface. Our SFG experiment shows that the surface concentration of the surface-active component increases sharply as its bulk concentration increases. For BSP/PHE (and BF/PHE) in air, the surface of the polymer blend is fully covered by BSP (and BF) at a bulk concentration of 3.5 wt % (and 1 wt %). The contact angle measurements and the XPS studies yield compatible results. Comparison of results for BSP/PHE, BS/PHE (published before[1]), and BF/PHE polymer blends shows that the lower the surface energy of the surface-active component (surface tension: BF < BS < BSP), the easier it is for the component to segregate to the surface (the minimum bulk concentration to saturate the surface is BF (1 wt %) < BS (1.7 wt %) < BSP (3.5 wt %)). After exposure to water, SFG spectra indicate that the surface layer of a polymer blend could be restructured. For BSP (3.5 wt %)/PHE, the hydrophobic end groups of BSP submerge while the hydrophilic polyurethane backbone emerges. For BF (1 wt %)/PHE, PHE emerges at the surface after exposure to water, but for BF (5 wt %)/PHE, the BF component dominates the surface in both air and water. Our results demonstrate the bifunctionality of polymer blends and show that the surface chemistry of polymer blends may be dominated by a minor component, while the mechanical stability of the polymer is controlled by the major component.

1. Introduction

To design suitable polymers for use in medical devices and artificial organs, both surface and bulk properties must be carefully considered. Synthetic polymers have been widely employed as biomaterials, and this makes the understanding and control of their properties of great practical interest.[2−4] In general, the bulk composition of a polymer governs its mechanical properties, while the surface composition dominates its interactions with biological systems. Polymer blends are widely used as means of tailoring both the bulk and the surface properties of polymeric materials for various industrial and biomedical applications.[5,6] A unique feature of these polymer blends is that the surface composition and structure, and consequently, the surface properties of the material, are often markedly different from those of the bulk. This is due to surface enrichment of a specific component that will minimize the total surface free energy of the system.[7] A challenging problem to us is how to monitor the surface composition and structure of

polymer blends and therefore gain a molecular-level understanding and control of the interfacial composition of such macromolecular mixtures.

Previous studies of similar polymer blends have been reported using attenuated total reflection infrared spectroscopy (ATR-IR)[8] and Raman[9] spectroscopy. The optical penetration depth of ATR−IR and Raman is on the order of 100 nm to a few thousands of nanometers, so that the spectra are often dominated by contribution from the polymer bulk. In a previous paper, we reported an investigation of a two-component polymer blend, Biospan-S (BS) and Phenoxy (PHE), using a combination of surface techniques: sum frequency generation (SFG),[10] atomic force microscopy (AFM),[11] and contact angle measurements,[12] all of which have a surface sensitivity of ~1−10 nm. Correlation of these properties can provide a more detailed picture of the polymer surface. In this paper, we report our study of two similar polymer blends by SFG, contact angle measurements, and XPS. We compare the surface properties of these three polymer blends deduced from our measurements.

The polymer blend chosen in our previous study[1] is composed of two thermodynamically compatible components: Biospan-S (BS) and the phenoxy base polymer (PHE). The two polymer blends studied in this paper are Biospan-SP (BSP)/Phenoxy (PHE) and Biospan-F (BF)/Phenoxy (PHE). The molecular

* To whom all correspondence should be addressed. Email: somorjai@socrates.berkeley.edu. Fax: 510-643-9668.
† Department of Chemistry, University of California at Berkeley.
‡ Lawrence Berkeley National Laboratory.
§ The Polymer Technology Group Inc.
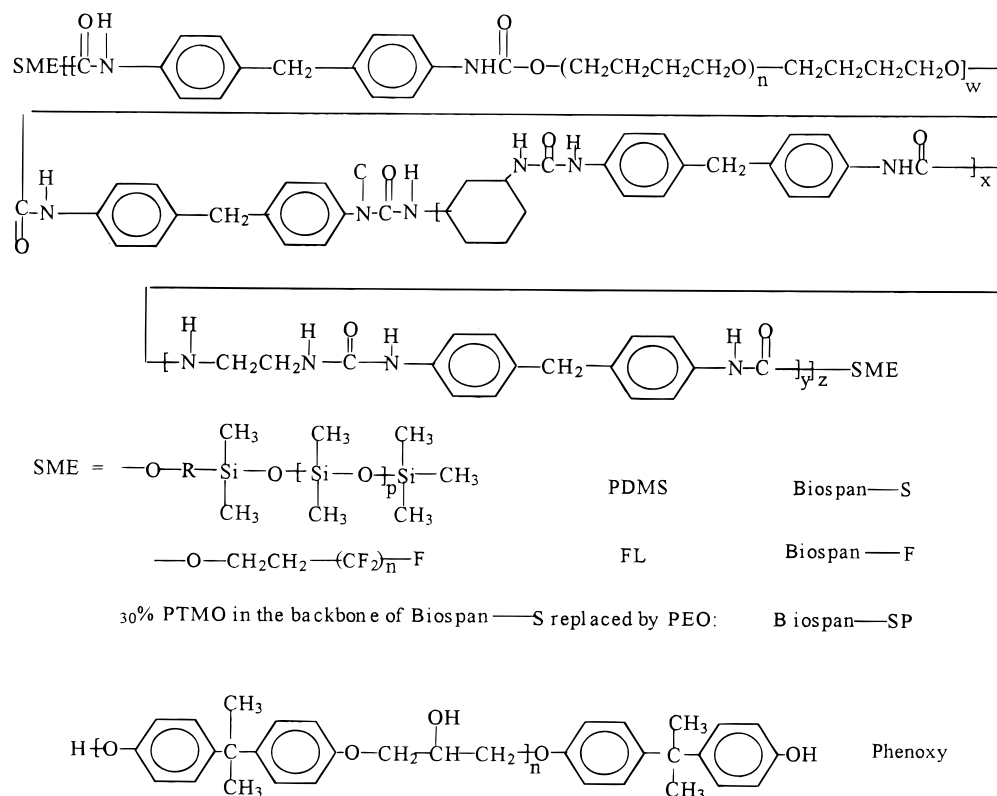∥ Department of Physics, University of California at Berkeley.

