

Spectroscopic Study on Water Diffusion in Poly(ester urethane) Block Copolymer Matrix

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The diffusion of water in a phase-separated biodegradable poly(ester urethane) shape-memory polymer with poly(ϵ -caprolactone) (PCL) as the soft segment was investigated using time-resolved FTIR-ATR. On the basis of the band fitting and water ordering in drawn films, the broad water band in the 3800–2800 cm^{-1} region was decomposed into four bands located at 3620, 3510, 3400, and 3260 cm^{-1} , and the first two components at 3620 and 3510 cm^{-1} were assigned to the vibrations of antisymmetric and symmetric stretching of water hydrogen bonded with the C=O group of the soft segment. The other two were associated with water bonded to the urethane hard segments in the forms of N–H:O–H:O=C bridge hydrogen bond and double hydrogen bonds with two C=O groups, respectively. Furthermore, band fitting and two-dimensional correlation analyses revealed that in the diffusion process, water first diffuses into the continuous soft-rich PCL phase and then into the hard-rich urethane domains, forming double hydrogen bonds with two C=O groups prior to the bridge hydrogen bond in the form of N–H:O–H:O=C.

Introduction

Water is one of the simplest and most significant molecules. When polymer materials are in service, water can adsorb to the polymers and have large effects on their physical and chemical properties. At the same time, the water adsorbed to the polymers exhibits a different structure from bulk water. The diffusion and structure of water in homopolymers have been widely studied, and remarkable progress has been achieved.^{1–7} Compared to homopolymers, copolymers generally have more complex morphological structures due to phase separation and segregation, and water diffusion in copolymers is more complicated. During the past two decades, water diffusion into copolymers has been studied; however, the published work focused mainly on permeability and structure/property relationships of the polymers.^{8–11} Few reports concerned the interactions between water and copolymers at the molecular level,¹² and the structure and diffusion behavior of water in phase-separated copolymer matrixes are still not well-understood.

Shape-memory polymers (SMPs) have aroused great attention from academic researchers because they can remember and recover their permanent shape under certain conditions^{13–17} and, therefore, have potential applications in areas such as smart fabrics,¹⁸ intelligent medical devices,¹⁹ and implants for minimally invasive surgery.^{20,21} As an important kind of SMPs, polyurethane SMPs consist of two components forming separated domains due to immiscibility of the two segments, and the hard domains serve as the net points, and the soft domains, the switching segments.^{13–17} Biodegradable SMPs²⁰ further combine biodegradability with shape-recoverability; they would restore their permanent shape to function after insertion in a compressed temporary shape and then would neither stay in the human body for a long time after operation nor require a second surgery to be removed from the human body. With these desirable properties, they are expected to find extensive ap-

plications in medical devices. In these applications, water contact is the first event when a biodegradable SMP is inserted into the human body, and it is critical to understand the interactions between water and the SMP, for they may affect or determine the biocompatibility, biodegradability, and mechanical properties of the inserted material. However, previous studies on polyurethane SMPs were largely focused on the synthesis and thermomechanical properties.^{13–17} Even though limited amount of information on the water absorption may be inferred from the thermomechanical properties of the copolymers,^{22,23} it is necessary to explore the interactions between water and the copolymers at the molecular level.

Various experimental methods have been used to investigate water diffusion into polymers, including gravimetric sorption,²⁴ laser interferometry,²⁵ quartz crystal microgravimetry,²⁶ nuclear magnetic resonance spectroscopy (NMR),²⁷ dielectric relaxation spectroscopy,²⁸ and Fourier transform infrared spectroscopy (FTIR).^{2–7,29–38} Among these methods, FTIR shows some distinct advantages, for it can provide information relating to the interactions between water and the polymer at the molecular level and is more general and more sensitive than other methods. In particular, in the attenuated total reflection (ATR) mode, with a penetration depth of the IR beam into polymer films in the range of 0.1–5 μm , FTIR-ATR is convenient, rapid, and accurate and can monitor water diffusion in polymers in real time.³⁰ Recently, generalized two-dimensional (2D) correlation FTIR spectroscopy proposed by Noda³⁹ has been developed to analyze various kinds of spectral data, which can not only enhance spectral resolution of overlapped FTIR bands but also provide inter- and intramolecular interactions and the specific sequence during a dynamic process.

