

Review

Water in Epoxy Coatings: Basic Principles of Interaction with Polymer Matrix and the Influence on Coating Life Cycle

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Abstract: This review describes the interaction of epoxy coatings with water, the kinetics of water uptake in epoxy resins, and the methods of studying the latter (gravimetric, IR (Infrared) and NMR (Nuclear magnetic resonance) spectroscopies). The analysis of experimental data requires using mathematical models which simulate the processes that occur during water uptake in a polymer matrix. This review classifies the numerous models applied for the study of water absorption into two large groups: Fickian and non-Fickian models. Fickian models involve the Fickian diffusion model and its development for the case of anomalous diffusion, as well as the models of Jacobs–Jones, Berens–Hopfenberg, and the time-varying diffusion coefficient model. The Carter–Kibler approach is provided as an example of a non-Fickian or Langmuir-type model. A critical analysis of the experimental methods is provided, including advantages and possible experimental errors. The methods used for processing experimental data are discussed as well as the effect of water on the exploitation properties and life cycle of epoxy coatings.

Keywords: epoxy coatings; water uptake; kinetic study; water state; coating performance; life cycle



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1. Introduction

Polymer coatings are widely used as the most accessible tool to protect metal and wood. Water on Earth ensures the existence of life on Earth; on the other hand, it is one of the main sources that destroy objects produced by humankind. The infusion of water stimulates corrosion processes in the materials underlying protective coatings. In polar regions, it can result in the destruction of coatings and coated materials as a result of multiple freeze–thaw cycles.

In this study, water is considered a complex liquid. The polarity of its molecules in combination with the possibility of a hydrogen bond network being formed results in a multilevel structure of liquid water. Such structures may persist during the infusion of water into the polymer matrix, which influences the diffusion processes and the infiltrate in the polymer bulk. Hence, the study of water infusion in coatings requires a multimethod approach using modeling and spectroscopic structural analysis.

Epoxy resins, with their network structure and excellent mechanical performance, high barrier properties, and thermal and chemical stability, are widely used as coatings and matrices for composite materials. Their high rigidity leads to their fragility and void formation during their preparation, which largely affects their water permeation.

The aim of most studies in this field is to examine the water permeation of common epoxy-based coatings across a range of commercially relevant temperatures (from room temperature to +80 °C). Water absorption can induce damage to the epoxy network, induce distinctive cavity formation in the coating films, and increase the aggregative porosity of the coatings. Hence, the analysis of the processes of water uptake is crucial for protecting

transport pipelines, tanks, industrial constructions, and other objects. Vapor transport analysis in a broad range of temperatures from deep freezing to high sunshine is important for epoxy composites used in the aircraft industry because any damage to an aircraft is crucial. Other important engineering plastics are polyamides 6 and 6.6, which are widely used as materials for bearings, shafts, and other construction elements in the ship-building industry. The high uptake of water by these plastics and its influence on the performance characteristics of products is a topic that is not directly related to this review and would be the subject of another research. However, the main methods of studying water absorption appear to be common for all plastics and are referred to in the papers discussed.

The study of water uptake to epoxies has a long history [1]. The performance of epoxy coatings during moisture absorption has been described to decrease as a result of swelling [2], the fluctuation of bulk mechanical properties [3], the plasticization effect [4], the chemical destruction of the epoxy matrix [5], and other factors. In this study, these changes are considered to involve both experimental [6] and molecular simulation [7] methods. The complexity of this task requires new insights to advance the molecular-level understanding of the water interaction with the epoxy matrix and justifies the need for new strategies, including 2D IR spectroscopy [8] and solid-state NMR using multi-quantum filter techniques [9]. Methods based on electrochemical noise measurement have been shown to be promising as reliable quantitative indicators of corrosion [10–13].

This review includes the following sections: the experimental methods used for studying the water uptake of epoxy resins, the kinetics of this process, the water state in the epoxy matrix, the influence of water absorption on the material properties of epoxy coatings, and the molecular origin of these changes.

2. Methods for Studying Water Uptake

2.1. Gravimetric Analysis

Gravimetric analysis is one of the most popular methods used to characterize water absorption in polymers and polymer composites [14–16]. Rectangular samples (10 mm wide, 10 mm long, and 1 mm thick) are immersed in distilled water at room temperature or higher. Water absorption is monitored as a function of the immersion time. The samples are regularly removed from the liquid and wiped with filter paper to measure the water uptake. The change in the water content, M_t (%), is calculated using Equation (1):

$$M_t = \frac{w_t - w_d}{w_d} \times 100 \quad (1)$$

where w_t is the weight of the sample immersed in water at the time t , and w_d is the weight of the dry sample.

The resulting diffusion plots normally represent curves with an oblique linear initial portion and a subsequent horizontal representation of the equilibrium statement. On the other hand, the immersion time is a very important parameter that affects the type of curve that is produced. Often, researchers have achieved pseudo-equilibrium due to the measurement time not being long enough.

In many cases, the nature of water absorption at the initial stages is consistent with Fick's law, since the absorption of water molecules in the volume occurs due to their penetration into the free volume of the polymer network. Further absorption is usually related to hydrogen bond formation, polymer network degradation, segmental relaxation, swelling, and many other negative factors. Therefore, a gradual increase in water content after reaching a pseudo-equilibrium state is typical for long-term tests [17–25].

The diffusion plots are easy to calculate and refer to, and thus can fit various mathematical models. These models make it possible to define the water diffusion coefficient and some other diffusion parameters. There are multiple mathematical models, and they have different solutions for calculating the kinetic parameters of water absorption [14,26–28].

Today, commercial epoxy coatings are very complex polymer systems containing many components including an epoxy binder, hardener, fillers, anti-corrosion pigments,

solvents, reactive diluents, plasticizers, dispersants, coupling agents, thixotropic additives, and other substances of various nature. The behaviors of these compositions under water diffusion will vary depending on the morphology, structure, crosslink density, and free volume of each polymer system [29,30]. Thus, the behavior of diffusion can be described by any of the two large groups of models: Fickian and non-Fickian models.

2.1.1. Fickian Diffusion Model

The Fickian diffusion model is a straightforward approach to evaluate the water absorption of epoxy compositions [15,16,31–33]. Fick's law describes the transfer of water into a polymer by diffusion only without considering intermolecular interactions and/or changes in the topology of the polymer network. In a one-dimensional system with a substance concentration gradient dC/dx in the x direction, the rate of change in the substance concentration at a given point is a function of diffusion, and it is determined by Fick's second law (Equation (2)):

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \quad (2)$$

Equation (2) can be presented for a three-dimensional system:

$$\frac{dC}{dt} = D_x \frac{d^2C}{dx^2} + D_y \frac{d^2C}{dy^2} + D_z \frac{d^2C}{dz^2} \quad (3)$$

where C is the concentration of the diffused substance; D , D_x , D_y , and D_z are the diffusion coefficients; and x , y , and z are the diffusion directions.