Figure 1. Molecular structures of Biospan-S (BS), Biospan-F (BF), Biospan-SP (BSP) and Phenoxy (PHE).

structures of all the polymers are shown in Figure 1. BS is a polyurethane capped with poly(dimethylsiloxane) (PDMS) end groups. BSP is similar to BS but with 30% PTMO (poly-(tetramethylene oxide)) in the BS polyurethane backbone replaced by PEO (poly(ethylene oxide)). BF is composed of the same polyurethane as BS, but the polyurethane is capped with fluoroalkyl ($-(-CF_2-)_n-$) end groups. As seen from their chemical structures, BS, BSP, and BF all contain both hydrophobic (PDMS or ($-(-CF_2-)_n-$)), and hydrophilic (ether and urethane segments) components. Such blends of phenoxy with several different block or segmented copolymers can produce extrudable and moldable compounds that soften at a glass transition temperature determined by the composition of the blend. The dramatic difference in stress relaxation rate above and below glass transition give these blends shape-memory properties. Such blends, with a glass transition between room temperature and body temperature are thus ideal candidates for various biopolymer applications, such as intravenous catheter tubings that will soften after insertion into the veins. Since the surfaces of these blends are to be in contact with blood after insertion, the ability to control their surface properties is of great interest in order to prevent possible complications related to thrombosis and embolization caused by contact of blood with a foreign surface. From our previous studies,[13,14] it was found that the more hydrophobic tail (e.g., PDMS or fluoroalkyl chains) would dominate at the pure BS, BSP, or BF surface in air. Such hydrophobic surfaces are known to extend blood clotting time and reduce blood platelet adsorption and thrombosis in vivo.[15,16] However, the polymer surface structure could change in response to different environments. For a biopolymer intended to be used as an implant in contact with living tissues or blood in a body, it is very important to know the structure of the biopolymer surface in the hydrated state. We have therefore used SFG spectroscopy to study the polymer blends in both air and water.

2. Experimental Section

2.1. Infrared−Visible SFG Surface Vibrational Spectroscopy.
Vibrational spectra are very useful for identifying composition since different chemical species have unique vibrational modes. SFG is surface-specific and capable of providing surface vibrational spectra. The technique has been described in detail elsewhere.[17,18] In our experiment, sum frequency spectra were obtained by overlapping a visible and a tunable IR beam of ∼100 μm in diameter on a polymer surface, at incident angles of 45 and 50°, respectively. The visible beam at 532 nm was generated by frequency-doubling the fundamental output pulses of a 20 ps pulse width from a Continuum Nd: YAG laser. The IR beam, tunable from 2500 to 3600 cm^{-1}, was generated from an optical parametric generation/amplification system pumped by the Nd:YAG laser. The sum frequency (SF) signal reflected from the polymer surface was collected by a gated integrator and photon counting system. The surface vibrational spectra were obtained by measuring the SF signal as a function of the input IR frequency. In this work, we present only results with the ssp polarization combination (for s-polarized SF output, s-polarized visible input, and p-polarized infrared input). All spectra were collected at 300 K and atmospheric pressure.

2.2. Contact Angle Goniometry.
A Rame-Hart NRL contact angle goniometer was employed to measure the contact angle of liquids of known surface tension on polymer films, using the sessile drop technique.[19] The liquids used in this study were water (surface tension 72.8 dyne/cm) and methylene iodide (50.8 dyne/cm). The advancing contact angle was measured directly using the movable protractor scale of the goniometer. The spatial size probed (in the plane of the surface) was 1−2 mm in diameter.

The following geometric mean equations[20] were used to calculate the surface tension for each sample from the measured contact angles.

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$$(1 + \cos\theta_w)\gamma_w = 2[(\gamma_w^d\gamma_s^d)^{1/2} + (\gamma_w^p\gamma_s^p)^{1/2}] \quad (1)$$

$$(1 + \cos\theta_m)\gamma_m = 2[(\gamma_m^d\gamma_s^d)^{1/2} + (\gamma_m^p\gamma_s^p)^{1/2}] \quad (2)$$

where θ_w and θ_m are the contact angles of water and methylene iodide on the sample respectively, γ_w, γ_m, and γ_s are the surface tensions of water, methylene iodide, and the polymer sample, respectively, and the superscripts d and p denote the dispersive (nonpolar) and polar components of the surface tensions. By measuring θ_w and θ_m, and inserting known values for γ_w^p, γ_w^d, γ_m^p, and γ_m^d, the solution of the two equations yields γ_s^p and γ_s^d. The total surface tension or surface energy of the polymer is given by $(\gamma_s^d + \gamma_s^p)$.

2.3. X-ray Photoemission Spectroscopy. XPS experiments were performed on a Perkin-Elmer PHI 5300 XPS spectrometer with a position sensitive detector and a hemispherical electron energy analyzer. The Mg Kα X-ray emission was used as the probe and was generated with 400 W (15 kV acceleration voltage) at the Mg cathode. A pass energy of 178 eV was used for survey spectra with a 45° takeoff angle. For angle-resolved high-resolution spectra, a pass energy of 17.9 eV was used. F 1s (685 eV), C 1s (285 eV), N 1s (398 eV), and O 1s (531 eV) regions were acquired with variable takeoff angles, where the takeoff angle is defined as the angle between the detector and the sample surface. At small takeoff angles, the detector collects electrons emitted from a shallow region near the surface. At larger takeoff angles, the detector collects electrons emitted from deeper layers as well. By changing the takeoff angle, it is possible to obtain a chemical profile of the uppermost layers of a polymer blend. Relative abundances of elements were calculated from the integrated peak areas.

