

# Change in Mechanical Properties, Composition, and Structure of Hydrated Polyurethaneurea

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**ABSTRACT:** Relative to the extensive study on the relationship between the structure and properties of polyurethane (PU) and polyurethaneurea (PUU), basic information available on hydrated PUU is limited. In this study, PUU films were immersed in a saline solution (0.9 wt % NaCl, 37°C) for periods of up to 60 days and evaluated by the change in static and dynamic mechanical properties, composition, and hydrogen-bonding structure. It was found that immersion in a saline solution could greatly increase the average molecular weight and degree of phase separation, which enhanced the mechanical strength and reduced the flexibility. The increase in the average molecular weight is believed to come from the chain extensions or crosslink reactions between intramolecules and/or between intermolecules and from the leaching out of poly(tetramethylene oxide) (PTMO) oligomers. FTIR analysis indicated that H<sub>2</sub>O molecules did not obviously alter the hydrogen-bonding structure of PUU. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 252–260, 2001

**Key words:** polyurethane/polyurethaneurea; molecular weight; mechanical properties; hydrogen bonding

## INTRODUCTION

It has been commonly recognized that segmented polyurethane (PU) and segmented polyurethaneurea (PUU) are the most desirable candidate materials used for artificial hearts and blood vessels because of their excellent mechanical properties such as high flexibility, high strength, high ductility, and antithrombogenicity. These unique properties are directly related to their two-phase microstructure with the hard domains acting as reinforcing fillers and/or physical crosslinking agents, dispersing into the soft-segment matrix, and strongly depend upon their multiblock copolymer composition and hydrogen-bonding struc-

ture between intramolecules and between intermolecules. For example, in a series of articles by Sung et al.,<sup>1–6</sup> asymmetry in the diisocyanate structure, as in 2,4-toluene diisocyanate (2,4-TDI), led to an amorphous hard-segment domain, while in the symmetric 2,6-TDI PU, a crystalline hard segment was observed. The polyester-based soft segment was found to contribute to greater phase mixing than did the polyether-based soft segment. In the symmetric diisocyanate-based polymers, the PUUs extended with diamine demonstrated much better phase separation than that of PUs extended with diol, indicated by a much lower  $T_g$  of the soft-segment phase and by a much higher  $T_g$  of the hard-segment domain in PUUs due to the presence of three-dimensional hydrogen bonding within the hard-segment domains in PUUs, where one urea carbonyl oxygen is bonded to two NH groups. This three-dimensional hydrogen bonding was also observed by Wang and Co-

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per<sup>7</sup> and confirmed independently by Bonart et al.<sup>8</sup> using X-ray scattering studies.

Shibayama et al.<sup>9-14</sup> studied the deformation mechanism of segmented PUUs during uniaxial stretching and fatigue processes based on deformations of spherulities. The spherulities were selectively destroyed at the equatorial zone of the spherulite with respect to the stretching direction and then fragmented hard segments were dispersed into the soft-segment matrix, causing phase mixing and accompanied by an increase in the hydrogen bonds of urethane groups and a decrease in the hydrogen bonds of urea groups with increasing elongation. Mechanical fatigue resulted in the dissociation of hard-segment microdomains, increasing the degree of phase mixing judged by weaker hydrogen bonds: the index of the cohesive force between the hard segments.

