Probing the Surface Chemistry of a Hydrated Segmented Polyurethane and a Comparison with Its Dry Surface Chemical Structure

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ABSTRACT: A biochemical approach has been used to analyze the surface chemistry of a hydrated polyester−urea−urethane. Using an enzyme-catalyzed hydrolysis reaction, the surface chemistry of the polyurethane was probed by having the enzyme remove the polymer chain components making up the surface. The surface-derived products were analyzed using high performance liquid chromatography (HPLC), and product identification was carried out by mass spectrometry. The qualitative and quantitative analysis of the removed surface-derived products provided the necessary information required to reconstruct the chemistry of the hydrated polymer surface. The results indicated that urethane and urea linkages were present on the hydrated surface. However, their concentrations were lower than in the bulk polymer. In addition, the ratio of urea to urethane groups was substantially reduced at the hydrated surface relative to the bulk polymer stoichiometry. The data obtained for the hydrated surface were also compared to the analysis of the dry surface, carried out using X-ray photoelectron spectroscopy (XPS). The hydrated polymers contained higher urethane and ester groups than that shown on the dry surface. While XPS was able to identify the presence of urethane linkages on the dry surface, these could not be accurately quantified. Furthermore, the content of urea linkages could not be specifically determined by XPS because they were masked by the ester groups.

Introduction

Interest in the surface chemistry of polymers, specifically for polyurethanes, has increased over the past decades as these materials have found numerous applications as membranes, coatings, and adhesives as well as applications where surfaces undergo interaction with biological solutions.[1−3] Surface characterization becomes an important parameter in the specification of the materials, particularly where biological interactions between the polymer and a tissue/blood interface exists.[4] In such cases, the environment may change the polymer surface by hydration, protein adhesion, and cell attachment. Among the various polymers of interest in aqueous environments, microphase-separated segmented polyurethanes are one group whose surfaces have been extensively investigated. This is primarily due to inherent differences between their surface and bulk phase, the nature of which has been the subject of many investigations.[2]

Several articles[2,3] have reviewed the most common techniques used to probe material surfaces with respect to their chemistry, surface energy, morphology, and microheterogeneity. Techniques that have been used to investigate the interaction of polymers with aqueous environments have included contact angle measurements and attenuated total internal reflection infrared spectroscopy (ATR−IR). However, they are limited in their ability to provide a detailed chemical profile of the polymer surfaces. Alternate techniques often used to characterize the surface chemistry of polymers have consisted of X-ray photoelectron spectroscopy (XPS)[5−16] and secondary ion mass spectrometry (SIMS).[8,15−17] Of these two techniques, perhaps XPS has received the greatest attention. Low resolution XPS is used prevalently to provide atomic composition of the surface within the top 10 nm. High resolution XPS is usually used to determine chemical linkages around the atoms by curve-fitting. The latter approach relies on the condition that the chemical groups of interest have exhibited signals with a high enough relative intensity to permit their accurate curve-fitting. In the case of polyurethane elastomers, it has been noted that the low content of urethane and urea groups in polyurethane elastomers can limit the accuracy of their high-resolution C 1s XPS analysis. SIMS is an effective technique used to identify the chemical structure of particular polymer segments which can be fragmented by an ion beam.[2,8] But quantification is difficult. Both XPS and SIMS require the analytical environment to be maintained under high vacuum. This is often unlike the environments in which the materials are applied. For example, these methods cannot characterize the polymer in aqueous media. In the case of polymers interfacing with proteins and other complex biological solutions there has been a concern that the surface nature in the vacuum environment does not adequately represent the material surface as it would be in the aqueous environment of a biological system.[1] In attempts to overcome this problem, investigators have analyzed the surface composition of prehydrated polyurethanes in a cold stage following freeze-drying.[18,19] The XPS results have shown an increase in nitrogen concentration for samples which were hydrated and then freeze-dried, relative to untreated dry samples. This indicated changes in the more polar urethane component.

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In this study, in addition to XPS, a nonconventional approach is used to obtain more comprehensive surface chemical analysis information on polymers whose surface groups are capable of undergoing hydrolysis in an aqueous/enzyme medium. It involves the surface erosion by enzymes interfacing with the polymer surface, followed by the characterization of the medium-soluble breakdown products, using well-defined chemical analysis techniques for organic compounds. In this manner, the enzymes are used as a tool to assist in probing the original hydrated surface chemistry. The versatility of this approach would be practical since numerous studies[20−27] have reported on the ability of selected enzymes to erode the surface of polymers in aqueous biological systems. These enzymes can bind to surfaces and cleave the polymer surface groups to release surface-derived products from the aqueous/polymeric interface.[28,29] As an example, cholesterol esterase (CE) was found to be an effective enzyme for the degradation of urethane,[30] carbonate[31] and ester-containing groups in polyurethanes.[32] As well, various poyesters and polyurethanes have been shown to be susceptible to erosion by lipases.[25,33,34] Hence, either of these enzymes would be well suited for the proposed biochemical approach to the surface characterization of a hydrated phase-separated polyester−urea−urethane. Out of convenience, CE was selected for this current study. The results of the quantitative and qualitative chemical analysis of the surface-derived products will be used to reconstruct the chemical nature of the polyurethane surface. Radiolabeling of the polyurethane will also be used to assess the quantity of surface-derived product as well as the nature of the individual polymer components found at the surface.

