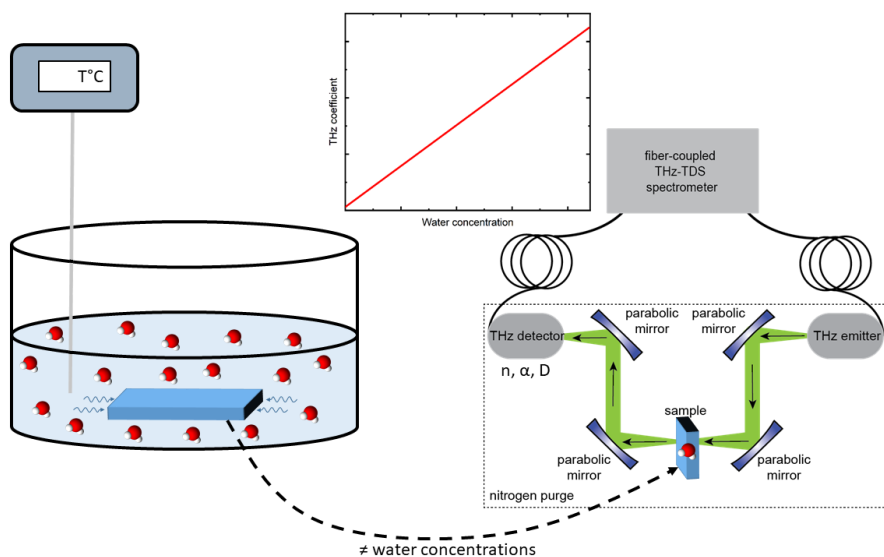


Graphical Abstract

Extraction of Fickian water diffusion in polymers using terahertz time-domain spectroscopy

Sebastian Engelbrecht, Vincent Pichot, Thomas Goepfert, Hungyen Lin, Bernd M. Fischer



Extraction of Fickian water diffusion in polymers using terahertz time-domain spectroscopy[★]

Sebastian Engelbrecht^{a,*}, Vincent Pichot^a, Thomas Goepfert^a, Hungyen Lin^b and Bernd M. Fischer^a

^a*French-German Research Institute of Saint-Louis, 5 rue du Général Cassagnou, Saint-Louis, 68301, , France*

^b*Department of Engineering, Lancaster University, Gillow Awe, Lancaster LA1 4YW, , United Kingdom*

ARTICLE INFO

Keywords:

Polymers

Fickian water diffusion

THz spectroscopy

ABSTRACT


The dynamic behavior of polycarbonate and poly(methyl methacrylate) upon water immersion at temperatures of 40°C and 70°C was studied by gravimetric measurements and by terahertz time-domain spectroscopy. Time-resolved measurements of the terahertz refractive index and absorption coefficient show a good agreement to the gravimetric measurements. Assuming a Fickian diffusion mechanic the diffusion coefficients were extracted from both methods. It was found that the terahertz measurements provide a reliable non-contact way to study the water diffusion in polymers. Especially, the THz absorption coefficient seems to be a robust method to determine the diffusion coefficients.

1. Introduction

Today polymeric materials are widely used in numerous fields of application, ranging from simple packaging materials, to protective coatings or even ballistic protective devices due to their relatively low cost, a high mechanical strength and a low weight. However, the exposure to environmental conditions (temperature, humidity, or ultraviolet radiation) can have a significant effect on their durability and longevity. Extensive studies on the influence of the environmental parameters on the properties of polymeric materials can be found in the literature [1, 2]. For example, it was shown that a thermal pretreatment can have a strong influence on the impact strength [3], while humidity can impact the fracture strain or glass transition temperatures [4], as well as the scratch resistance [5] and transparency [6]. Even ductile-brittle transitions with a decrease of the tensile strength were observed when subjected to humidity and temperatures [7]. In addition to the pure polymers, studies with composites have also been made [8–10]. In laminated glass, the moisture and temperature can cause delaminations [11, 12]. These studies showed the importance of water/polymer interaction. In order to make a lifetime prediction for application relevant polymers a good knowledge about the water diffusion coefficients is therefore important, as they will give the temporal frame in which the water absorption will occur. This, however, has been classically determined using gravimetric or capacitive measurements [13]. The water diffusion in general can be classified into three regimes [14]: (1) Case I (Fickian diffusion) in which the polymer relaxation is much faster than the water diffusion, (2) Case II where the diffusion is much faster than that of the relaxation and (3) Super Case II in which the diffusion rate is equal to the relaxation. This paper will focus on the Fickian diffusion, which was shown to be the main type of diffusion in the studied polymers [15, 16].

The recent years have seen the maturity of novel techniques like terahertz time-domain spectroscopy (THz-TDS). The technique proved to be especially useful for the characterization of polymers due to their semi-transparent properties at these frequencies [17]. As such, it was shown that it can be used to measure glass transition temperatures [18], determine the content of additives in thermoplastics [19] and elastomers [20], study the fiber orientation in compounds [21, 22] or analyze the quality of glued or welded plastic joints [23–25]. THz-TDS also provides information on the crystallization [26, 27], crystalline structure [28, 29] or crystallization dynamics [30]. Moreover, it also has a unique sensitivity to water in plants [31, 32], papers [33], or epoxy-resins [34] and is able to distinguish the diffusion type in porous media [35].

