

Sensing the hygroscopicity of polymer and copolymer materials using terahertz time-domain spectroscopy

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Received 9 February 2009; revised 17 March 2009; accepted 17 March 2009;
posted 26 March 2009 (Doc. ID 107173); published 14 April 2009

We present the hygroscopicity of polymer and copolymer materials in the low terahertz (THz) frequency range using a linear absorption model. We identify COC 6013 and COC 5013 as optimal THz window materials, possessing both low hygroscopicity and high transmission in the THz regime. The correct choice of window material is of significance for transmission THz spectroscopy and of particular interest for THz liquid spectroscopy. © 2009 Optical Society of America

OCIS codes: 160.4670, 160.4760, 160.5470.

1. Introduction

Terahertz (THz) radiation, or T rays, is a relatively unexplored part of the electromagnetic spectrum and lies between the millimeter and the far-infrared bands at approximately 0.1 THz to 10 THz, which corresponds to the wavelength range of $30\text{ }\mu\text{m}$ to 3 mm [1]. Over the past two decades, there has been a tremendous growth in THz technology. Many potential applications, including medical diagnostics [2,3], spectroscopy of biomolecules [4], security [5–7], and communications [8,9], have been explored. A number of significant studies have motivated the need for THz spectroscopy of liquids, including characterizing hydration state in solution [10], investigation of inflammable liquids [11], solvent diffusion in polymers [12], solvation dynamics of liquid mixtures [13,14], spectroscopy of liquid using evanescent field of a silicon waveguide [15], characterization of aqueous alcohol solutions in bottles [16], microfluidic devices for THz spectroscopy of biomolecules [17], and spectroscopy of liquids using double-modulated differential time-domain spectroscopy [18]. Due to the fact that water significantly absorbs THz, i.e., approximately 230 cm^{-1} at 1 THz [19], a window ma-

terial that is high in transmission and has low hygroscopicity is required for liquid spectroscopy applications. Although a number of papers on polymer window materials for THz spectroscopy have been presented [20–25], the hygroscopicity of polymer windows that could hamper THz transmission has not been investigated yet. Thus, we present hygroscopicity measurements on selected polar and nonpolar polymer materials using transmission mode THz time-domain spectroscopy (THz-TDS). The frequency range of our results is in the 0.2 to 2.0 THz band.

A. Polymers and Hygroscopicity

A polymer is a substance composed of molecules containing a repetition of structural units or monomers connected by chemical bonds. Polymers can be classified into two groups: polar and nonpolar. A polar polymer has an incomplete covalent bond, and an imbalance occurs in the electrons of the molecules. The imbalance in the electrons creates a dipole polarization in the presence of an electric field [26]. As for the nonpolar polymers, complete covalent bonds and symmetrical molecules can be seen. An absence of a dipole polarization can be noticed in the presence of an electric field on these materials. However, due to its electron polarization, a slight movement of the

electrons in the direction of the electric field can still be observed [26].

Hygroscopicity is the ability of a substance (e.g., a polymer) to absorb water molecules. The hygroscopicity measurement of polymer materials has been well explored using techniques such as Fourier transform infrared–attenuated total reflectance [27] and the standard ASTM D570 weight test method for water absorption of polymers [28]. However, to our knowledge investigation in the THz regime to identify optimal polymer window materials with low hygroscopicity has not yet been reported. Therefore, we investigate the hygroscopicity of polar and nonpolar polymer materials using THz radiation. In this technique, the hygroscopicity of polymer materials is determined by observing the changes in the absorption coefficient (α) before and after hydration of the polymer materials in distilled water. We have selected several polar polymers [i.e., polymethyl methacrylate (PMMA), polycarbonate (PC), polyvinyl chloride (PVC)], nonpolar polymers [i.e., high-density polyethylene (HDPE), polytetrafluoroethene (PTFE)], and nonpolar copolymers [i.e., cyclic-olefin copolymer (COC) 6013, COC 5013] for this investigation.