Experimental Section

Materials and Synthesis. 2,4-Toluene diisocyanate (TDI), labeled with ^{14}C in the phenyl ring (lot no. 3104-168, NEN, Du Pont, Boston, MA), was supplied in amber glass ampules each containing 0.24 mCi in 0.55 mL of anhydrous toluene. Aldrich Chemical (Milwaukee, WI) supplied nonlabeled TDI (98% purity), ethylenediamine (ED, 99+% purity), *N*,*N*-dimethylacetamide (DMAC, 99% purity), ethyl alcohol (EtOH, anhydrous), butylamine (BA, 99+%), and polycaprolactone diol (PCL) with an average molecular weight of 1250. 1-Butanol (BuOH, 99.5% purity) and HPLC grade tetrahydrofuran (THF, 99.9% purity) were obtained from BDH (St. Louis, MO). Dimethyl sulfoxide (DMSO, 99.9% purity) was received from Sigma Chemical (St. Louis, MO). HPLC-grade methanol (MeOH, 99.9% purity) was supplied by Mallinckrodt (Paris, KY). Cholesterol esterase (CE, lot No. 31010) was obtained from Genzyme (Cambridge, MA).

The synthesis and purification of the radiolabeled polyurethane [^{14}C]-TDI−PCL−ED with a 2.2:1:1.2 stoichiometry of TDI, PCL, and ED was described in detail elsewhere.[35] Following the synthesis, the polymer product was precipitated from the reaction solution in distilled water by dropwise addition, washed, and then dried. When dry, the polymer was redissolved in DMAC (10 wt %/vol) and centrifuged. The precipitation and washing steps were repeated, and the polymer was then dried in a vacuum oven at 50 °C.

Three model compounds BuOH−TDI−BuOH, EtOH−TDI−EtOH, and BA−TDI−BA were synthesized to assist in the interpretation of mass spectroscopic characterization data and were used as standards for the quantification of surface-derived products. BuOH was dried by distillation in the presence of sodium within 4 h of required use prior to the synthesis. Sodium wire was added into BuOH, and the mixture was boiled under reflux until the metal was dissolved. Then the BuOH was distilled off at 118 °C.[37] The three model compounds were synthesized in DMAC, and the reaction temperature was maintained between 60 and 70 °C for BuOH−TDI−BuOH and EtOH−TDI−EtOH and under 30 °C for BA−TDI−BA. The products were recovered and characterized by mass spectrometry and HPLC for their purity (see Biochemical Surface Analysis section for the detailed description of these methods).

Polymer Characterization. To compare the bulk polymer to the surface polymer chemistry elemental analysis of the bulk polymer for nitrogen, oxygen and carbon was carried out by Guelph Chemical Laboratories Ltd. (Guelph, ON, Canada). The polystyrene-equivalent molecular weight of the polymer was measured by gel permeation chromatography (GPC) in order to assess the distribution of the polymer chains and to ensure that unreacted monomers were removed during polymer processing. The details of the GPC system were previously reported.[35]

The specific radioactivity of the polymer was determined using a 1217 liquid scintillation counter (Rackbeta; LKB, Cambridge, U.K.). Samples were prepared in triplicate by dissolving weighed polymer (0.01−0.03 g) in 1 mL of DMAC and adding 10 mL of a LSC cocktail (formula-989; Packard Instrument Corp.).

Prior to enzyme-catalyzed hydrolysis of the surface, the surface chemistry of the dry polyurethane was characterized by X-ray photoelectron spectroscopy (XPS), using a Leybold MAX 200 XPS apparatus (located at the Centre for Biomaterials, University of Toronto, Toronto, ON, Canada). Samples were cast onto glass coverslips using the same solutions and curing protocol as described in the next section for the biochemical surface analysis. A monochromatic Al Kα beam was used as the X-ray source. Surface atom concentrations for the elements were derived from spectra obtained in a low-resolution mode (pass energy 192 eV). The spectral regions of interest were also run in a C 1s high-resolution mode (passing energy 49 eV) in order to provide information on the different chemical groups within the surface. Angle-resolved XPS was also performed at 90, 30, and 15° in order to provide depth profiles. Angles were defined relative to the plane of the sample. All data were processed using Matlab 4.2b software (Mathwork Inc., Natick, MA).