The introduction of polydimethylsiloxane in the main chains reduced the crystallization capability of the soft segments and increased the degree of microphase separation between the soft and hard segments characterized by a higher activation energy for the glass transition of the soft segment, and the higher was the molecular weight of soft segment, the lower was the  $T_g$  of the soft segment, that is, the higher was the degree of completion in microphase separation. Similar results were also reported by Cooper et al.<sup>7,15</sup> and Takahara et al.,<sup>16</sup> who further found that the phase separation in PUUs was also dependent upon the number of methylene units within the diamine. The PUUs with an even number of methylene unit-based diamines showed a remarkably greater degree of phase separation between the hard and soft segments than did those with an odd number of methylene unit-based diamines, accompanied by a higher hydrogen-bonding concentration of urea carbonyl groups in an even number of diamine-based hard segments than that in an odd number of diamine hard segments. At the same time, Ishihara et al.<sup>17-19</sup> also studied the deformation mechanism of a more crystallizable PUU that exhibited a spherulitic texture using wide- and small-angle X-ray diffraction. They observed that the hard segments have a well-defined crystal structure—an anisotropic supermolecular structure, that is, a spherulitic crystalline texture. The microdomain structure was a function of the molecular weight of the soft segments, with phase separation becoming distinct with an increase in the molecular weight of the soft segment. On deformation, the hard segment oriented preferably transverse to the

stretch direction up to high elongation, and it showed a hysteresis of orientation.

Generally, the PUUs with better phase separation exhibit better mechanical properties, such as higher elongation at break, greater toughness, lower hysteresis, and a slower rate of stress relaxation.<sup>4,7</sup> Furthermore, the phase separation of PUUs is directly connected to the blood compatibility. For instance, Takahara et al.<sup>16,20,21</sup> and Shibatani et al.<sup>22,23</sup> found that PUUs with greater phase segregation revealed less platelet adhesion and deformation than did those with greater phase mixing. The blood compatibility of PUU was better than that of the homopolymer of each hard or soft segment which constituted PUU, suggesting that the degree of microphase separation and the microphase domain size have a considerable influence upon the blood compatibility of PUU.

Up to now, however, relative to developments on the study of the relationship between the structure and properties of the original (as-received) PU and PUU, basic information on the change in the mechanical properties, composition, and structure of hydrated PUU or hydrated PU was very limited<sup>24,25</sup> and some confusing conclusions were drawn.<sup>26-28</sup> Since PUU or PU is a typical polar polymer and usually used in an aqueous environment when serving as an artificial heart or as blood vessels, it is of great importance and interest to obtain insight into the possible change in mechanical properties, composition, and structure of hydrated PUU. The objective in this study was to design some *in vitro* experiments to obtain information on the effect of hydration on the mechanical properties, composition, and structure of PUU.

## EXPERIMENTAL

### Materials

PUU films were supplied by Arrow International, Inc. (Reading, PA). PUU solutions were synthesized by the Polymer Technology Group, Inc. (Emeryville, CA) based on 4,4'-diphenylene diisocyanate (MDI), poly(tetramethylene oxide) (PTMO,  $M_w = 2000$ ), and diamines, in which PTMO is the soft segment, whereas the MDI and diamines constitute the hard segment. The PUU solutions in dimethylacetate (DMAC) were cast onto clean glass plates to obtain about  $13 \times 10 \times 0.06$ -cm

films which were immersed into a saline solution (0.9 wt % NaCl, 37°C) for some period of time.

### Mechanical Testing

The mechanical tests were conducted on specimens set in air at room temperature (23°C, as received) or in a saline solution. An Instron Model 4201 tensile testing machine at a crosshead speed of 500 mm/min was employed for the tensile test. The specimens for the tensile test were dumbbell cut from PUU films according to Die C of ASTM-D412. A 25-mm benchmark and the original cross-sectional area were utilized to calculate their tensile properties. The tensile strength at break ( $\delta_b$ ), the secant modulus ( $E_{50}$ , at 50% elongation in our experiments), and the ultimate elongation ( $\varepsilon$ ) can be automatically calculated by the computer connected to the Instron. The average of at least eight measurements for each sample is reported. The experimental error is <10%.

### Gel Permeation Chromatographic Analysis

The molecular weight and molecular weight distribution were obtained by running a 0.05 wt % PUU solution in dimethylformamide (DMF) with 0.05M lithium bromide (LiBr) to prevent aggregation through a Waters liquid chromatograph at 80°C. This system consisted of a Waters 510 pump, 410 differential refractometer, and two PL-gel 5  $\mu$ m mixed-C columns. A 0.05M solution of LiBr in DMF was degassed and used as the eluent phase. Elution volumes were converted to apparent molecular weights using narrow distribution poly(ethylene oxide) (PEO) standards. The calibration coefficient of the PEO standard curve is <0.999, and the experimental uncertainty is <10%. The average of at least two measurements is reported.