In the present study, time-resolved FTIR-ATR is used to monitor the diffusion of water into biodegradable polyurethane SMP to understand the diffusion process in phase-separated systems and the molecular interactions between water and the different domains. This is also important to the compatibility

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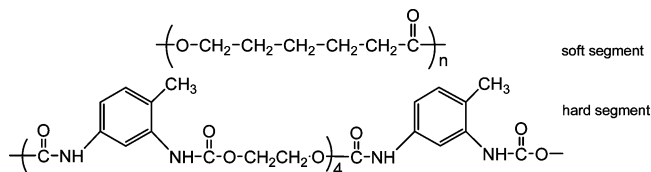


Figure 1. Chemical structures of the soft and hard segments of the PEU.

and mechanical properties of the SMP when inserted into the human body.

Experimental Section

Sample Preparation. A biodegradable poly(ester urethane) (PEU) SMP with poly(ϵ -caprolactone) (PCL) as the soft segment, 2,4-toluene diisocyanate (TDI)–ethylene glycol (EG) as the hard segment, shown in Figure 1, was used in this study. The number-average molecular weight of the soft segment was 5000, and the composition was PCL/TDI/EG = 1:5:4. Details of the sample synthesis and thermomechanical and shape recovery properties have been reported previously.¹⁷ A solution was prepared by dissolving the polymer in chloroform (CHCl_3) at a concentration of 10 mg/mL. Chloroform was purchased from Beijing Chemicals Co. (China) and used as received. Water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was prepared using a Millipore Simplicity unit and used for water absorption measurements.

Time-Resolved FTIR-ATR Spectroscopy. The films used for ATR measurements were cast from the PEU solution at room temperature, which was maintained under vacuum at 40°C for 24 h to remove residual CH_3Cl . The thickness of the film was $\sim 20 \mu\text{m}$. Time-resolved FTIR-ATR measurements were carried out on a Bruker Vertex-70 spectrometer equipped with a horizontal ATR accessory (ZnSe crystal, 45°). All spectra were taken by coadding 16 scans at a resolution of 4 cm^{-1} . For the diffusion experiments, a PEU film was sandwiched between the ZnSe crystal and a piece of filter paper, and the assembly was mounted in the ATR cell. Ultrapure water was then injected into the filter paper, and data acquisition was started simultaneously. The subtraction spectra were obtained via differential spectroscopy using the C–H stretching band as the reference, for there is little interaction between water and the C–H groups. The penetration depth was assumed to be almost constant during the diffusion process, and quantitative analysis was available.³⁴

Polarized FTIR Spectra. A drawn film of the copolymer was prepared by stretching a thin film on a homemade machine at a stretch rate of 0.01 mm/s . Polarized spectra were collected with a gold wire grid polarizer (Specac) mounted between the sample and the detector. The stretch direction was defined as the reference (parallel) direction, and the dry film was used as the background. Each spectrum was collected with 16 scans and 4 cm^{-1} resolution.

Two-Dimensional Correlation Analysis. At least eight spectra at equal time intervals in certain wavenumber ranges were selected for 2D correlation analysis using 2D Pocho software composed by Daisuke Adachi (Kwansei Gakuin University). The 2D correlation spectrum is in the center, and the time-averaged 1D reference spectrum is at the left side and top of the map. In the 2D correlation maps, unshaded and shaded regions are defined as the positive and negative correlation intensities, respectively.