Biochemical Surface Analysis. One unit of CE activity was defined as the amount of CE required to generate 1 nmol/min of *p*-nitrophenol from *p*-nitrophenylacetate, at 25 °C and pH 7.0.[29] Two polymer groups were incubated. Group 1 consisted of 500 polyurethane-coated glass tubes (25 mm × 2.0 mm i.d. × 3.0 mm o.d.) with 4 units/mL (approximately 0.06 mg/mL) of CE in sodium phosphate buffer (0.05 mol/L) at pH 7.0. Group 2 contained the same number of polymer-coated glass tubes but was incubated with the buffer solution alone. The total polymer surface area per incubation sample was approximately 2000 cm^2. The procedures for polymer coating were described previously.[32] All samples were incubated for 7 days at 37 °C using previously described methods.[36]

The incubation solutions containing the surface-derived products were collected and counted for their radioactivity. UF-20 and UF-CL filter units (Millipore Co., Bedford, MA) were used to filter the incubation solutions and remove protein from the enzyme solution. The filtered solutions were dried by lyophilization in a freeze-dryer. The solid deposits were extracted six times using HPLC grade methanol and THF sequentially. The combined extracts were dried and dissolved in 4.0 mL of the HPLC mobile phase. The sample preparation process was monitored for product recovery by radioactivity measurements taken between the individual steps.

A Waters HPLC system was used for chromatographic separation of the compounds. A Waters' C18 μBondapak column (4.6 mm × 250 mm) was used in combination with a gradient mobile phase, starting with 90% (vol) of an 0.005 mol/L ammonium acetate buffer (pH 7.0) and 10% (vol) of a HPLC grade MeOH and ending at 30% (vol) of the buffer and 70% (vol) of MeOH. The flow rate was 1.0 mL/min. The HPLC fractions that contained surface-derived products were collected for the mass spectrometric analysis. Using the calibration curves for three model compounds, the surface-derived products were quantified.

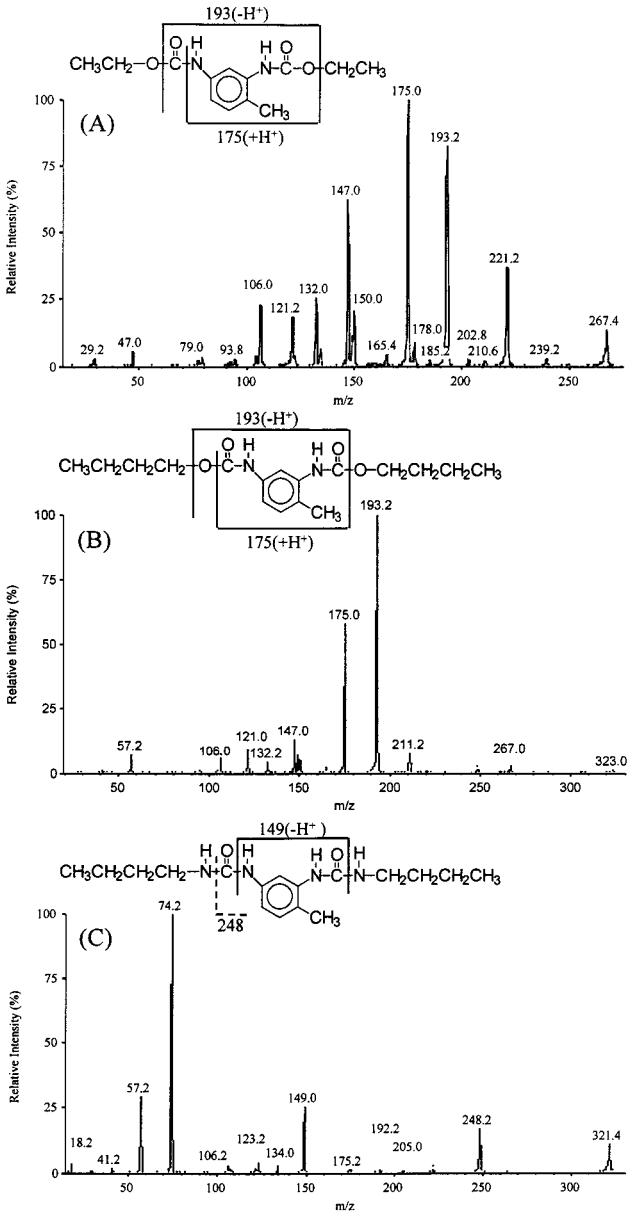


Figure 1. Chemical structure and MS spectra of three model compounds.

Ion spray tandem mass spectrometry analysis was carried out on an API-III triple quadrupole mass spectrometer (MS−MS) (Perkin-Elmer/Sciex, Concord, ON, Canada), located at the Carbohydrate Research Centre, University of Toronto. The degree of product fragmentation was adjusted by changing the pressure of the collision gas (argon) in the second quadrupole. The voltage applied to the tip of the spray needle was 5.00 kV and the voltage applied to the orifice was 80 V. The accuracy of the *m*/*z* measurement, within the range of 100−2000 atomic mass units (amu), was ±0.5 amu.