2. Experimental Method

The THz-TDS setup for the hygroscopicity measurement of the polymer materials is shown in Figure 1. A MiraSeed (Coherent) Ti:sapphire femtosecond mode-locked laser is used as the source of the optical

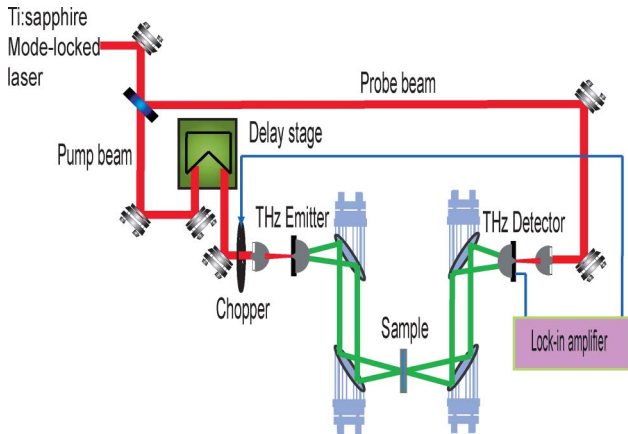


Fig. 1. (Color online) THz-TDS spectrometer schematic for polymer hygroscopicity measurement. This schematic diagram depicts a standard THz spectrometer configured for characterizing the hygroscopicity of a polymer. The Ti:sapphire mode-locked laser generating a train of <50 fs pulses at 76 MHz is used as a source of optical pulses. This source is split into a pump beam and a probe beam using a beam splitter. The pump beam generates the THz pulse as the laser is incident on an emitting photoconductive antenna. The generated THz pulse is collimated and focused onto the polymer sample using the first pair of off-axis parabolic mirrors. The transmitted THz pulse is recollimated and refocused onto the detector using the second pair of off-axis parabolic mirrors. The probe beam gates the incoming transmitted THz pulse by focusing the probe laser beam onto the photoconductive antenna at the detector. The detected signal is fed into the lock-in amplifier for signal extraction and processing.

pulses. It is pumped by a Verdi (Coherent) V6 with a wavelength of 532 nm. The femtosecond laser produces an output pulse duration less than 50 fs at a repetition rate of 76 MHz. The laser has an output power of 1 W with a center wavelength of 800 nm. The femtosecond source is split into the probe beam and the pump beam using a beam splitter. At the pump beam, the laser is modulated at 300 Hz by an optical chopper before focusing onto a photoconductive THz emitter that is biased at 90 Vdc. As the modulated laser beam hits the emitter, a THz pulse is generated. The generated pulse is focused onto the detector using four off-axis gold-plated parabolic mirrors. The probe beam is designed to gate the incoming THz pulse at the detector. The entire THz waveform can be sampled by varying the time delay of the delay stage.

A. Sample Preparation

Two sets of the polar and nonpolar polymer materials are investigated under two conditions: (i) dehydrated in a vacuum oven and (ii) hydrated in distilled water. The temperature used in the vacuum oven to dehydrate the samples is 80 °C. The lowest and the highest melting temperatures T_m for all the polymer materials measured are 130 °C and 330 °C, respectively. Thus, dehydrating the conditioned samples in the vacuum oven at 80 °C is well below the melting point. Based on these conditions, the polymer materials are measured after 24 h and 120 h. Five average scans are used to increase the signal-to-noise ratio of the measurements. Moreover, the measurements are conducted in a nitrogen-purged environment to minimize the effect of water lines interfering with the results. The excess water on the surface of the sample is removed before the measurement. Also, in order to increase the accuracy of the measurements, the samples are measured immediately after conditioning. The thickness of the measured samples is approximately 3 mm. The experiments are conducted at room temperature.