In this manuscript, THz-TDS is used to study the water absorption dynamics in Polycarbonate (PC) and Poly(methyl methacrylate) (PMMA) at different temperatures upon water immersion. In particular, we extract the Fickian diffusion

 sebastian.engelbrecht@isl.eu (S. Engelbrecht)

ORCID(s): 0000-0002-7980-7514 (S. Engelbrecht); 0000-0002-3327-1371 (H. Lin)

Table 1

Polymer properties: number average molecular weight (M_n) and weight average molecular weight (M_w) were determined by gel permeation chromatography and glass transition temperatures by differential scanning calorimetry.

Polymer	Density (g/cm ³)	M_n (g/mol)	M_w (g/mol)	T_g (°C)
PC	1.2	36631	1.4×10^6	148
PMMA	1.2	187896	77.1×10^6	111

coefficients non-destructively and contact-free for comparisons against conventional gravimetric measurements, where a good agreement is found.

2. Materials and Methods

THz-TDS allows the coherent measurement of the refractive index and absorption coefficient over a broad frequency range. The spectroscopic measurements were carried out using a commercially spectrometer based on a 1550 nm laser (TOPTICA Teraflash, Germany) [36]. In this system the THz radiation is generated and detected using antennas based on InGaAs photoconductive switches. A system of four off-axis parabolic mirrors was used to focus the THz beam onto the sample and the detector, respectively [37]. All measurements were done under nitrogen atmosphere to prevent additional absorption caused by water vapor.

The samples were cut into plates at a size of 35x35 mm² and a thickness of 2 mm (PC: Technoplast Kunststoffe, Germany, PMMA: S-Polytec Polymertechnologie, Germany). In Tab. 1 some physical parameters of the used polymers are given. Before the measurements took place, the samples were dried in a furnace at 50°C for 72 h to remove any residual water. Preliminary experiments found that after 72 h drying was sufficient to remove any residual water as there was no observable mass change. After the initial characterization, the samples were placed in a water bath filled with DI water at a temperature of 40°C and 70°C. In the beginning of the measurements, the samples were withdrawn each 30 min from the water bath, any excess water removed by careful wiping with tissues, their weight be measured by a fine scale (Mettler Toledo NewClassic MF ML54, USA) and their thickness determined by a micrometer screw (Mitutoyo No.293-340, Japan). Afterwards the THz response has been measured under N₂ purge (humidity in purge chamber was below 2%). Before placing them back in the water bath, the weight and thickness have been measured once again to check for a possible water loss while being in the N₂ purged box during the THz measurement. Within the accuracy of the used scale, no significant change in mass nor thickness was observed. Overall, the duration out of water for each sample/time step was between 4 and 5 min. However, here it should be emphasized that the time out of water indeed is crucial as preliminary experiments found that if this took longer than 10 min, this would result in a significant change in mass. For each polymer, there were three repeats. Once the initial fast water uptake slowed down, the time steps of measurements were consecutively increased.

3. Results and Discussion

Figure 1 shows the refractive index and absorption coefficient for both polymers once in dry state (solid line) and once after water saturation has been reached (dashed lines). In both cases the spectra show a featureless response which can be described by a Debye model (not shown) [38, 39] and agree well with previously published data [40]. As can be expected from previous experiments studying the influence of water on the THz response [34] an increase of both the refractive index and the absorption coefficient can be observed with increasing water content. Overall, the differences between dry and saturated state are larger in PMMA than in PC, which can be explained by the higher amount of water incorporated into the samples. While the saturation concentration was around 0.34% at 40°C and 0.49% at 70°C for PC, for PMMA the values were significantly higher with 1.98% at 40°C and 2.19% at 70°C. In all cases the saturation concentration was slightly higher for the higher temperature. Overall the obtained values are in good agreement with values published in the literature [41–44].

Figure 2 shows the thickness variation over the water immersion time. In PMMA a significant increase with increasing water content can be observed. At saturation a change of around 14 μm at 40°C and 22 μm at 70°C compared to the dry values is seen. In PC in opposite the changes are much smaller. If the accuracy/repeatability of the used

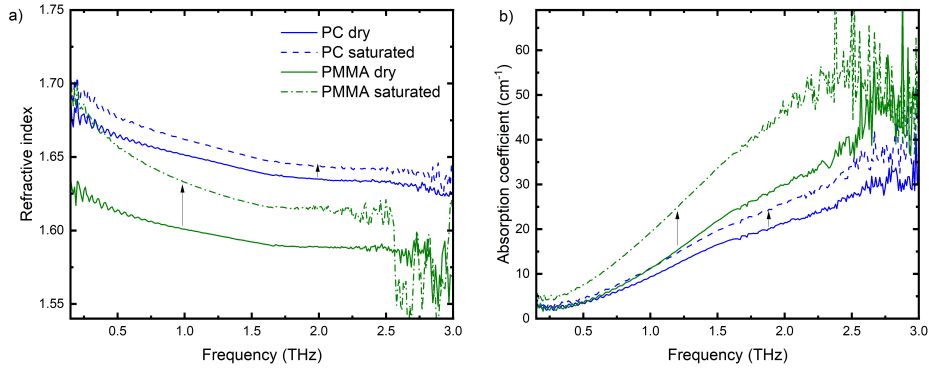


Figure 1: (a) Refractive index and (b) absorption coefficient of PC and PMMA in dried and water saturated state for the water immersion at 40°C.