Results and Discussion

Polyurethane SMP is a good example of block copolymer.^{9–11} Due to the thermodynamic immiscibility between the hard and

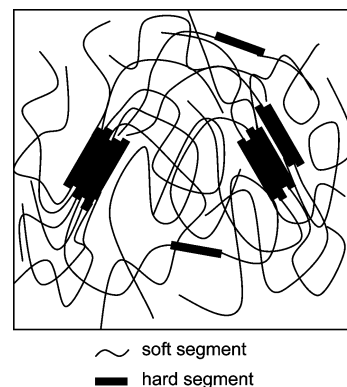


Figure 2. Schematic illustration of the phase-separated PEU SMP.

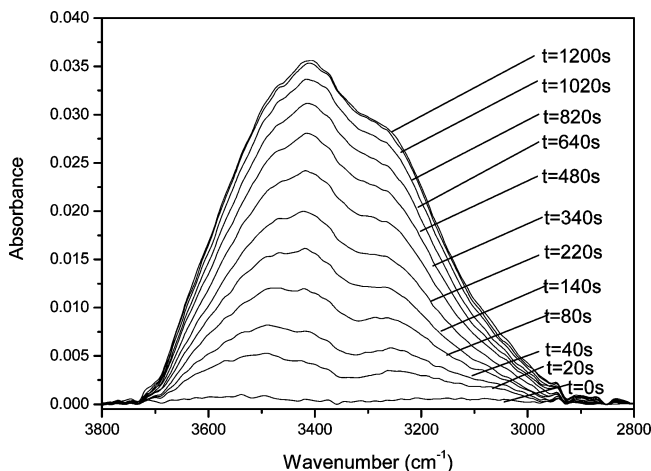


Figure 3. Time-resolved FTIR-ATR spectra collected during water diffusion process, with time of collection indicated for each spectrum.

soft segments, they phase-separate and form hard-rich and soft-rich domains,¹⁶ as illustrated in Figure 2. Water absorbed to polyurethane SMPs can form different kinds of hydrogen bonds due to the polarity of C=O in the ester and the urethane domains, and there are two kinds of hydrogen bonds between water molecules and the urethanes,²² the firmly bonded hydrogen bond and the loosely bonded hydrogen bond, like that in polyamides.^{40,41}

IR Spectra of Water. It is well-known that the fundamentals of the stretching and the deformation vibrations of water are present in the regions of $3800\text{--}3000$ and $1700\text{--}1600 \text{ cm}^{-1}$, respectively. In our case, the $1700\text{--}1600 \text{ cm}^{-1}$ region is highly overlapped with the C=O stretching vibration. Thus, the discussion will be focused in the $3800\text{--}3000 \text{ cm}^{-1}$ region. In addition, it has been proved that more information about hydrogen bonding can be obtained from the O–H stretching band in this region.⁵ Time-resolved FTIR-ATR subtraction spectra in the range of $3800\text{--}3000 \text{ cm}^{-1}$ for water diffusing into the PEU film are shown in Figure 3, which indicate the increase in water content in the film with time.

Band Fitting and Assignment. More detailed analysis of the spectra can be achieved by band-fitting the broad band in the region of $3800\text{--}3000 \text{ cm}^{-1}$, and the band decomposition was achieved using the local-least-squares routine provided in the OPUS software package. The adopted procedure used four parameters—peak position, intensity, bandwidth, and shape—that were allowed to vary upon iteration, and the “best” fitting obtained as the root-mean-square deviation was minimized.

The O–H stretching of water diffused into the PEU copolymer matrix in the $3800\text{--}3000 \text{ cm}^{-1}$ is displayed in Figure 4,

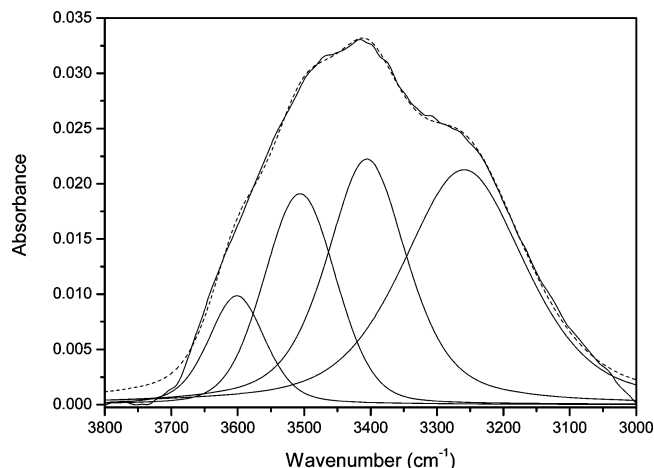


Figure 4. Band fitting for water diffused into the PEU matrix at equilibrium.