Results and Discussion

Material Characterization. The polystyrene-equivalent weight and number-average molecular weights and polydispersity, measured by GPC, were 1.3×10^5, 8.1×10^4, and 1.7, respectively. They are consistent with the values reported previously.[32] The specific radioactivity was measured to be 8.0×10^3 CPM/mg.

Figure 1 shows the MS spectra of the three synthesized model compounds, along with their chemical structure. It was noted that two dominant fragments, having mass-to-charge ratios (*m*/*z*) of 175 and 193 (Figure 1, parts A and B), were characteristic fragment ions for the TDI−urethane segment contained in EtOH−TDI−EtOH and BuOH−TDI−BuOH. Two ions at *m*/*z* 149 and 248 (Figure 1C) were characteristic fragments of BA−TDI−BA. These will be used to identify similar fragments in the mass spectrometry of the surface-derived products.

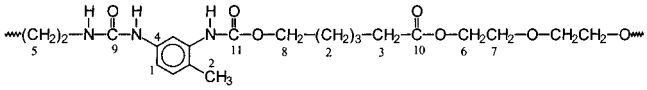
Table 1. Surface and Bulk Elemental Composition (Atomic %) by XPS at Various Takeoff Angles and by Elemental Analysis

takeoff angle (deg)	O	N	C	Si
15	21.44	0.86	74.17	2.53
30	21.96	2.14	74.60	1.28
90	22.02	2.55	76.51	0.93
bulk (elem anal.)	28.60	4.53	66.8	

Table 2. XPS C 1s Bonding Energy of Different Functional Groups[38] and % Atomic Composition at Different Take-off Angles

a	group	bond energy (eV)	C1s peaks	15°	30°	90°
1	phenyl C	284.58, 284.64	A	74.8	69.2	66.4
2	C−C	285.00	A			
3	C−C	285.55	A			
4	phenyl C	285.88, 285.75	A			
5	C−N	285.88	A			
6	C−O	286.54	B	16.9	19.8	20.7
7	C−O	286.54	B			
8	C−O	286.61	B			
9	N−CO−N	288.84	C	7.11	10.1	11.3
10	CO−O	289.08	C			
11	N−CO−O	289.60	D	0.85	1.09	1.6

[a] Carbon positions are shown in the following chemical structure.



XPS Characterization of the Dry Polymer. XPS analysis data in Table 1 show the elemental composition of O, N, C, and Si for the dry polyurethane at takeoff angles of 15, 30, and 90°, corresponding to depths of 3, 5, and 10 nm, respectively. Si is suspected to be derived from dimethylsiloxane-based contaminants since they are some of the most commonly encountered agents in chemical laboratories. For comparison, Table 1 also includes the elemental composition of the bulk polymer as determined by classical elemental analysis. A significant decrease in N concentration from the bulk to the surface was observed. Since N was only associated with the urethane and urea linkages, the XPS data indicate that the urethane and urea content at the upper surface was much less than their content in the bulk. This has been previously observed in many polyurethane systems.[18]

The XPS C 1s data are given in Table 2. On the basis of the chemical structure of the polymer it was determined that the carbon atoms in the polymer chain were located within 11 different functional groups and these were related to their different binding energies[38] (given in Table 2). Since the bonding energy for some functional groups are very close and would be to difficult to resolve in the curve fitting analysis, these groups were combined and classified into four component groups, A, B, C, and D, in Table 2. A Gaussian curve-fitting process was used to obtain the percentage contribution to the C 1s spectra reported in Table 2. Peak B primarily reflected the C−O contribution from the PCL soft

segment. The decrease of the peak B percentage, as the surface was being approached (i.e., decreasing angle), suggested that the ether groups preferentially resided under the top surface of the polymer. As shown in Table 2, C−O linkages are found in the diethylene/oxycaproate-containing soft segments and urethane components. Since the low resolution XPS data (Table 1) indicated a depletion of N-containing groups and therefore an enrichment of PCL soft segments on the surface, it is suggested that the decrease of peak B on the surface would reflect in part the reduction of the urethane linkages. Peak C contains the combined contribution of ester and urea linkages, which represented both the soft and hard segments. The enrichment of the PCL soft segment on the surface, relative to the depletion of hard segments (Table 1), was again used to explain in part the decrease of peak C within the upper surface and suggests that the decrease was associated with a depletion of urea linkages and not the ester linkages. Peak D was solely related to the urethane linkage at the surface. Since the percent contribution of this group was so low (∼1%) and the curve-fitting overlapped with that of peak C, it was impossible to obtain reliable quantitative information about the urethane groups.