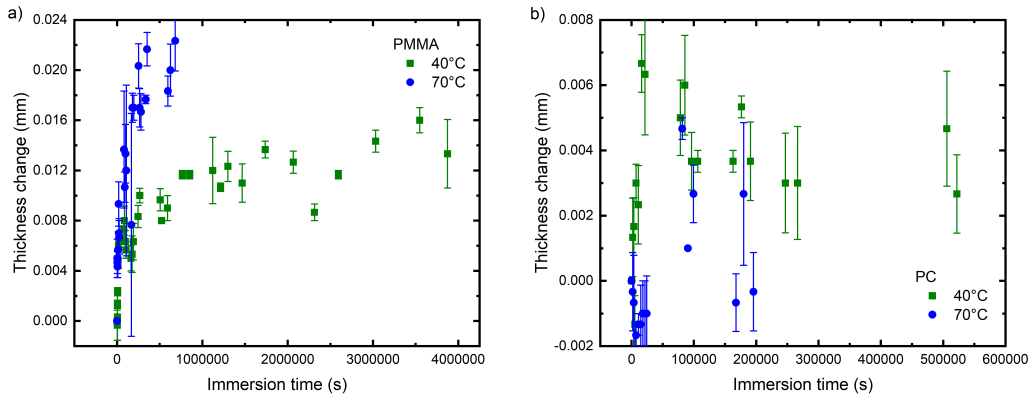


Figure 2: Thickness variation in PMMA (a) and PC(b) for water absorption experiments at 40°C and 70°C.

micrometer screw is considered ($\pm 3 \mu\text{m}$), the measured changes are probably negligible for PC. Besides the accuracy of the used device, the accurate thickness determination is additionally hindered by two factors: 1) since the samples are not perfectly flat, it is difficult to repeatedly measure the exact same spot in the different measurements already causing some variation in the results and 2) the samples inherently soften as part of the ageing process making the accurate thickness determination notably more difficult. All factors combined lead to the relatively large variation observed between the three samples for each polymer/temperature causing the large error bars observed in Fig. 2. Nevertheless, a clear trend can be observed for the PMMA samples, which might give some insights into the mechanisms how the water is included in the polymers. In general, there can be two mechanisms describing how the water molecules can be incorporated in the polymers [5, 16]. The first being that the water molecules can fill up the free volume between the polymer molecules which increases the density (i.e. increase of the mass without changing the polymer dimensions). Secondly, the water molecules can build a polar bond to the polymer chains modifying the dimensions of the sample. Considering the structural formulas (inset of Fig. 3 of PMMA and PC) both polymers show a strongly polar carbonyl group ($\text{C}=\text{O}$). However, in PC this group has oxygen atoms on both sides, suppressing the ability to bind water molecules [4]. Therefore, in PC the water just can fill up the free volume of the polymer, while in PMMA the polar water molecules also can additionally build a polar bond to the carbonyl group in addition to filling the free volume. As a result, this leads to a swelling of the PMMA, while the thickness in PC more or less remains constant during the water intake.

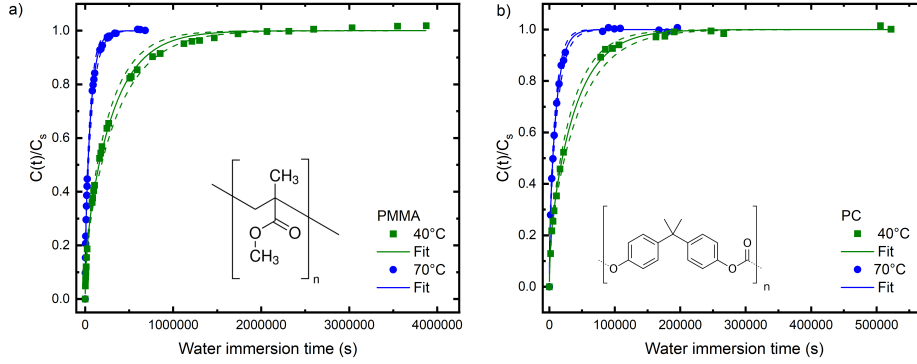


Figure 3: Mass fraction of water in PMMA (a) and PC (b) for water absorption experiments at 40°C and 70°C determined from gravimetric measurements. Insets show the structural formulas for PMMA and PC, respectively.

The measured mass data dependent on the water immersion time can be used to extract the Fickian diffusion coefficient by [45]

$$\frac{C(t)}{C_S} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\frac{-D(2n+1)^2 \pi^2 t}{4l^2} \right], \quad (1)$$

where D is the Fickian diffusion coefficient, t the time in s, l half the thickness of the film, C_S the saturation concentration and $C(t)$ the time dependent water concentration determined by