2.4. Sample Preparation. The biopolymers BS, BF, and BSP were synthesized by The Polymer Technology Group, Inc. of Berkeley, California.[21] BS (MW = 65 000) is a polyurethane based on methylene diisocyanate with mixed diamine chain extenders of ethylenediamine and 1,3-cyclohexanediamine, and poly(tetramethylene oxide) (PTMO)) capped with poly(dimethylsiloxane) (PDMS) end groups that exhibit thromboresistance properties. BF is a similar biopolymer with polyurethane as the backbone but with fluoroalkyl $-(-CF_2-)_n-$ as the end groups. BSP has the same end group (PDMS) as BS, but the polyurethane backbone is modified with 30% PTMO substituted by PEO. The homopolymer of PHE (MW = 16 000) was purchased from Union Carbide. The molecular structures of these polymers are shown in Figure 1. Except for pure BF, all the polymer films were prepared by casting the polymer blends from their *N,N*-dimethylacetamide (~1 wt % of the polymer) solutions onto flat quartz substrates. Then the films were dried in air at 65 °C for 24 h. The film thickness was measured to be around 100 μm at room temperature using an Alpha-Step 50V surface profiler. Due to the difficulty in preparing a flat polymer film of pure BF on a quartz substrate by casting, all pure BF films were obtained by spin coating the polymer between 500 and 3000 rpm, depending on the polymer concentration.

3. Results and Discussion

3.1. Polymer Blends Surfaces in Air. *3.1.1. Brief Review of Studies of BS/PHE Blends by SFG, Contact Angle Goniometry, and AFM.* From the previous SFG study,[1] we find that the BS component likes to segregate to the surface of BS/PHE blend and approaches a full BS surface coverage when its bulk concentration is only 1.7 wt %. If the BS concentration is lower than 0.17 wt %, the polymer blend surface is dominated by
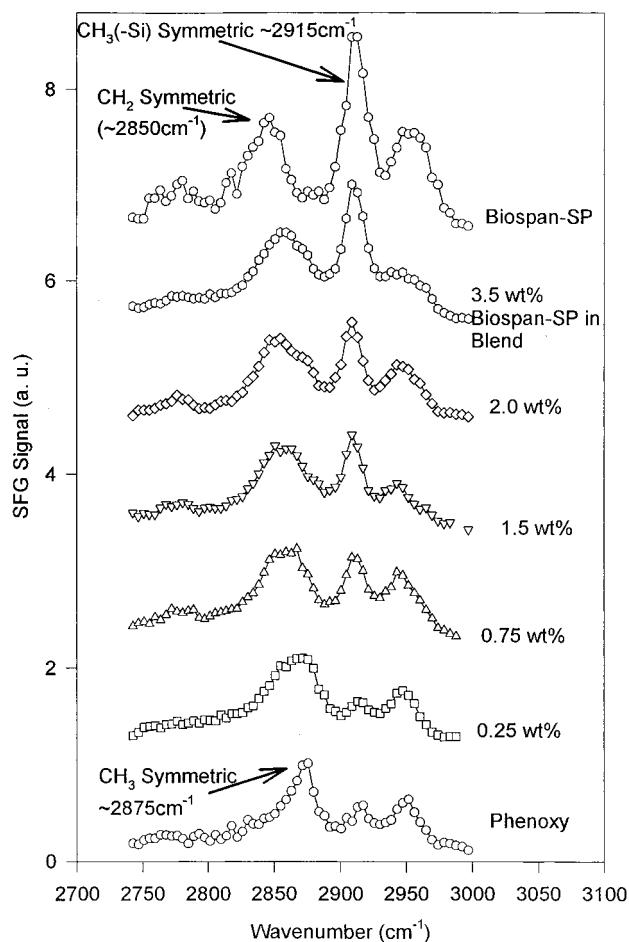

Figure 2. SFG spectra of pure PHE, pure BSP, and BSP/PHE blends for different BSP bulk concentrations in wt %.

PHE. In the intermediate BS bulk concentration region, 0.17−1.7%, the relative surface content of PHE decreases rapidly with the addition of BS. These findings correlate well with the contact angle results, which show that the surface free energy decreases in the same way. They indicate the fact that, in air, the surface likes to be enriched by the component of lower surface energy. From the AFM measurements, we find that below 0.17 wt % of BS in PHE, the surface morphology of the polymer blend is very similar to that of pure PHE; while above 1.7 wt %, it resembles that of pure BS. Between 0.17% and 1.7% there appears to be a phase separation of BS and PHE into separate domains at the surface. By measuring the spatial variations of friction of the polymer blend, the two components on the surface could be distinguished in this concentration regime. The combination of the three techniques thus provides a more complete physical picture of the polymer blend surface at the molecular level.