In view of the above discussion, it was concluded that XPS provided a limited ability to assign a defined compositional structure for the individual linkages present in low concentrations or having similar bonding energies. This weakness renders the reconstruction of the surface chemistry, solely on the basis of XPS, difficult.

Biochemical Analysis of the Hydrated Polymer Surface. On the basis of the measurement of the released radioactivity from the surface into the incubation solution (4.3×10^4 counts/min for the enzyme treated group), the estimated amount of surface-derived compounds could be calculated using the specific radioactivity of the polymer. This value was 5.4 mg per 0.2 m^2 of polymer surface area and was 10 times greater than the value for the buffer incubation, thus indicating the effectiveness of the enzyme in rapidly generating the surface-derived products. In previous work,[35] using the same degradation system as was used in the current study this level of product was estimated to represent approximately 1% of the total weight of polymer found on the coated tubes. Given that the polymer coating is on the order of 1 μm thick, then it can be estimated that the surface analyzed by the biochemical approach would relate to roughly the top 10 nm of the surface. This is similar to the range studied by the XPS data reported in this paper.

Consideration in the interpretation of the total radioactivity measurement as an absolute measure of mass released from the surface should however take into account the following consideration. It can be seen that while a TDI−PCL segment within the surface region, having an average molecular weight of 1424, and a TDI−ED segment, which has a molecular weight of 234, would each contain one ^{14}C-TDI segment, their inherent radiolabel concentration per segment would be different. As a result of the inherent heterogeneity in polyurethane elastomers,[1] the distribution of TDI−PCL soft segment and the TDI−ED hard segment found at the surface would introduce different levels of specific radioactivity among the surface microdomain phases present. Specifically, the surface TDI−PCL soft segment would contribute to a lower ^{14}C-TDI content than the TDI−ED hard segment components. As well, it should be noted that the specific radioactivity of the polymer reflects the average radioactivity contributed from the combined TDI−PCL soft segments and the TDI−ED hard segment components. Since the XPS analysis suggests an enrichment of the soft segment domains near the surface rather than hard segment domains, the erosion at the surface would be expected to preferentially release the radiolabel from the soft segment domains. Therefore, an estimate of mass loss from the surface based on soft segment radioactivity would be greater than one based on the specific radioactivity of the whole polymer. In conclusion, the estimated mass of surface-derived products (5.4 mg/0.2 m^2), computed above may be a low estimate. This will be discussed further following the surface-derived product analysis.

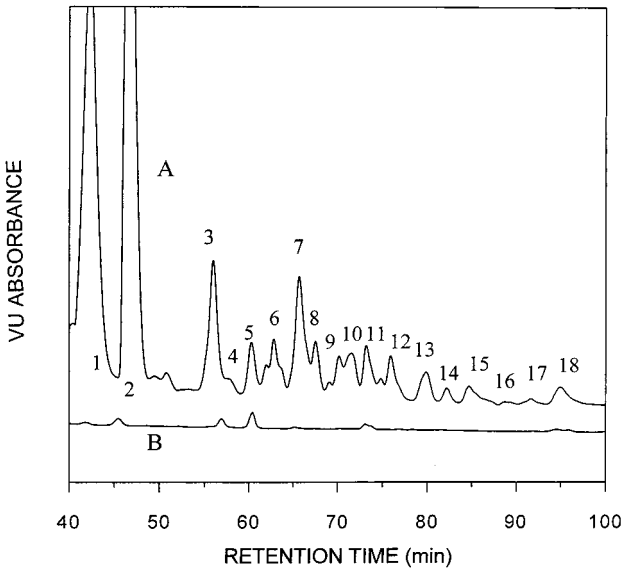


Figure 2. HPLC chromatograms: (A) group 1 (polymer incubated with CE solution); (B) group 2 (polymer incubated in buffer).

Figure 2 shows HPLC chromatograms A and B for the surface degradation products from groups 1 (CE incubation) and 2 (buffer−incubation), respectively. In the enzyme treated surface a significant amount of products were found between the retention times of 40 and 60 min. Again, this illustrates the more comprehensive level of chemical information that may be acquired from the enzyme eroded surface. Previous work[35,36] has shown that the deproteinization process was efficient and the contamination of residual protein contributed minimally to the observed HPLC peaks. The chemical identification and quantification of the surface-derived products in chromatogram A can therefore be used to depict the chemistry of the polymer surface which has been eroded away by CE. It should be noted that scanning electron micrographs of the polymer-coated glass tube surfaces have previously shown that within the incubation time frame studied here there were no observable changes in the smooth surface features of the original material.[32] This indicates that the chemical changes occurring at the surface related to a submicroscopic scale.[32]

Previous work[35,36] had identified products from peaks 1, 2, and 3 found in Figure 2 and their chemical structure is given in Table 3. The MS spectra of products from peaks 4, 6, 7, 12, 13, and 15 were assigned to other structures reported in Table 3. Products from peaks 13 and 15 showed similar fragmentation patterns and were