### Dynamic Mechanical Analysis (DMA)

Dynamic mechanical measurements were carried out on a DMS 110 bending module instrument (Seiko Instruments Inc., Japan). The specimens of 50  $\times$  10 mm and 0.5 mm thick were immersed in a saline solution for 30 and 60 days, respectively, then taken out and equilibrated at room temperature for 1 week to release the water, followed by being positioned in the flexure mode. Dynamic measurements were performed at 1 Hz with the heating rate of 2°C/min from -150 to 200°C. Samples were cooled quickly to -150°C by liquid nitrogen and allowed to equilibrate at

-150°C for 5 min before the measurements were begun. A sample temperature signal was calibrated by the glass transition temperature (117°C) of poly(methyl methacrylate) at 1 Hz with the heating rate of 2°C/min.

### Infrared Spectral Analysis

Spectra were acquired on a Bio-Rad Digilab Model FTS-45 Fourier transform infrared (FTIR) spectrometer at a resolution of 2  $\text{cm}^{-1}$ . A minimum of 50 scans was signal-averaged. PUU film was obtained by the solution-cast method by spreading a small amount of a 20% solution (w/v) in DMAC on a precleaned standard glass microscopic slide. The solvent was removed by putting this slide into a hood at room temperature for 1 day followed by vacuum drying at 50°C for 1 more day. This polymer film was immersed in a saline solution for different days and taken out and blotted with clean lens paper to remove the residual liquid on the surface and then scanned by an FTIR spectrometer. The same film was repeatedly immersed into the same saline solution for a much longer time. Thus, FTIR spectra of the same polymer film were taken in the original and 1-, 30-, and 60-day immersed states. A curve-fitting technique and an iterative least-squares computer program were used to obtain the best fit of the experimental data by varying the frequency ( $\gamma$ ) and the area ( $A$ ). For urethane carbonyl groups of PUU, the fraction of hydrogen-bonded carbonyl groups ( $X_b$ ) was calculated by

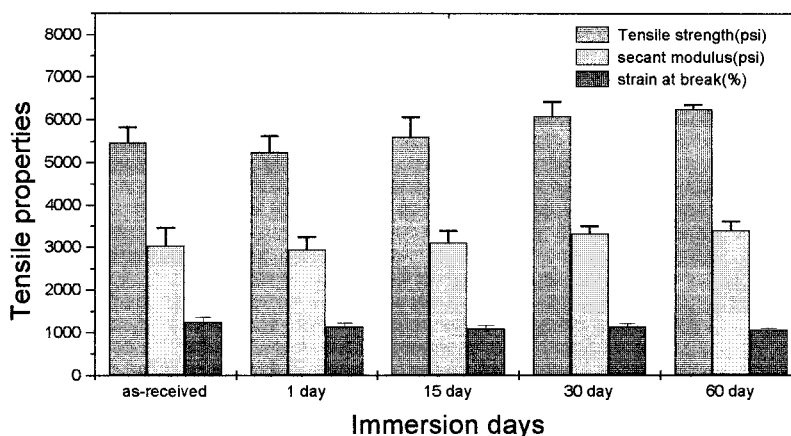
$$X_b = (A_b/E_b)/([A_f + (A_b/E_b)]) \quad (1)$$

where  $A_b$  and  $A_f$  are the absorbency intensity of the hydrogen-bonded and free urethane carbonyls, respectively.  $E_b$  is the extinction coefficient for the H-bonded urethane carbonyl groups and equals 1.2 in PU and PUU.<sup>7</sup> In addition, since the free urea carbonyl is usually not present<sup>17</sup> and NH absorption coefficients are strongly frequency-dependent, as indicated by Coleman et al.,<sup>29</sup> the  $\text{CH}_2$  stretching vibration of an aromatic near 2857  $\text{cm}^{-1}$  was used as the normalized factor to characterize any possible change in the absorbency intensity of H-bonded NH and H-bonded urea carbonyl groups.