3. Analysis

Assuming that the THz radiation is incident to the measured polymer materials, the spectral components at angular frequency ω of the electric field of the THz wave transmitted through the sample and reference can be written as [29]

$$\tilde{E}_{\text{sam}}(\omega) = T_{12}(\omega) \cdot P_2(\omega, d) \cdot T_{23}(\omega) \cdot A(\omega) \cdot \text{FP}(\omega), \quad (1)$$

$$\tilde{E}_{\text{ref}}(\omega) = T_{13}(\omega) \cdot P_{\text{air}}(\omega, d) \cdot A(\omega), \quad (2)$$

where $\tilde{E}_{\text{sam}}(\omega)$ and $\tilde{E}_{\text{ref}}(\omega)$ are the complex spectral components of the sample and the reference pulses, respectively. P_2 and P_{air} refer to the propagation coefficient of the polymer and air, respectively. Here, T_{ab} is the transmission coefficient of the THz wave from medium a to b . Also $A(\omega)$ accounts for the amplitude of each frequency component, and d is the thickness

of the polymers. The $FP(\omega)$, Fabry–Perot reflection term is ignored for this measurement since the thickness of the samples measured is sufficiently thick to avoid multiple reflections. The ratio of the transmission spectra is as follows:

$$\tilde{T}(\omega) = \frac{\tilde{E}_{\text{sam}}}{\tilde{E}_{\text{ref}}} \quad (3)$$

Thus, based on the ratio, the extinction coefficient (κ) and absorption coefficient (α) of the polymers can be extracted based on the following formulas:

$$\kappa(\omega) = -\frac{c_0}{\omega d} \ln \left(\frac{(1 + n(\omega))^2}{4n(\omega)} p(\omega) \right), \quad (4)$$

$$\alpha(\omega) = 2 \frac{\kappa(\omega)\omega}{c_0}. \quad (5)$$

Here, $p(\omega)$ is the magnitude obtained from the ratio of the transmission spectra, and $n(\omega)$ is the refractive index. The speed of light is denoted as c_0 . The hygroscopicity is determined by using the linear absorption model, which can be written as follows [30]:

$$\alpha_H(\omega) = (1 - c_x)\alpha_{DH}(\omega) + c_x\alpha_w(\omega), \quad (6)$$

where $\alpha_H(\omega)$ is the absorption coefficient of the hydrated polymer. The $\alpha_{DH}(\omega)$ is the absorption coefficient of a dehydrated polymer (after drying at 80 °C) and $\alpha_w(\omega)$ is the absorption coefficient of distilled water at 1 THz. Here, c_x denotes the water absorption, which is also known as the water concentration [30]. Rearranging the above equation gives the following formula to calculate the amount water absorbed by the samples:

$$c_x = 100 \frac{\alpha_H(\omega) - \alpha_{DH}(\omega)}{\alpha_w(\omega) - \alpha_{DH}(\omega)}. \quad (7)$$

Here, c_x for 24 h measurement is obtained by comparing $\alpha_w(\omega)$ of 24 h with $\alpha_{DH}(\omega)$ of 24 h and c_x for 120 h measurement is obtained by comparing $\alpha_w(\omega)$ of 120 h with $\alpha_{DH}(\omega)$ of 120 h.

4. Results and Discussion

Measurements on seven different polymer materials are conducted. The experimental results of the absorption coefficients are presented in Figs. 2–4. These figures illustrate the variation in the absorption coefficients between hydrated and dehydrated polymers. In these figures, the error bars have not been plotted for clarity, as they are about the same size as the characters that represent the data points.

Figure 2 shows the absorption coefficient of PMMA measured at different hydration levels. It is noted that as the hydration period increases, the hydration level increases. However, PMMA shows no difference in a hydration level after 24 h. This is because it has

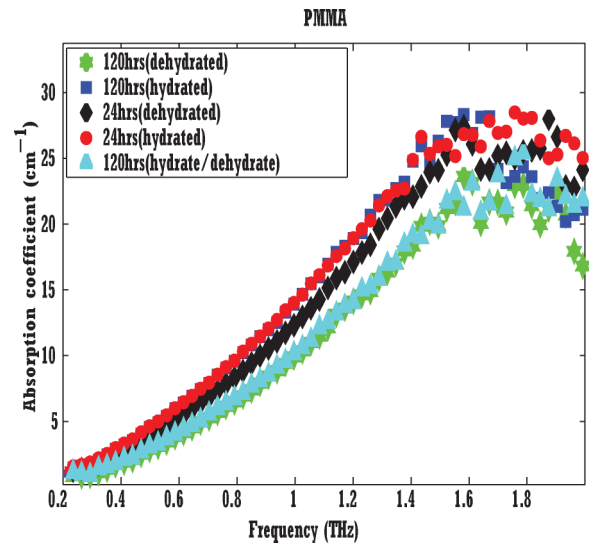


Fig. 2. (Color online) Absorption spectra of PMMA. This figure illustrates the absorption coefficient of PMMA at different hydration levels. It can be observed that there is a distinct difference between the hydrated and the dehydrated state. Also, it is noted that the hydration state of PMMA saturates after 24 h. The hygroscopicity measurement indicates that the PMMA absorbs 0.75% of water after 24 h and 1.8% after 120 h of hydration. The increase in absorption after the hydration for 24 h and 120 h is due to its methyl (CH_3) polar group, which binds strongly to water molecules.

reached the saturation point. To show that the optical properties of PMMA are not affected by the hydration and dehydration process, the sample is then dehydrated again for 120 h in a vacuum oven at 80 °C after the hydration and dehydration process. The results obtained show that the absorption coefficient remains unchanged compared to the original dehydrated sample, which indicates that the optical properties of PMMA are unchanged after 120 h of the hydration and then the dehydration process.

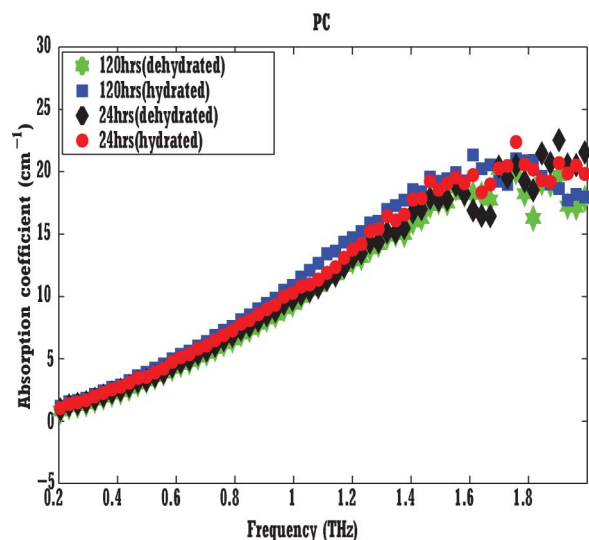


Fig. 3. (Color online) Absorption spectra of PC. This figure depicts the absorption coefficient of PC at different hydration levels.

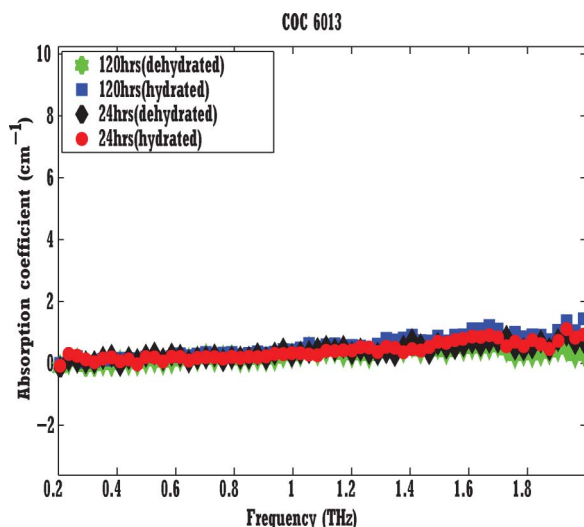


Fig. 4. (Color online) Absorption spectra of COC 6013. This figure compares the absorption coefficients of nonpolar polymer COC 6013 at different hydration levels. It is clear that the effects of hydration are much less compared to PC and PMMA.

In Fig. 3, the absorption spectra for PC are presented. The hydration level is proportional to the hydration period. The increase in the hydration level is due to the strong polar group ($C=O$), which strongly binds the water molecules. The hygroscopicity measured at 1 THz is 0.21% for 24 h of hydration and 0.69% for 120 h of hydration. The absorption spectra for COC 6013 are presented in Fig. 4. Note that COC 6013 is a crystal clear nonpolar polymer that has a symmetrical molecular structure. Such a structure prevents water molecules from binding with polymer molecules. Thus, it can be seen from Fig. 4 that the hydration process has less effect on the COC 6013. The hygroscopicity measured at 1 THz is less than 0.01% for 24 h of hydration and 0.09% for 120 h of hydration. A summary on the variation of the absorption coefficient at 1 THz for all the measured polymer materials is shown in Table 1. Also, the hygroscopicity of the polymers obtained using Eq. (7) is given in Table 1. The hygroscopicity obtained from the literature based on the ASTM D570 weight test method is also included in the table to verify agreement.

Based on Table 1, all nonpolar polymer materials have absorption coefficients less than 1 cm^{-1} at 1 THz. This is obviously due to their covalent bonds and symmetrical molecular structures, which do not create any dipole polarization in the presence of an electric field. However, polar polymer materials exhibit strong absorption. This is mainly caused by the imbalance of electrons, which creates a dipole polarization in the presence of an electric field. According to Table 1, the experimental data show a very close agreement on the hygroscopicity measurement. The measured data are compared with American Society for Testing and Material standard ASTM D570 [31]. It is an international standard used for water absorption in polymer materials for 24 h. However, no document has been presented by the ASTM for a water absorption for 120 h. Thus, our measurements conducted for 120 h are not compared with the literature. All the nonpolar polymer and copolymer materials measured exhibit a very low hygroscopicity for both 24 and 120 h of hydration and dehydration cycles. However, polar polymer materials such as PMMA have a very high hygroscopicity and absorption coefficient, which may not be suitable as window materials in THz regime. Therefore, according to Table 1, HDPE, PTFE, COC 6013, and COC 5013 are identified as optimal window materials with low hygroscopicity and a low absorption coefficient in the THz regime.

5. Conclusion

In this paper, we have demonstrated the hygroscopicity of polymer and copolymer materials using the linear absorption model in the THz frequency band. This is achieved by observing the changes in the absorption coefficients of the measured samples before and after hydration for 24 h and 120 h. Good agreement in hygroscopicity is produced when compared with the ASTM D570 water absorption standard [31]. All measured nonpolar polymer and copolymer materials are potential window materials for liquid spectroscopy applications since they exhibit a low absorption coefficient and are less affected by water absorption, however, in certain liquid spectroscopy applications, PTFE and HDPE may not be suitable

Table 1. Variation in Absorption Coefficient and Hygroscopicity of Polymer Materials for 24 h and 120 h Measurements at 1 THz^a

Polymer	Absorption (cm^{-1})				Hygroscopicity (%)			
	24 h		120 h		Experimental		Literature	
	Hydrated	Dehydrated	Hydrated	Dehydrated	24 h	120 h	24 h [28]	120 h
COC 6013	0.269	0.240	0.361	0.160	0.01	0.09	0.01	—
COC 5013	0.334	0.315	0.485	0.290	0.01	0.08	0.01	—
HDPE	0.259	0.215	—	—	0.02	—	0.01	—
PTFE	—	—	0.552	0.450	—	0.04	0.01	—
PMMA	14.020	12.393	14.015	10.000	0.75	1.80	0.5	—
PVC	22.218	22.087	22.263	21.998	0.06	0.11	0.06	—
PC	10.346	9.800	10.977	9.457	0.21	0.69	0.25	—

^aHygroscopicity data obtained from Eq. (7) are compared with the standard test method for water absorption of polymers (ASTM D570) to verify agreement.

as window material due to their optical opaqueness. This is because the optical opaqueness of PTFE and HDPE prevents visual inspection, which could hinder liquid measurements. Thus, we recommend COC 6013 and COC 5013 as optimal window materials for THz liquid spectroscopy applications.

The authors are grateful to Dotmar Engineering Plastic Products and Polyplastics for providing the polymer sheets. The authors also thank Sigma Tools for technical assistance. This research was supported under the Australian Research Council (ARC) Discovery Projects funding scheme (project number DP0771243).

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