Table 3. Amounts of Degradation Products

products from peak no.	chemical structure	MW	peak area (V s)	amounts[a] (nmol or μg)
1	$HOOC(CH_2)_5O-TDI-O(CH_2)_5COOH$	438	31	39 or 17
2	$HOOC(CH_2)_5O-TDI-O(CH_2CH_2O)_2H$	412	33	41 or 18
3	$H(OCH_2CH_2)_2O-TDI-O(CH_2CH_2O)_2H$	386	5.9	7.4 or 2.8
4	$HOOC(CH_2)_5O-TDI-ED-TDI-O(CH_2)_5COOH$	672	0.53	1.2 or 0.81
6	$HOOC(CH_2)_5O-TDI-ED-TDI-O(CH_2CH_2O)_2H$	646	1.9	4.3 or 2.8
7	$HOOC(CH_2)_5O-TDI-O(CH_2)_5COO(CH_2CH_2O)_2H$	526	6.0	7.5 or 3.9
12	$H(OCH_2CH_2)_2O-TDI-ED-TDI-O(CH_2CH_2O)_2H$	620	1.9	4.3 or 2.7
13	$H(OCH_2CH_2)_2O-TDI-O(CH_2CH_2O)_2CO(CH_2)_5OH$	500	1.4	1.7 or 0.86
15	$H(OCH_2CH_2)_2O-TDI-O(CH_2CH_2O)_2CO(CH_2)_5OH$	500	0.83	1.0 or 0.51
total				107 or 49.4

[a] Contained in 80 μL HPLC injection volume of total CE/polymer sample solution.

suspected to be isomers having the two polymer chain segments in alternate positions relative to the methyl group on TDI's phenyl ring. The two ions, m/z 175 and 193, which were identified in the MS spectra of the model compounds in Figure 1, parts A and B, and related to TDI−urethane segments, were found in the MS spectra for products associated with peak 7 as well as peaks 13 and 15. Another ion, m/z = 115, was common to products in peaks 1, 2, 4, 6, 7, 13, and 15 and was assigned to the caproic acid group. Similarly, mass ions of 107, 89, and 45 found in MS spectra for products isolated from peaks 3, 6, 12, 13, and 15 in Figure 2, were attributed to the diethylene glycol group associated with PCL. A mass ion of 261 shown in Figure 3 for the mass spectra of products from peaks 4, 6, and 12 in Figure 2 was specifically related to the TDI−ED segment.

The HPLC analysis of the degradation products made it possible to quantify each of the products using the three model compounds (Figure 1) as standards. Products 1, 2, and 3 showed superimpossible UV spectra in previous work.[36] Hence, it was proposed that the different capping groups on the TDI−urethane-containing compounds would not generate very different molar extinction coefficients. This was confirmed in the current study since the TDI−urethane-containing model compounds EtOH−TDI and BuOH−TDI showed overlapping calibration curves (Figure 4). As a result, the peak areas for products 1, 2, 3, 7, 13, and 15 in Table 3 were converted to the amount of product reported in Table 3.

The TDI−urea-containing model compound (Figure 1C) has a different calibration curve slope from that of the TDI−urethane-containing model compounds in Figure 4. This indicates that the molar extinction coefficient of TDI-containing compounds depends primarily on the linkages adjacent to the phenyl ring, for example, urethane vs urea. In the instance of urethane−TDI−urea containing products, it is difficult to synthesize and purify model compounds that have a urethane−TDI−urea structure in order to specifically represent products 4, 6, and 12. For these products, it was assumed that the UV absorbance would result from a combined contribution of a urethane−TDI−urethane chromophore and a urea−TDI−urea chromophore. Therefore, the amount of product determined for these compounds (Table 3) was calculated based on a theoretical calibration curve generated from the TDI−urethane calibration curve and the TDI−urea calibration curve in Figure 4. With the use of these data, it was possible to provide a profile for the chemistry of the degraded polymer surface.