## RESULTS AND DISCUSSION

### Static Mechanical Properties and Molecular Weight

Figure 1 demonstrates the static mechanical properties of PUU as a function of the immersed



**Figure 1** Static tensile properties of PUUs as a function of the immersion time.

time in a saline solution. After 1-day immersion, the static mechanical properties of the hydrated PUU do not obviously vary in comparison with those of the as-received PUU within the experimental error range, although both the tensile strength and secant modulus tend to decrease. But after a 15-day immersion, both the tensile strength and secant modulus show an increasing trend, while the elongation tends to decrease. Orang et al.<sup>26</sup> immersed Biomer<sup>®</sup> into a saline solution at 37°C for 66 days and found that Biomer<sup>®</sup> in the undried state showed an increase in the ultimate strain and a decrease in the tensile strength, whereas the dried films after hydration showed a decrease in both tensile strength and ultimate strain, suggesting that the plasticization of the adsorbed water had an important influence on the *in vitro* mechanical behavior. Hayashi et al.<sup>27,28</sup> studied the mechanical properties of three kinds of PU or PUU immersed in a saline solution for 1 month and found that the secant modulus and tensile strength decreased and the ultimate elongation increased for Toyobo TM5<sup>®</sup> (PU made in Japan) and the secant modulus increased and both the tensile strength and ultimate elongation

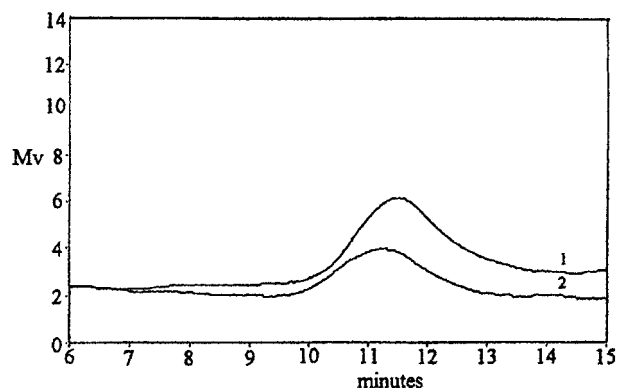
decreased for Biomer<sup>®</sup> (PUU). Both the secant modulus and strength increased and the ultimate elongation decreased for Avcothane51<sup>®</sup> [block copolymer of 90% poly(ether urethane) and 10% polydimethylsiloxane]. It was believed that the plasticization of the adsorbed water caused the decrease in the tensile strength and modulus, but the considerably large change in the tensile properties of Avcothane51<sup>®</sup> during immersion in the saline solution might result from the crosslinking of a reactive silicone moiety onto a performed urethane chain under the activating force of atmospheric moisture.

Table I summarizes the average molecular weight and water content adsorbed by PUU as function of the immersion time. Just like most polar organic compounds, PUU can absorb water molecules very quickly, as shown in Table I. The PUU film reaches equilibrium after 5-h immersion, absorbing around a 1.2% H<sub>2</sub>O content. The average molecular weight increases as the immersion time is extended, even increasing to 24 and 31% for  $M_n$  and  $M_w$ , respectively, after immersion for 60 days. The increase in the average molecular weight after immersion has been occa-

**Table I** Molecular Weight and Adsorbed H<sub>2</sub>O Content

Specimen	$M_n$	$M_w$	$M_w/M_n$	Absorbed H <sub>2</sub> O (%) <sup>a</sup>
As-received	29,900	62,000	2.07	
1-Day immersion	30,400	65,000	2.13	1.05 (2 h)
15-Day immersion	33,000	70,000	2.14	1.17 (5 h)
30-Day immersion	35,000	77,000	2.21	1.17 (1 day)
60-Day immersion	45,000	93,000	2.09	1.17 (15 days)

<sup>a</sup> In the parentheses are the immersion times.