Fick's second law has more than one analytical solution, but the most common equation is given by Crank [16,27,34–36]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{l^2}\right) \quad (4)$$

where M_t is the water absorption at time t , M_∞ is the equilibrium water absorption, n is an integer representing the number of terms in the series, l is the sample thickness, and t is the diffusion time.

An analytical simplification of Equation (4) for a short exposure time takes the following form for $M_t/M_\infty < 0.5$:

$$\frac{M_t}{M_\infty} = \frac{4}{l} \sqrt{\frac{Dt}{\pi}} \quad (5)$$

and for $M_t/M_\infty > 0.5$, it takes the following form:

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-7.3 \left(\frac{Dt}{l^2}\right)^{0.75}\right] \quad (6)$$

The Fickian behavior of water diffusion in cured epoxy resin is only typical for its early stages. However, many epoxy compositions exhibit behaviors that tend to deviate from Fick's law after a long-term immersion [6,17,35,37]. The movement of water molecules into the polymer depends not only on the penetration of water into the free volume, but also on the complexity of the intermolecular interactions between the polymer network and the water. Polar groups in the structure, the crosslink density, free volume, and the results of the water–polymer interactions (including segmental relaxation, plasticization, swelling, and the destruction of the macromolecular structure) make it impossible to completely describe the diffusion process using Fick's law [24,38,39].

2.1.2. Non-Fickian (Anomalous) Diffusion Models

Polar functional groups in cured epoxy resins and the relaxation processes resulting from the interaction with water molecules is the cause of an eventual deviation from the

classical Fick's law. There has been ample research to achieve a deeper understanding of the water absorption process in epoxy materials and to propose more efficient models. As a result, the following four models were proposed for anomalous diffusion in epoxies: two-phase polymer dual-diffusivity model (Jacobs–Jones model) [14,40], coupled diffusion–relaxation model (Berens–Hopfenberg model) [41], time-varying diffusion coefficient model [42,43], and “Langmuir-type” model (Carter–Kibler model) [44]. They include some additional factors: bound and unbound phases of water; phases with different structures of macromolecules formed within polymers; relaxation effects due to swelling; and variability of diffusion coefficients over time, to name a few. All of these models rely on experimental observations to determine their parameters and coefficients. This paper focuses on the four above-mentioned models and does not regard those used for describing nano- and reinforced composites (for example, the hindered diffusion model [28,45], barrier models [46,47], and the model proposed by Shen and Springer [48]).

Jacobs–Jones Model (Two-Phase Polymer Dual-Diffusivity Model)

The Jacobs–Jones model assumes that a polymer has a two-phase structure, including highly crosslinked and low crosslinked regions. The first stage of water absorption is suggested to correspond to the rapid absorption of water. In this case, the diffusion of molecules occurs both in the highly crosslinked phase and in the low crosslinked one. Further, the diffusion process slows down due to water absorption only into the highly crosslinked phase. Both stages follow Fick's law, and the resulting equation is as follows [14,40]:

$$\frac{M_t}{M_\infty} = V_d \left\{ 1 - \exp \left[-7.3 \left(\frac{D_d t}{l^2} \right)^{0.75} \right] \right\} + (1 - V_d) \left\{ 1 - \exp \left[-7.3 \left(\frac{D_l t}{l^2} \right)^{0.75} \right] \right\} \quad (7)$$

where D is the diffusion coefficient of the dense (highly crosslinked) phase, D_l is the diffusion coefficient of the less dense (low crosslinked) phase, and V_d is the volume fraction of the highly crosslinked phase. This model neglects the interaction between the water and the polymer network.

Maggana and Pissis [14] suggested a modified Jacobs–Jones model. The main difference is the final interpretation of the two phases above. Thus, there is the main (the first) phase, in which most of the water is absorbed, and the second phase with a different density and/or hydrophilic characteristics.

Berens–Hopfenberg Model (Coupled Diffusion–Relaxation Model)

The Behrens–Hopfenberg model is based on the relaxation phenomena resulting from the polymer swelling during the diffusion. The diffusion of water in a glassy polymer is facilitated by Fickian diffusion and relaxation changes in the polymer network occurring with the free volume changes [41,49]. Thus, the main equation of the model can be expressed as follows (Equation (8)):

$$M_t = M_F + M_R = M_{\infty F} \left(1 - \exp \left[-7.3 \left(\frac{D_d t}{l^2} \right)^{0.75} \right] \right) + M_{\infty R} \left(1 - \exp(-kt^2) \right), \quad (8)$$

where M_F is the amount of absorbed water, related to the Fickian diffusion process, M_R is the amount of absorbed water, related to relaxation, $M_{\infty F}$ is the water saturation value disregarding any stress relaxation, $M_{\infty R}$ is the water saturation value related to the relaxation effect, and k is a constant related to the relaxation rate of the polymer.

Research on absorption in polymers has revealed that the rate-controlling process depends on the size of the penetrant [41]. When the absorption starts rapidly but slows down at the later stages, the diffusion outpaces the relaxation. However, if these processes operate simultaneously, it becomes challenging to differentiate them based on the absorption curve.

Time-Varying Diffusion Coefficient Model

A one-dimensional time-varying diffusion coefficient model is a modified Fickian model (Equation (2)) interpreting the diffusion coefficient as a time-dependent function. Weistman [42] suggested the following equation for a diffusion model with a time-varying diffusivity:

$$\frac{\partial C}{\partial t} = D_0 \exp\left[-\frac{B}{\theta(t)}\right] \frac{\partial^2 C}{\partial x^2} \quad (9)$$

where D_0 and B are material constants and $\theta(t)$ is the absolute temperature.

According to Roy et al. [43], moisture uptake can be expressed by Equation (10):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\frac{(2n+1)^2 \pi^2}{l^2} \times \left[D_0 t + \sum_{r=1}^R D_r \left[t + \tau_r \left(e^{-\frac{t}{\tau_r}} - 1\right)\right]\right]\right\} \quad (10)$$

The main parameters, M_∞ , D_0 , D_r , and τ_r , are determined by fitting Equation (10) to the experimental data.

This model is often used for water diffusion in epoxy composites and adhesives [34,42,43,47,50–53]. Despite obtaining good approximation results for composites and adhesives, the model with a time-varying diffusion coefficient has been rarely found to describe the water absorption process in epoxy coatings.