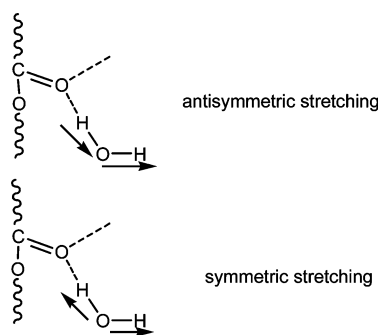


Figure 5. Hydrogen bonding of water with the PCL soft segment.

and four bands are resolved at 3620, 3510, 3400, and 3260 cm^{-1} , respectively. According to the band assignments for pure water,⁶ these four components are due to the O–H stretching vibrations of free and weakly, moderately, and strongly hydrogen-bonded water molecules, respectively. These assignments correlate the band position order with the strength of the hydrogen bonding, but do not carry much structural information. On the basis of a more recent literature report,⁵ the 3620 and 3510 cm^{-1} bands are further assigned to the antisymmetric and symmetric O–H stretching vibrations of water partially hydrogen-bonded with the C=O groups in the PCL, as illustrated in Figure 5, and these assignments are consistent with our findings on states of water in drawn film discussed below. The assignments of the other two bands at 3400, and 3260 cm^{-1} need to be further clarified.

There are two kinds of hydrogen bonds between water and polyurethane,²² as illustrated in Figure 6. Some absorbed water molecules can form double hydrogen bonds with two C=O groups (site “a” in Figure 6), and other water molecules can form hydrogen bonds bridging the gap between the N–H and the C=O groups (site “b” in Figure 6). It has been pointed out that the water molecule in site a is more firmly bound, and the hydrogen bond is stronger compared to that in site b.⁴⁰ On the other hand, it is known that the 3260 cm^{-1} band is associated with O–H that is more strongly hydrogen-bonded than that for the 3400 cm^{-1} band. Therefore, we assign these two bands to the water hydrogen-bonded with the urethane hard segments. More specifically, the 3260 cm^{-1} band is associated with water forming double hydrogen bonds with two C=O groups in the hard segments, and the 3400 cm^{-1} band is assigned to the O–H with bridge hydrogen bond of N–H:O–H:O=C form. The assignment of the latter is also consistent with simulation results reported in the literature.⁴²

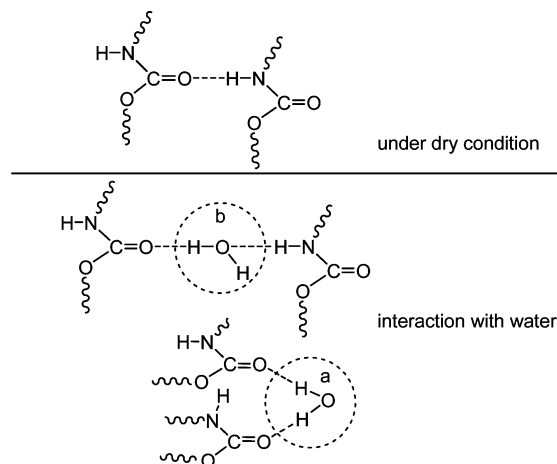


Figure 6. Interactions between water and the urethanes (modified from the literature^{22,40,41}).