**Figure 2** GPC traces between original and 60-day immersed PUUs: (1) original PUU; (2) 60-day immersed PUU.

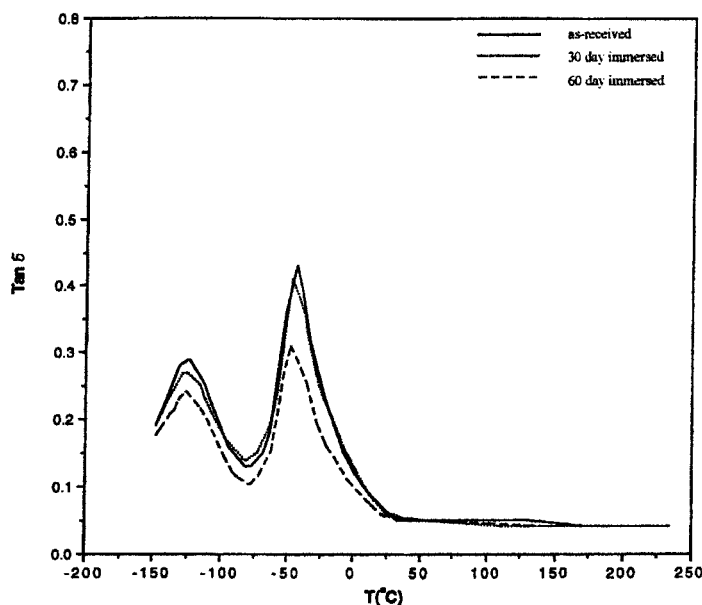
sionally reported by some researchers using *in vitro* and *in vivo* systems,<sup>2,30-34</sup> but no unanimous conclusions on the sources for the increase in the average molecular weight were drawn.

Comparison of the GPC traces between as-received and 60-day immersed PUU films, as shown in Figure 2, shows an obvious shift toward less retention time direction, at both the low molecular weight and high molecular weight ends. The shift of the high molecular weight end in the GPC trace to less retention time strongly suggests that this increase in the average molecular weight is certainly contributed to partially by the increase

of the individual molecular size. This increase probably comes from the chain extensions by residual free isocyanate groups upon exposure to an aqueous medium. The shift of the low molecular weight end in the GPC trace to less retention time implies that some low molecular weight oligomers become larger and larger by the chain-extension reaction or some low molecular weight oligomers leach out during immersion. Thus, it would be thought that during the early stage of hydration, such as 1 day, the adsorbed water molecules have the function of acting as a plasticizer, trying to decrease the mechanical strength of PUU although the average molecular weight slightly increases. But as the immersion time is extended, the average molecular weight continues to increase and eventually results in an increase in the tensile strength and secant modulus.

### Phase Separation

Figure 3 illustrates the mechanical loss tangent,  $\tan \delta$ , as function of the immersion time. The  $\gamma$ - and  $\alpha_a$ -absorption are observed around  $-125$  and  $-46^\circ\text{C}$ , respectively. The  $\gamma$ -absorption is assigned to the amorphous relaxation due to local motions of methylene sequences of the main chain, while the  $\alpha_a$ -absorption arises from micro-Brownian segmental motion of the amorphous PTMO associated with the glass transition.<sup>26, 28</sup> As the im-