Carter–Kibler Model (“Langmuir-Type” Model)

The Langmuir model and its modifications consider chemical interactions between water molecules and polar groups of the epoxy polymer in contrast to the above-mentioned models. The Langmuir-type model assumes that there are two states of absorbed water molecules: bound and free. According to the model, the state of water molecules at any time and in any place in the polymer unit may regularly change from bound to free (this can happen with probability β) and from free to bound (with probability γ). The coefficients β and γ are also referred to as the desorption and absorption coefficients, respectively. The Langmuir equation for the one-dimensional case has the following form [33,54–57]:

$$\frac{dC_f}{dt} + \frac{dC_b}{dt} = D \frac{d^2 C}{dx^2} \quad (11)$$

$$\frac{dC_b}{dt} = \gamma C_f - \beta C_b \quad (12)$$

$$\gamma C_{f\infty} = \beta C_{b\infty} \quad (13)$$

where C_f and $C_{f\infty}$ are the concentration of «free» water and its maximum concentration, respectively, and C_b and $C_{b\infty}$ are the concentration of «bound» water and its maximum concentration, respectively.

Carter and Kibler [44] derived Equation (14) for calculating water absorption:

$$\frac{M_t}{M_\infty} = \left\{ 1 - \frac{8}{\pi^2} \sum_{i=1}^{\infty} \frac{r_i^+ \exp(-r_i^- t) - r_i^- \exp(-r_i^+ t)}{i^2 (r_i^+ - r_i^-)} + \frac{8}{\pi^2} \left(\kappa \frac{\beta}{\beta + \gamma} \right) \sum_{i=1}^{\infty} \frac{\exp(-r_i^- t) - \exp(-r_i^+ t)}{(r_i^+ - r_i^-)} \right\} \quad (14)$$

$$r_i^\pm = \frac{1}{2} \left[(\kappa i^2 + \gamma + \beta) \pm \sqrt{(\kappa i^2 + \gamma + \beta)^2 - 4\kappa\beta i^2} \right] \quad (15)$$

$$\kappa = D_\gamma \left(\frac{\pi}{l} \right)^2 \quad (16)$$

These equations can be simplified for ease of calculation:

$$\frac{M_t}{M_\infty} = \frac{\beta}{\gamma + \beta} e^{-\gamma t} y(t) + (1 - e^{-\beta t}) + \frac{\beta}{\gamma + \beta} (e^{-\beta t} - e^{-\gamma t}) \quad (17)$$

$$y(t) = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-(2n+1)^2 \kappa t \right] \quad (18)$$

A typical water absorption curve can be presented as the sum of free (unbound) and bound water (Figure 1). There are normally two stages of absorption—the first one (characteristic of unbound absorption) and the second one (characteristic of bound absorption).

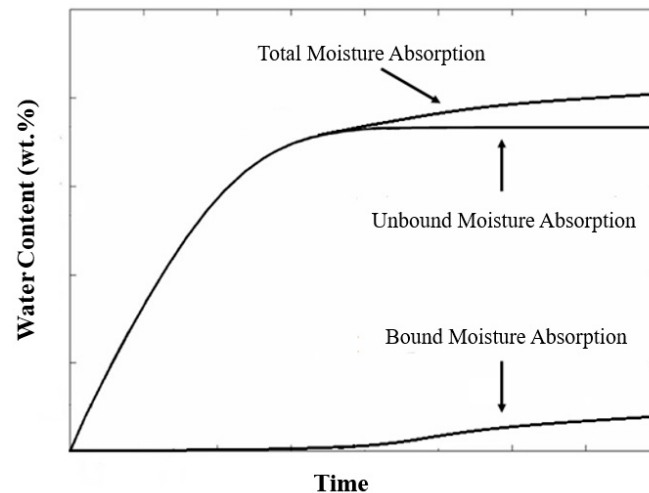


Figure 1. Typical curve for Langmuir-type model.

The absorption coefficient γ and the desorption coefficient β are very important parameters of the Carter–Kibler model. Scott and Lees [55] reported some difficulties in selecting the method for calculating these parameters and compared a number of methods used to estimate the coefficients β and γ . The authors chose a simplex algorithm to evaluate the non-linear regression corresponding to the experimental data.

The Langmuir-type model showed the greatest efficiency among those described for non-Fickian diffusion in epoxy coatings [9,26,34,37,39,51,54–59]. For example, Glaskova et al. [51] quantified the performance of a number of the above models for a selected commercial epoxy resin and found that Langmuir-type and relaxation models provide results that have adequate agreement with the experimental data. Other researchers [55,58,59] also showed that Langmuir-type models provide highly convergent results and can properly predict a further increase in mass from a set of obtained experimental data.

On the other hand, a good approximation of the data does not always confirm the validity of the model. Two models with different permissible physical justifications may equally approximate the same water absorption data. Therefore, the true applicability of the model has to be confirmed by other control tests (e.g., absorption–desorption test and elevated temperatures) or by studying water absorption using spectral analysis methods.

Using gravimetric measurements without any comparison with other methods (e.g., IR or NMR) may also lead to an interpretation error. Unfortunately, gravimetric analysis does not allow for the study of the diffusion mechanism, the relaxation behavior, and the interactions between the penetrant and the polymer. Nevertheless, the absorption kinetics obtained by gravimetric analysis is essential for studying the water absorption of epoxy compositions.

2.2. Infrared Spectroscopy (IR)

Another widely used method is infrared (IR) spectroscopy in the middle and near-infrared ranges [19,31,60–69]. FTIR spectroscopy has been successfully used to investigate water diffusion in a thermoset and, in particular, in epoxy materials. In contrast to gravimetric analysis, it is not only possible to observe the concentration dependencies of water

molecules in the polymer volume, but also to determine the interaction of the penetrant and the polymer network at a molecular level.

The equipment available today contributes to a more accurate investigation of the diffusion processes in polymer systems compared to the facilities that existed 30–40 years ago. For example, the development of in situ measurement technology has improved the accuracy of analyzing the changes in polymer systems during moisture absorption. Measurements are performed in real time with continuous spectrum removal using special tooling or techniques (in situ time-resolved spectroscopy, difference spectroscopy, or 2D correlation spectroscopy). Many studies are performed using FTIR-ATR (attenuated total reflectance) spectroscopy. This technique is often criticized due to a number of drawbacks: insufficient contact between the specimen and the crystal; a more complex relationship between absorbance and water concentration compared to transmission; and the “skin effect” and multilayer structures in thin films that make interpreting the resulting data difficult [20]. However, the influence of these factors is negligible. The most common research approach is to collect spectra in the middle range ($4000\text{--}400\text{ cm}^{-1}$) of dry and wet samples at different time intervals [8,70–72]. The further quantitative analysis is performed by the deconvolution of the spectra in the ranges of $3700\text{--}3100\text{ cm}^{-1}$ (stretching vibrations of hydroxyl groups) and of $1700\text{--}1600\text{ cm}^{-1}$ (deformation vibrations of hydroxyl groups). These ranges contain information about both intermolecular and intramolecular hydrogen bonding. The region from 3700 to 3100 cm^{-1} is more intense and contains more information about the hydrogen bonds, while that of $1700\text{--}1600\text{ cm}^{-1}$ is less informative due to the overlapping with other functional groups and low signal intensity [9,60,66].

