

Non-destructive monitoring and quantitative analysis of moisture absorption in epoxy using THz time-domain spectroscopy and a three-phase effective medium model

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ABSTRACT

Water uptake in epoxy resins significantly affects their mechanical and dielectric properties, leading to long-term reliability concerns. However, conventional gravimetric methods are limited in their ability to distinguish among absorbed water states and to provide non-destructive evaluation. In this study, we propose a non-contact, non-destructive method based on terahertz time-domain spectroscopy (THz-TDS) for the quantitative analysis of moisture absorption in epoxy. The complex permittivity of water-immersed DGEBA epoxy was extracted as a function of immersion time and analyzed using a coupled model that combines a three-phase Landau-Lifshitz-Looyenga (LLL) dielectric mixing model with a Kohlrausch-Williams-Watts (KWW) kinetic model. This approach enables model-based estimation of the effective volume fractions of bound water (BW) and free water (FW). Compared with the conventional two-phase model, which considers only BW, the proposed three-phase LLL-KWW model showed substantially improved agreement with both gravimetric measurements and terahertz-derived complex permittivity, particularly under high-uptake conditions and during prolonged immersion. The model maintained high accuracy, with mean errors of 0.41% and 4.21% for the real and imaginary parts of permittivity, respectively, and demonstrated robust performance across the full frequency range. The results further indicate that the contribution of FW becomes increasingly significant during long-term immersion, providing a physically consistent interpretation of non-Fickian moisture absorption behavior. These findings demonstrate that THz-TDS, combined with a three-phase dielectric mixing framework, offers a reliable, non-destructive method for analyzing water uptake in epoxy, with strong potential for condition monitoring and lifetime assessment of polymer-based materials.

1. Introduction

Epoxy resins are widely used as adhesives, encapsulants for electronic devices, and waterproof coating materials. Accordingly, their long-term reliability and lifetime prediction are of critical importance [1]. Prolonged moisture absorption in epoxy has been reported to lower the glass transition temperature, induce plasticization, promote the formation of microcracks and voids, and alter dielectric properties, ultimately degrading the functional performance of the resin [2–4]. Therefore, a reliable method is needed to accurately evaluate moisture penetration in epoxy resins.

Conventionally, water uptake and its underlying mechanisms have

been investigated by immersing epoxy specimens in water or exposing them to high-humidity environments, followed by monitoring weight changes over time using gravimetric methods [5,6]. Although gravimetry is effective for quantifying total moisture absorption, it has inherent limitations in practical applications. Separate specimens must be prepared specifically for weight measurements, making direct evaluation of in-service structures difficult. In addition, conventional methods are often contact-based or require sample pretreatment. More importantly, gravimetric analysis provides only the total amount of absorbed moisture and cannot distinguish between bound water (BW) and free water (FW), nor can it reveal the spatial distribution of moisture within the epoxy [7,8]. These limitations highlight the need for a non-destructive

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approach capable of estimating the effective contributions of BW and FW. For these reasons, there is an increasing demand for non-contact and non-destructive inspection techniques that can monitor moisture states inside epoxy and support long-term reliability prediction [9]. Terahertz time-domain spectroscopy (THz-TDS) is a non-contact and non-destructive technique that can extract the complex refractive index and complex permittivity of materials in the 0.1 THz to several-THz range. Because water molecules exhibit strong absorption in the THz region, even small changes in moisture content can be detected with high sensitivity through variations in the transmitted THz amplitude [10–15]. Beyond moisture sensing, THz-TDS has also been used for material characterization by exploiting amplitude, phase, and spectral information [16,17]. Recent advances in THz source, modulation, and sensing platforms have further broadened the applicability of THz-based material evaluation [18–20]. Based on the strong moisture sensitivity and non-contact nature of THz-TDS, this technique was adopted in the present study as a quantitative probe for moisture-induced dielectric changes in epoxy.

In particular, when the frequency-domain permittivity spectrum is combined with dielectric mixture models based on effective medium theory (EMT) [21], such as the Landau-Lifshitz-Looyenga (LLL) [22], Birchak [23], and Silberstein [24] models, the volume fraction and dielectric properties of absorbed water can be quantitatively analyzed. More recently, THz-TDS and EMT have also been combined to evaluate the dielectric properties of heterogeneous materials [25–27]. These studies further support the use of THz-TDS-EMT analysis as a methodological basis for dielectric characterization of multicomponent systems. This approach enables more comprehensive characterization of material properties than simple transmission-based analysis [14,28].

In the context of moisture quantification, previous studies have combined THz-derived complex permittivity with dielectric mixture models, particularly the LLL model, to quantify moisture content in polymers, soils, and aged epoxy systems [14,28,29]. For example, Lin et al. used THz-TDS in combination with the LLL model to estimate water uptake in hydrothermally aged epoxy systems and reported a strong correlation between THz optical constants and gravimetric water uptake [28]. In parallel, the classification of absorbed water in epoxy and related polymers into BW/FW or mobile/bound states has been investigated using complementary techniques such as gravimetric analysis, NMR, ATR-FTIR, dielectric spectroscopy, and THz-TDS. Popineau et al. combined gravimetric analysis and NMR measurements for an epoxy adhesive and reported water populations with different mobilities [7], while Maggana and Pissis interpreted the moisture sorption behavior of a DGEBA/TETA epoxy system using a two-phase diffusion framework based on structural heterogeneity of the epoxy matrix [30]. In the time-resolved 2D ATR-FTIR study by Liu et al., water molecules in cured epoxy were shown to preferentially interact with polar or hydrophilic groups during the initial stage, whereas the contribution of less hydrogen-bonded or free-like water gradually increased as immersion proceeded [31]. In addition, THz-TDS/effective-medium analyses by Jördens et al. and Lin et al. showed that the dielectric contribution of absorbed water in polymers and moisture-aged epoxy can be reflected in the measured complex permittivity [14,28]. In the present framework, BW is interpreted as water molecules whose mobility is restricted by interactions with polar or hydrophilic groups in the epoxy network, whereas FW is treated as relatively less constrained, bulk-like water associated with free volume, microvoids, or water clusters. These different molecular environments are expected to contribute differently to the measured THz complex permittivity because of differences in molecular mobility, hydrogen-bonding state, orientational relaxation, and dipolar response.

However, several important limitations remain. First, previous epoxy studies adopted a two-phase model consisting of dry epoxy and a single BW-like water phase, implicitly assuming that all absorbed water behaves as bound water [28]. Although the LLL model can be extended to multicomponent systems, such extensions have not been implemented

for quantitative BW/FW separation in moisture-aged epoxy. Second, the discrepancy between experimental results and model predictions increases substantially in the high-uptake region. In particular, the applicability of the two-phase model becomes limited when the moisture content exceeds approximately 2–4% [28], underscoring its inability to account for the increasing contribution of FW during prolonged immersion [7,8]. Third, analysis of the non-Fickian behavior observed during long-term immersion remains limited [30].