**Figure 3** Temperature dependencies of mechanical loss tangent with increasing immersion time.

mersion time is extended, the  $\alpha_a$ -absorption temperature decreases, namely, the  $T_g$  of the soft segments decreases, indicating an increase in the degree of phase segregation between the hard and soft segments since thermal motion within the soft segment is less restricted with the hard segment by phase separating, which is coincident with the results that PTMO, with a higher molecular weight, led to a greater degree of phase separation between the hard and soft segments.<sup>7,15,16</sup> On the other hand, since  $\alpha_a$ - and  $\gamma$ -relaxation processes are associated with the micro-Brownian segmental motion of amorphous PTMO and the local mode motion of methylene sequences of PTMO, respectively, the lowering of the  $\alpha_a$ - and  $\gamma$ -absorption peaks indicates a decrease in the quantity of the amorphous PTMO chain. This provides us the evidence that the leaching out of some low molecular weight PTMO oligomers had occurred during immersion. What is astonishing is that since the low molecular weight soft segments—PTMO oligomers—have the function of being a plasticizer the decrease in the concentration of the PTMO oligomers during immersion should increase the glass transition temperature. But the current decrease in the glass transition temperature with increasing immersion time gives us a hint that the increase in the molecular weight (or molecular size) causes a considerably great phase separation, which not only balances the increase in  $T_g$  due to the loss of PTMO oligomers, but also further decreases the  $T_g$  of the soft segments. Further discussion was presented in refs. 33 and 34.

### Hydrogen-bonding Structure of PUU

Hydrogen bonding of PU and PUU has been extensively studied using Fourier transform infrared (FTIR) spectroscopy.<sup>7,16,17,24,35</sup> The fraction of H-bonded carbonyl groups characterized by both urethane carbonyl and urea carbonyl groups hydrogen-bonded to NH groups of urethane and urea within the hard segments was used as an index of the extent of phase separation. The hydrogen bonding between the ether oxygen to NH groups of the hard segment represents the degree of phase mixing between the hard and soft segments. It was found that an increase in the elongation decreases the strength of the hydrogen bonds in the hard-segment domains—the cohesive force in hard-segment domains—making the hard-segment domains to be broken into small fragments and to be dispersed in the soft-segment

**Table II Curve-fitting Results of H-bonded NH Stretching Region**

Specimen	H-bonded NH Groups		CH <sub>2</sub> Band Near 2857 cm <sup>-1</sup>	
	$\gamma_b$ (cm <sup>-1</sup> )	$A_{\text{NH}}$	$A_{\text{CH}_2}$	$A_{\text{NH}}/A_{\text{CH}_2}$
Original	3317	18	51.2	34.2
1 day immersion	3318	30	71.6	41.9
30 day immersion	3318	35	84.6	40.9
60 day immersion	3318	29	73.3	39.6

matrix, but the increase in molecular weight or chain length of the soft segments is favorable for enhancing the fraction of H-bonded carbonyl groups in the hard-segment domains.<sup>7,12</sup> As the temperature increases, the average strength of the hydrogen bonds decreases, indicating the progress of phase mixing and reduction in the cohesive force in the hard-segment domain.<sup>1,11,27,36</sup> Moreover, Sung et al.,<sup>1</sup> Teo et al.,<sup>36</sup> and Seymour and Cooper<sup>37</sup> further obtained the temperature for the dissociation of hydrogen bonding between hard-hard segments and between hard and soft segments by investigating the effect of temperature on the hydrogen bonding in PU and PUU.

In this section, we study the effect of hydration on the hydrogen bonding of PUU. The polymer films used in this study were sufficiently thin to be within an absorbency range where the Beer-Lambert law is obeyed. No matter how long this film was immersed, the infrared bands near 3318 and 3443 cm<sup>-1</sup> can be observed, corresponding to the H-bonded NH and free (not hydrogen-bonded) NH group's stretching vibration, respectively. If we could borrow the integrated extinction coefficient  $E_f = 3.44 \times 10^3$  L/(mol cm<sup>-1</sup>) for the free NH group and  $E_b = 1.19 \times 10^4$  L/(mol cm<sup>-1</sup>) for the H-bonded NH groups from the measurement on 2,4-TDI-based PU reported by MacKnight and Yang<sup>38</sup> and use eq. (1) to calculate the fraction of H-bonded NH groups from the curve-fitting peaks, the results display that around 95% of the NH groups are H-bonded in accordance with the values reported by Sung and Schneider.<sup>39</sup>