According to the research [9,15,60,66,73,74], the intensity of the bands corresponding to OH-group vibrations increases, and the peak broadens with the increasing diffusion time. The selected region has a single overlapping broad peak that cannot be used in diffusion studies without some additional processing. Therefore, according to the results of deconvolution, it is customary to distinguish the following ranges: $3800\text{--}3500\text{ cm}^{-1}$ (S_0 , free/mobile water molecules), $3600\text{--}3400\text{ cm}^{-1}$ (S_{1L} , water molecules bound by weak hydrogen bonds), $3500\text{--}3200\text{ cm}^{-1}$ (S_{2L} , moderately bound water molecules), and $3300\text{--}3100\text{ cm}^{-1}$ (S_{2T} , strongly bound water molecules) [9,15,60,62,63,66,71,75]. Figure 2 illustrates the possible deconvolution peaks.

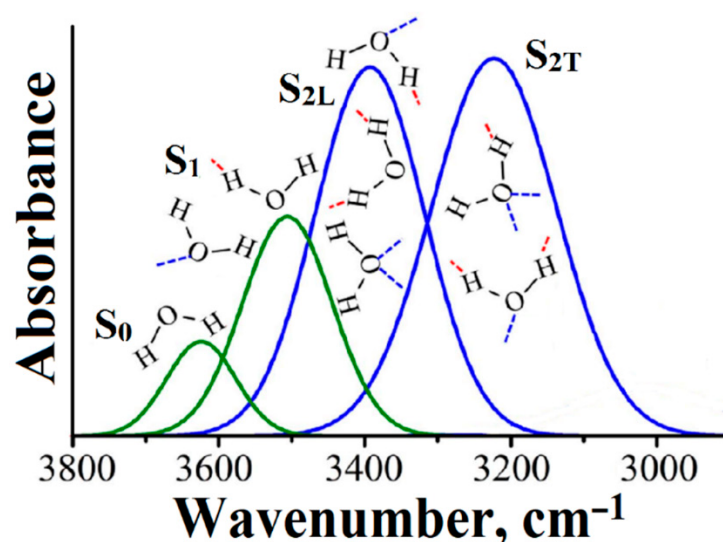


Figure 2. Band deconvolution corresponding to OH-group vibrations in the range of $3800\text{--}3000\text{ cm}^{-1}$.

The number of water molecule states differs from one study to another; however, most researchers agree on the definitions of free, weakly related, and strongly related states.

In addition to the middle range, the near infrared (NIR) range is of particular interest for studying water diffusion by evaluating the stretching and bending vibrations during

hydrogen bond formation. The NIR region of the infrared spectrum has a wavelength range of 8000–4000 cm^{-1} . The current study focuses on two ranges, 7300–6300 cm^{-1} and 5400–4800 cm^{-1} , that correspond to the –OH stretching vibration band and the –OH bending vibration band, respectively. Although the 5500–4800 cm^{-1} range provides qualitative information at the molecular level, quantitative analysis is very difficult, as the hydrogen bond has opposite effects on stretching and bending vibrations, which reduces the ability to separate different components of a complex profile [73,76]. Therefore, the interval of the hydroxyl group stretching vibration is often analyzed in more detail [62,76–81].

The deconvolution of the 7300–6300 cm^{-1} range shows three overlapping peaks (Figure 3): a peak at 7080–7050 cm^{-1} , attributed to the free state of water molecules (type S_0); a peak at 6850–6810 cm^{-1} , assigned to singly hydrogen-bound water molecules (type S_1); and a peak at 6580–6535 cm^{-1} , attributed to strong hydrogen-bound interactions (type S_2).

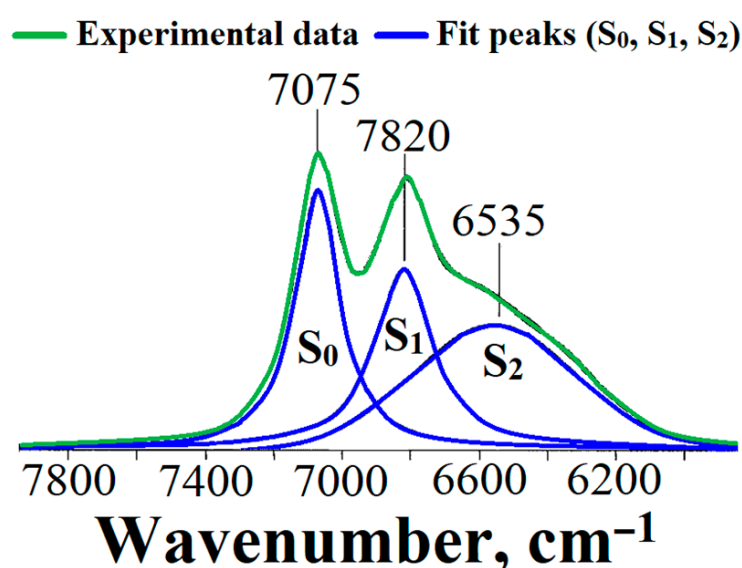


Figure 3. Band deconvolution corresponding to OH-group vibrations in the range of 7800–6000 cm^{-1} .

As water is absorbed, the width and the height of the peaks change due to many factors. These changes allow for the determination of the exact nature of hydrogen bonding as well as the resulting changes in properties. Polar groups, the structure and branching of the polymer network, its defectiveness, and the compatibility of the system components are among the factors that will determine the diffusion rate and the ways water molecules will penetrate into the polymer system volume.

An isolated spectrum of absorbed water is required for adequate data analysis. Using difference spectroscopy, the spectra of absorbed water are isolated by eliminating the interference of the epoxy network spectra [15,75]:

$$A_{\text{dif}} = A_{\text{wet}} - KA_{\text{dry}} \quad (19)$$

where A_{dif} , A_{wet} , and A_{dry} are the absorbances of the difference spectrum, wet spectrum, and dry spectrum, respectively, and K is the subtraction factor, i.e., an adjustable parameter used to compensate for possible thickness changes between the sample and the reference spectra [15,75,79]. Usually, K is equal to 1 because the thickness changes upon water absorption are negligible for most specimens.

The resulting time-resolved spectra are studied using generalized 2D correlation spectroscopy. This method better distinguishes the overlapping peaks and determines the correlation between them. Two-dimensional correlation FTIR spectroscopy has a number of advantages: it can detect overlapping spectroscopic information, it can easily search for

minor changes in peaks, and it can identify specific sequence of events occurring in the system under the influence of external factors [9,15,60,62,65].

