Terahertz dielectric properties of polystyrene foam

Guozhong Zhao, Maarten ter Mors, Tom Wenckebach, and Paul C. M. Planken

Delft University of Technology, Faculty of Applied Sciences, Department of Applied Physics, Lorentzweg 1, 2628 CJ Delft, The Netherlands

Received October 23, 2001; revised manuscript received December 13, 2001

We have performed terahertz time-domain spectroscopy measurements on three types of polystyrene foam. We find that between 0.2 and 4 THz, the extinction of this material is low and that it has a remarkably low refractive index of 1.017 to 1.022 in this range, with little variation as a function of frequency. In foam produced with HCFC 142b gas (1-chloro-1,1-difluoroethane) as the blowing agent, we find an additional absorption band at 0.5 THz caused by rotational transitions in this gas. The low extinction and refractive index make polystyrene foam a very suitable material to be used as a dichroic filter that blocks the near-IR and transmits THz radiation with small losses of less than 1.5 cm^{-1} for frequencies of <4 THz, and as a substrate for THz imaging. © 2002 Optical Society of America

OCIS codes: 300.6270, 300.6250, 320.7150, 300.6390.

In recent years, terahertz time-domain spectroscopy (TDS) has grown in popularity as a spectroscopic tool that surpasses conventional Fourier transform spectrometers in an otherwise difficult to reach frequency range of 0.1 to 10 THz.[1–6] Basically, terahertz TDS uses a visible or near-IR femtosecond laser pulse to generate a broadband free-space THz pulse from a suitable nonlinear material. Terahertz TDS is now used in many laboratories as a tool for spectroscopy and imaging.[7–9] One of the problems still facing workers in the terahertz field, however, is to find suitable materials that can be used as filters or substrates. For example, silicon is often used as a filter to block the near-IR laser pulse while simultaneously transmitting the THz pulse after optical rectification in ZnTe. Silicon, however, has a THz refractive index of ~3.4.[2] When the THz pulse is perpendicularly incident on the silicon, each reflection off an air–silicon interface corresponds to a loss of 30 percent in THz power. This can in principle be overcome by putting the material under Brewster's angle, but at 74 deg this angle is inconveniently large. Ideally, materials to be used as sample substrates or filters should have little absorption and a refractive index as close to unity as possible.

Here, we report that a commonly available material, polystyrene foam, satisfies these demands. We have measured the frequency-dependent extinction and refractive index of three kinds of polystyrene foam: one produced with 1-chloro-1,1-difluoroethane (also called HCFC 142b) as a blowing agent and two with CO_2 as the blowing agent. We find that for all three samples the overall THz extinction is small ($\kappa < 0.6\ \mathrm{cm}^{-1}$ below 2 THz), where the material with the highest mass density has the smallest extinction. An interesting absorption and refractive-index feature is observed at ~0.5 THz in the foam blown with HCFC 142b, which we attribute to rotational absorption by the molecular gas still contained in the closed cells of the foam. The refractive indices of the materials are extremely low and show little dispersion over the measurement range from 0.1 to 4.0 THz, with values between 1.016 and 1.022, depending on the sample. Polystyrene foam is therefore very well suited as a substrate for low-frequency (<4 THz) THz imaging and is an ideal material to be used as a filter to block the near-IR laser beam while transmitting the THz pulse with only small losses.

The experimental setup to generate and detect THz pulses uses a 72-MHz-repetition-rate Ti:sapphire oscillator from Femtolasers Produktions (Austria) capable of generating 15-fs pulses. Approximately 200 mW of optical power is used to illuminate a biased GaAs emitter. The transient current in this emitter generates an electromagnetic transient containing THz frequencies. The THz average power, measured with a pyroelectric detector calibrated with a HeNe laser, is estimated to be of the order of 40 μW. The THz electric field is measured with a standard electro-optic and differential-detection setup incorporating a (110) oriented 100-μm-thick GaP crystal.[10] The setup is enclosed in a box that is purged with dry nitrogen to reduce the effects of THz absorption by water vapor. A complete THz electric field as a function of time is measured with and without polystyrene samples by rapidly scanning the delay between the THz pulse and the probe pulse. From the two measurements, the refractive index and the absorption coefficient of the polystyrene foam can be calculated independently as a function of frequency.