3.1.2. SFG and Contact Angle Results for BSP/PHE Blends in Air. SFG spectra were taken between 2700 and 3100 cm^{-1} (C−H stretching region) for pure BSP, pure PHE, and BSP/PHE blends as a function of BSP bulk concentration in wt % (Figure 2). For pure PHE, the most intense peak at 2875 cm^{-1} is assigned to the symmetric stretch of the methyl group. The less intense peak at ~2915 cm^{-1} is due to the antisymmetric stretch of CH$_2$ and the peak at ~2950 cm^{-1} is due to the antisymmetric stretch of CH$_3$ and the Fermi resonance band of CH$_2$. For subsequent analyses of spectra from the blended polymers, the symmetric stretch of CH$_3$ at 2875 cm^{-1} was taken as the characteristic band for PHE. For pure BSP, three prominent peaks are present in the SFG spectrum (Figure 2).
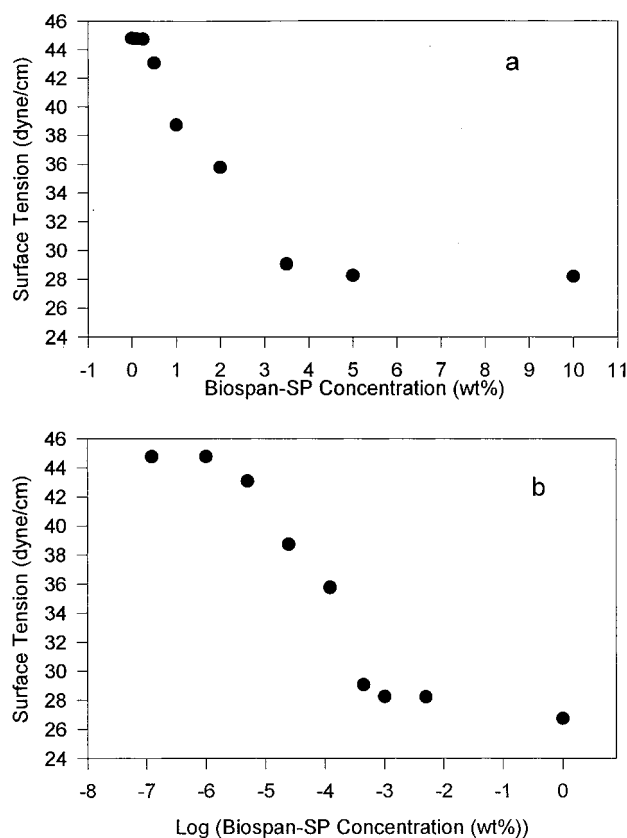
Figure 3. (a) Surface tension of the BSP/PHE polymer blend as a function of BSP bulk concentration in wt %. (b) Surface tension of BSP/PHE as a log function of BSP bulk concentration.

Figure 4. SFG spectra of pure PHE, pure BF, and BF/PHE blends for different BF bulk concentrations in wt %.

According to a previous study,[13] we can assign the peaks at $\sim$2915 cm^{-1} to the symmetric stretches of CH$_3$ of PDMS. The symmetric stretch of the methyl group was shifted from 2875 cm^{-1} in PHE to 2915 cm^{-1} in BSP because the group is bound to Si in PDMS, which is the end group on BSP. The peak at $\sim$2950 cm^{-1} is the antisymmetric stretches of CH$_3$ and the Fermi resonance of CH$_2$. The peak at 2850 cm^{-1} is due to the symmetric stretch of CH$_2$ of Biospan. The strong PDMS modes in the SFG spectrum suggest that the BSP surface is well populated by PDMS, yielding a hydrophobic surface.

As the concentration of BSP was increased in the BSP/PHE blends, the spectra show the segregation of BSP to the surface of the polymer (Figure 2). The SFG spectrum of BSP/PHE blend with 0.25 wt % BSP bulk concentration is very similar to that of PHE. The lack of a peak at 2915 cm^{-1} indicates the surface is not covered by the end groups of BSP. A weak peak at 2850 cm^{-1} may be due to the polyurethane of BSP, which was brought to the surface by the hydrogen bonding between PEO in the polyurethane backbone of BSP and $-$OH groups in PHE. The key features of the observed spectral changes with increasing BSP bulk concentration are the weakening of the prominent methyl resonance of PHE at 2875 cm^{-1} and the strengthening of the prominent 2915 cm^{-1} band for the CH$_3$ groups and $\sim$2850 cm^{-1} band for the CH$_2$ groups of BSP. These changes clearly show an enrichment of the BSP component at the BSP/PHE polymer blend surfaces in air.

To explore the possibility that surface tension was the driving force behind the enrichment of BSP at the surface, the surface tensions for the polymer blend surfaces as functions of BSP bulk concentration were measured (Figure 3). The surface tensions of pure PHE and BSP are 45 and 26 dyne/cm, respectively. When the BSP bulk concentration is lower than
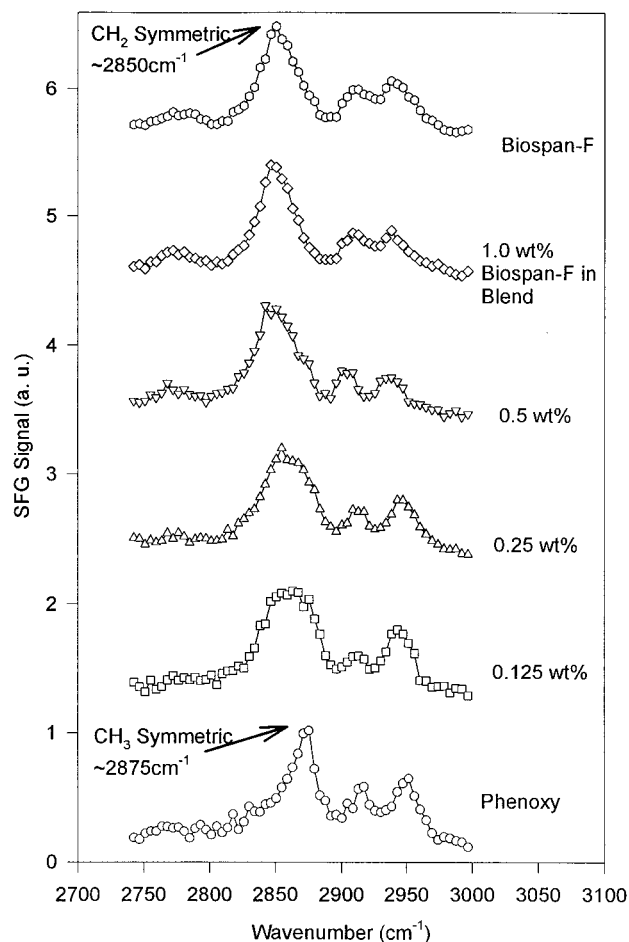
0.25 wt %, the surface tension of the BSP/PHE blend is very close to that of pure PHE and when the BSP concentration is higher than 3.5 wt %, it approaches that of pure BSP. In the intermediate region of 0.25$-$3.5 wt % of BSP, the surface tension of the blend decreases almost linearly with increasing BSP concentration. The variation of surface tension of the polymer blends correlates well with the relative BSP/PHE surface compositions measured by SFG. These results support the claim that the low surface-energy component (BSP) enriches the surface in order to minimize the overall surface free energy of the binary macromolecular system.