Noda [82] proposed the basic principles of 2D IR spectroscopy based on the 2D NMR correlation method. The generalized 2D method considers signals as arbitrary functions of time, temperature, pressure, concentration, or any other physical variable, and defines the intensity of synchronous and asynchronous correlations (Equation (20)):

$$\Phi(v_1, v_2) + i\Psi(v_1, v_2) = \frac{1}{\pi(T_{\max} - T_{\min})} \int_0^\infty Y_1(\omega) \cdot Y_2^*(\omega) d\omega \quad (20)$$

where $\Phi(v_1, v_2)$ is the synchronous two-dimensional correlation intensity; $\Psi(v_1, v_2)$ is the asynchronous two-dimensional correlation intensity; $Y_1(\omega) = \int_{-\infty}^\infty \tilde{y}(v_1, t) e^{-i\omega t} dt$ is the Fourier transformation of changes in spectral intensity, observed for a certain spectral variable $\tilde{y}(v_1, t)$ relative to the external variable t ; $Y_2^*(\omega) = \int_{-\infty}^\infty \tilde{y}(v_2, t) e^{+i\omega t} dt$ is the variation of spectral intensity $\tilde{y}(v_2, t)$ at another spectral variable v_2 ; ω is the Fourier frequency; and t is the fixed interval of some external variable between $T_{\min}$ and $T_{\max}$.

The synchronous spectrum characterizes the degree of coherence between the dynamic fluctuations of the IR signals measured at two different wavenumbers and shows a general similarity between the two separate spectral intensity changes. In contrast, the asynchronous spectrum describes the independent and inconsistent fluctuations and indicates that the bands v_1 and v_2 vary in phases relative to each other during the diffusion. The typical synchronous and asynchronous spectra are shown in Figure 4.

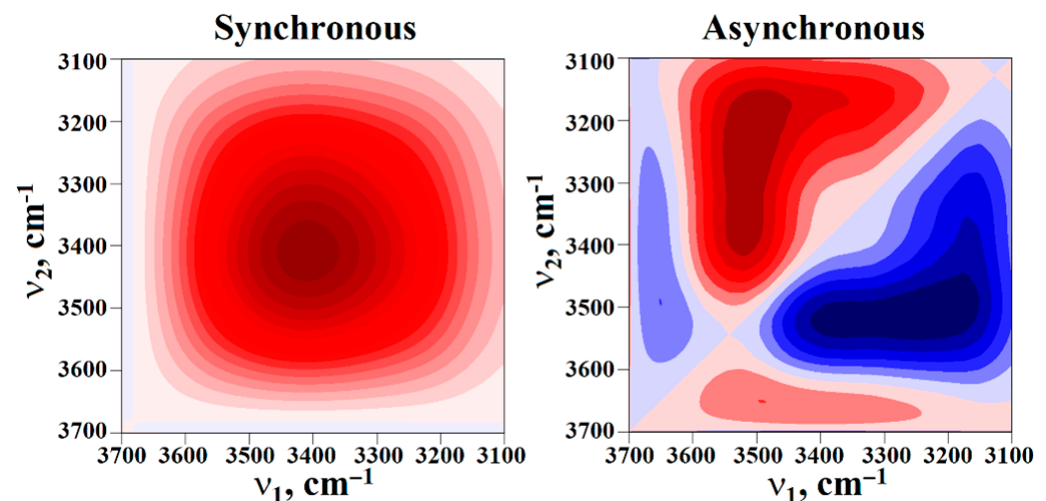


Figure 4. Typical 2D correlation spectra of water absorption into epoxy composition in the 3700–3100 cm^{-1} range.

According to Noda's rule, if $\Phi(v_1, v_2) > 0$ and $\Psi(v_1, v_2) > 0$, the band v_1 changes before the band v_2 . And if $\Phi(v_1, v_2) > 0$ and $\Psi(v_1, v_2) < 0$, the band v_1 changes after the band v_2 . The red regions in the 2D correlation spectra generally indicate a positive correlation, and the blue regions indicate a negative one. The coordinates of the cross-peaks, e, located below the correlation diagonal, are to be indicated as (v_1, v_2) , where v_1 and v_2 refer to the spectrum frequencies by the X-axis and Y-axis. The coordinate values also have a "+" or "-" sign depending on the positive or negative value of the peak, respectively.

These approaches can be used for both medium and near-infrared ranges. More details on the test methodology and interpretation can be found in [15,31,33,60,62,64–67].

Besides the features described above, spectroscopy also provides the diffusion coefficient, absorption kinetic plots and profiles, concentration plots, volume change during water uptake, and other parameters [19,20,31,64,70,74,75,83].

2.3. Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful technique for investigating water diffusion in epoxy coatings [4,84,85]. NMR exploits the behavior of atomic nuclei in a magnetic field and provides valuable information about molecular mobility, diffusion behavior, and the interaction between water molecules and the polymer matrix. Using various NMR methods, researchers can quantitatively analyze water diffusion, probe water–polymer interactions, and evaluate coating performance. By applying magnetic field gradients and analyzing the resulting changes in the NMR signal, researchers can determine the diffusion coefficient and the spatial and temporal distribution of water molecules [86].

Using NMR techniques can provide an understanding of the effects of temperature, humidity, and of the coating structure on diffusion. Moreover, NMR spectroscopy can be combined with other NMR-based methods, such as relaxometry and imaging, to gain some further information about water diffusion processes and their impacts on coating properties [34,58,87–89].

When studying the water–epoxide interaction using NMR spectroscopy, it is deuterium oxide, D_2O , that is used as the diffusing liquid, rather than hydrogen oxide, H_2O . This is explained by the fact that the 1H isotope makes an essential proportion of the epoxy composition, making the 1H signal from the polymer dominant in the NMR signal, while the content of deuterium, 2H , is very small. Therefore, using D_2O and 2H -NMR will provide the data that refers only to diffusing heavy water [34,59,90,91].

The sensitivity of 2H -NMR experiments allows for the assessment of molecular mobility and, consequently, the physical state of water molecules. The 2H NMR spectra (Figure 5) can be interpreted as a superposition of only two subspectra corresponding to water molecules reorienting either very rapidly or very slowly. The decomposition of the spectra may be related to the mobile/“fast moving” phase (narrow peak) and bound/“slow-moving” phase (wide peak) of heavy water [9,59,90]. The relative proportions of highly mobile and less mobile water molecules can be determined by analyzing the intensity of narrow and broad components of the 2H NMR spectrum.