To address these limitations, this study proposes a gravimetry-assisted THz-TDS analysis framework in which the conventional two-phase BW-only LLL approach is extended to a KWW-constrained three-phase model consisting of dry epoxy, BW, and FW. Unlike previous THz-TDS/LLL-based approaches that mainly treated aged epoxy as a dry-epoxy/single-water-phase system, the present framework extends the analysis to a constrained three-phase inverse model that separately estimates the time-dependent dielectric contributions of BW and FW [14, 28,30,31]. This formulation enables the time-dependent volume fractions of BW and FW to be estimated while mitigating the non-uniqueness inherent in the inverse EMT problem. To provide input data for this framework, a DGEBA/TETA epoxy specimen was immersed in distilled water at 75 °C, and the time-dependent complex permittivity was measured using THz-TDS transmission experiments. The accuracy of the proposed framework was validated by comparison with the gravimetric value and the measured frequency-dependent complex permittivity. This framework not only quantifies the moisture content at a given aging time but also enables non-destructive estimation of the temporal evolution of BW and FW in epoxy, thereby providing insight into complex moisture absorption mechanisms including non-Fickian behavior.

2. Experimental

2.1. Sample preparation

In this study, the DGEBA epoxy shown in Fig. 1(b) was used. The epoxy specimen was prepared as follows. First, the epoxy resin (Kukdo Chemical, YD-128) and curing agent (TETA) were weighed according to the stoichiometric ratio (YD-128, 18.7 g; TETA, 2.5 g) and mixed at room temperature for 5 min. Second, the mixture was placed in a vacuum chamber and degassed for 1 h to remove entrapped air bubbles. The degassed mixture was then poured into a metal mold, cured at room temperature for 1 h, and post-cured at 80 °C for 2 h. The fabricated epoxy sheet was machined into the specimen geometry used for the immersion and THz-TDS measurements, and dried in an oven at 55 °C for 24 h to ensure a fully dry initial state. For the immersion test, accelerated aging was carried out by immersing the specimen in heated distilled water. As shown in Fig. 1(a), the immersion setup consisted of a hot plate equipped with a temperature sensor, which maintained the distilled water at 75 °C.

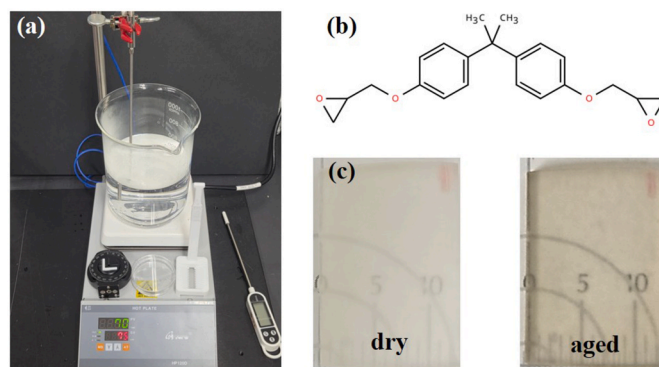


Fig. 1. (a) Heated immersion setup used for the epoxy immersion experiment. (b) Chemical structure of DGEBA. (c) Photographs of the epoxy specimen before immersion (0 h, dry state) and after 552 h of immersion.

The immersion temperature (75 °C) remained below the reported glass transition temperature of similar DGEBA/TETA epoxy systems (~124 °C) [32], minimizing thermally induced network softening effects during water uptake.

2.2. Terahertz time-domain spectroscopy and immersion test protocol

A THz-TDS system based on a mode-locked Ti:sapphire laser was employed, with a center wavelength of 800 nm, a pulse width of ~150 fs, and a repetition rate of 80 MHz, shown in Fig. 2. The output beam was split into pump and probe paths for THz generation and detection, respectively. In the pump path, THz radiation was generated using a photoconductive antenna (PCA) excited by the laser pulse. Four off-axis parabolic mirrors were used to collect and refocus the emitted THz pulses, producing an intermediate focus at the sample plane, where the specimen was positioned. For detection, the delayed probe beam and the THz beam were spatially overlapped in a 1 mm-thick, (110)-cut ZnTe crystal. The THz-induced birefringence in the ZnTe crystal was measured by polarization analysis. Specifically, a quarter-wave plate and a Wollaston prism split the probe beam into two orthogonally polarized components, which were then detected using a balanced photodetector. All measurements were performed at room temperature under a dry-air purge to minimize atmospheric absorption.

THz transmission measurements were conducted on the same DGEBA/TETA epoxy specimen over a total immersion period of 552 h using an ex-situ time-tracking protocol. At each measurement time, the specimen was removed from distilled water maintained at 75 °C, gently blotted to remove residual surface water, and weighed using an electronic balance (Daehan, WBA-220A; 0.1 mg). The specimen mass was determined from five repeated measurements. The dry epoxy mass measured prior to immersion was approximately 539 mg. The specimen dimensions, including the thickness at the THz-TDS measurement position, were measured five times using a digital micrometer (Mitutoyo, MDC-25PX; 1 μm), and the averaged value was used for permittivity extraction and water-volume-fraction calculation. At each immersion time, three THz-TDS waveforms were recorded and averaged for analysis. All measurements were completed within 10 min, after which the specimen was immediately re-immersed.

3. Theoretical background

3.1. Extraction of complex refractive index and dielectric constants from THz-TDS

Using THz-TDS, the complex refractive index and complex dielectric constant of aged epoxy were extracted as functions of immersion time. The reference electric field in air, $E_{\text{ref}}(t)$, and the electric field trans-

mitted through the sample, $E_{\text{sam}}(t)$, were measured in the time domain. A fast Fourier transform (FFT) was then applied to both signals to obtain the corresponding complex electric-field spectra in the frequency domain, $\tilde{E}_{\text{ref}}(\omega)$ and $\tilde{E}_{\text{sam}}(\omega)$. The normalized transmission function is expressed as follows [28,33,34]:

$$\frac{\tilde{E}_{\text{sam}}(\omega)}{\tilde{E}_{\text{ref}}(\omega)} = A(\omega) \exp^{-i\phi(\omega)} \quad (1)$$

where $A(\omega)$ and $\phi(\omega)$ represent the amplitude and phase of the complex transmission function respectively.