Each of the three samples consists of a block of polystyrone foam approximately 40 mm × 40 mm × 20 mm cut from a large plate.[11] Sample A (Styrodur 2500) is produced with HCFC 142b as a blowing agent, whereas samples B (Styrodur 2500 C) and C (Styrodur 4000 CS) are blown with CO_2. Their measured mass densities are 31.6 kg/m^3, 34.6 kg/m^3, and 39.9 kg/m^3, respectively. Visual inspection under an optical microscope revealed that the samples consisted of irregularly shaped cells with average sizes that differed for the three samples. We estimate an average cell diameter of 75 μm ± 25 μm for sample A, 150 μm ± 40 μm for sample B, and 65 μm ± 20 μm for sample C. In Fig. 1 we plot an example of the measured THz waveforms obtained with and without polystyrene foam C in the focus of the THz beam. The

0740-3224/2002/061476-04$15.00

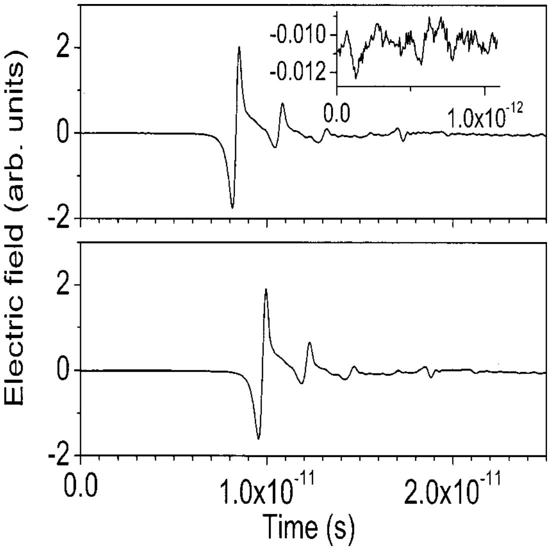

Fig. 1. Measured THz electric fields of the reference pulse (top) and of sample C, a polystyrene foam produced with CO_2 as the blowing agent (bottom). The inset in the top panel shows the noise floor of this measurement.

signal taken without the sample in the THz focus shows several peaks corresponding with multiple reflections in the GaP detection crystal and the GaAs emitter crystal. The peak THz electric field in this measurement is ~95 V/cm. With the polystyrene foam in the beam we observe an only slightly decreased THz peak amplitude and a shift toward longer delays of ~1.4 ps as the main features of the trace. The shift toward longer delays is very clear but extremely small, considering that the sample is ~20 mm thick. We note, for comparison, that a block of silicon of the same thickness would give a shift toward longer delays of 160 ps. The THz time-domain signals for samples A and B are similar.

The extinction coefficient and the refractive index of the materials can be calculated from the Fourier transform of the measured electric fields. We write $k_r(\omega) = k_r'(\omega) + ik_r''(\omega)$ and $k_s(\omega) = k_s'(\omega) + ik_s''(\omega)$ for the THz wave vectors in air and polystyrene, respectively. We assume that the absorption in the nitrogen atmosphere is negligible and that the refractive index is 1.0006 so that we can write $k_r''(\omega) = 0$ and $ck_r'(\omega)/\omega = 1.0006$. Designating the amplitude spectrum of the pulse at the exit face at position d of the polystyrene sample as $E_s(d, \omega)$ and the amplitude spectrum of the reference pulse as $E_r(d, \omega)$, we can write

$$\frac{E_s(d, \omega)}{E_r(d, \omega)} = \exp i\left\{\left[k_s'(\omega) - \frac{\omega}{c}\right]d\right\}\exp[-k_s''(\omega)d]. \quad (1)$$

This equation shows that from $E_s(d, \omega)$ and $E_r(d, \omega)$, which are calculated from the measured electric fields, $k_s'(\omega)$ and $k_s''(\omega)$—and thus the extinction coefficient and refractive index—can be determined. It should be noted that these simple calculations have to be amended when a sample is studied in which multiple reflections in the sample occur or when the sample has a high (and frequency-dependent) refractive index giving rise to frequency-dependent reflections.[12] Fortunately, in our samples the refractive index is so low that reflections are extremely small and can be ignored altogether, allowing us to use the above simple analysis.