$$C(t) = \frac{m(t) - m_0}{m_0}, \quad (2)$$

where $m(t)$ is the mass at time t and m_0 the dry mass at $t=0$. Figure 3 shows the experimentally obtained relative mass fraction of water $C(t)/C_S$ averaged over the three studied samples (symbols) for PMMA (a) and PC (b) for both studied temperatures. As can be seen, in all cases an increase in the mass and hence in the water concentration was observed. Since the water diffusion coefficient follows an Arrhenius law [6], the higher the temperature the faster is the water absorption. Moreover, in Fig. 3 it can be seen that the water absorption in PC goes much faster than in PMMA. While in PC the saturation is reached after 20 h at 70°C (66 h at 40°C), PMMA needs 126 h at 70°C (536 h at 40°C). Using Eq. 1 the data can now be fitted to extract the Fickian diffusion coefficients. The fits are shown as solid lines in Fig. 3, while the dashed lines are calculated assuming a 15% variation of the diffusion coefficient. As can be seen Eq. 1 describes the experimental data pretty well. The obtained diffusion coefficients are summarized in Tab. 2. The obtained values are in good agreement with previously published values for PC and PMMA using gravimetric methods [15, 16, 44]. However, we observe a small deviation from the ideal Fickian behavior for relative mass fractions larger than 0.9 C_S in PMMA. In particular, once the mass fraction is close to saturation, the Fickian description slightly overestimates the water intake, meaning the water absorption process happens slightly slower than is expected by the theory. We note that this effect is present at both studied temperatures, with the deviation being slightly smaller at 70°C. A possible reason to this might be related to the mechanism how the water molecules are being incorporated into the polymer. For example, water molecules can hydrogen bond to the carbonyl group in PMMA and once a relative high concentration of water is reached where all available places are occupied, this could result in a slow down of water absorption. This effect is smaller at high temperatures where additional heat induces the reorganisation of the mobile polymer molecules resulting in more places available for hydrogen bonding.

Figure 4 shows the dependence of the refractive index (a) and absorption coefficient (b) at 1 THz on the water concentration. First of all, it can be noticed, that there are some small variations in the absolute values of the refractive index and absorption coefficients between the samples used for the 40°C and 70°C measurements in the dry state, probably caused by some minor variations in the samples used for the different runs. Nevertheless, the behavior of the different samples upon water intake is pretty similar. In all cases and temperatures, a linear increase of the optical

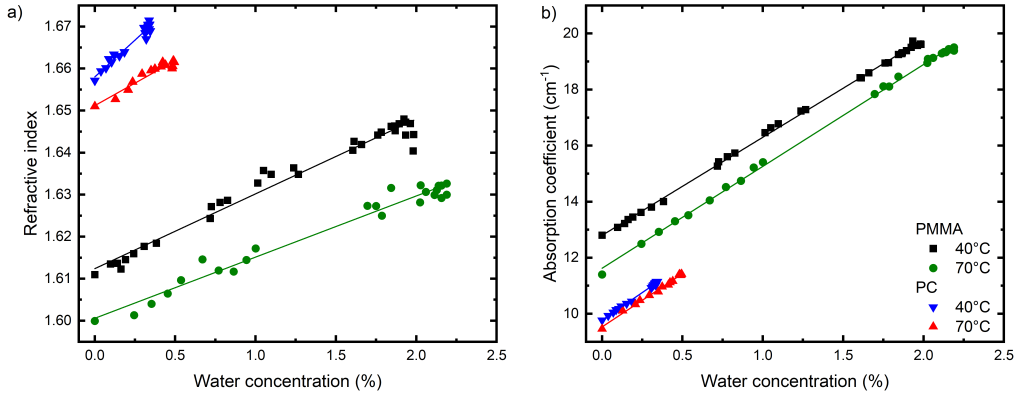


Figure 4: (a) Refractive index and (b) absorption coefficient at 1 THz in dependence of the water concentration. Solid lines show the linear regression of the experimental data.

constants with increasing water content is observed, which is in agreement with which was found in the investigation of water absorption in papers [33]. The behavior of the absorption coefficient shows the same slope independent of temperature for each polymer, which is expected, since the higher temperature should just impact the time-scale of the water absorption. Between the PMMA and the PC a small difference can be observed, with PC having around 18% higher values. For the refractive index the situation is more complex. Here, the differences between the different samples and temperatures are larger. However, also the scattering of the experimental data is much larger compared to the absorption coefficient. This is probably caused by the inaccuracies of the thickness determination. Since the refractive index is much more sensitive to an inaccurate thickness determination than the absorption coefficient [34], the imprecision in thickness is the probable reason for the differences observed in Fig. 4 (a) and the absorption coefficient seems to be the more robust parameter.

As it was found that there is a linear relationship between the water concentration and the optical constants at THz frequencies, it should be possible to use an adapted version of Eq. 1 to also describe the THz results. In order to do so, the normalized water concentration $C(t)/C_S$ in Eq. 1 was replaced by the refractive index/absorption coefficient normalized to their respective saturation value. Figure 5 shows the respective data for both polymers at 1 THz. The experimental values are averaged over the three studied samples. As in Fig. 3 the solid line shows the fit according to the adapted Eq. 1 and dashed lines are plotted for a variation of 15% of the extracted diffusion coefficients. The absorption coefficient data is almost perfectly described by the adapted Eq. 1, while the scattering of the data is much larger for the refractive indices. Here, the variation between the three samples was much larger than for the absorption coefficient, as can be seen on the error bars in the figure. The reason for the larger scattering in the refractive index is, as previously discussed, the inaccuracy of the thickness determination. In addition, the absorption coefficient data for PMMA closely follows the gravimetric measurements showing the same deviation from the ideal Fickian behavior.

The analysis of Fig. 5 was done at a frequency of 1 THz, but of course THz-TDS gives the optical constants over a broad frequency range as can be seen in Fig. 1. So the analysis was repeated for the whole measured frequency band and the results are shown in Fig. 6. Solid lines show the results obtained by the absorption coefficient data, while dashed lines were extracted using the refractive index one. The diffusion coefficients obtained by the absorption coefficient show a very flat response, i.e. no frequency dependent behavior is observed. However, at low frequencies as well as very high frequencies, some oscillations around the actual value can be observed. Similar oscillations can also be observed at the low frequencies in the spectra in Fig. 1 and arise due to an inaccuracy in the thickness determination, leading to oscillations at low frequencies [46]. At the high frequencies, the available bandwidth of the system is reached, leading to a scattering of the data making a proper extraction of the diffusion coefficients difficult. For the diffusion coefficients retrieved by the refractive indices, the difference to the gravimetric measurements is much larger and also there seems to be a slight frequency dependence. However, over the different materials and temperatures there is no clear trend in the frequency dependence and it's probably caused just by the inaccurate thickness determination, making the scattering of the data much larger which in consequence leads to an overestimation of the extracted diffusion coefficients.

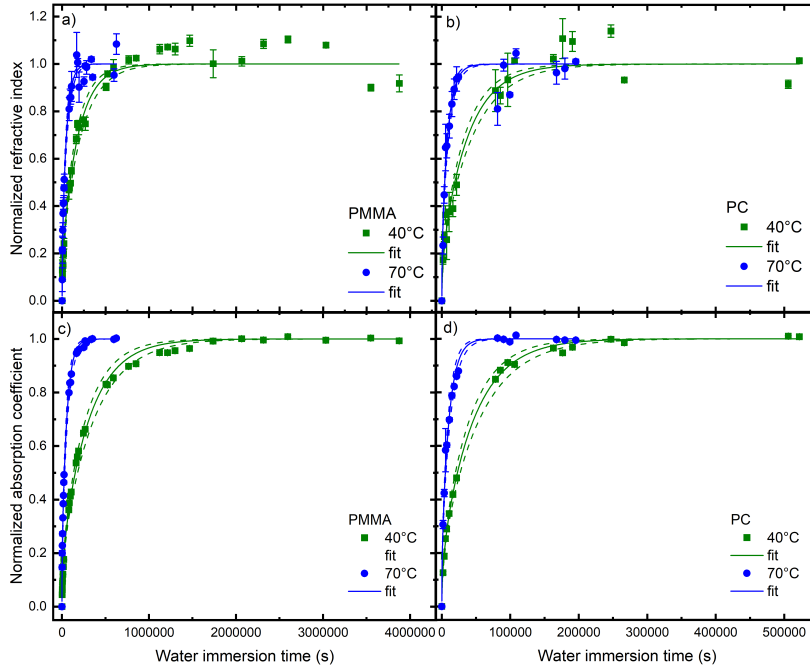


Figure 5: Normalized refractive index (a,b) and absorption coefficient (c,d) at 1 THz in dependence of the water immersion time for PMMA (a,c) and PC (b,d), respectively.

In order to check the quality of the THz fits, a variation of 10%, 15% and 20% of the initially obtained diffusion coefficient has been assumed and the number of experimental points inside these confidence intervals has been counted for each frequency. Figure 7 shows an example of this analysis for the PC sample immersed at 40°C. Solid lines show the results for the absorption coefficient, while the dashed ones for the refractive index. As can be seen, at frequencies below 0.6 THz and above 1.7 THz the percentage of points inside the intervals quickly decrease for the absorption coefficients. However, inside this frequency interval the fits according to Eq. 1 describe the experimental data very well. This frequency range also corresponds to the flat parts in Fig. 6, showing that the method allows to retrieve the diffusion coefficients with a high accuracy. Since at the lower and higher frequencies the scattering of the experimental data is larger, the percentage of points inside the confidence intervals decrease rapidly and the extracted values for the diffusion coefficients start to oscillate around the real value. For the refractive index data the picture is much worse. Here, the initial data shows a large scattering (Fig. 5 (b)), leading to a small confidence in Fig. 7, which explains the differences observed in Fig. 6.

Compared to conventional methods of gravimetrics and capacitive measurement, THz-TDS is an emerging technique that does not require physical contact thus minimising prior preparations. As the technique is point based, there is the added opportunity to investigate spatial variations of water diffusion across sample area, which is not possible with existing methods that only provide bulk information. However, for accurate parameter extraction, there is a need to determine sample thickness, which becomes practically difficult under prolonged ageing resulting in sample softening. However, this can potentially be mitigated using iterative processing algorithms to simultaneously extract thickness and optical constants [47]. **Our proposed demonstrations will therefore further motivate developments in THz-TDS to realise the potential as an interesting complementary technique, opening up opportunities for future rapid**

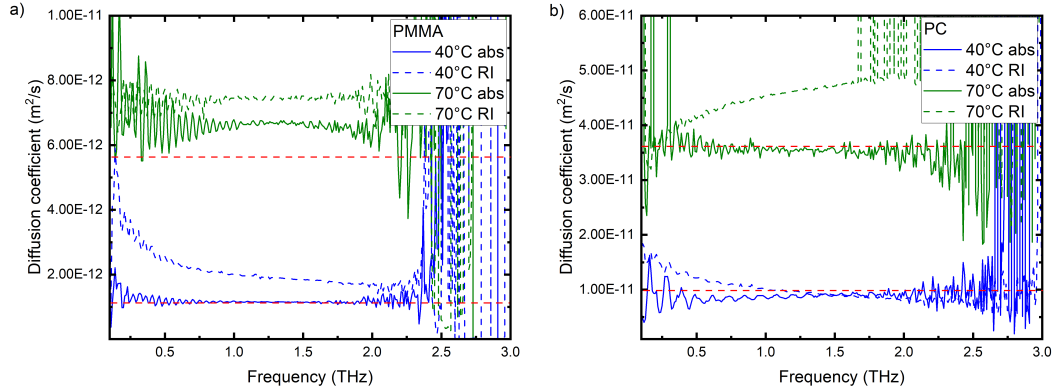


Figure 6: Extracted diffusion coefficients for (a) PMMA and (b) PC. Red dashed lines show the respective values extracted from the mass data.