3.1.3. SFG and Contact Angle Results for BF/PHE Blends in Air. The SFG spectra of pure PHE (the lowest spectrum), pure BF (the top spectrum), and BF/PHE polymer blends in the C$-$H stretching region are shown in Figure 4. Unfortunately, the C$-$F stretching frequencies are out of range of the current SFG system. Instead, the vibrational peak at 2850 cm^{-1} from the polyurethane in the Biospan-F was used as the spectral signature of this polymer. The other two peaks at 2915 and 2950 cm^{-1} are also from the polyurethane in BF. The intensity of CH$_3$ symmetric stretch ($\sim$2875 cm^{-1}) in PHE is still used as the indicator of PHE surface concentration. As seen in Figure 4, the peak at $\sim$2850 cm^{-1} from CH$_2$ on BF increases as the bulk BF concentration in the BF/PHE blend is increased, while the $\sim$2875 cm^{-1} PHE peak decreases. The BF can be detected on the surface even with a bulk concentration below 0.125 wt %. At 1 wt %, BF entirely covered the polymer blend surface.

Contact angle measurements provide further evidence that BF segregated to the surface (Figure 5). BF has a very low surface tension of 16 dyne/cm, which is close to Teflon. The
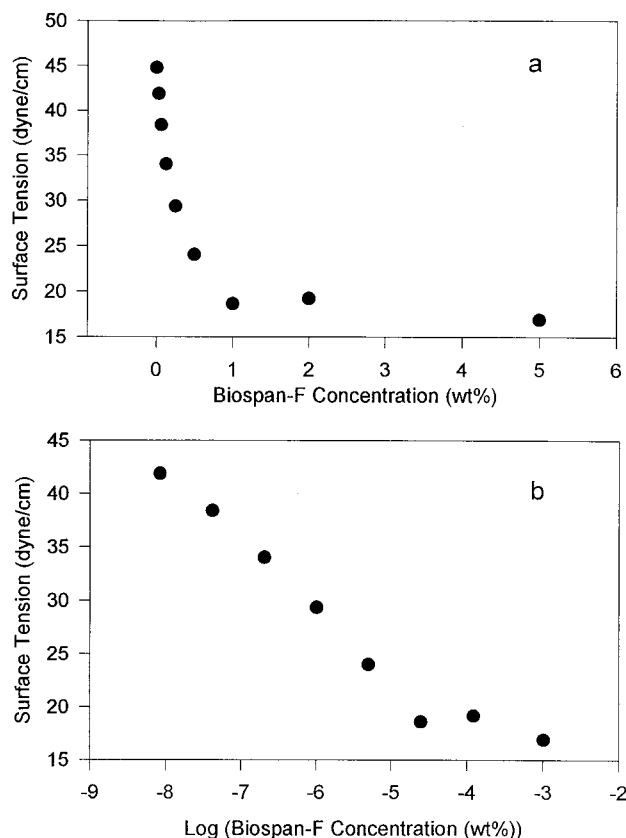
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Figure 5. (a) Surface tension of BF/PHE as a function of BF bulk concentration in wt %. (b) Surface tension of BF/PHE as a log function of BF bulk concentration.

Figure 6. Angle-resolved XPS measurements of F atomic concentrations for different BF/PHE samples.

surface tension of the BF/PHE blend begins to drop when the bulk concentration of BF reaches 0.031 wt %. With increasing BF concentration, it decreases further and saturates to the value of pure BF at a bulk BF concentration of 1 wt %. This indicates that having only 1 wt % of BF in the BF/PHE blend the surface is already completely covered by BF. These contact angle measurements correlate very well with the SFG results.

3.1.4. XPS Results for BF/PHE Blends. As mentioned above, the C−F stretch is out of the range for our SFG system and therefore the C−H stretch of polyurethane backbone in BF was used as the indicator for BF. To provide further evidence of surface segregation of BF, the BF/PHE blend was investigated using angle-resolved XPS, which can provide concentration depth profiles. Although XPS requires a vacuum to operate and has a poorer surface sensitivity than SFG and contact angle goniometry, it can accurately measure the concentration of almost all the elements, in particular F.

Angle-resolved XPS spectra from four BF/PHE blends show that the detected F concentration decreases as the takeoff angle increases (Figure 6). When the bulk concentration of BF reaches 0.063 wt %, prominent F concentration can be detected by XPS on the surface. At bulk BF concentrations higher than 1 wt %, the emission ceases to significantly increase, indicating that the surface is completely covered by BF.