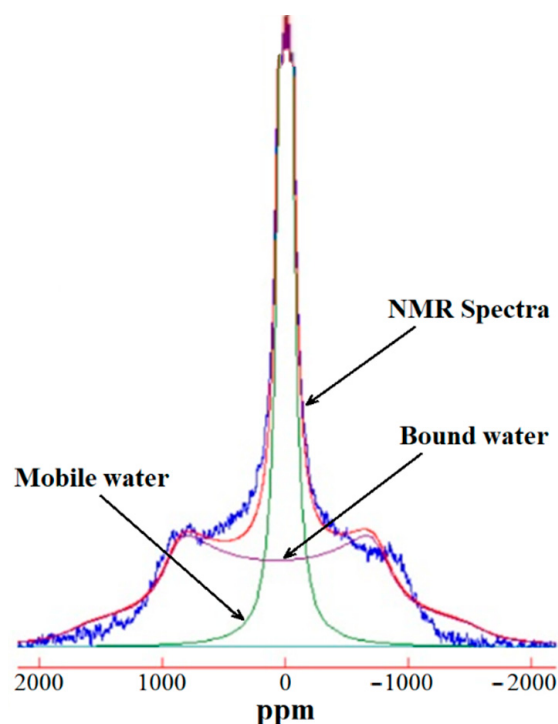


Figure 5. Example of a deconvoluted 2H NMR peak.

The interpretation and comparison of absorption data obtained using different methods of analysis have revealed an interesting fact. Some authors [59,90] obtained time

dependencies of water absorption in epoxy compositions for each type of water by integrating the two peaks of the NMR signal. Despite good convergence between the results obtained using NMR spectroscopy and using the Carter and Kibler model (gravimetric analysis), there was a striking difference in the interpretation of the terms “mobile” and “bound” water for each of them. Popineau et al. [59] noted that the “mobile” water in the Langmuir-type model is actually the “bound” phase in NMR spectroscopy, and vice versa. From a kinetic perspective, the following explanation can be given: the “free” phase refers to individual water molecules with high mobility that can easily permeate into the polymer’s bulk. On the other hand, the “bound” phase represents the water molecules that have formed hydrogen bonds and occupy the microcavities and channels within the polymer. These water molecules are constrained by the available free volume within the polymer matrix. The authors emphasize that the “mobile” and “bound” states are related to kinetic concepts, and not directly to intermolecular water–polymer interactions.

NMR Imaging

NMR imaging, including Magnetic Resonance Imaging (MRI), provides spatially resolved information on water diffusion patterns within epoxy coatings [34,87,92]. These imaging techniques provide a visualization and mapping of the water distribution and the penetration depth. By acquiring multiple images over time, researchers can also monitor the progression of water diffusion. NMR imaging provides valuable insights into the spatial heterogeneity of water diffusion and can guide the optimization of coating designs for improved water resistance.

The principles of NMR imaging are similar to NMR spectroscopy, with spatial encoding added. In NMR imaging, a strong, homogeneous magnetic field is applied to the sample, which aligns the nuclear spins of the water molecules. Radiofrequency pulses are then applied to perturb the spins, followed by the detection of the resulting NMR signal. Spatially varying magnetic field gradients applied during the experiment provide the NMR signal encoding.

The reconstructed NMR images provide visual information about the transport and distribution of water within the epoxy matrix. A quantitative analysis can be performed on the images to extract parameters including water diffusion coefficients, water uptake profiles, water concentration gradients, and other parameters [34,87,92].

NMR imaging allows for the non-destructive observation of dynamic processes, including water diffusion and flow, in real time. By varying the imaging parameters, it is possible to study various aspects of water transport in a polymer, including the diffusion rates, spatial distribution, and the effects of temperature, humidity, and composition on water transport behavior.

To summarize, NMR spectroscopy offers essential opportunities for studying water diffusion in epoxy coatings. Through quantitative analysis, the investigation of water–polymer interactions, and the assessment of coating performance, NMR techniques provide valuable information on diffusion kinetics, molecular dynamics, and coating behavior. These data contribute to the development of more water-resistant epoxy coatings for various applications.

2.4. Electrochemical Impedance Spectroscopy (EIS)

The basic principle of EIS involves applying an AC electrical signal to the polymer–water system and measuring the resulting impedance response across a range of frequencies. The impedance (Z) is a complex quantity that consists of two components: resistance (R) and reactance (X). The resistance component represents the ohmic losses in the system, while the reactance component reflects the capacitive and inductive effects.

EIS can be utilized to assess the transport properties of water within the polymer matrix. As water diffuses into the polymer, it influences the electrical conductivity and impedance of the system. The analysis of the impedance spectra obtained through EIS provides valuable information about the water diffusion process [93] that increases the

material's polarizability. This enhanced polarizability raises the polymer permittivity. Measuring impedance quantifies the rise in permittivity through the derivation of capacitance. The relationship between the permittivity of the polymer film and the capacitance is expressed by Equation (21) [19,94].

$$C = \frac{\epsilon\epsilon_0 A}{d} \quad (21)$$

where A is the area of the sample, d is the sample thickness, ϵ is the dielectric constant of the medium, and ϵ_0 is the permittivity of free space.

Assuming that the changes in capacitance are directly proportional to the changes in the dielectric constant (while keeping the geometrical parameters constant), using Equation (6) with any given time " t " and at time zero estimates the volume water uptake (Brasher–Kingsbury equation):

$$\chi_V = \frac{\log(C_t/C_0)}{\log \epsilon_w} \quad (22)$$

where C_t is the capacitance at time t , C_0 is the dry coating capacitance, which is generally obtained by extrapolating t to zero, and ϵ_w is the dielectric constant of water. The volume water uptake χ_V obtained from the EIS experiments on coatings can be compared to the mass water uptake χ_m determined through gravimetric measurements. This comparison was made possible by following the procedure described in [25,95]. The resulting absorption curves can be fitted to calculate the diffusion coefficient using various Fickian and non-Fickian models that have been considered above for gravimetric analysis [19,95–97].

The impedance spectra obtained from EIS measurements provide valuable information about water transport features, including the diffusion of water molecules through the epoxy matrix, the water-filled voids or channels present, and the interaction of water with the epoxy surface or interfaces. The spectra can be analyzed using equivalent circuit models. These models consist of various circuit elements that represent the electrochemical processes occurring during water diffusion, including charge transfer at interfaces, Warburg impedance for diffusion, and solution resistance. Fitting the experimental data to the equivalent circuit model provides the information about the underlying transport mechanisms and diffusion coefficients [69,98,99].

In addition, EIS provides an evaluation of the electrochemical barrier performance of epoxy coatings against water and corrosion. Measuring the impedance response of the coated system assesses the resistance to ion transport and the effectiveness of the epoxy coating in preventing the penetration of corrosive species and other corrosion processes. The impedance modulus at the low-frequency domain (0.1 or 1 Hz) can generally be regarded as an indicator of systematic barrier properties of a coated metal [62,99,100]. The double-layer capacitance C_{dl} and the charge transfer resistance R_{ct} were the electrochemical parameters related to the corrosion reaction to the metal/coatings interface, and they were obtained from fitting the EIS spectra [68,69,97,98].