Table II shows the curve-fitting analysis of the H-bonded NH groups in the FTIR spectra as function of the immersion time. An iterative least-squares computer program was used to obtain the best fit of the experimental data by varying the

**Table III** Curve-fitting Results of Urethane and Urea Carbonyl Stretching Region

Specimen	Urethane Carbonyl					H-bonded Urea Carbonyl		
	$\gamma_f$ ( $\text{cm}^{-1}$ )	$A_f$	$\gamma_b$ ( $\text{cm}^{-1}$ )	$A_b$	$X_b$ (%)	$\gamma_{\text{UA}}$ ( $\text{cm}^{-1}$ )	$A_{\text{UA}}$	$A_{\text{UA}}/A_{\text{CH}_2}$ (%)
Original	1734	5.79	1709	4.20	37.7	1638	7.94	15.5
1 day immersion	1733	9.04	1710	6.73	38.8	1638	10.9	15.3
30 day immersion	1733	10.3	1710	7.85	38.9	1636	11.4	13.4
60 day immersion	1733	8.15	1710	6.12	38.5	1637	8.88	13.2

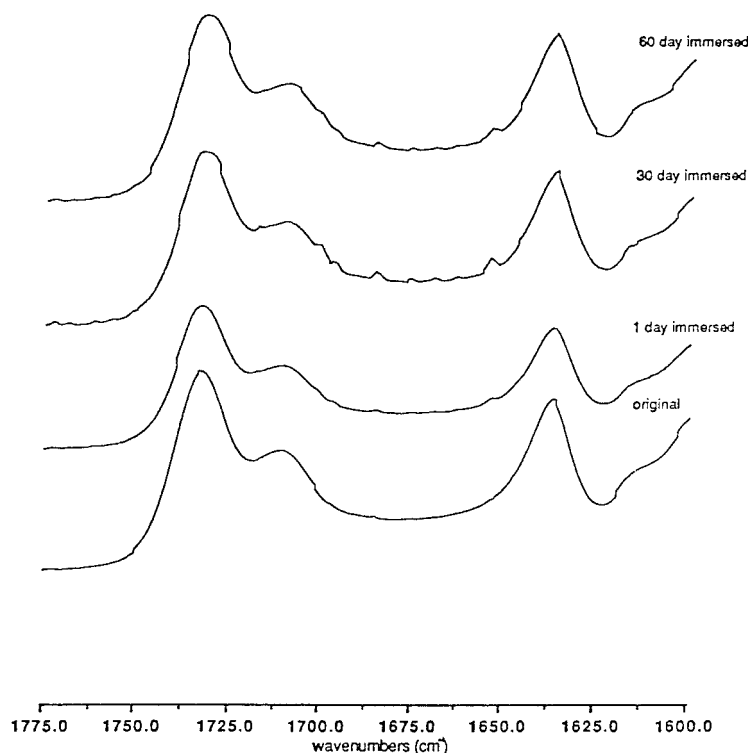
frequency ( $\gamma$ ) and the absorbing area ( $A_{\text{NH}}$ ). The change in fraction of H-bonded NH groups can be characterized by the normalized peak area of H-bonded NH groups ( $A_{\text{NH}}$ ) with the peak area of the  $\text{CH}_2$  stretching vibration ( $A_{\text{CH}_2}$ ). The data show that hydration in a saline solution generates a small increase in the normalized peak area of H-bonded NH groups ( $A_{\text{NH}}/A_{\text{CH}_2}$ ), that is, the fraction of H-bonded NH groups slightly increased. Obviously, this increase is at the expense of sacrificing free NH groups. But the absorbing frequency of H-bonded NH remains essentially constant from the original to the 60-day immersion, indicating that the strength of the interaction between urethane NH to the oxygen of  $\text{H}_2\text{O}$  molecules is comparable to those of urethane NH to urethane  $\text{C}=\text{O}$  and to ether oxygen.<sup>38</sup> But it should be noted here that this strength of interaction is only comparable, not exactly the same. In effect, it has reported recently<sup>36</sup> that the area of the NH hydrogen-bonded to ether oxygen decreased more significantly than that of the NH hydrogen-bonded to carbonyl groups with increasing temperature; in other words, the hard-soft segments are more weakly hydrogen-bonded than are the hard-hard segments. Thus, it should be reasonable to consider that the oxygen of  $\text{H}_2\text{O}$  competes mainly with the ether oxygen, not the carbonyl, to form  $\text{NH} \cdots \text{OH}$  hydrogen bonding, and this competition is still very limited since only about 1.2% of the  $\text{H}_2\text{O}$  molecules were adsorbed in the PUU as shown in Table I. Extending the immersion time does not further increase the peak area of the H-bonded NH groups.