3.1.5. Comparison of Surfaces of Three Polymer Blends: BSP/PHE, BS/PHE, and BF/PHE. We now compare results from the three polymer blends, including the BS/PHE studied previously.[1] As mentioned earlier, the only structural difference between BS and BSP is that in BSP, 30% of soft PTMO segments of the polyurethane backbone in BS is replaced by PEO, which is very hydrophilic and has higher surface tension. From the previous SFG study, we found that the polymer blend
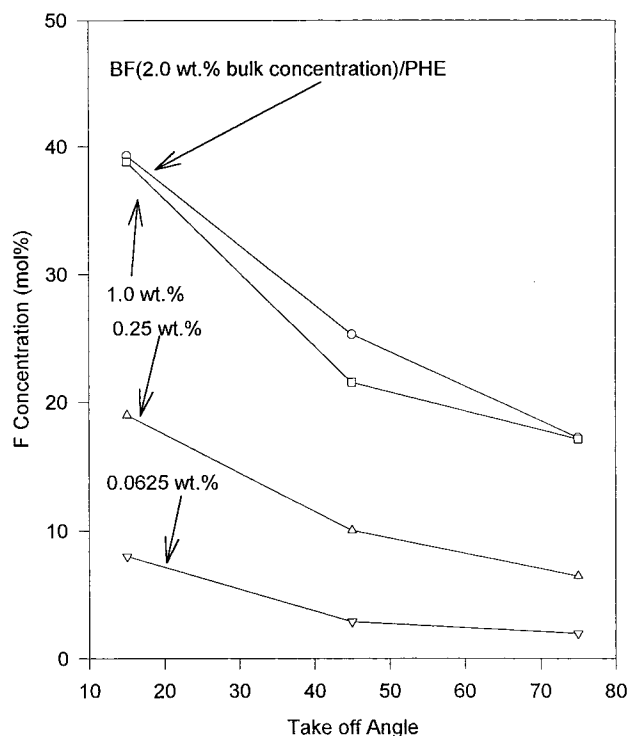
surface was saturated by the BS component when its bulk concentration reached 1.7 wt % but was fully covered by PHE when the BS concentration was lower than 0.17 wt %. For the BSP/PHE blend we have studied here, the surface is fully covered by PHE when the BSP concentration is below 0.25 wt % and the surface was covered completely by BSP at bulk concentrations of 3.5 wt % and higher.

The differences between BS/PHE and BSP/PHE demonstrate that BSP is not as surface-active as BS. This can be explained by the lower surface tension of BS (22 dyne/cm) than BSP (26 dyne/cm). The lower surface tension means lower surface free energy. In air, the component with lower surface tension in the polymer blend is likely to appear at the surface so that the free energy of the system will be reduced. The higher surface tension of BSP, as compared to BS, comes from the replacement of 30% PTMO in BS by PEO, which is more hydrophilic and has higher surface tension. This makes BSP less surface-active than BS and explains the differences in surface properties between BS/PHE and BSP/PHE blends.

On the contrary, BF surface has a lower surface tension (16 dyn/cm) than that of BS so that BF is more surface-active. This can be proved by the comparison between polymer blends BF/PHE and BS/PHE. Our experiments show that the BF component begins to appear on the BF/PHE blend surface when its bulk concentration reaches 0.031 wt % and fully covers the surface when the concentration reaches 1 wt %.

The surface tensions of all three polymer blends are present in Figure 7. The curves show that the lower the surface energy of the surface-active polymer (surface tension: BF < BS < BSP), the easier it is for it to saturate the polymer blend surface (minimum bulk concentration for surface saturation: BF (1 wt %) < BS (1.7 wt %) < BSP (3.5 wt %)). Surface activity should increase with the difference in surface tension between the base polymer (solvent) and surface-active additive polymer (surfactant). Figure 8 describes the roughly linear correlation between these minimum bulk concentrations and the surface free energy differences of the PHE base polymer and the three surface-
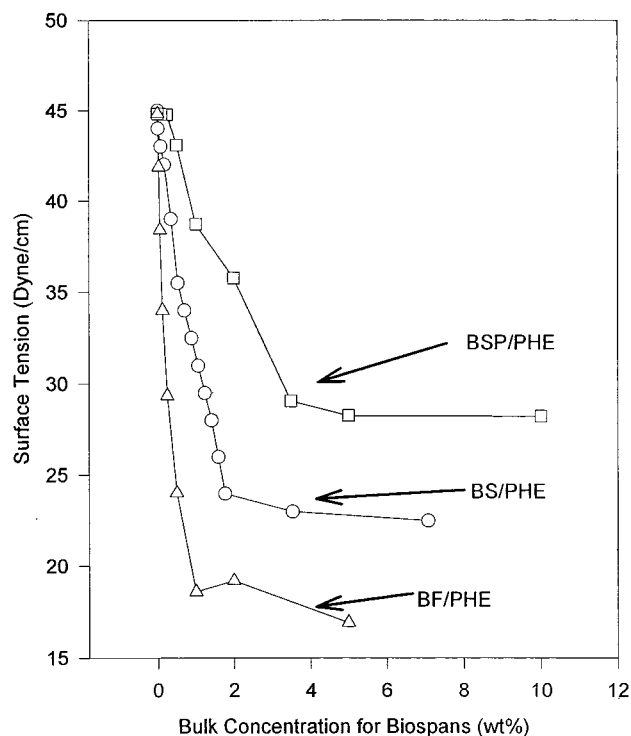
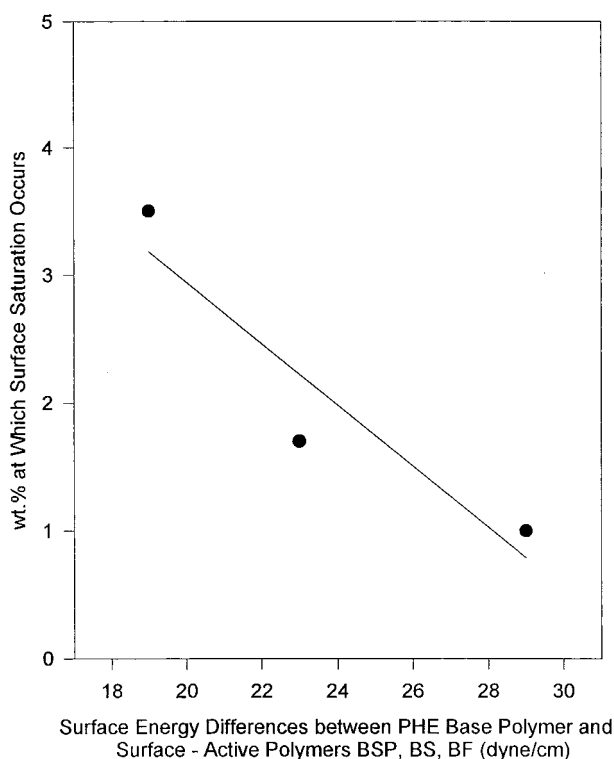**Figure 7.** Comparison of surface tensions of three polymer blends: BS/PHE, BSP/PHE, and BF/PHE.