EIS offers a versatile and non-destructive method for studying water transport in epoxy materials and assessing their anticorrosive performance. By providing information about water diffusion, coating integrity, and electrochemical barrier properties, EIS provides an understanding of the behavior of epoxy coatings in corrosive environments and supports the development of improved corrosion protection strategies.

2.5. Other Methods

2.5.1. Fluorescence

Fluorescence-based techniques offer a powerful approach to study water diffusion in polymer materials [101–103]. Fluorescent probes or dyes can help to track and visualize the movement of water molecules within the polymer matrix.

One common method is to incorporate a fluorescent dye or probe into the epoxy material. The dyes or probes are sensitive to water, and their fluorescence properties change upon the interaction with water molecules. Trans-4-nitro-4'-aminostilbene (NAS) [104], tri-

cyanovinyljulolidene (TCJ) [103], 5-Dimethylamino-1-naphthalene-sulfonylchloride (DNS-Cl) [105,106], 5-Dimethylaminonaphthalene-1-[N-(2-aminoethylenesulfonamide)] (DNS-2), and 5-Dimethylaminonaphthalene-1-[N-(2-aminopentylenesulfonamide)] (DNS-5) [107] were used as external fluorophores to control the absorption of water molecules into epoxy resins. As water diffuses into the epoxy, the fluorescence signal can be monitored and analyzed to understand the dynamics of water diffusion.

Fluorescence microscopy or spectroscopy can be employed to observe and quantify the diffusion of water in a polymer. Exciting the fluorescent dye with a specific wavelength of light allows for the measurement of the emission intensity or lifetime of the fluorescence signal. As water molecules diffuse, the fluorescence signal can change, providing information about the spatial and temporal distribution of water within the material.

Furthermore, fluorescence correlation spectroscopy (FCS) can be used to measure the diffusion coefficients and dynamics of water in coatings at the microscopic level. FCS analyzes the fluctuation in the fluorescence signal caused by the diffusion of fluorescently labeled water molecules. By analyzing these fluctuations, it is possible to determine the diffusion coefficient and investigate the mechanisms of water diffusion in the polymer matrix [108].

2.5.2. Atomic Force Microscope-Infrared Spectroscopy (AFM-IR)

When investigating water diffusion in polymers using AFM-IR, water molecules' distribution and movement within the polymer matrix can be visualized and characterized. AFM provides topographical information, identifying surface features and defects. Meanwhile, IR spectroscopy provides chemical identification and mapping based on the absorption of infrared light by various molecular species [109].

The AFM-IR setup allows us to directly observe and analyze the diffusion of water molecules in polymers. Water absorption and diffusion in a polymer can cause changes in its chemical composition and structure. These changes can be detected and monitored through variations in the infrared absorption spectra obtained by AFM-IR. By mapping these changes, it is possible to visualize the movement and diffusion of water at a high spatial resolution.

Thus, Morsch and colleagues [8,110,111] were able to directly visualize the water absorption in epoxy-phenolic compositions on a submicron scale using the AFM-IR method, as well as characterize the distribution of absorbed water and study the morphology of the coating.

2.5.3. Positron Annihilation Lifetime Spectroscopy (PALS)

PALS involves the use of positrons, which are positively charged antiparticles of electrons. When positrons are implanted into a material, they rapidly annihilate with electrons, resulting in the emission of gamma rays. Measuring the time delay between the positron injection and annihilation provides information about the free volume and defects within the material. PALS not only determines the amount of free volume, but also the distribution of free-volume holes [112,113]. As mentioned earlier [18,30,85], polarity, the topology of the polymer structure, and molecular mobility determine the absorption kinetics. Polarity has the greatest influence on the equilibrium moisture absorption; the greater the polarity of the polymer units, the more water is absorbed [22].

It is often a very challenging task to estimate the topological and polar contributions to the absorption process. However, two separate research groups [22,114] managed to isolate and study the influence of topological contribution on the nature of absorption. One of the groups used various amine isomers to obtain polymer networks that were fundamentally different in terms of their structure and packing density while maintaining identical chemical compositions and network polarity [114]. The second group selected the "epoxy resin-hardener-chain extender" system and synthesized the epoxy compositions, in which the polarity remained constant, while the topology systematically changed [18]. In

both cases, the kinetics of the penetrant absorption was found to strongly depend on the size of the free-volume holes.

3. Influence of Water on Glass Transition Temperatures of Epoxy Coatings

The glass transition temperature (T_g) is a crucial parameter for epoxy coatings as it strongly affects the material's mechanical, thermal, electrical, and chemical properties. Understanding and controlling the T_g is essential for achieving desirable coating performance and durability. The influence of water on the glass transition temperature of epoxy coatings is one of the most important considerations for designing and formulating coatings for various applications. Understanding the plasticization effect of water can help engineers and coating manufacturers optimize formulations to ensure long-lasting performance, even in water-exposed environments. Effective mitigation strategies produce highly durable and protective epoxy coatings for a wide range of applications.

When water diffuses into an epoxy coating, this can lead to changes in the T_g of the epoxy. Water molecules can affect the mobility of polymer chains. Water molecules can act as plasticizers (so that polymer chains can move more easily) and reduce the T_g of the epoxy coating. As water diffuses into the coating, it disrupts the polymer chains, increasing their mobility. This increased mobility lowers the T_g and can result in a softer and more flexible material. Usually, the decrease in T_g due to the plasticizing effect ranges from 10 to 20 °C for every percent of water molecules in the epoxy material [6,53,115–118].

Water diffusion highly depends on the polymer structure, crosslink density, environmental conditions (including temperature, pressure, humidity, and presence of salts), steric effect, polymer–penetrant interaction, and thermal and mechanical history. Since the relaxation phenomena also have significant effects on the changes in the nature of absorption, Fickian diffusion predominates in an amorphous polymer at temperatures much higher than T_g , while non-Fickian behavior regularly occurs in polymers at the glass transition temperature and below. This is explained by the relaxation of the polymer, which is essential for penetrant molecules to diffuse into the molecular network. This rearrangement results in a significant macroscopic swelling related to the diffusion of vapors and liquids into polymers [119–121].

When water penetrates into the epoxy matrix, there is a change in the effective crosslink density as a result of the interaction of the polymer and water molecules. This leads to an increase in the distribution of molecular weights and in the relaxation time. The effect of this process can be observed on thermograms when measuring the glass transition temperature using the DMA method. As the water content increases, the $\tan \delta$ peak in the glass transition region broadens towards lower temperatures [61,122,123]. Often, the $\tan \delta$ peak can become separated into two peaks with low- and high-temperature maxima [5,6,122,124]. The high-temperature maximum corresponds to a less plasticized network, while the low-temperature one corresponds to a highly plasticized network. The $\tan \delta$ peak will change until the water saturation is reached. After that point, no evolution in the shape of the peak is observed. This is often explained by the plasticizing effect. Nogueria et al. [5] explained the observed phenomenon by the plasticizing effect and two additional factors: the free volume and the epoxy–water interactions. The formation of hydrogen bonds between water molecules and polymer chains requires breaking the interchain hydrogen bonds, which leads to an increased mobility of the chain in the glass transition region and a corresponding decrease in the effective crosslink density.

