Terahertz Spectroscopy for Characterization of Hydrogen Bonding and Cross-linked Structure Dynamics in Polyurethane

Hiromichi Hoshina¹ • Yuichi Saito¹ • Takumi Furuhashi² • Tomomi Shimazaki² • Manabu Sawada² • Yasunori Hioki² • Chiko Otani¹

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Abstract

Terahertz (THz) absorption spectra of cross-linked polyurethane films were observed at 30–180 °C. The obtained spectra displayed characteristic absorption bands. A band observed at 2.6 THz was assigned to the C=O···N-H hydrogen bond vibration using previously reported data. DFT calculation results confirmed that a band at 7.5 THz arises owing to the torsional vibration of cross-linked molecules containing urethane bonds. The slight changes in the temperature-dependent spectra were analyzed by the first derivative of absorption intensity with temperature. The thermal behavior of absorption intensities indicates the dynamics of hydrogen bonds and cross-linked structures in polyurethane films.

Keywords Terahertz spectroscopy · Polymer · Hydrogen bond · Polyurethane · Cross-linked structure

1 Introduction

Because terahertz (THz) frequencies are significantly lower than infrared (IR) light frequencies, absorption features in the THz region can be mainly attributed to the vibrations of weaker intermolecular interactions (e.g., hydrogen bonds or van der Waals interactions) in massive molecules, such as molecular aggregates or macromolecular structures [1, 2]. THz spectroscopy can be used to elucidate higher order structures within macromolecules. Absorption

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✉ Hiromichi Hoshina
hoshina@riken.jp; <https://orcid.org/0000-0002-4770-2005>

¹ RIKEN Center for Advanced Photonics, Sendai, Miyagi 980-0845, Japan

² Murata Manufacturing Co., Ltd., Nagaokakyo, Kyoto 617-8555, Japan

frequencies and intensities provide rich information about the conformation of higher order structures, which imparts macromolecular properties [3–6]. Therefore, THz spectroscopy is expected to become a novel tool to characterize macromolecular structure and dynamics.

In our previous studies, we observed THz spectra of polymers with hydrogen bonds. Based on the THz polarization spectra and low-frequency Raman spectra, the vibrational modes of crystalline polymers were determined [6–10]. In addition, we developed a computational method to enable the precise assignment of each vibrational mode [8–10]. As a result, we determined that polymers having similar structures exhibit comparable absorption features in their THz spectra. For example, poly(hydroxybutyrate) displays an intense absorption band at 2.5 THz, which is assigned to the coupled bending motion of C=O and CH₃ [8]. A similar vibrational band (bending motion of C=O and CH₂) is observed in the spectrum of poly(glycolic acid) at 2.7 THz [9]. These modes are characteristic of hydrogen bond between C=O and CH_x. Importantly, the vibration frequency red shifts at higher temperatures due to changes in hydrogen bond lengths caused by thermal expansion [7, 9, 10].

Furthermore, characteristic bands are found in polymers with C=O⋯N-H hydrogen bonds. It has been reported that polyamides exhibit intense absorption bands at approximately 3 THz [11–15]. Recently, the bands observed at 3.2 THz in the spectrum of nylon-6 were assigned to the coupled bending motion of C=O, N-H, and neighboring CH₂ using DFT calculations [10]. The characteristic band for a C=O⋯N-H hydrogen bond is also observed at 3.4 THz in organic gels containing C=O⋯N-H hydrogen bonds [16]. The frequency of the band reflects the supramolecular structure of the gel; the frequency drastically changes with a sol-gel phase transition [16]. Polyurethane also contains C=O⋯N-H hydrogen bonds. Zavodov et al. reported absorption bands around 100 cm⁻¹ (~3 THz) in the far-IR spectra of all samples of segmented polyurethane [17].

In this study, the THz spectra of cross-linked polyurethane films, a thermosetting plastic used for electric devices, are determined at different temperatures. The cross-linked structure comprises urethane bonding, in which the C=O functional group is included in C=O⋯N-H hydrogen bonds. Macromolecular structures and their dynamics are discussed according to the frequencies and intensities observed in THz absorption spectra.

2 Materials and Methods

In this study, two different polyurethane films were evaluated—samples A and B. Figure 1 shows the macromolecular structure of cross-linked polyurethane and the molecular structures of samples A and B. Poly(hydroxy ether) of bisphenol-A (BPAP) and phenoxy copolymer from bisphenol-TMC and TMDHB (BP-TMC-co-TMDHB) were used as the main agents for samples A and B, respectively; 4,4'-diphenylmethane diisocyanate (MDI) was used as the curing agent.

To construct a film sample, a two-step process was used. First, a 70:30 (wt%) ratio of main agent to curing agent was mixed and dissolved in methyl ethyl ketone (MEK) at 20 wt%. Next, the mixture was spread onto a polyethylene terephthalate (PET) film to form a film with the thickness of 3 μm, the typical thickness used for electric devices. The film was warmed to 60 °C over 20 h, and then was maintained at 60 °C for 20 h. Under these conditions, approximately 50% cross-linked structure was formed. Films were then removed from the PET films, stacked to 100 sheets, and heat-pressed at 73.4 MPa and 80 °C for 5 min to form a single film with a thickness of 250 μm, which is appropriate for THz measurements. To complete the cross-linking reaction, the samples were gradually heated to 180 °C over 1 h, and then maintained at 180 °C for 4 h.

Sample A

Sample B

Fig. 1 Macromolecular structure of cross-linked polyurethane and molecular structures of samples A and B

Sample crystallinity was assessed using wide angle X-ray diffraction; no peak was observed. The macromolecular structure of the sample is amorphous. The glass transition temperature, T_g , measured by differential scanning calorimetry, was 175 °C for sample A and 245 °C for sample B.

THz absorption spectra were observed using Fourier-transform far-IR spectrometer (FT-FIR) (JASCO: FARIS) combined with a superconducting bolometer (QMC: QNbB/PTC), which detects THz frequencies with higher sensitivity and stability than those of conventional bolometers. A high-pressure mercury lamp was used as the light source and a wire-grid beam splitter was used for measurements with a resolution of 0.06 THz. A total of 200 scans were accumulated in 3 min to obtain a single spectrum. The schematics of the heated sample holder are shown in Fig. 2. The sample film was sandwiched between a pair of aluminum holders and set to Brewster's angle, θ_B , to reduce multiple internal reflections (to avoid fringe in the absorption spectrum) [18]. Brewster's angle was set to 55° using the typical index of refraction for polymers ~ 1.5 [5]. The THz beam was linearly polarized using a wire-grid polarizer. The temperature of the sample holder was changed from 30 to 180 °C by controlling the rubber heater current using a PC running a PID program, which monitors temperature using a Pt-100 sensor. Prior to measurements, the temperature difference between the sample and Pt-100 sensor was confirmed. The difference of the temperature was less than 3 °C for the temperature range measured. For convenience, the value of Pt-100 is denoted as “temperature” herein.

3 Results and Discussions

Figure 3 shows the absorption and second derivative spectra of samples A and B measured at 30 °C. In this paper, smoothing is applied for all the absorption spectra to remove spike noise originated in the absorption of the residual water vapor in the sample chamber. The spectra were averaged by Origin™ software with adjacent average option with 100 points (~ 0.7 THz), which does not “over-

Fig. 2 Schematics of the heating sample holder with Brewster's angle

Fig. 3 THz absorption spectrum measured at 30 °C (upper panel) and its second derivative (lower panel) for **a** sample A and **b** sample B. Arrows in the second derivative spectra show the negative band position

smooth” spectra. Also, smoothing was applied with 100 points when the second derivative spectra was calculated. By taking the second derivative of the absorption intensity with frequency, the broad baseline is removed, and the resulting absorption band structure appears as negative peaks. In addition, the intensity of the peak in the second derivative is proportional to the absorption intensity of the band if the width and shape of the band are the same.

Absorption bands are observed at 2.6, 5.4, and 7.3 THz for sample A, and at 2.6, 5.3, 6.2, and 7.5 THz for sample B. Similar band structures appear at 2.6 THz in both samples. As described in the introduction, the characteristic absorption band for C=O $\cdots$ N-H hydrogen bonds is observed in this region. Therefore, it is reasonable to assign this band to the C=O $\cdots$ N-H hydrogen bond vibration. However, the peak frequency is lower than those observed for nylons. This vibrational frequency red-shifting likely correlates to differences in the reduced mass. In nylons, this mode is the coupled vibration of C=O, N-H, and neighboring CH₂. [10] In contrast, samples A and B contain phenyl groups near the urethane bond, which may increase reduced mass. Another possible culprit is weaker hydrogen bond. Since samples A and B are amorphous polymers, their average intermolecular distance may be longer than that of crystalline nylons, which would weaken hydrogen bond interactions.

Fig. 4 **a** Simulation model for molecular vibrations in sample A. The vibrational mode at 7.5 THz is also depicted using vectors. **b** THz absorption spectrum of sample A and vibrational modes obtained from quantum calculations

To assign the other bands, first principles quantum chemistry calculations were performed. For the lower frequency region of THz spectra, THz vibrational modes result mainly from intermolecular motion; a large number of atoms must be included in the simulation. In addition, weak intermolecular interactions must be considered, in order to reproduce anharmonic vibrational potentials. As a result, *ab initio* calculations for the THz vibrational spectra require extensive resources compared to those for IR spectroscopy. In the last decade, the frequencies of THz vibrational modes in crystalline samples have been calculated with some success using software that considers the periodic boundary conditions of the crystal [19–21]. Yamamoto et al. have developed a method (Cartesian-coordinate tensor transfer

Fig. 5 **a** Simulation model for molecular vibrations in sample B. The vibrational mode at 7.4 THz is also depicted using vectors. **b** THz absorption spectrum of sample B and vibrational modes obtained from quantum calculations

method) to assign polymer spectra using DFT calculations for a fragment of the crystalline polymer [8–10]. However, these methods can be applied only to crystalline samples. To simulate the spectrum of an amorphous structure, more advanced methods, such as *ab initio* molecular dynamics simulations, are required [22].

Conversely, vibrational modes at higher frequencies (far-IR) are rather straightforward to calculate, because the contribution of intramolecular motion becomes dominant [23, 24]. Some of the bands can be simulated by considering a small number of atoms. Figure 4 a shows a simulation model for sample A, in which MDI bridges two BPAP chains. To extract the model from the actual material, cross-sections of BPAP chains are capped by hydrogen atoms. The geometric structure was optimized and the vibrational frequencies of the simulation model were calculated using the Gaussian 09 program. Optimization and spectrum calculations were executed at the B3LYP/6-311G(d) level. We used the scale factor of 0.966 to compensate the anharmonic effect in the quantum chemistry IR (THz) calculations [25].

Figure 4 b presents the observed THz absorption spectrum and calculated vibrational modes for sample A. The majority of the calculated modes are coupled vibrations of many atoms in BPAP and MDI. The obtained frequencies for these modes are not reliable; the frequencies change with the size of the simulation model. On the other hand, the vibrational mode at 7.5 THz is completely intramolecular. Arrows in Fig. 4a demonstrate the atomic motions of that mode. (Also shown as a movie in the supplemental data.) Atoms in the cross-linked

Fig. 6 THz absorption spectra measured in 5 °C increments from 30 to 180 °C (upper panel) and its second derivative (lower panel) **a** for sample A and **b** sample B

structure, including the urethane bond, move, but the other atoms in the BPAP moiety remain stationary. This mode is completely “local,” thus the obtained frequency is reliable. We assigned this band to the torsional vibration motion in the cross-linked structure, coupled with the bending motion of urethane bonds.

Figure 5 a shows a simulation model for sample B, in which MDI bridges BP-TMC-co-TMDHB chains. The geometric structure was optimized and the vibrational frequencies were calculated with same method and basis set with sample A, and the scale factor of 0.966 was applied. Figure 5 b presents the observed THz absorption spectrum and calculated vibrational modes for sample B. Same as the sample A, the vibrational mode at 7.4 THz is mainly due to intramolecular motion, and we assigned this band to the torsional vibration motion in the cross-linked structure, coupled with the bending motion of urethane bonds.

Figure 6 shows the THz absorption spectra of samples A and B measured with heating at 5 °C increments from 30 to 180 °C, as well as their second derivative spectra. The bands at

Fig. 7 The first derivative of absorption intensity with temperature calculated by the absorption spectra shown in Fig. 6 for (a) sample A and (b) sample B. The dashed lines indicate the frequency shift of the negative peaks

2.6 THz shift toward lower frequencies with temperature monotonically. In our previous studies with crystalline polymers, we observed similar red shifts in the characteristic absorption bands for hydrogen bonds with temperature [7, 9, 14]. The observed rates of frequency shift were approximately 0.1–0.2 THz/100 °C and were attributed to the reduction of intermolecular interactions due to increased intermolecular distances resulting from thermal expansion. The shift in frequency of the 2.6 THz band for samples A and B can also be attributed to reduced intermolecular hydrogen bonds at higher temperatures.

Conversely, the band at 7.5 THz does not exhibit remarkable shifts in frequency with temperature, but the intensity of the second derivative spectrum decreases. This indicates that the static structure shown in Fig. 4a is not maintained at higher temperatures. Thermal motion likely deforms the structure around the cross-linked molecules, which causes weakening or broadening of the vibrational band.

To clearly visualize the change in absorption intensity, the first derivative of absorption intensity (α) with temperature (T), $\partial\alpha/\partial T$ was calculated. Figure 7 shows two-dimensional plot of $\partial\alpha/\partial T$ with frequency and temperature. The dashed lines in Fig. 7 indicate the frequency

shift of the negative peaks, which correspond to the hydrogen bond vibration at 2.6 THz. Since the band features are tilted by the slope of their baselines, their frequency shift causes a decrease in the absorption intensity. (See Fig. 6) Therefore, a negative peak appears at a slightly higher frequency in the plot of $\partial\alpha/\partial T$. A broad negative band centered at 3 THz appears at 160 °C only in the plot of sample A, which clearly indicates a change in spectral intensity at the glass transition temperature. A drastic decrease in the intensity of the hydrogen bond vibration occurs at the glass transition temperature. Most probably, hydrogen bonds formed in the glassy structure break when the polymer changes to a rubbery state.

A broad negative area above 3 THz is observed below 90 and 100 °C for samples A and B, respectively. Since the bandwidth of this spectral feature is quite broad, this absorption feature may originate with liquid molecules, such as remaining MEK or unreacted MDI. It is difficult to assign molecular structure using the THz spectra alone. However, DSC, NMR, and dielectric spectroscopy measurements do not indicate corresponding structural changes at these temperatures. The origin of this spectral change remains unknown.

4 Conclusion

In this research, THz absorption spectra of cross-linked polyurethane films were observed and peaks in the obtained spectra were assigned using *ab initio* calculations. A characteristic absorption band at 2.6 THz was assigned to C=O...N-H hydrogen bond vibration. Another band at 7.5 THz was assigned to the torsional vibration of cross-linked molecules with urethane bonds using DFT calculations. Temperature-dependent spectra and its first derivative spectra clarify slight changes in the broad vibrational bands. Thermal dependence of the absorption intensities indicates the dynamics of hydrogen bond and cross-linked structures in the polyurethane films. Thus, we have demonstrated the potential for THz spectroscopy to analyze hydrogen bond interactions and cross-linked structures in polymers.

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