Figure 8. Linear correlation between the wt % at which saturation of the surface-active component occurs and the surface free energy differences of the PHE base polymer and the surface-active polymers BF, BS, and BSP.

active polymer components, BF, BS, and BSP. This relation may be used to predict the wt % of other surface-active polymers that would be required to mix into PHE and fully cover the surface of the polymer blend.

3.2. Polymer Blend Surfaces in Water. It is very important to study biopolymer surfaces in the hydrated state because the biopolymers are used as implants in the body and in contact
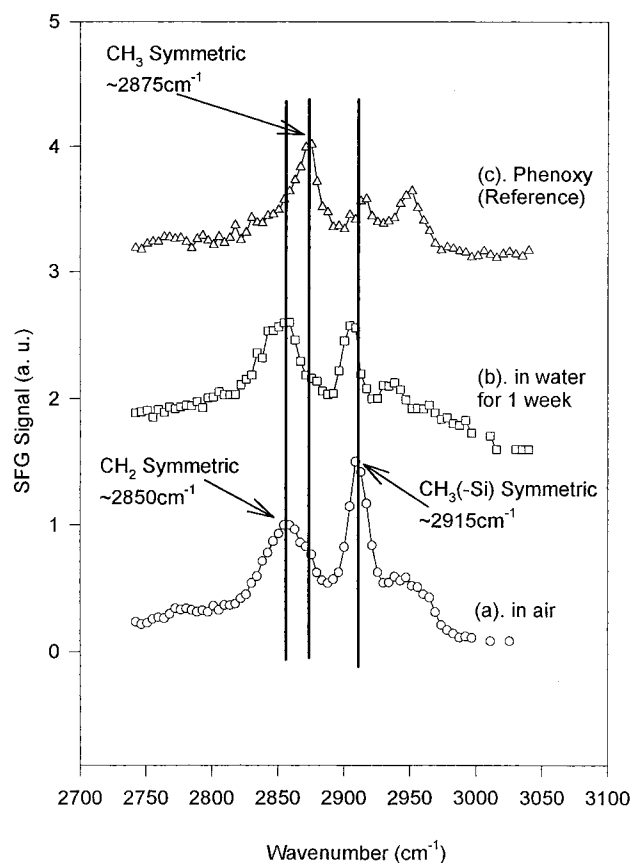

Figure 9. SFG spectra of BSP/PHE with 3.5 wt % BSP bulk concentration in air and in contact with water.

with living tissues or the blood. We have studied the surface changes of three polymer blends after being immersed in water. The three polymer blends are BSP/PHE with 3.5 wt % BSP bulk concentration, BF/PHE with 1 wt % and 5 wt % bulk BF concentration.

3.2.1. SFG Results of BSP/PHE Blends Exposed to Water. When a 3.5 wt % BSP/PHE blend polymer is in contact with water for 1 week, the SFG spectra in Figure 9 show that the surface is still dominated by BSP. The characteristic peak at $\sim$2875 cm^{-1} for PHE is hardly detectable. However, the surface concentration of the BSP end groups (PDMS) does decrease, so that the surface is covered more by the polyurethane part of the BSP. The changes are similar to that seen in pure BS or pure BSP after being in contact with water.[13,14] Clearly, the interaction of water with the polymers is unable to overcome the diffusion barrier for PHE to emerge although it is more hydrophilic than BSP. Yet it is strong enough for the BSP (or BS) backbone and end groups at the surface to rearrange so that the more hydrophobic PDMS would tend to submerge and the more hydrophilic polyurethane backbone emerge.