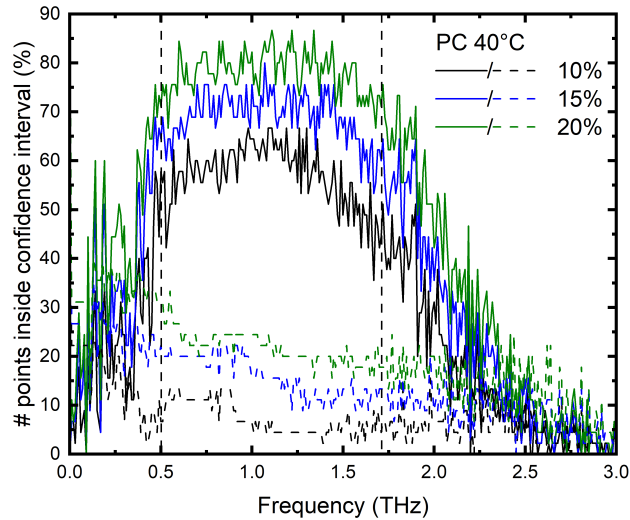


Figure 7: Percentage of points inside the interval for an uncertainty of 10%, 15% and 20% in the diffusion coefficient. Solid lines show the results for the absorption coefficients, while dashed lines are for the refractive index.

degradation testing and material understanding especially in multi-component systems [48], where the technique has already shown sensitivity [49–51].

4. Conclusion

In summary, this paper studied the water diffusion dynamics in polycarbonate and poly(methyl methacrylate) at temperatures of 40°C and 70°C by gravimetric methods and terahertz time domain spectroscopy. Fickian diffusion coefficients were extracted from the experimental data, where it was found that the THz measurements open up a novel way to determine these parameters contact-free. A good agreement to the gravimetric measurements was found. Moreover, it was seen that the THz absorption coefficient is a more robust parameter to extract these values.

Acknowledgment

H. L. acknowledges financial support from the Australian Defence Science and Technology Group.

Table 2

Extracted diffusion coefficients and obtained saturation concentrations. Due to the frequency dependence of D_{RI} , the value at 1 THz is shown. For comparison values from the literature are also given.

T (°C)	D_{grav} (m ² /s)	D_{RI} (m ² /s)	D_{Abs} (m ² /s)	D_{lit} (m ² /s)	C_s	C_s^{lit}
PC						
40	9.9×10^{-12}	1.0×10^{-11}	8.7×10^{-12}	2.95×10^{-11} [41]	0.34%	0.31% [41]
70	3.6×10^{-11}	4.5×10^{-11}	3.5×10^{-11}	5.27×10^{-11} [41]	0.49%	0.3% [41]
PMMA						
40	1.1×10^{-12}	2.0×10^{-12}	1.1×10^{-12}	0.67×10^{-12} (24°C) [44]	1.98%	1.2% (24°C) [44]
70	5.6×10^{-12}	7.4×10^{-12}	6.7×10^{-12}	-	2.19%	-

CRediT authorship contribution statement

Sebastian Engelbrecht: Conceptualization, Methodology, Data Analysis, Writing, Editing. **Vincent Pichot:** Methodology, Measurements, Editing. **Thomas Goepfert:** Measurements, Editing. **Hungyen Lin:** Conceptualization, Data Analysis, Editing. **Bernd M. Fischer:** Administration, Funding, Editing.