Under the low-loss condition ($n \gg \kappa$), the real part of the refractive index, $n(\omega)$, and the extinction coefficient, $\kappa(\omega)$, are given by [34]:

$$n(\omega) = 1 + \frac{c}{2\pi f d} \phi(\omega) \quad (2)$$

$$\kappa(\omega) = \frac{c}{2\pi f d} \ln \left[\frac{4n(\omega)}{A(\omega)(n(\omega) + 1)^2} \right] \quad (3)$$

where c is the speed of light and d is the sample thickness.

The complex dielectric constant is then obtained from the complex refractive index as:

$$\tilde{\epsilon}(\omega) = \tilde{n}(\omega)^2 = \begin{cases} \epsilon'(\omega) = n(\omega)^2 - \kappa(\omega)^2 \\ \epsilon''(\omega) = 2n(\omega)\kappa(\omega) \end{cases} \quad (4)$$

3.2. Effective medium modeling: two-phase and three-phase LLL model

In this study, a dielectric mixing model based on effective medium theory (EMT) was employed to quantify the volume fraction of absorbed water, F_{Water} , in epoxy using the complex permittivity of the immersed (aged) epoxy, $\tilde{\epsilon}_{\text{aged}}$, extracted from THz-TDS measurements. EMT provides a theoretical framework for describing the effective permittivity of a heterogeneous mixture based on the known permittivities and volume fractions of its constituent phases [21].

Among various EMT models, the LLL model has been widely applied to moisture absorption in heterogeneous systems because it does not require explicit information about the geometry of the constituent phases [14,28].

In previous studies, moisture-absorbed epoxy was modeled as a two-phase mixture consisting of dry epoxy and BW. Here, the two-phase representation refers to a mixture of dry epoxy and a single BW-like water phase. Under this assumption, all absorbed water is treated as BW, and the dielectric response is described by the relationship between the volume fraction F and the complex permittivity $\tilde{\epsilon}$ of each component, namely dry epoxy and BW. The two-phase LLL model is expressed as follows:

$$\begin{cases} \tilde{\epsilon}_{\text{aged}}^{1/3} = F_{\text{dry}} \tilde{\epsilon}_{\text{dry}}^{1/3} + F_{\text{BW}} \tilde{\epsilon}_{\text{BW}}^{1/3} \\ F_{\text{dry}} + F_{\text{water}} = 1 \end{cases} \quad (5)$$

However, as immersion time increases, particularly in the high-uptake regime, the moisture absorption behavior becomes nonlinear and deviates from the initial Fickian-like trend. This deviation can be associated with the increasing contribution of less-bound or FW-like water within the epoxy. Under such conditions, the two-phase model, which assumes that all absorbed water exists as a single BW-like phase, is insufficient to explain the observed changes in permittivity during prolonged immersion.

Water sorption in polymers, composite resins, and epoxy systems has commonly been interpreted using Fickian diffusion for diffusion-controlled uptake [35]. Deviations from ideal Fickian behavior have been modeled using Langmuir/Carter–Kibler-type mobile/bound-water exchange models [7,36], Berens–Hopfenberg diffusion–relaxation models [37], cyclic moisture-uptake models for absorption/desorption histories [5], time-dependent diffusivity models for nonconstant

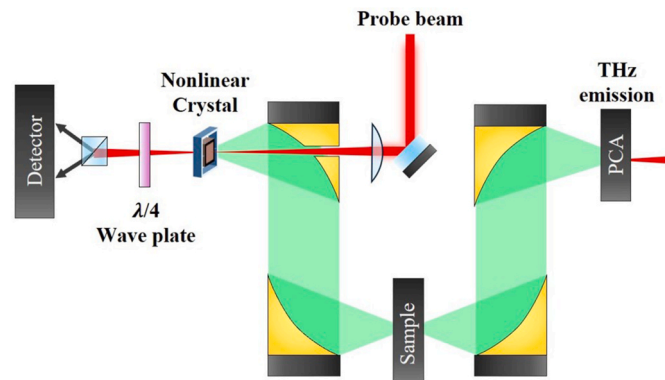


Fig. 2. THz-TDS setup for transmission measurements of the epoxy samples. Schematic illustration of THz generation and detection and sample positioning in the terahertz time-domain spectroscopy (THz-TDS) system.

transport properties [38], and two-phase or heterogeneous-network diffusion frameworks for matrix heterogeneity [30,38]. These models are useful for analyzing total gravimetric uptake and relaxation-related anomalous sorption behavior. In contrast, the present LLL-KWW framework is not intended to replace established diffusion or sorption models. Rather, it uses KWW-type temporal constraints to regularize the inverse estimation of effective BW and FW fractions from THz-derived complex permittivity.

As a reference, an ideal Fickian uptake is considered. For a homogeneous polymer of thickness $2L$ exposed to a constant moisture environment on both faces, the short-time solution of Fick's second law predicts that the gravimetric uptake increases linearly with $\sqrt{t}$ until $M(t)/M_\infty \approx 0.6$, after which it gradually approaches an equilibrium plateau [35]. However, deviations from this ideal Fickian saturation behavior have been widely reported in epoxy and fiber-reinforced polymer composite systems under prolonged moisture exposure [39, 40], motivating effective-medium frameworks that can accommodate later-stage uptake beyond the short-time Fickian regime.

These observations, together with the limitation of the BW-only two-phase approximation, motivated the extension of the conventional two-phase LLL model to a three-phase LLL model consisting of dry epoxy, BW, and FW. The FW component is assumed to occupy free volume and/or microvoids that develop during long-term immersion. The phase fractions are defined as:

$$F_{\text{dry}} = 1 - F_{\text{BW}} - F_{\text{FW}} \quad (6)$$

$$\begin{cases} \tilde{\epsilon}_{\text{aged}}^{1/3} = F_{\text{dry}} \tilde{\epsilon}_{\text{dry}}^{1/3} + F_{\text{BW}} \tilde{\epsilon}_{\text{BW}}^{1/3} & (t \leq t_c) \\ \tilde{\epsilon}_{\text{aged}}^{1/3} = F_{\text{dry}} \tilde{\epsilon}_{\text{dry}}^{1/3} + F_{\text{BW}} \tilde{\epsilon}_{\text{BW}}^{1/3} + F_{\text{FW}} \tilde{\epsilon}_{\text{FW}}^{1/3} & (t > t_c) \end{cases} \quad (7)$$

$$F_{\text{dry epoxy}} + F_{\text{Water}} = 1$$

Here, t_c is introduced as an operational marker for the early BW-dominant calibration window used in Section 3.4 to estimate the effective BW permittivity. This condition does not imply the physical absence of FW at $t \leq t_c$. In the subsequent three-phase LLL-KWW analysis, $F_{\text{BW}}(t)$ and $F_{\text{FW}}(t)$ are both considered as time-dependent volume fractions that can evolve continuously during immersion.