3.2.2. SFG Results of BF/PHE Blends Exposed to Water. The Phenoxy base polymer (PHE) was not detected on 1 wt % BF/PHE surface in air (Figure 4). However, after contacting with water for 5 days, the characteristic peak of PHE at $\sim$2875 cm^{-1} showed up, as seen in Figure 10. This indicates that the PHE component had emerged to the surface. This is due to the more hydrophobic property of BF than Phenoxy base polymer. The different responses of 1 wt % BF/PHE and 3.5 wt % BSP/PHE polymer blends to the environmental change from air to water are due to (1) BF is more hydrophobic than BSP and (2) the wt % of BF in the blend (1%) being lower than BSP (3.5%). After drying this BF/PHE polymer blend in the air, the PHE part goes
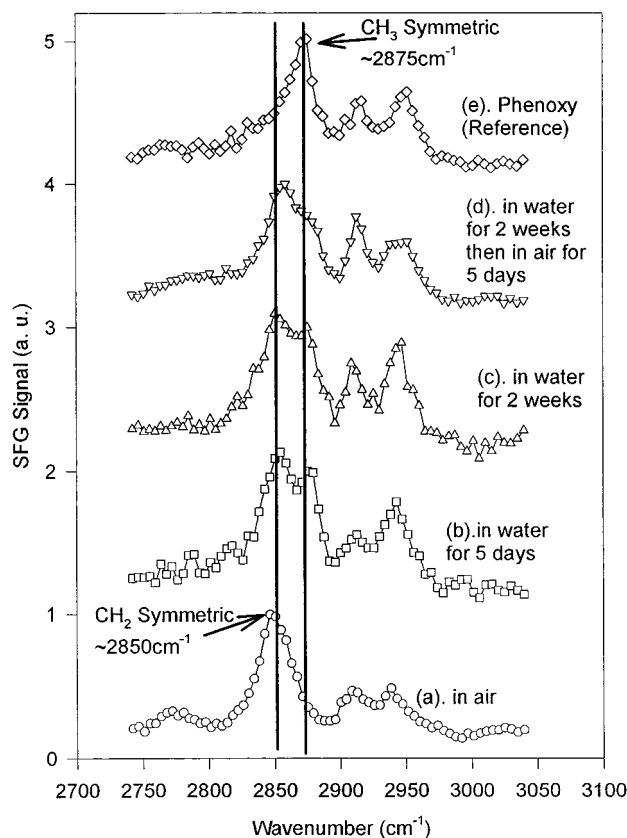
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Figure 10. SFG spectra of BF/PHE with 1 wt % BF bulk concentration in air, in contact with water, and later dried in air again.
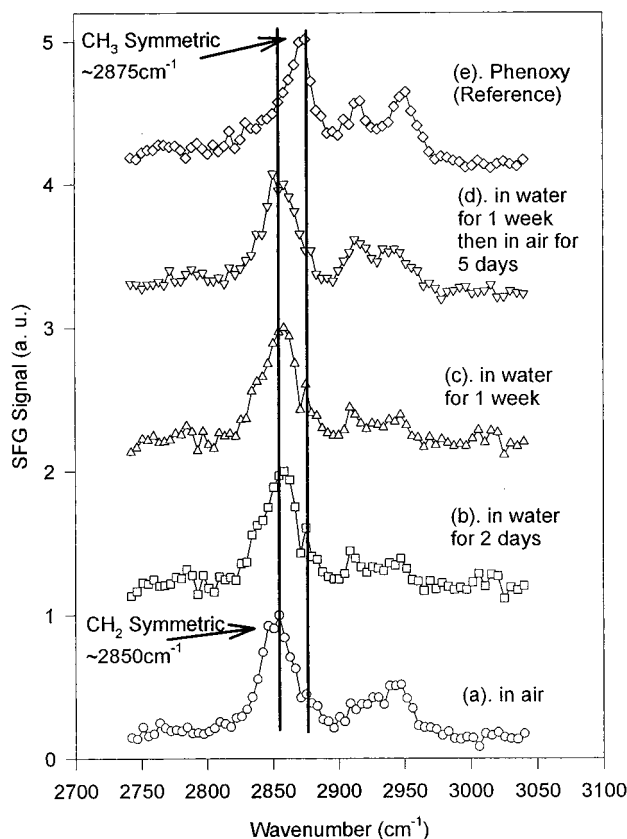

Figure 11. SFG spectra of BF/PHE with 5 wt % BF bulk concentration in air, in contact with water, and later dried in air again.

back to the bulk, although not completely as the $\sim$2875 cm^{-1} peak can still be detected by SFG. Figure 11 shows that for 5

wt % BF/PHE blend, the surface is always completely dominated by BF, whether it is in air or in water. The PHE component is barely visible in the SFG spectra after the surface is in contact with water. This must be due to the thicker BF layers on the 5 wt % BF/PHE surface than that on the 1 wt % BF/PHE surface, which inhibits migration of PHE to the surface.

4. Conclusions

Surface properties of two polymer blends Biospan-SP/Phenoxy (BSP/PHE) and Biospan-F/Phenoxy (BF/PHE) have been studied by SFG, XPS, and contact angle goniometry. Comparison of results for three polymer blends BSP/PHE, BS/PHE (published before[1]), and BF/PHE shows that the surface of polymer blends is sensitive to (a) bulk concentrations, (b) surface energy of the surface-active polymer in the blend, and (c) chemical environments.

From the SFG results, it was found that in air the surface of BSP/PHE is fully covered by BSP when its bulk concentration reaches 3.5 wt %, while for BS/PHE and BF/PHE, the surface is saturated by BS or BF at 1.7 wt % (BS) or 1 wt % (BF). The surfaces are covered by Phenoxy when the bulk concentrations of BSP, BS, and BF are lower than 0.25, 0.17, and 0.125 wt %, respectively. The surface compositions change sharply from one limit to the other in the intermediate range. The contact angle measurement and the XPS show compatible results. The polymer with a lower surface tension (BF = 16 dyn/cm, BS = 22 dyne/cm, BSP = 26 dyn/cm) saturates the surface at a lower bulk concentration, BF (1 wt %)/PHE, BS (1.7 wt %)/PHE, BSP (3.5 wt %)/PHE.

The polymer blends respond differently to aqueous environment, which would induce the more hydrophilic component of the polymer to segregate to the surface. BSP dominates the surface of 3.5 wt % BSP/PHE in both air and water, but its hydrophilic and hydrophobic parts at the surface reorient after exposure to water. The BF (1 wt %)/PHE blend surface is completely covered by BF in air, but some PHE component diffuses to the surface after contact with water. At 5 wt % BF the surface is fully covered by BF in both air and water.

Our results show that, in general, the surface composition of a polymer blend can be very different from the bulk composition. The lower surface tension component would effectively segregate to the surface in order to minimize the surface free energy of the system. Furthermore, aqueous environments stabilize different functional groups of the polymer, so it is necessary to study the surfaces under the conditions that the polymer blends are expected to be employed.

References and Notes

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