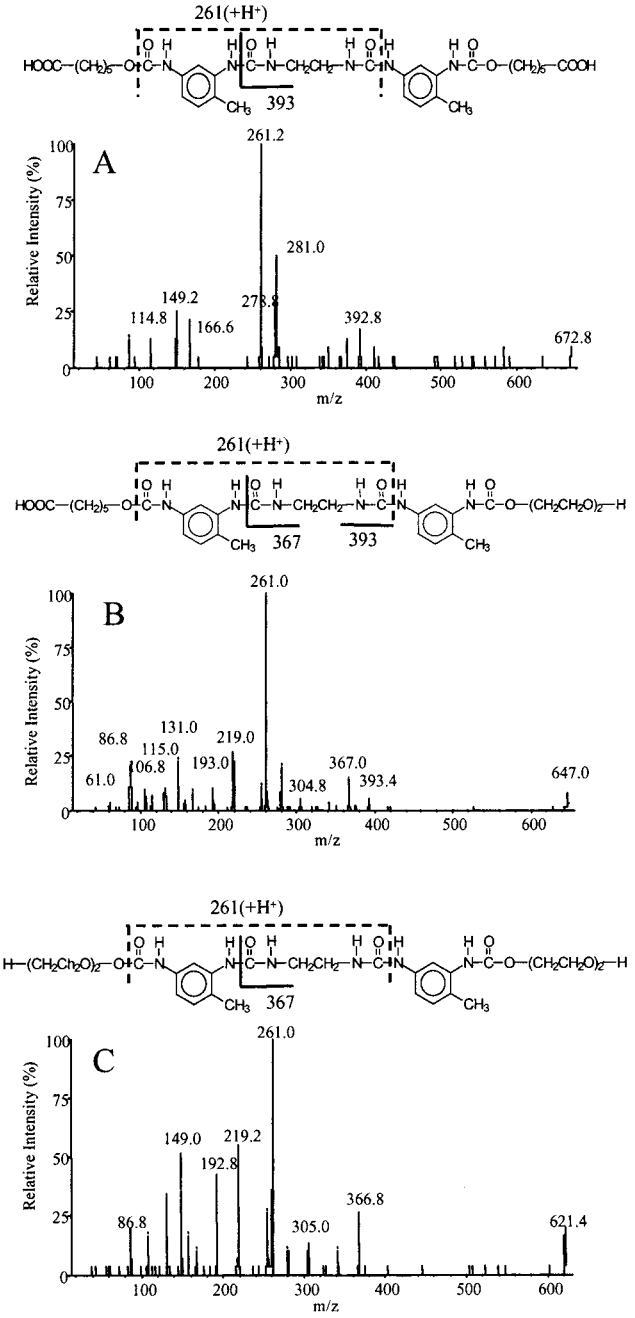


Figure 3. MS spectra of the protonated molecular ions for degradation products with an m/z = 261. Data are ploted as percent relative intensity for the different mass ion signals. HPLC peak numbers in the following legend refers to the labeled peaks in Figure 2, i.e.: (A) product from peak 4; (B) product from peak 6; (C) product from peak 12.

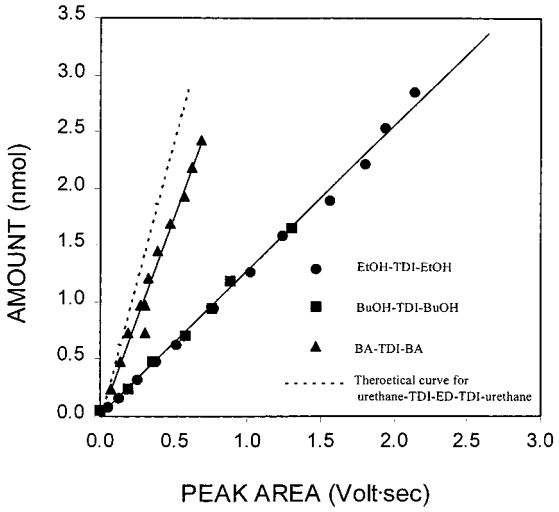


Figure 4. Calibration curves using three model compounds as standards.

Surface Chemistry of the Hydrated Polyurethane. It was estimated that a total of 107 nmol of surface-derived product was generated from the nine dominant TDI-related products (Table 3), contained within an 80 μL HPLC injection volume. More than 90 mol % of the identified products were composed of the six products related to HPLC peaks 1, 2, 3, 4, 6, and 12, while the amount of the intermediate sized products associated with peaks 7, 13, and 15 made up less than 10 mol % of the total identified degradation products. As a result, it was proposed that the other unidentified intermediate products, which likely have yet larger molecular weights than products found in peaks 7, 13, and 15, would contribute to even smaller amounts of the overall composition for the TDI-containing products. Hence, it was assumed that their contribution could be omitted in the final analysis of the surface composition. The total amount of products 4, 6, and 12 generated from the TDI−urea hard segments on the polymer surface was determined to be 9.1 mol % of the total identified surface-derived products.

On the basis of the chemical structure of the polymer there would be on average, 10 oxycaproate repeating units and one diethylene glycol unit between TDI segments in the polymer. The generation of 107 nmol of the TDI-related products (see Table 3) indicates the presence of 10 × 107 nmol of oxycaproate units and 107 nmol of diethylene glycol units between the TDI-containing products within the surface. On the basis of this profile of degradation products, it was proposed that the oxycaproate and diethylene glycol units would be released as the TDI-containing segments were released. On the basis of this analysis, it was estimated that the total amount of surface-derived product would be approximately 7.9 mg per 0.2 m^2 of polymer surface, which is greater than the 5.4 mg per 0.2 m^2 estimated earlier by the radioactivity calculation. This result would confirm the suggestion that the microheterogeneous distribution of the surface's ^{14}C-labeled TDI segments have led to a low estimate of the total surface-derived products from radioactivity data. These findings highlight the differences in chemical structure that exist at the hydrated surface of the polyurethane vs within the bulk polymer and agrees with the XPS findings for the dry polymer (Table 1) which showed a soft segment enriched surface.

Table 4. Percent Composition of the Four XPS Curve-Fitting Groups of Chemical Linkages for the Degraded Surface

component A		component B	component C		component D
C−C C=C	C−N[a]	C−O	COO (ester)	HN−CO−NH	HN−CO−O
64.4	0.5	18.7	13.4	0.3	2.7
64.9		18.7	13.7		2.7

[a] The carbon was in the ED segments.

Upon examination of the data in Table 3, it was also noted that the concentration of the urethane groups was approximately 10 times greater than that of the urea groups on the surface, although the theoretical ratio of urethane to urea would be expected to be 1/1.2, based on the synthesis stoichiometry of this polymer. These data indicate that the urea segments were significantly depleted from the surface in comparison to the urethane segments. Since the specific information on the urea groups in the XPS data (Table 2) was masked by the esters, it was not possible to appreciate the relative depletion of hard segment at the surface.

While the atomic % values for oxygen and carbon were 23.1 and 74.5%, respectively, the nitrogen composition calculated from the biochemical technique was 2.37%. This was greater than the XPS measured value of 0.86 atomic % at a 15° takeoff angle (Table 1) but was similar to 2.14% at 30° and 2.55% at 90°. These data indicate that the biochemical method provides elemental distribution values which are in the range of the XPS data and indicate that polar urethane and urea groups remain depleted (relative to the bulk) even in an aqueous medium.

While XPS provided a depth profile analysis, the current biochemical data did not attempt this. However, further work could consider profiling different depths using this biochemical approach. This should be possible since the depth of analysis for the biochemical technique will likely depend on the enzyme's activity and the hydrolysis period.[32] It should, however, be kept in mind that as the top surface is eroded at later time points, the polymer matrix at the water/polymer interface may undergo a change due to the preferential migration of selected polymer segments resulting from hydration. Hence, analysis of the dynamic state rather than a static depth profile may be only permissible by this approach.

According to the definition of the four component peaks for carbon atoms given in the XPS analysis of the dry surface in Table 2, the percentages of the same four components in the analyzed surface layer of the hydrated polyurethane were calculated and are given in Table 4. The values are best comparable to the 90° takeoff angle data in Table 2, in that the A components are similar for the dry and hydrated surfaces. Otherwise, it was noted that the hydration led to an increase of the polar urethane content to 2.7% (Table 4) from 1.6% (Table 2) for the dry surface. It was also interesting to note that the hydrated sample showed a higher component C content (by ≈2 atomic %) vs the XPS data, but a lower ether content (component B) between the two analyses. This likely reflects the difference in polarity between the carbonyl vs ether groups and the fact that the aqueous environment of the biochemical study would favor attracting more carbonyl groups to the surface. The urea content was estimated to be approximately 0.3% for the hydrated surface, however this value could not be compared to the XPS analysis

since the latter method was not able to provide the urea content. Also present in Table 4 is specific information on the chain extender component (i.e., −C−N), which was not available in the XPS study.

Conclusions

Biochemical surface analysis data have been used to gain insight into the surface chemistry of a hydrated polyurethane surface. Using this approach it was possible to account for the content of all the chemical components on the polyurethane surface and to depict a detailed chemical structure of the hydrated polymer surface. While the data compared well with the anticipated surface chemistry changes relative to the bulk chemistry, as analyzed by established methods such as XPS, they indicated that there was an increased presence of urethane and urea linkages within the hydrated surface, relative to the dry surface. In addition there was a selective migration of the polar urethane linkages to the surface relative to the urea groups. Since the biochemical method can detect low levels of degradation products due to the high sensitivity of HPLC and MS analysis, this method can be used as an effective tool for the analysis of material surfaces having very low concentrations of specific chemical linkages within this region. Such information will be relevant for the study of interfacial systems involving polyurethanes and possibly other polymers used in membrane, adhesive, and biological studies.

Having said this, it should be noted that the solubility of products in the incubation media is a potential limitation of the biochemical surface analysis approach. Although many of the anticipated low molecular weight products were soluble and collected in this system, low levels of large size intermediate products would be insoluble and were omitted in the analysis. Therefore, some caution should be exercised in the interpretation of data in systems that may have products with limited solubility. Nevertheless, the method described in this study, provided a valuable analytical approach toward gaining further insight into the surface structure of the polyurethane system, and this was particularly important since this material as well as other polyurethanes, is able to undergo important changes between the bulk structure and the surface interfacing with aqueous media.

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