Because the three-phase LLL model contains both $F_{\text{BW}}(t)$ and $F_{\text{FW}}(t)$ as unknowns at each immersion time, direct extraction of these quantities can lead to non-unique or physically unrealistic solutions. To mitigate this underdetermined inverse problem, KWW-type stretched exponential terms were introduced as phenomenological time-evolution constraints on the effective volume fractions of BW and FW [41,42].

The KWW functions were not used as fundamental diffusion equations or as analytical solutions of Fick's law. Instead, they were used to regularize the time-dependent evolution of the BW and FW fractions in the inverse LLL problem. The KWW model has been widely used to describe non-exponential relaxation phenomena, including non-Debye dielectric relaxation, photoconductive decay, and stress relaxation [43–45]. In this study, it was employed to represent the time-dependent evolution of BW and FW volume fractions. The parameters $F_{\text{BW,max}}$, $F_{\text{FW,max}}$, τ_{BW} , τ_{FW} , β_{BW} , and β_{FW} were optimized independently for the two water states:

$$F_{\text{BW}}(t) = F_{\text{BW,max}} \left[1 - \exp \left\{ - \left(\frac{t}{\tau_{\text{BW}}} \right)^{\beta_{\text{BW}}} \right\} \right] \quad (8)$$

$$F_{\text{FW}}(t) = F_{\text{FW,max}} \left[1 - \exp \left\{ - \left(\frac{t}{\tau_{\text{FW}}} \right)^{\beta_{\text{FW}}} \right\} \right] \quad (9)$$

where, $F_{\text{BW,max}}$ and $F_{\text{FW,max}}$ are the saturation volume fractions of each component, τ is the characteristic time constant, and β is the stretched exponent ($0 < \beta \leq 1$).

To obtain physically meaningful solutions, non-negativity constraints were imposed on the BW and FW volume fractions, and the total water volume fraction was constrained as $F_{\text{FW}} + F_{\text{BW}} \leq 3.5\%$. This upper

bound was derived from the 552 h gravimetric uptake of 3.016 wt%. Using the dry epoxy mass $m_0 = 0.53904$ g, specimen area $A = 2.41098314 \text{ cm}^2$, thickness $d_0 = 0.192$ cm, and water density $\rho_w = 1 \text{ g/cm}^3$, the measured uptake was converted to a total water volume fraction of approximately 0.0351, corresponding to 3.5 vol%. Therefore, the upper-bound condition later written in Eq. (15) uses the apparent near-saturation uptake as a physically constrained upper bound, not as evidence of complete saturation.

The complex permittivities of dry epoxy, BW, and FW were treated as fixed model inputs. The dry-epoxy permittivity was obtained from THz-TDS measurements, the effective BW permittivity was estimated from the early BW-dominant calibration window, and the FW permittivity was calculated using the double-Debye water model. The measured complex permittivity of moisture-absorbed epoxy was used as the fitting target. The adjustable fitting parameters were the KWW-related parameters governing the time-dependent evolution of the BW and FW fractions. These parameters were optimized by minimizing the squared error between the modeled complex permittivity calculated using Eqs. (7)–(9) and the experimentally measured complex permittivity. During the optimization process, physical constraints including non-negativity, monotonic increase, saturation behavior, and an upper bound on the total water volume fraction were imposed to ensure physically meaningful solutions. Through this constrained optimization procedure, the BW and FW volume fractions were estimated as functions of immersion time.

3.3. Physical interpretation of BW and FW in the three-phase model

The BW and FW phases introduced in the three-phase LLL model are physically interpreted as follows. Bound water refers to water molecules that interact with hydrophilic or polar functional groups in the epoxy network through hydrogen bonding or dipole-dipole interactions, whereas free water refers to water that exists in free volume or microvoids of the material in a more bulk-like state [7,31]. These distinct molecular environments can produce distinguishable dielectric responses for BW and FW in the THz/microwave range. Henry et al. showed by dielectric measurements that a clear contrast exists between the loss responses of FW and BW [46]. THz-based studies by Jördens et al. and Lin et al. also treated BW as a state having dielectric parameters distinct from those of bulk/free water [14,28]. In general, FW retains a relatively mobile hydrogen-bond network and therefore exhibits stronger THz absorption, whereas the orientational and vibrational responses of BW are more restricted by water-polymer interactions [14, 28]. In addition to these dielectric contrasts, the temporal evolution of the two water states has also been investigated directly. Liu et al. used time-resolved 2D ATR-FTIR spectroscopy to show that water molecules in cured epoxy first interact with hydrophilic groups and that the contribution of free or cluster-like water gradually increases as immersion proceeds [31]. Therefore, separating BW and FW is important for interpreting the transition from the initial rapid uptake regime to the later non-Fickian regime in epoxy.

3.4. Permittivity of bound water and free water

$$F = \frac{m_{\text{aged}} - m_{\text{dry}}}{\rho A d} \quad (10)$$

$$\tilde{\epsilon}_{\text{BW},t}^{1/3} = \frac{\tilde{\epsilon}_{\text{aged},t}^{1/3} - F_{\text{dry},t} \tilde{\epsilon}_{\text{dry},t}^{1/3}}{F_{\text{BW},t}} \quad (11)$$

$$\tilde{\epsilon}_{\text{BW}} = \frac{1}{3} \sum_{i=1}^3 \tilde{\epsilon}_{\text{BW},i} \quad (12)$$

The effective complex permittivity of bound water was estimated from the first 3 h of immersion, which was used as an early BW-

dominant calibration window. This assumption does not indicate that FW is physically absent at the initial stage. Instead, the 3 h interval was adopted as a practical calibration period because it corresponds to the initial rapid water uptake regime observed in the present gravimetric data, where water–polymer interactions are expected to be relatively dominant [14,28,31].

For this calibration, the volume fraction of absorbed water was calculated from the mass difference between the dry and aged epoxy specimens, the specimen thickness, and the exposed surface area using Eq. (10). The density of water was approximated as 1 g/cm³ for the mass-to-volume conversion. The complex permittivities of the aged and dry epoxy specimens obtained by THz-TDS were then substituted into the two-phase LLL model (Eq. (5)) to estimate the apparent BW permittivity at immersion times of 1, 2, and 3 h using Eq. (11). These three values were averaged to obtain the representative BW permittivity used in the subsequent analysis, as shown in Eq. (12).

In the following three-phase LLL-KWW analysis, this BW permittivity was fixed as an effective calibrated parameter, while the BW and FW volume fractions were treated as time-dependent fitting variables.

For the FW phase, the complex permittivity was calculated using the double-Debye model proposed by Liebe et al. (1991) [47]:

$$\tilde{\epsilon}_{FW}(f) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_1}{1 - i(2\pi f)\tau_1} + \frac{\epsilon_1 - \epsilon_{\infty}}{1 - i(2\pi f)\tau_2} \quad (13)$$

In this calculation, commonly reported parameter values for water at room temperature were used. Here, ϵ_s is the static permittivity, ϵ_{∞} is the optical-limit permittivity, τ_1 and τ_2 are the slow and fast relaxation times, respectively, and ϵ_1 is an intermediate permittivity constant representing the dielectric response in the high-frequency region.

4. Results and analysis

4.1. Time-dependent moisture absorption and THz transmission spectrum

Fig. 3 shows the complex refractive indices of dry epoxy and epoxy aged for 216 h, extracted from the THz-TDS transmission data using Eqs. (1)–(3) as representative cases. The complex refractive index is expressed as $\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$ where $n(\omega)$ and $\kappa(\omega)$ represent the refractive index and extinction coefficient, respectively. These results confirm that moisture ingress induces changes in both the real and imaginary components of the complex refractive index, thereby providing the optical basis for the subsequent analyses of time-dependent THz transmission, complex permittivity, and LLL-based moisture quantification.

The evolution of water uptake, specimen thickness, and THz transmission as functions of immersion time is presented in Fig. 4. The total water uptake was calculated as the weight gain (wt%), defined as:

$$\text{wt\%} = 100 \times \frac{m_{\text{aged}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (14)$$

where m_{aged} is the mass of the epoxy specimen after immersion and m_{dry} is the mass of the specimen in the initial dry state.

Fig. 4(b) shows the gravimetric water uptake with error bars representing the standard deviation of repeated measurements. In the initial uptake regime, $\sqrt{t} = 0\text{--}3.87\sqrt{h}$, corresponding to approximately 0–15 h, the uptake increased almost linearly with $\sqrt{t}$, consistent with the short-time Fickian sheet-geometry solution [35]. Beyond this initial Fickian-like regime, the DGEBA/TETA epoxy under the present 75 °C immersion condition continued to absorb water, reaching 3.016 wt% at 552 h without a clear saturation plateau. This behavior is consistent with prolonged uptake beyond the short-time Fickian regime. Therefore, the measured value was treated as an apparent upper-bound uptake level at 552 h under the present accelerated immersion condition, rather than as a true equilibrium saturation state. This apparent near-saturation level was used to define the upper constraint for the total water volume

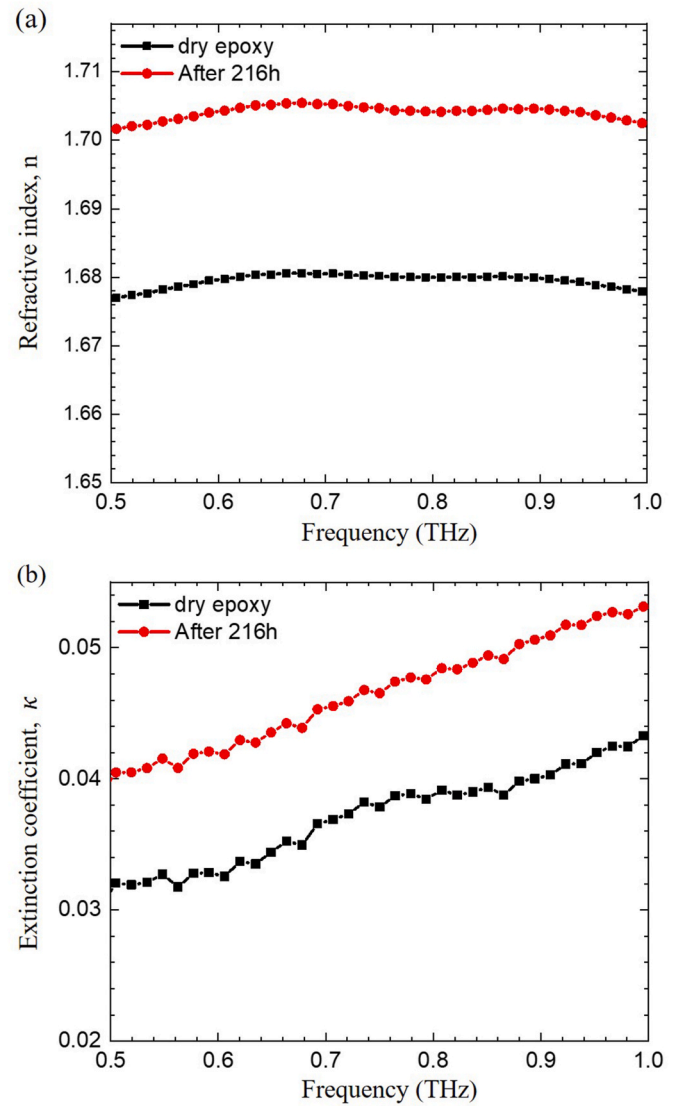


Fig. 3. (a) Refractive index and (b) extinction coefficient of dry epoxy and epoxy aged for 216 h in the terahertz frequency range.

fraction in Eq. (15), as described in Section 3.2. In addition, the relative variability of the repeated thickness measurements was less than 0.06%, and a sensitivity analysis showed that the resulting uncertainty in the extracted real permittivity was below approximately 0.05%.

The THz transmission spectra, normalized to the air reference and shown in Fig. 4(c), decrease across the entire frequency range as immersion time increases. This trend indicates enhanced THz-band absorption due to water uptake in the epoxy [10,28,46].

The complex permittivity of the epoxy as a function of immersion time is shown in Fig. 5. Both the real part, $\epsilon'(f)$, and the imaginary part, $\epsilon''(f)$, increase with immersion time. In particular, the increase in $\epsilon''(f)$ reflects the growth of dielectric loss associated with the strong THz absorption of water molecules, which is consistent with the decreasing transmission observed in Fig. 4(c). In addition, $\epsilon'(f)$ exhibits a systematic increase across the entire frequency range as immersion time increases, indicating the progressive accumulation of moisture-induced dielectric changes within the epoxy.

4.2. Model fitting results: two-phase vs three-phase LLL-KWW

Fig. 6 compares the conventional two-phase LLL model consisting of dry epoxy and BW with the proposed three-phase LLL-KWW model

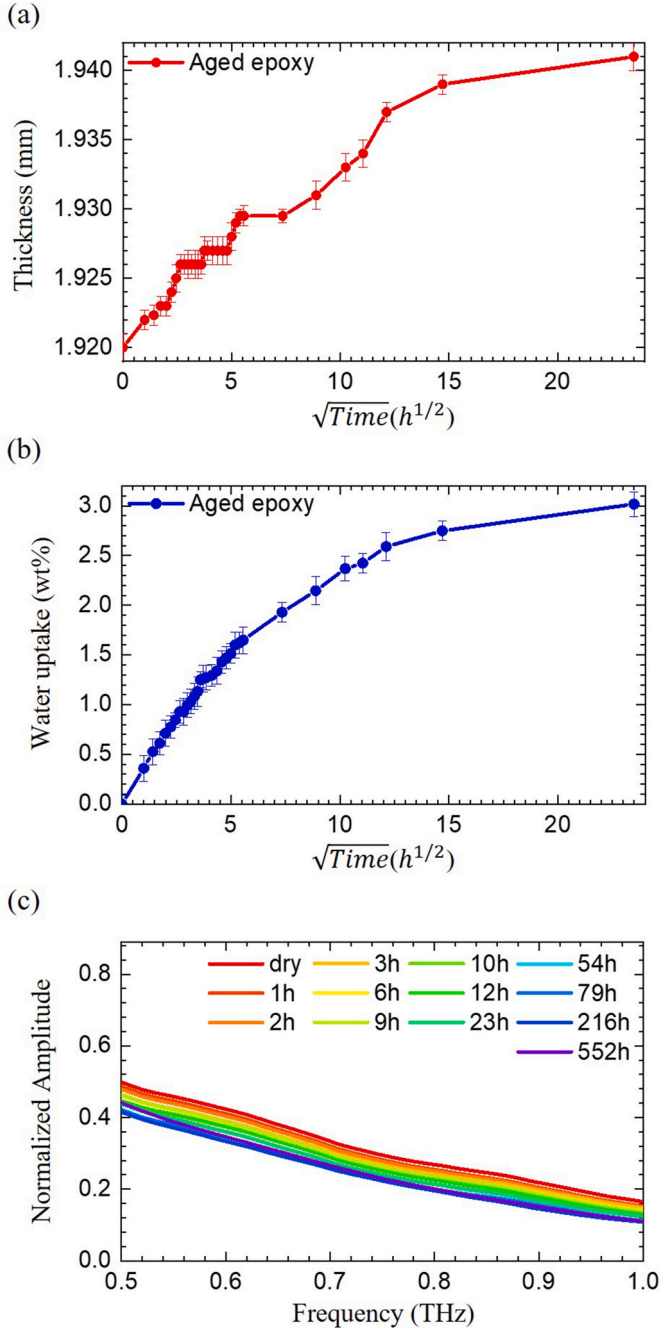


Fig. 4. Changes in water uptake and THz transmission characteristics as a function of immersion time: (a) change in epoxy thickness with immersion time; (b) total water uptake (wt%) measured by the gravimetric method; and (c) THz transmission spectra normalized to the air reference.

consisting of dry epoxy, BW, and FW, using THz-TDS data. A representative fitting frequency of 0.85 THz was used in this analysis. The rationale for selecting this frequency and the corresponding frequency-sensitivity check are discussed together with Fig. 7 in the subsequent cross-frequency validation.

First, the two-phase LLL model (Eq. (5)), which assumes that all absorbed moisture exists as BW, was applied. The volume fraction of BW (F_{BW}) was calculated by substituting the complex permittivities of the aged and dry epoxy obtained from THz-TDS, along with the bound water permittivity estimated from the initial absorption stage, into Eq. (5). The corresponding absorbed water mass was then calculated using Eq. (10). The result, shown as the blue curve in Fig. 6(a), agrees well with

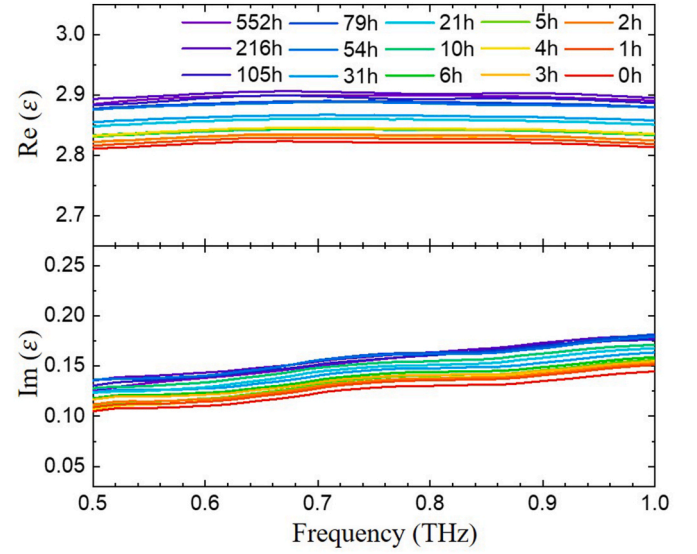


Fig. 5. Frequency-domain spectra of the complex permittivity of immersed epoxy: real part, $\epsilon'(f)$, and imaginary part, $\epsilon''(f)$, as functions of immersion time.

gravimetric measurements during the early stage of immersion. However, the discrepancy increases with immersion time, indicating that the two-phase model fails to account for the growing contribution of free water (FW) during prolonged immersion.

To address this limitation, a three-phase LLL model incorporating a FW component (Eq. (7)) was adopted. The time-dependent BW and FW volume fractions were constrained by the KWW model (Eqs. (8) and (9)) and by the upper-bound condition $F_{FW} + F_{BW} \leq 3.5\%$ (Eq. (15)), derived in Section 3.2 from the apparent upper-bound uptake level at 552 h. The final three-phase LLL-KWW fitting expression is therefore given as follows.

$$F_{BW} + F_{FW} \leq 3.5\% \quad (15)$$

$$\begin{aligned} \tilde{\epsilon}_{\text{aged}}^{1/3} = & F_{\text{dry}} \tilde{\epsilon}_{\text{dry}}^{1/3} + F_{\text{BW,max}} \left(1 - e^{-(t/\tau_{\text{BW}})^{\beta_{\text{BW}}}} \right) \tilde{\epsilon}_{\text{BW}}^{1/3} \\ & + F_{\text{FW,max}} \left(1 - e^{-(t/\tau_{\text{FW}})^{\beta_{\text{FW}}}} \right) \tilde{\epsilon}_{\text{FW}}^{1/3} \end{aligned} \quad (16)$$

As shown by the red curve in Fig. 6(a), the three-phase LLL-KWW model agrees closely with the gravimetric value over the entire immersion period. Although the three-phase model contains more adjustable parameters than the two-phase model, its improvement is most pronounced in the high-uptake regime, where the two-phase model exhibits large deviations from the gravimetric value, whereas the three-phase model remains consistent with it. The fitting results of the three-phase LLL-KWW model also show good agreement with the measured complex permittivity, as illustrated in Fig. 6(b), with mean errors of 0.41% and 4.21% for the real and imaginary parts, respectively.