The extent of the T_g change depends on the concentration of water diffusing into the epoxy coating. Higher water concentrations typically result in more important reductions in T_g . The relationship between the water concentration and T_g change may not be linear, and different epoxy systems may exhibit varying sensitivity to water plasticization. Intramolecular interactions, post-cure, swelling, microcracking, physical aging, hydrolysis, and chain scission at higher temperatures also result in a different T_g [39,49,125–127].

Understanding the effect of water uptake on T_g and subsequent chemical resistance is essential for selecting appropriate coatings for environments where exposure to chemicals

is a concern. Prediction models for the glass transition temperature of epoxy coatings during water diffusion are based on various approaches, ranging from empirical equations to more complex theoretical models. The goal of these models is to estimate how T_g changes with the water content in the increasing epoxy matrix. Some of the most commonly used methods are the Fox, Kelley-Beuche (free volume model) and Simha-Boyer equations.

The Fox equation is an empirical model that relates the glass transition temperature of a polymer to the weight fractions of various components. The equation can be modified for epoxy–water systems to consider the effect of water (or other low-molecular-weight diluent) uptake [114,125,128]:

$$\frac{1}{T_g} = \frac{w_p}{T_{gp}} + \frac{w_w}{T_{gw}} \quad (23)$$

where T_{gp} and T_{gw} are the glass transition temperature of the polymer and water, respectively, and w_p and w_w are mass fractions of polymer and water, respectively. According to [129,130], the experimentally obtained value of T_g of the water is in the range between 124 and 138 K.

The Fox equation is formulated based on the assumption of ideal volumetric additivity at T_g , and it neglects any specific interactions between the two components. Therefore, this model, in most cases, poorly describes the change in the glass transition temperature during water absorption as there are specific interactions between the water and the polar groups within the epoxy network.

The free volume theory (Kelley-Bueche equation) suggests that the glass transition is related to the available free volume in the polymer matrix. By considering the effect of water uptake on the free volume, the T_g changes can be estimated [131–133]:

$$T_g = \frac{\alpha_{gp} V_p T_{gp} + \alpha_{lw} (1 - V_p) T_{gw}}{\alpha_{gp} V_p + \alpha_{lw} (1 - V_p)} \quad (24)$$

where α_{gp} is the difference in the coefficient of thermal expansion (CTE) of a polymer between the glassy and rubbery states; α_{lw} is the CTE of water; and V_p is the volume fraction of the polymer. The value of V_p can be calculated using the following equation [134]:

$$V_p = \frac{1}{1 + 0.01 M_m \left(\frac{\rho_p}{\rho_w} \right)} \quad (25)$$

where M_m is the equilibrium water content, and ρ_p and ρ_w are the densities of the polymer and water, respectively.

This approach requires knowledge of the epoxy's free volume properties and their variation with water uptake. All parameters required to calculate the glass transition temperature can be obtained from the literature (for example, the CTE and T_g of water are taken as $4 \times 10^{-3}/\text{K}$ and 277 K, respectively [133–135]) or experimentally (for example, the thermal expansion coefficients α_{lw} and α_{gp} are determined with a TMA experiment). This model has been used by many authors [124,132–136] and has proven to have good agreement with experimental data.

The Simha-Boyer equation is another empirical model that describes T_g changes with the water uptake. It is given in [137] as follows:

$$\frac{1}{T_g} = \frac{1}{T_{gp}} + \left(\frac{1}{T_{gw}} - \frac{1}{T_{gp}} \right) V_w \quad (26)$$

where V is the volume fraction of water in the polymer. As mentioned above, the T_g of water is in the range between 124 and 138 K. It was also mentioned [117,118] that this method is able to adequately describe the decrease in the glass transition temperature as a result of the water penetrating into the polymer.

In addition to empirical and theoretical models, there are molecular simulation methods and techniques that can be used to predict the glass transition temperature during water uptake in the epoxy. Molecular dynamics (MD) simulations can provide insights into the behavior of polymers at the molecular level. By simulating the interactions between epoxy and water molecules, MD simulations can offer predictions of T_g changes during water uptake. However, MD simulations require detailed knowledge of the epoxy molecular structure and parameters, as well as ample computational resources [135,138].

It is important to note that each method has its own limitations and may not accurately capture the specific behavior of the epoxy system selected. Therefore, accurate predictions may require a combination of approaches along with an experimental validation. Additionally, a specific formulation, curing agents, and environmental conditions of the epoxy system can influence the T_g changes, and accounting for these factors would improve the accuracy of the predictions.

4. The Effect of Water Absorption on Mechanical Properties of Epoxy Materials

Epoxy materials are the basis for preparing composites used in the production of aircrafts, wind, and tidal turbine blades [139]. They are in direct contact with atmospheric water (moisture), rain, or sea water. As a result, they undergo humidity damages during their operation. Composite materials were shown to absorb more water from the environment compared to common polymers [140]. This has a detrimental effect on the mechanical, electrical, and thermal properties of epoxy composites and reduces their service lives [141].

A high moisture uptake can lead to obvious mechanical degradation and even severe failure and damage [142]. The inclusion of fillers was found to decrease the moisture absorption, increase the glass transition temperature, and slightly reduce the detrimental effect on the mechanical properties after hygrothermal conditioning [143]. However, no long-term durability of epoxy resins seems to have been comprehensively documented.

Water attacks epoxy-based composites at every level. The fibers, matrix, fiber–matrix interface, and adhesives are all susceptible to deterioration. Absorbed water can increase creep and relaxation, introduce residual stresses, cause osmotic pressure, and degrade the epoxy matrix, fillers, and filler/matrix interfaces via hydrolysis and chemical nucleophilic attack and acid or alkali catalysis. Water accelerates the fatigue degradation of composites and shortens their fatigue life. Additionally, fatigue damage offers new paths for moisture ingress and significantly increases the rate of moisture-related damage. However, the effect of fluids tends to be contradictory. For example, fluids result in improved impact resistance. This may be due to the impacting object being resisted by a larger volume of fibers. However, over time, impact damage may allow more routes for moisture to penetrate into the composite, and, thus, impair its properties over time [144].

Moisture damage begins near the surface of the material and spreads inward over time, with cracks tending to grow parallel to the free surface. This damage is often localized, resulting in a small number of large cracks [145]. