



Structure and dynamics of bound water in poly(ethylene-vinylalcohol) copolymers studied by terahertz spectroscopy

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ABSTRACT

Poly (ethylene-vinylalcohol) copolymer (EVOH) films under different humidity conditions were studied by THz absorption spectroscopy to obtain information about the bound water. An intermolecular stretching mode of bound water was observed at around 6 THz, similar to that in liquid water; and the very weak librational mode indicates that this water is frozen. By generalized two-dimensional correlation spectroscopy (2DCOS) and perturbation-correlation 2D moving window (PCMW2D) correlation spectroscopy, the bound water was categorized into three types: frozen with amorphous structure (I), liquid-like with librational motion (II), and nearest neighboring water with weaker hydrogen bonding network (III). The strongly inhomogeneous intermolecular stretching band of water I shows that the frozen bound water is amorphous. The frequency shift of this band in water III indicates a weaker hydrogen bonding network around the ethylene group. Changes in the films' oxygen permeability are discussed and correlated with the dynamics of bound water.

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1. Introduction

Due to the recent development of terahertz (THz) wave technology, THz spectroscopy and imaging applications have attracted keen interests in applied physics and chemistry [1,2]. In polymer science, THz absorption spectroscopy gives detailed information about the higher order structures and their hydrogen bonding interaction, because the low-frequency vibrational modes observed in THz frequencies are mainly due to the skeletal vibration of polymer chains or the vibration of hydrogen bonds [3–11]. Since such information is closely correlated with the properties and functions of polymers, THz spectroscopy is expected to become an important tool for inspecting polymer products. Another advantage of THz spectroscopy is that it is a non-destructive analysis method. THz spectroscopy can be used for diagnosis in polymer products, such as time-lapse monitoring of polymer degradation and imaging the crystalline distribution in polymer sheets [10]. These *in-situ* measurements are difficult by conventional methods such as differential scanning calorimetry (DSC), NMR, and X-ray diffraction.

Another virtue of THz absorption spectroscopy is the high

sensitivity for liquid water ($\sim 250 \text{ cm}^{-1}$ at 1 THz) [12]. THz imaging can clearly show slight differences of water concentration in the samples [1,2,13–15], and THz spectra provide rich information about the structure and dynamics of water molecules. Spectra in the lower frequency region below 1 THz reflect rotational relaxation [16–20]. The mechanism of water hydration has been studied at the lower frequency region by THz time-domain spectroscopy and dielectric relaxation spectroscopy [21–27]. On the other hand, spectra at higher frequencies (>3 THz) reflects intermolecular stretching vibration and librational motion [12]. However, only a few studies have been performed in this frequency region, probably because of the difficulty in obtaining good signal-to-noise ratio.

In this paper, THz spectra of bound water in Poly (ethylene-vinylalcohol) copolymers (EVOH) film are studied. The bound water can drastically change the property and function of the polymer. Therefore, the structure and dynamics of bound water have been studied with various methods. Its amount can be estimated by DSCs [28–30], which however does not directly provide the structural information. There are studies observing bound water by infrared [31] and near infrared spectroscopy [32]. Yet the observed shift of OH stretching mode provides much less information of hydrated water. In contrast, THz spectroscopy could provide clear analysis of bound water in terms of the intermolecular vibrational modes, which gives direct information about the intermolecular

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conformation and dynamics.

EVOH, a random copolymer consisting of ethylene and vinyl-alcohol (VOH), is widely used due to its low oxygen permeability. However, the mobility of gas molecules in EVOH has been known to change with humidity, resulting in unstable oxygen permeability of the related products. In this study, we measured the spectra of bound water in EVOH samples prepared under different humidity conditions. The obtained data were analyzed using generalized two-dimensional correlation spectroscopy (2DCOS) [33–36] and perturbation-correlation 2D moving window (PCMW2D) correlation spectroscopy [37,38]. These analytical methods help to separate the overlapped absorption bands with different origins and works as powerful tools for examining THz absorption spectra, in which the bands are broad and overlapped at room temperature [39,40]. By using these methods, we successfully extracted information of bound water in different environments. The dynamics of bound water obtained by THz spectroscopy was compared with those obtained by DSC. The mechanism of the oxygen permeability in EVOH film is discussed in terms of the bound water dynamics as revealed by THz spectroscopy analysis.

2. Experimental section

2.1. Sample preparation

EVOH monolayer films with three different ethylene contents were provided by Kuraray Co. Ltd. The sample sheets with the thickness of 60 μm were formed by the extrusion on a roll at 80 $^{\circ}\text{C}$, and then annealed for 10 min to control the crystallinity. Table 1 summarizes the sample codes and preparation conditions (i.e., ethylene content and annealing temperature). For each EVOH composition, two different annealing temperatures were used to change their crystallinity, which becomes higher upon increasing the annealing temperature, as found in a previous study [41].

The obtained EVOH sheets were cut into pieces and numbered. Each sample was measured by a contact thickness meter (Nikon: MF-501) with the accuracy of 0.6 μm at 3 different positions, and the averaged value was used for calculating the absorption coefficient. Initially, the samples were vacuum dried at 40 $^{\circ}\text{C}$ for 1 week, then their THz absorption spectra and weight were measured in a nitrogen gas purge. Next, the samples were stored in 10 different humid environments at room temperature controlled by saturated solutions of inorganic salts for 2 weeks, at 11% RH (LiCl), 22% RH (KCOOCH_3), 33% RH (MgCl_2), 44% RH (K_2CO_3), 55% RH ($\text{Mg}(\text{NO}_3)_2$), 66% RH (NH_4NO_3), 76% RH (NaCl), 86% RH (KCl), 90% RH (ZnSO_4) and 100% RH. After moisturizing the samples, their THz absorption spectra and weights were measured again.

2.2. THz spectroscopy

High-quality spectra in the frequency range of 1–9 THz were obtained by the combination of a Fourier transform far infrared spectrometer (FT-FIR) (JASCO: FARIS) and a superconducting bolometer (QMC: QNbB/PTC), which detects THz waves with higher

sensitivity and stability than conventional ones. A high-pressure mercury lamp was used as the light source, and a wire-grid beam splitter was used for the measurement with the resolution of 0.06 THz. A total of 360 scans were accumulated in 5 min to obtain a single spectrum. A film sample with the size of 26 mm \times 11 mm was placed in the measurement chamber with a volume of 1.6 L. The chamber was purged by a continuous flow of nitrogen gas (20 L/min) to reduce the absorption of water vapor. After introduction, the sample was left for 7 min in the chamber before the measurement, which was performed at room temperature (23 ± 1 $^{\circ}\text{C}$).

The absorption coefficient $\alpha(\nu)$ of the sample was obtained by the following equation

$$\alpha(\nu) = -\frac{1}{l} \text{Log}_{10} \left(\frac{I_s(\nu)}{I_r(\nu)} \right) \quad (1)$$

where $I_s(\nu)$ and $I_r(\nu)$ are the power spectra of the sample and reference, respectively, and l is the length of the optical path. In this study, the sample was set to Brewster's angle to reduce multi-reflection within, which causes fringe in the absorption spectrum. The THz beam was linearly polarized by the wire-grid polarizer, and the sample was tilted to Brewster's angle $\theta_B = 57^{\circ}$ against the p-polarized THz beam. The optimal Brewster's angle was obtained by changing the tilting angle in 1 $^{\circ}$ steps to maximize the transmitted power at 6 THz. Due to refraction in the sample, the optical path length l is

$$l = \frac{d}{\sin \theta_B} \quad (2)$$

where d is the measured sample thickness.

For each measurement, two samples were prepared under the same condition, and their absorption spectra obtained independently to confirm the reproducibility. Typically, the difference in their spectral intensity is less than 1% absorbance. The averaged spectra of the two samples are shown here.

2.3. Water content

To estimate the amount of water adsorbed in the sample, the EVOH films were weighted by an electronic balance. For each sample condition, three sheets of EVOH with the size of 40 mm \times 30 mm were prepared and treated in the same manner as those for THz spectroscopy. The water content in the samples was obtained by the difference in averaged mass between the dried and humid samples.

3. Results and discussion

3.1. THz absorption spectra of vacuum-dried EVOH

Fig. 1 shows the absorption spectra of vacuum-dried EVOH. In all samples, the absorbance increases at higher frequency, showing two broad band structures at 2–4 and 5–6 THz. According to previous studies, the THz absorption bands of polymers are mainly due to vibration of the crystalline structure [3,8,42]. Amorphous structures show weaker and broader absorption feature than for the crystalline polymer. In Fig. 1, the absorbances of all samples increase with the annealing temperature, suggesting that the observed THz absorption is mainly due to the crystalline structure.

The spectral shape of EVOH is completely different from that of polyethylene, which shows the B_{1u} lattice mode at 2.2 THz [8,43–45]. Moreover, the absorbance of EVOH is more than 10 times higher. Since the THz absorption becomes stronger when the

Table 1
Ethylene content and annealing temperature of the EVOH samples.

	Ethylene Content (mol %)	Annealing Temperature ($^{\circ}\text{C}$)
EVOH24-L	24	80
EVOH24-H	24	175
EVOH32-L	32	80
EVOH32-H	32	160
EVOH44-L	44	80
EVOH44-H	44	140

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