To evaluate the physical plausibility of the three-phase LLL-KWW fitting results, the optimized saturation fractions of BW and FW were compared with the gravimetric value and previously reported literature values. The fitted saturation volume fractions were $F_{\text{BW,max}} \approx 0.7\%$, $F_{\text{FW,max}} \approx 2.7\%$, giving a total water volume fraction of approximately 3.4%. When converted into specimen-based water mass fractions, these values correspond to approximately 0.62 wt% for BW, 2.38 wt% for FW, and 3.00 wt% for total uptake, which is in good agreement with the gravimetric value. The model-estimated total uptake (~ 3.0 wt%) is within the uptake range reported for epoxy systems under elevated-temperature water immersion [8,30], and the estimated FW contribution (~ 2.38 wt%) is consistent with previously reported free-like water uptake of approximately 2–3 wt% in epoxy systems [30]. At 552 h, the gravimetric value was 16.26 mg. The three-phase LLL-KWW model predicted a total water mass of 16.18 mg at 0.85 THz, whereas the

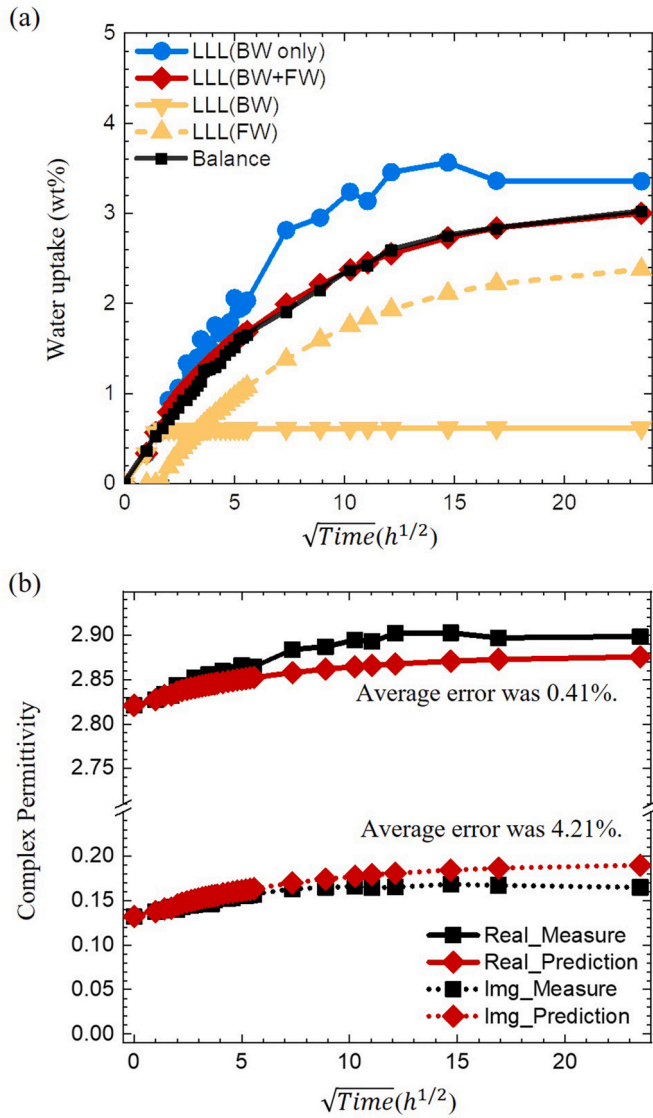


Fig. 6. (a) Comparison of water uptake predicted by the two-phase (dry epoxy + BW, blue line) and three-phase (dry epoxy + BW + FW, red line) LLL-KWW models at 0.85 THz, together with gravimetric measurements (black dots). The yellow solid and dashed lines represent the individual contributions of BW and FW, respectively. (b) Complex permittivity of the immersed epoxy at selected immersion times. Solid and dashed lines denote ϵ' and ϵ'' , respectively. Black and red curves correspond to THz-TDS measurements and three-phase LLL-KWW model fits.

conventional BW-only LLL model predicted 18.10 mg. This comparison indicates that explicitly incorporating the FW contribution improves not only the dielectric fitting but also the gravimetric-equivalent estimation accuracy of the absorbed water mass. However, because the BW/FW decomposition is obtained through a constrained inverse fitting procedure, the separated BW and FW fractions should be interpreted as model-based estimates rather than directly measured fractions. A similar interpretive consideration applies to the fitted KWW exponent β , which is regarded as a phenomenological parameter describing the breadth of the time-scale distribution involved in the accumulation of BW or FW. When $\beta = 1$, the corresponding process follows single-exponential saturation, whereas $\beta < 1$ indicates non-single-exponential uptake behavior with a broader distribution of time scales. Therefore, fitted values of $\beta < 1$ should be interpreted not as direct measurements of specific microstructural features, but as effective parameters indicating that water uptake in the epoxy network involves a broad distribution of

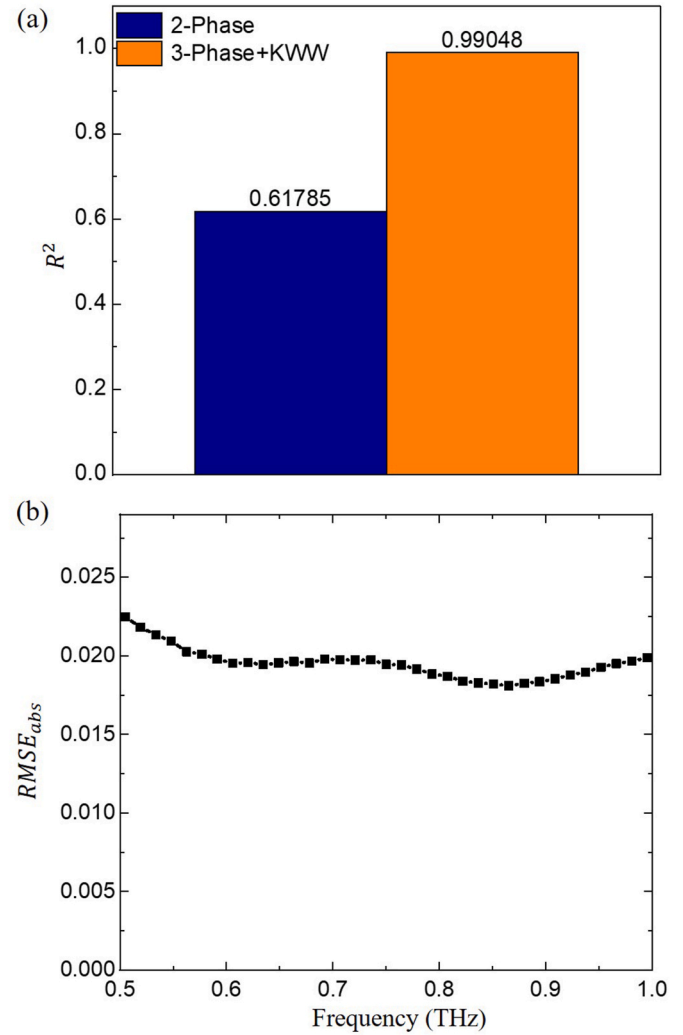


Fig. 7. (a) Comparison of fitting performance between the two-phase (BW-only) and three-phase (BW + FW) LLL models based on R^2 . (b) Absolute root mean square error ($RMSE_{abs}$) of the complex permittivity when volume fractions fitted at 0.85 THz are applied across the full frequency range (0.85 THz: 0.48%; full band: <1%).

time scales.

Because the three-phase model contains more adjustable parameters than the two-phase model, a simple R^2 comparison alone cannot be used as decisive evidence of model validity. We therefore primarily assess the models by their consistency with the gravimetric value (Fig. 6(a)) and with the measured complex permittivity (Fig. 6(b)), and present the R^2 values in Fig. 7(a) only as supplementary information. As shown in Fig. 7(a), the R^2 values evaluated at 0.85 THz are higher for the three-phase model than for the two-phase model, consistent with the gravimetric-value comparison in Fig. 6(a), in which the deviation of the two-phase model from the gravimetric value grows markedly in the high-uptake (long-term immersion) regime while the three-phase model remains consistent with it across the entire immersion period.

To further assess model performance, the absolute root mean square error ($RMSE_{abs}$) was evaluated as:

$$RMSE_{abs} = \sqrt{\frac{1}{N} \sum_{t=1}^N |\tilde{\epsilon}_{\text{model},t} - \tilde{\epsilon}_{\text{meas},t}|^2} \quad (17)$$

where $\tilde{\epsilon}_{\text{model},t}$ and $\tilde{\epsilon}_{\text{meas},t}$ denote the modeled and measured permittivities, respectively, at immersion time t . The error was computed over all

measurement time points.

Here, $RMSE_{abs}$ does not have a separate physical unit because it is calculated from the real and imaginary parts of the relative complex permittivity. This RMSE-based analysis was further used to examine whether the fitting results were dependent on the selected representative frequency.

In this study, the BW and FW volume fractions were determined by fitting the three-phase LLL-KWW model at the representative frequency of 0.85 THz. This frequency was selected because it lies within a spectrally stable region of the THz-TDS setup and provides a favorable balance between measurement stability and moisture-induced dielectric sensitivity. In contrast, higher-frequency regions can make stable analysis more difficult because of stronger water absorption and reduced spectral stability.

To evaluate the sensitivity of the model results to this frequency selection, the same fitting procedure was additionally performed at 0.65 and 1.10 THz, alongside the reference frequency of 0.85 THz. The total water masses estimated at these three frequencies were 15.90, 16.18, and 16.23 mg, corresponding to approximately 2.95, 3.00, and 3.01 wt %, respectively. These values are in close agreement with the gravimetric value of 16.26 mg, or 3.016 wt%. This indicates that the estimated values obtained in this study are not strongly dependent on a single selected frequency. To further verify that the BW and FW volume fractions obtained at 0.85 THz are not specific to that frequency, the same optimized fractions were substituted into Eq. (7), together with the frequency-dependent permittivities of BW, FW, and dry epoxy, to calculate the predicted permittivity over the entire measured frequency range. The predicted values were then compared with the measured permittivity of aged epoxy at each frequency. As shown in Fig. 7(b), the RMSE at 0.85 THz is approximately 0.018, corresponding to an error of 0.48% relative to the measured permittivity. Across the entire measured frequency range, the error remains below 1%. These results confirm that the volume fractions obtained at 0.85 THz are not limited to a specific frequency but are broadly applicable over the measured frequency range. This demonstrates that the proposed three-phase LLL-KWW model can reliably predict moisture-induced dielectric and gravimetric changes using a single set of volume-fraction parameters.

5. Conclusion

Prolonged water uptake in epoxy resins induces plasticization and degradation of material properties, while cumulative changes in the internal structure can lead to non-Fickian absorption behavior. In this study, the complex permittivity of epoxy was extracted using non-contact, non-destructive terahertz time-domain spectroscopy (THz-TDS), and the moisture absorption behavior of water-immersed epoxy was quantitatively analyzed using a coupled framework that combines a three-phase Landau-Lifshitz-Looyenga (LLL) dielectric mixing model with a Kohlrausch-Williams-Watts (KWW) kinetic model.

The proposed three-phase LLL-KWW model enables estimation of the volume fractions and masses of BW and FW. The model shows substantially improved accuracy compared with the conventional two-phase (BW-only) model for both measured water uptake and complex permittivity, particularly in the high-uptake, long-term immersion regime where prediction errors increase in the conventional two-phase model. The extracted BW/FW evolution also provides an improved interpretation of non-Fickian behavior that cannot be captured by the conventional model. This improvement arises from two complementary aspects of the framework: the explicit inclusion of the free-water component, which becomes increasingly important during long-term immersion, and the application of KWW-based constraints to the temporal evolution of the BW/FW volume fractions. By combining these two elements, the framework enables nonlinear moisture absorption behavior to be analyzed within a single model.

However, because the BW/FW decomposition is derived from a constrained inverse model, the separated BW and FW values should be

interpreted as model-based estimates rather than directly measured quantities. To improve the applicability of the proposed THz-TDS-based approach, the model-based BW/FW decomposition should be further validated using independent techniques such as DSC, NMR, or FTIR, which can provide complementary information on freezable water, water mobility, and hydrogen-bonding states. Future work should include desorption tests, longer-term aging, temperature-dependent THz-TDS measurements, and validation under various specimen and environmental conditions to evaluate reversibility, hysteresis, condition-dependent variability, and the Arrhenius-type behavior of the KWW time constants. Although the present experiment was conducted using an ex-situ immersion protocol, the proposed THz-based approach could be extended in future work to practical on-site or spatially resolved moisture inspection, since localized water uptake in epoxy-containing structures is expected to modify the local THz transmission or reflection response. Such extension may allow the proposed THz-TDS-based moisture diagnostic technique to serve as a condition-based monitoring tool and contribute to improved maintenance strategies and lifetime management.

CRediT authorship contribution statement

Hun Choi: Conceptualization, Data curation, Investigation, Methodology, Writing – original draft. **Yong Hwa Son:** Data curation, Investigation, Methodology. **Seunghwa Yang:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Geunchang Choi:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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