In Figs. 2 and 3 we plot the frequency-dependent refractive index and extinction coefficient calculated from the data shown in Fig. 1 for sample C, and from similar data for samples A and B. The calculations give an almost constant and extremely small value for the refractive index of ~1.0175 for sample A, ~1.0185 for sample B, and ~1.0215 for sample C. In all three samples, the refractive index increases slightly with increasing frequency for frequencies >0.7 THz. The extinction of all three samples remains less than the value of 1 cm^{-1} for frequencies <2.5 THz, but for samples A—and especially C—it remains <1.5 cm^{-1} over the whole measured range. As we will discuss below, a small but reproducible absorption band with a peak value of 0.3 cm^{-1} at a central frequency of 0.5 THz and a FWHM of 0.45 ± 0.05 THz is observed for the polystyrene sample blown with the HCFC 142b. Etalon oscillations associated with the reflection in GaAs are observed in both figures for increasing THz frequencies. At these frequencies, the SNR of the foam measurements is smaller than those of the reference measurement, giving rise to imperfect cancellation of these oscillations in the calculation of the extinction and the refractive index. The error bars show our estimate of the resulting uncertainty in the calculated values of the extinction coefficient and the refractive index.

The results so far show that sample C has especially favorable properties in the THz range <4 THz because the extinction generally remains <1.5 cm^{-1}. An attractive feature of the foams studied in this paper is that they diffusively scatter visible and near-IR light while transmitting THz radiation with only small losses. This means that they can be used as optical filters to block the laser beam while transmitting a THz beam. In addition, we are now successfully using them as sample substrates for THz imaging experiments.

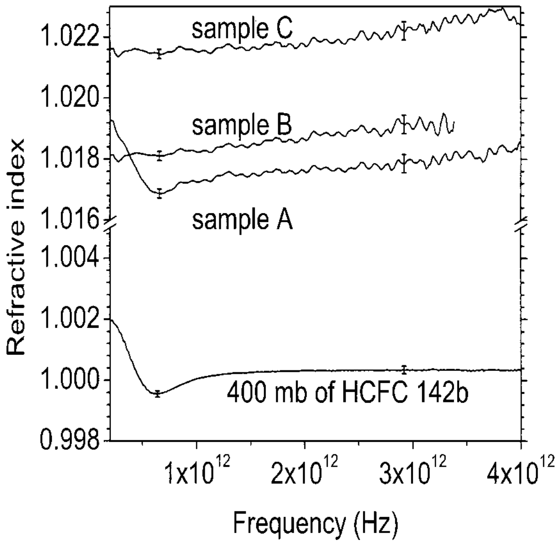

Fig. 2. THz frequency dependence of the refractive index of three types of polystyrene foam and 0.4 bar of HCFC 142b gas, calculated from the electric fields shown in Fig. 1 for sample C and from similar measurements for samples A and B and the gas sample. Note the break in the vertical axis. The error bars give an estimate of the uncertainty in the calculated values.

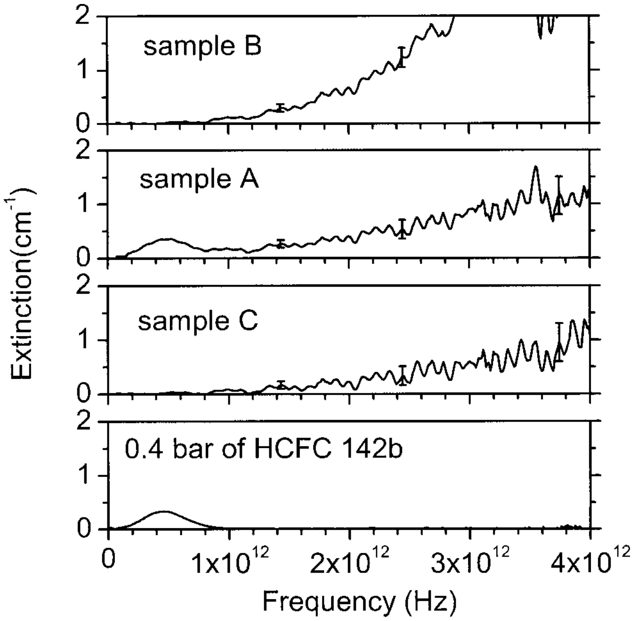

Fig. 3. THz frequency dependence of the extinction coefficient of polystyrene samples A, B and C and for 0.4 bar of HCFC 142b gas, calculated from measured electric fields such as the one shown in Fig. 1. The absorption feature at ~0.5 THz in sample A is most probably caused by rotational transitions of the molecular gas (HCFC 142 b) contained by the foam. The error bars indicate the estimated uncertainty in the calculated values. The estimated uncertainty in the measured peak value of the extinction coefficient of the molecular gas is less than 5%.

We now turn to the absorption peak at ~0.5 THz observed in sample A. The presence of this band also leaves its mark on the frequency dependence of the refractive index. When going from 1 THz to 0.1 THz, the refractive index of this sample first decreases somewhat to a value of nearly 1.017 at 0.7 THz and then increases to ~1.0195 at 0.2 THz. Neither the absorption nor the refractive-index features at ~0.5 THz are observed in the samples produced with CO_2 as the blowing agent, indicating that the HCFC 142b blowing agent is responsible for the absorption. The polystyrene samples we have investigated have a closed cell structure, and HCFC 142b is known to diffuse only slowly out of the polystyrene foam over a time period of decades. CO_2, on the other hand, being a much smaller molecule, diffuses through the material almost immediately after production and is replaced by ordinary air. To confirm that HCFC 142b is responsible for the observed features, we have performed THz TDS measurements on this gas at different pressures. We find near identical features at exactly the same frequency as the features observed in sample A. At a pressure of 0.4 bar, the frequency-dependent refractive index and extinction obtained from these measurements (plotted in Figs. 2 and 3) have almost the same amplitude as in the foam. This suggests that the partial pressure of the HCFC in the foam is approximately 0.4 bar.

Concerning the rotational transitions, we note that we do not observe "THz commensurate photon echoes,"[3] that is, the emission of a train of THz pulses due to periodic dephasing and rephasing of the excited rotational transitions of the gas molecules. A possible explanation for this is the limited length of our temporal scan in relation to the rotational line spacing. This is currently under investigation.

We would like to point out that our measurements on sample A provide a clear example of the advantage of THz TDS over mid-infrared spectroscopy, in that it allows us to measure, in a nondestructive manner, the presence of a gas contained inside a medium. Although HCFC 142b absorbs in the mid-infrared,[13] the strong scattering of the foam in that frequency region makes it difficult to perform measurements.

The physical origin of the small refractive index of the foams is the low average mass density of the material, in combination with the material's consisting mainly of gas filled polystyrene cells with an average diameter smaller than the THz wavelengths. We note that bulk polystyrene has a refractive index of ~1.6 in the THz range.[14] As long as the wavelength of the THz light is much longer than the diameter of the foam cells, the refractive index is a weighted average of the refractive index of air (or an air and HCFC 142b mixture) and bulk polystyrene. The different values of the refractive index of the three foams can be related to the variations in their density. This can be seen from the dielectric function, which is linearly proportional to the density according to $\epsilon \equiv n^2 = 1.0006 + \xi N$, with n the refractive index, N the density, ξ a constant containing material parameters, and 1.0006 the dielectric constant of air. For example, the mass density of sample C is 1.153 times the mass density of sample B. The contribution to the dielectric constant of foam B at 1.5 THz is $\epsilon - 1.0006 = n^2 - 1.0006 = 1.0185^2 - 1.0006 = 0.0367$. Based on the larger density, the contribution to the dielectric constant of foam C would have to be $1.153 \times 0.0367 = 0.0424$. The predicted value of the refractive index is then $n = (1.0006 + 0.0424)^{1/2} = 1.0213$, which agrees well with the measured value of 1.0217. Similar comparisons between samples A and B and between samples A and C, taking the contribution to the dielectric constant and the mass density of the HCFC gas into account, show less quantitative agreement. As an example, we attempt to calculate the refractive index of sample A, starting from the measured refractive index of sample B. First, we note that the contribution to the dielectric constant at 1.5 THz of sample B is 0.0367, as calculated above. To now calculate the contribution to the dielectric constant of sample A, we have to multiply this number by the mass ratio of samples A and B. However, in sample A, the HCFC 142b gas contributes to the measured mass density of the foam. To get the correct polystyrene foam mass density, we have to subtract the contribution of the HCFC gas (which has a molecular weight of 100.5 g/mol) from the measured mass density. The corrected mass density is 30.06 kg/m^3, which is 1.54 kg/m^3 lower than the measured mass density. With 34.6 kg/m^3 the mass density of foam B, the contribution to the dielectric constant is then $0.0367 \times 30.06/34.6 = 0.0319$. The background dielectric constant of foam A, formed by the vacuum contribution of 1, together with the contribution of 0.6-bar (0.6×0.0006) air and the measured contribution of 0.4-bar HCFC 142b of 1.0005, yields $1 + 0.0005 + 0.6 \times 0.0006 = 1.00086$. The sum of all the contributions to the dielectric constant is then finally 1.0328, which gives a value of the refractive index $n = (1.0328)^{1/2} = 1.0163$ for sample A. This number is significantly lower than the measured value of 1.0174 seen in Fig. 2. We note, however, that samples B and C are both blown with CO_2, whereas sample A is blown with HCFC 142b, perhaps giving rise to slightly different dielectric properties of the polystyrene.

The extinction of the polystyrene in the THz range is most probably caused by scattering, not absorption (with the exception of the 0.5-THz absorption feature in sample A). With increasing frequencies, the wavelength of the THz light approaches the foam cell diameter, giving rise to increased scattering. Indeed, the extinction in sample C was smaller than for the other samples. Sample C has higher density and a smaller cell size and for the same wavelength, therefore the amount of scattering is expected to be smaller than for the other samples.

In conclusion, we have presented THz TDS measurements on three kinds of polystyrene foam that demonstrate that the material has an extremely low refractive index and a low absorption in the range from 0.1 to 4.0 THz. The results indicate that polystyrene foam is an excellent material for use as a filter to block near-IR light while transmitting THz light, and that it can be used as a sample substrate for THz imaging. In addition, we show that in the foam produced with HCFC 142b gas as the blowing agent, an absorption peak is found that we associate with rotational transitions of the molecule.

ACKNOWLEDGMENTS

We thank R. N. Schouten for expert electronics support and H. J. Bakker for stimulating discussions. This work was performed as part of the EU TERAVISION program (IST-1999-10154).

P. C. M. Planken may be reached by e-mail at planken @tnw.tudelft.nl.

REFERENCES AND NOTES

1. P. Y. Han, M. Tani, M. Usami, S. Kono, R. Kersting, and X.-C. Zhang, “A direct comparison between terahertz time-domain spectroscopy and far-infrared Fourier transform spectroscopy,” J. Appl. Phys. **89**, 2357–2359 (2001).
2. D. Grischkowsky, S. Keiding, M. van Exter, and Ch. Fattinger, “Far-infrared time-domain spectroscopy with terahertz beams of dielectrics and semiconductors,” J. Opt. Soc. Am. B **7**, 2006–2015 (1990).
3. H. Harde, R. A. Cheville, and D. Grischkowsky, “Terahertz studies of collision-broadened rotational lines,” J. Phys. Chem. A **101**, 3646–3660 (1997).
4. M. van Exter and D. R. Grischkowsky, “Characterization of an optoelectronic terahertz beam system,” IEEE Trans. Microwave Theory Technol. **38**, 1684–1691 (1990).
5. C. Weiss, R. Wallenstein, and R. Beigang, “Magnetic-field-enhanced generation of terahertz radiation in semiconductor surfaces,” Appl. Phys. Lett. **77**, 4160–4162 (2000).
6. A. Bonvalet, M. Joffre, J. L. Martin, and A. Migus, “Generation of ultrabroadband femtosecond pulses in the mid-infrared by optical rectification of 15 fs light pulses at 100 MHz repetition rate,” Appl. Phys. Lett. **67**, 2907–2909 (1995).
7. R. A. Cheville and D. Grischkowsky, “Time-domain terahertz impulse ranging studies,” Appl. Phys. Lett. **67**, 1960–1962 (1995).
8. D. M. Mittleman, R. H. Jacobsen, and M. C. Nuss, “T-ray imaging,” IEEE J. Sel. Top. Quantum Electron. **2**, 679–692 (1996).
9. S. Hunsche, M. Koch, I. Brener, and M. C. Nuss, “THz near-field imaging,” Opt. Commun. **150**, 22–26 (1998).
10. P. C. M. Planken, H.-K. Nienhuys, H. J. Bakker, and W. T. Wenckebach, “Measurement and calculation of the orientation dependence of terahertz pulse detection in ZnTe,” J. Opt. Soc. Am. B **18**, 313–317 (2001).
11. The material’s brand name is Styrodur and it is manufactured by BASF, Germany. It is primarily used for thermal isolation.
12. L. Duvillaret, F. Garet, and J.-L. Coutaz, “A reliable method for extraction of material parameters in terahertz time-domain spectroscopy,” IEEE J. Sel. Top. Quantum Electron. **2**, 739 (1996).
13. O. I. Baskakov, V. V. Ilyushin, E. A. Alekseev, H. Bürger, and G. Pawelke, “High-resolution infrared study of the ν_7, ν_8, and ν_{15} bands and millimeter-wave investigation of the $\nu_8 = 1$ state of $CF_2Cl - CH_3$,” J. Mol. Spectrosc. **202**, 285–292 (2000).
14. J. R. Birch, “The far-infrared optical constants of polypropylene, ptfe and polystyrene,” Infrared Phys. **33**, 33–38 (1992).