References

- [1] M. Narkis, S. Chaouat-Sibony, A. Nicolais, L. Apicella, J. Bell, Water effects on polycarbonate, *Polym. Commun.* 26 (1985) 339–342.
- [2] M. M. Qayyum, J. R. White, Effect of water absorption and temperature gradients on polycarbonate injection moldings, *J. Appl. Polym. Sci.* 43 (1991) 129–144.
- [3] G. A. Adam, A. Cross, R. N. Haward, The effect of thermal pretreatment on the mechanical properties of polycarbonate, *J. Mater. Sci.* 10 (1975) 1582–1590.
- [4] G. Baschek, G. Hartwig, F. Zahradnik, Effect of water absorption in polymers at low and high temperatures, *Polymer* 40 (1999) 3433–3441.
- [5] E. Moghbelli, R. Banyay, H.-J. Sue, Effect of moisture exposure on scratch resistance of pmma, *Tribol. Int.* 69 (2014) 46–51.
- [6] U. Schulz, G. Tjandraatmadja, The influence of rain and humidity on the lifetime of transparent polymeric roof materials, 2002.
- [7] R. J. Gardner, J. R. Martin, Humid aging of plastics: Effect of molecular weight on mechanical properties and fracture morphology of polycarbonate, *J. Appl. Polym. Sci.* 24 (1979) 1269–1280.
- [8] M. Haghighi-Yazdi, J. K. Y. Tang, P. Lee-Sullivan, Moisture uptake of a polycarbonate blend exposed to hygrothermal aging, *Polym. Degrad. Stab.* 96 (2011) 1858–1865.
- [9] W. Wang, X. Guo, D. Zhao, L. Liu, R. Zhang, J. Yu, Water absorption and hygrothermal aging behavior of wood-polypropylene composites, *Polymers* 12 (2020) 782.
- [10] M.-C. Li, X. Ge, U. Ryong Cho, Mechanical performance, water absorption behavior and biodegradability of poly(methyl methacrylate)-modified starch/sbr biocomposites, *Macromol. Res.* 21 (2013) 793–800.
- [11] R. Hartwell, M. Overend, Effects of humidity and the presence of moisture at the bond-line on the interfacial separation of laminated glass for flat glass re-use, Challenging Glass 7, Conference on Architectural and Structural Applications of Glas, Ghent (2020).
- [12] G. Rivers, D. Cronin, Influence of moisture and thermal cycling on delamination flaws in transparent armor materials: Thermoplastic polyurethane bonded glass-polycarbonate laminates, *Mater. Des.* 182 (2019) 108026.
- [13] C. Yang, X. Xing, Z. Li, S. Zhang, A comprehensive review on water diffusion in polymers focusing on the polymer-metal interface combination, *Polymers* 12 (2020).
- [14] H. L. Frisch, Sorption and transport in glassy polymers - a review, *Polym. Eng. Sci.* 20 (1980) 2–13.
- [15] S. I. Moon, C. W. Extrand, Water vapor permeation resistance of polycarbonate at various temperatures, *Ind. Eng. Chem. Res.* 48 (2009) 8961–8965.
- [16] D. T. Turner, Polymethyl methacrylate plus water: sorption kinetics and volumetric changes, *Polymer* 23 (1982) 197–202.
- [17] Y.-S. Lee, Principles of Terahertz Science and Technology, Springer Science+Business Media, 2008.
- [18] S. Wietzke, C. Jansen, T. Jung, M. Reuter, B. Baudrit, M. Bastian, S. Chatterjee, M. Koch, Terahertz time-domain spectroscopy as a tool to monitor the glass transition in polymers, *Opt. Express* 17 (2009) 19006–19014.
- [19] S. Wietzke, C. Jansen, F. Rutz, D. M. Mittleman, M. Koch, Determination of additive content in polymeric compounds with terahertz time-domain spectroscopy, *Polym. Test.* 26 (2007) 614–618.
- [20] O. Peters, M. Schwerdtfeger, S. Wietzke, S. Sostmann, R. Scheunemann, R. Wilk, R. Holzwarth, M. Koch, B. M. Fischer, Terahertz spectroscopy for rubber production testing, *Polym. Test.* 32 (2013) 932–936.
- [21] C. Joerdens, M. Scheller, M. Wichmann, M. Mikulics, K. Wiesauer, M. Koch, Terahertz birefringence for orientation analysis, *Appl. Opt.* 48 (2009) 2037–2044.

- [22] S. Katletz, M. Pfeleger, H. Puehringer, M. Mikulics, N. Vieweg, O. Peters, B. Scherger, M. Scheller, M. Koch, K. Wiesau, Polarization sensitive terahertz imaging: detection of birefringence and optical axis, *Opt. Express* 20 (2012) 23025–23035.
- [23] C. Jansen, S. Wietzke, H. Wang, M. Koch, G. Zhao, Terahertz spectroscopy on adhesive bonds, *Polym. Test.* 30 (2011) 150–154.
- [24] D. Zhao, J. Ren, X. Qao, L. Li, Application of terahertz time-domain spectroscopy in nondestructive testing of adhesion quality, *Proc. SPIE* 9674, AOPC 2015: Optical and Optoelectronic Sensing and Imaging Technology 96741P (2015).
- [25] S. Wietzke, C. Joerdens, N. Krumbholz, B. Baudrit, M. Bastian, M. Koch, Terahertz imaging: a new non-destructive technique for the quality control of plastic weld joints, *J. Eur. Opt. Soc. Publ.* 2 (2007).
- [26] S. Sommer, T. Raidt, B. M. Fischer, F. Katzenberg, J. C. Tiller, M. Koch, Thz-spectroscopy on high density polyethylene with different crystallinity, *J. Infrared, Milli. Terahz. Waves* 37 (2016) 189–197.
- [27] S. Wietzke, M. Reuter, N. Nestle, E. Klimov, U. Zadok, B. M. Fischer, M. Koch, Analyzing morphology and thermal history of polybutylene terephthalate by thz time-domain spectroscopy, *J. Infrared, Milli. Terahz. Waves* 32 (2011) 952.
- [28] S. Wietzke, C. Jansen, M. Reuter, T. Jung, D. Kraft, S. Chatterjee, B. M. Fischer, M. Koch, Terahertz spectroscopy on polymers: A review of morphological studies, *J. Mol. Struct.* 1006 (2011) 41–51.
- [29] H. Hoshina, S. Ishii, S. Yamamoto, Y. Morisawa, H. Sato, T. Uchiyama, Y. Ozaki, O. C., Terahertz spectroscopy in polymer research: Assignment of intermolecular vibrational modes and structural characterization of poly(3-hydroxybutyrate), *IEEE Trans. Terahertz Sci. Technol.* 3 (2013) 248–258.
- [30] S. Engelbrecht, K.-H. Tybussek, J. Sampaio, J. Boehmler, B. M. Fischer, S. Sommer, Monitoring the isothermal crystallization kinetics of pet-a using thz-tds, *J. Infrared, Milli. Terahz. Waves* 40 (2019) 306–313.
- [31] R. Gente, N. Born, N. Voß, W. Sannemann, J. Léon, M. Koch, E. Castro-Camus, Determination of leaf water content from terahertz time-domain spectroscopic data, *J. Infrared, Milli. Terahz. Waves* 34 (2013) 316–323.
- [32] R. Gente, A. Rehn, T. Probst, E.-M. Stuebling, E. Castro Camus, A. A. Covarrubias, J. C. Balzer, M. Koch, Outdoor measurements of leaf water content using thz quasi time-domain spectroscopy, *J. Infrared, Milli. Terahz. Waves* 39 (2018) 943–948.
- [33] D. Banerjee, W. von Spiegel, M. D. Thomson, S. Schabel, H. G. Roskos, Diagnosing water content in paper by terahertz radiation, *Opt. Express* 16 (2008) 9060–9066.
- [34] H. Lin, B. P. Russell, P. Bawuah, J. A. Zeitler, Sensing water absorption in hygrothermally aged epoxies with terahertz time-domain spectroscopy, *Anal. Chem.* 93 (2021) 2449–2455.
- [35] S. Yassin, K. Su, H. Lin, L. F. Gladden, J. A. Zeitler, Diffusion and swelling measurements in pharmaceutical powder compacts using terahertz pulsed imaging, *J. Pharm. Sci.* 104 (2015) 1658–1667.
- [36] N. Vieweg, F. Rettich, A. Deninger, H. Roehle, R. Dietz, T. Goebel, M. Schell, Terahertz-time domain spectrometer with 90 db peak dynamic range, *J. Infrared, Milli. Terahz. Waves* 35 (2014) 823–832.
- [37] P. U. Jepsen, D. G. Cooke, M. Koch, Terahertz spectroscopy and imaging - modern techniques and applications, *Laser Photon Rev.* 5 (2011) 124–166.
- [38] N. Nagai, R. Fukasawa, Abnormal dispersion of polymer films in the thz frequency region, *Chem. Phys. Lett.* 388 (2004) 479–482.
- [39] E. V. Fedulova, M. M. Nazarov, A. A. Angeluts, M. S. Kitai, V. I. Sokolov, A. P. Shkurinov, Studying of dielectric properties of polymers in the terahertz frequency range, *Proc. SPIE* 8337, Saratov Fall Meeting 2011: Optical Technologies in Biophysics and Medicine XIII (2012) 83370I.
- [40] Y.-S. Jin, G.-H. Kim, S.-G. Jeon, Terahertz dielectric properties of polymers, *J. Korean Phys. Soc.* 49 (2006) 513–517.
- [41] I. Ghorbel, F. Thominette, P. Spiteri, V. J., Hydrolytic aging of polycarbonate. i. physical aspects, *J. Appl. Polym. Sci.* 55 (1995) 163–171.
- [42] A. Golovoy, M. Zinbo, Water sorption and hydrolytic stability of polycarbonates, *Polym. Eng. Sci.* 29 (1989) 1733–1737.
- [43] K. Büyükkaya, Kinetics of long-term water absorption behavior of different organic waste dust/polymethylmethacrylate composites, *J. Chem. Technol. Metall.* 54 (2019) 339.
- [44] D. T. Turner, Water sorption of poly(methyl methacrylate): 1. effects of molecular weight, *Polymer* 28 (1987) 293–296.
- [45] B. C. Duncan, W. R. Broughton, Absorption and Diffusion of Moisture In Polymeric Materials, National Physical Laboratory, 2007.
- [46] T. D. Dorney, R. G. Baraniuk, D. M. Mittleman, Material parameter estimation with terahertz time-domain spectroscopy, *J. Opt. Soc. Am. A* 18 (2001) 1562–1571.
- [47] D. F. Alves-Lima, X. Li, B. Coulson, E. Nesling, G. Ludlam, R. Degl'Innocenti, R. Dawson, M. Peruffo, H. Lin, Evaluation of water states in thin proton exchange membrane manufacturing using terahertz time-domain spectroscopy, *J. Membr. Sci.* 647 (2022) 120329.
- [48] V. Loianno, G. Mensitieri, A. Baldanza, G. Scherillo, P. Musto, Combining ftir spectroscopy and pressure-decay techniques to analyze sorption isotherms and sorption kinetics of pure gases and their mixtures in polymers: The case of co₂ and ch₄ sorption in polydimethylsiloxane, *J. Membrane Sci.* 652 (2022) 120445.
- [49] P. U. Jepsen, U. Möller, H. Merbold, Investigation of aqueous alcohol and sugar solutions with reflection terahertz time-domain spectroscopy, *Opt. Exp.* 15 (2007) 14717–14737.
- [50] D. Bigourd, C. A., F. Hindle, S. Matton, R. Bocquet, G. Mouret, F. Cazier, D. Dewaele, H. Nouali, Multiple component analysis of cigarette smoke using thz spectroscopy, comparison with standard chemical analytical methods, *App. Phys. B* 86 (2007) 579–586.
- [51] M. Kaushik, B. W.-H. Ng, B. M. Fischer, D. Abbott, Terahertz scattering by granular composite materials: An effective medium theory, *Appl. Phys. Lett.* 100 (2012) 011107.