Table III assembles the quantitative analysis results of urethane carbonyl and ordered H-bonded urea carbonyl groups based on their FTIR spectra as shown in Figure 4. The free and H-bonded urethane carbonyl stretching vibrations are absorbed near 1733 and 1709  $\text{cm}^{-1}$ , respectively. The ordered H-bonded urea carbonyl stretching frequency ap-

pears near 1637  $\text{cm}^{-1}$ .<sup>40-42</sup> The free urea carbonyl stretching bands near 1693  $\text{cm}^{-1}$  are not present,<sup>13</sup> indicating that almost all the urea carbonyl groups are hydrogen-bonded.  $\gamma_f$ ,  $\gamma_b$ , and  $\gamma_{\text{UA}}$  correspond to the absorbing frequencies of free urethane carbonyl, H-bonded urethane carbonyl, and H-bonded urea carbonyl groups, respectively, while  $A_{\text{UA}}$  corresponds to the peak area of ordered H-bonded urea carbonyl groups. The results show that only around 38% of urethane groups are H-bonded and that a majority of the urethane carbonyl groups are free. Since a vast majority of NH groups are H-bonded, then the majority of the urethane NH groups must be H-bonded to urea carbonyl groups and poly(ether oxygen). Hydration in a saline solution does not increase the peak areas of H-bonded urethane carbonyl groups too much. Extending the immersion time results in a slight decrease in the normalized peak area of the H-bonded urea carbonyl groups. Since the interaction between NH and poly(ether oxygen) by hydrogen bonding is slightly weaker than that between NH and carbonyl,<sup>36</sup> accordingly, we would believe that the strength of the NH hydrogen bonded to oxygen of  $\text{H}_2\text{O}$  is also a little weaker than that of NH hydrogen bonded to the oxygen of urea carbonyl groups. Thus,  $\text{H}_2\text{O}$  molecules cannot disrupt the hydrogen bonds between interureas and interurethanes, even though they might destroy the orientation or the degree of crystallinity of the hard segment.

## CONCLUSIONS

PUUs, as the candidate materials used for artificial hearts and blood vessels, were immersed into a saline solution for periods of up to 60 days and evaluated by the change in the static mechanical properties, dynamic mechanical properties, molecular weight, and hydrogen-bonding structure. Immersion in a saline solution resulted in an



**Figure 4** FTIR spectra of carbonyl stretching region of PUU: (1) original; (2) 1-day immersion; (3) 30-day immersion; (4) 60-day immersion.

evident increase in the average molecular weight. The GPC traces and the DMA measurement show that this increase might be contributed to by the chain extension or crosslinking reaction, which caused the net increase in the individual molecular size, and from the leaching out of low molecular weight oligomers. At the same time, this increase in molecular weight led to considerable phase separation between hard and soft segments. The increase in both the molecular weight and phase separation and the decrease in the low molecular weight PTMO soft segments greatly enhanced the mechanical strength of PUU, but reduced the flexibility of this material. FTIR analysis of the hydrated PUU shows that H<sub>2</sub>O molecules cannot alter the hydrogen-bonding structure of PUU.

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