The State of Water in the PEU Matrix. Polarized FTIR in transmission mode was used to further investigate the interactions between water molecules and the PEU matrix. The undrawn and drawn films before and after equilibrated with water were analyzed, and Figure 7 shows the polarized spectra in the 3800–3100 cm^{-1} region. Although for the undrawn film, no preferred orientation is observed for the water as expected (i.e. the orientation of the hydrogen-bonded water is isotropic), perpendicular orientation of the O–H dipoles is found for the drawn film, indicating anisotropic distribution of hydrogen-bonding of water due to the orientation of the PEU chains. This kind of water ordering in oriented polymer matrix has been previously observed by solid state NMR using heavy water and oriented polyamides.^{43,44} The four component bands discussed in the previous section are then resolved by band fitting for the parallel and perpendicular spectra to assess the anisotropy of the hydrogen-bonded water molecules in the drawn film. The dichroic ratios are 0.41, 0.80, 0.71, and 0.78 for the 3620, 3530, 3420, and 3260 cm^{-1} bands, respectively. As we proposed above, the 3620 and 3530 cm^{-1} bands are assigned to the antisymmetric and symmetric stretching vibrations of water partially hydrogen-bonded with C=O in the PCL soft segment. By looking at Figure 5, it is obvious that the dipole moment for the antisymmetric mode has a greater perpendicular component than the symmetric mode. Therefore, upon stretching, the PCL (the soft segments) align along the stretch direction (the parallel direction), carrying the water molecules bound to the C=O groups together, and the 3620 cm^{-1} band should exhibit a lower dichroic ratio than the 3530 cm^{-1} band, which is what we observed. As for the 3420 and 3260 cm^{-1} bands, they have almost the same slight perpendicular orientation due to the orientation of the hard segments of the drawn film.

The Diffusion of Water in the PEU Matrix. The dynamics of water diffusion into the PEU matrix was examined by time-resolved FTIR-ATR measurements. The intensity of the spectra of adsorbed water in the PEU film saturates by 1000 s after onset of the flow of water through the filter paper. The spectra obtained over the diffusion process can be deconvoluted into four components with the same peak positions as discussed above. For each of the four bands, the variation of the peak intensity over time can be fitted with a single-exponential curve, as shown in Figure 8, and the relaxation time for each component is determined using the following equation,³

$$A = A_0[1 - \exp(-t/\tau)]$$

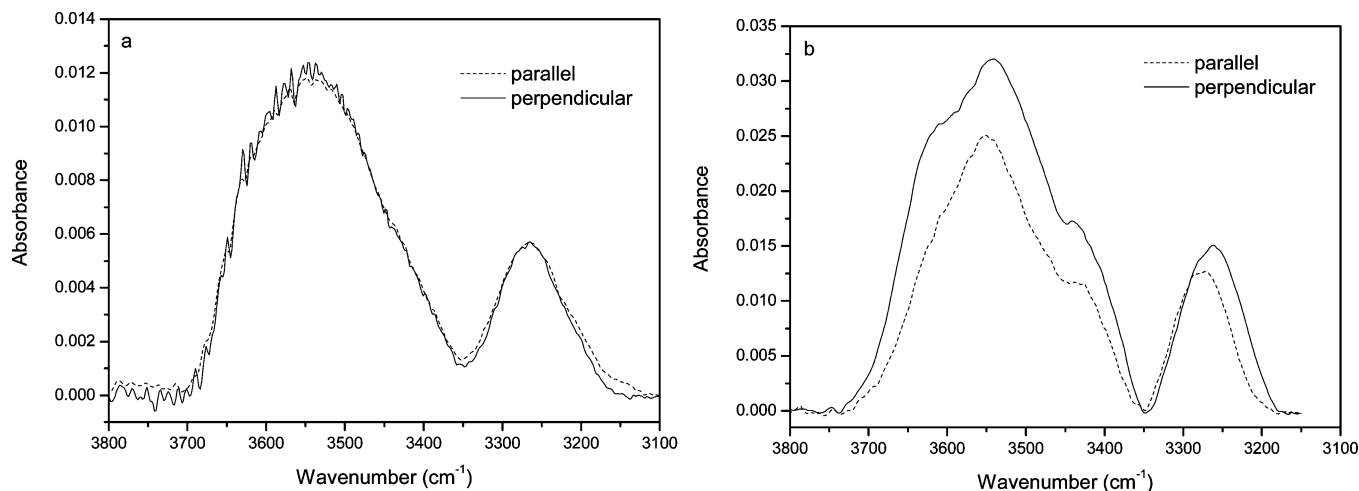


Figure 7. Parallel and perpendicular spectra in the 3800–3100 cm^{-1} region of water in (a) the undrawn PEU film and (b) the drawn PEU film.

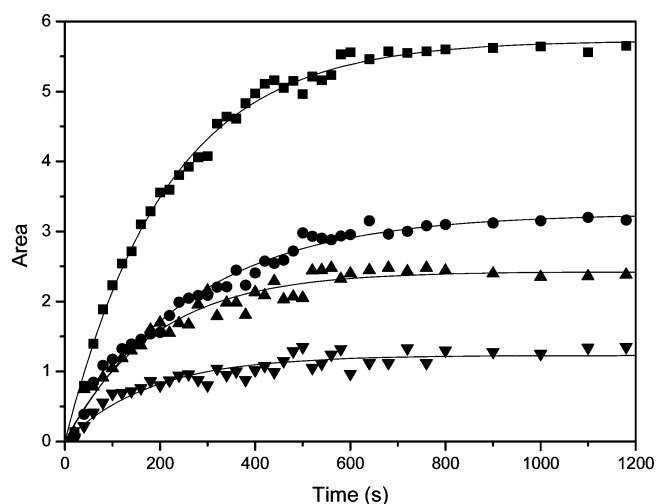


Figure 8. Evolution over time of the diffusion process of the four components of the O–H stretching band of water adsorbed to the PEU matrix at 25 °C (∇ , 3620 cm^{-1} ; \blacktriangle , 3510 cm^{-1} ; \bullet , 3400 cm^{-1} ; \blacksquare , 3260 cm^{-1}).

where A is the area for each component, A_0 is the maximal area, and τ is the relaxation time. The τ values for the components 3620, 3510, 3400, and 3260 cm^{-1} are 181, 188, 267, and 214 s, respectively. The relaxation times for the components at 3620 and 3510 cm^{-1} are about the same, which supports our above assignments of these two bands to the two vibrations of the same molecule. In addition, these numbers indicate that during water diffusion into the PEU matrix, the sequence order is the following: 3620, 3510 \rightarrow 3260 \rightarrow 3400 cm^{-1} .

Two-Dimensional Correlation Analysis. The synchronous and asynchronous 2D correlation spectra in the region of 3800–3000 cm^{-1} are shown in Figure 9. There is only one strong auto peak located at 3425 cm^{-1} in the synchronous spectrum, which is assigned to the O–H stretching of water. Bands originating from other components cannot be observed due to this strong band; thus, from the synchronous spectrum, we are not able to obtain solid information about the diffusion of water in the PEU copolymer. On the other hand, there are one broad positive cross-peak (3510/3400 cm^{-1}) and one negative cross-peak (3400/3260 cm^{-1}) in the asynchronous

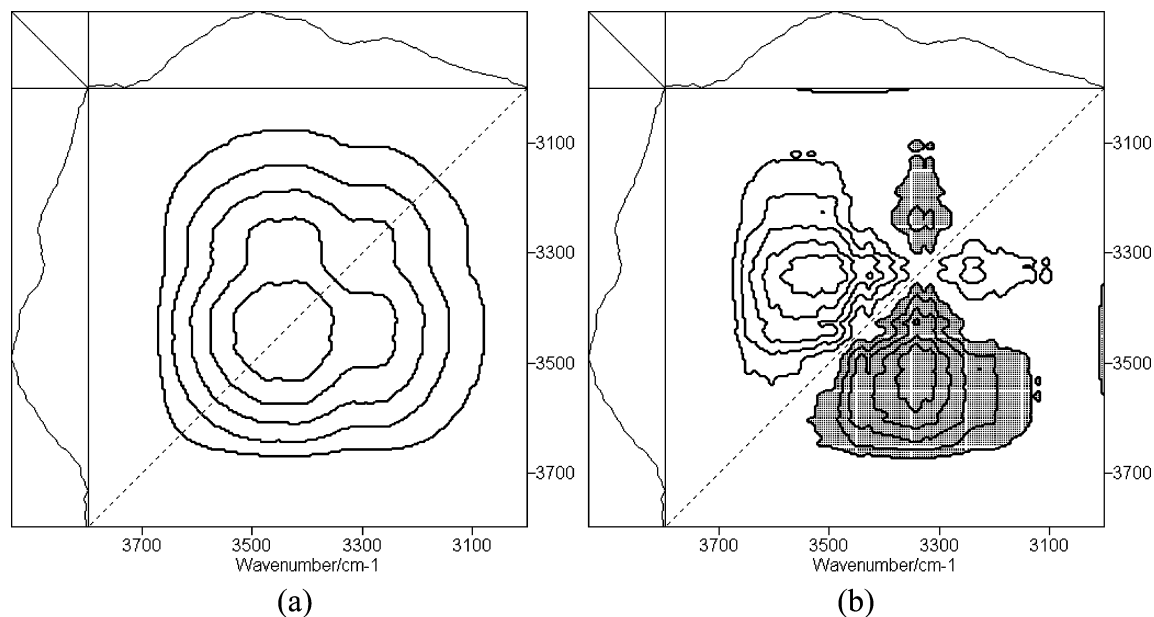


Figure 9. 2D correlation spectra of the OH stretching band in the range of 3800–3000 cm^{-1} : (a) synchronous and (b) asynchronous contour maps.

spectrum, indicating that the broad band in the region of 3800–3000 cm^{-1} consists mainly of three bands located at 3510, 3400, and 3260 cm^{-1} . Compared to the four components resolved by band fitting, the 3620 cm^{-1} band is not clearly observed here, likely hidden by the strong broad cross-peak at 3510 cm^{-1} , probably due to its low intensity and small variation during the diffusion process. The sign of the cross-peak in the asynchronous spectrum can provide information on the sequence order of events associated with the relevant bands. According to the rule of Noda,³⁹ the 3510 cm^{-1} band varied prior to the 3400 cm^{-1} band, the 3260 cm^{-1} band varied prior to the 3400 cm^{-1} band, and the 3510 cm^{-1} band varied earlier than the 3260 cm^{-1} band. Thus, the sequence order of the spectral changes of these three bands is 3510 \rightarrow 3260 \rightarrow 3400 cm^{-1} . This sequence is consistent with that derived from the band-fitting discussed above.

The Sequence Order of Water Diffusion. On the basis of all the spectroscopic results obtained, we are now in a position to describe the diffusion of water into the biodegradable PEU copolymer. Due to the thermodynamic immiscibility between the soft (PCL) and hard (urethane) segments, discrete hard-rich domains are formed in the soft-rich continuous phase in the PEU copolymer. When water diffuses into the copolymer, water molecules first enter the continuous soft-rich domains, forming hydrogen bonds with the C=O groups in the PCL soft segments, and then diffuse into the discrete hard-rich domains, forming double hydrogen bonds with two C=O groups of the urethanes prior to forming a bridge hydrogen bond between the C=O and the N–H groups. The formation of this bridge hydrogen bond would reduce the glass transition temperature and the mechanical properties of the polyurethanes.^{22,23}

Conclusions

In this work, time-resolved FTIR-ATR spectroscopy has been employed to study the water diffusion process into a PEU copolymer. The broad water band at 3800–3100 cm^{-1} region has been decomposed into four bands, which have been assigned on the basis of water ordering measurements in drawn films and comparison with previous studies. The intensity variations of these four components over the diffusion process and 2D correlation analysis of the broad water band revealed the sequence order of events occurring in the water diffusion into the copolymer matrix. This work provides insight into the diffusion of water into phase separated poly(ester urethane) copolymers at the molecular level.

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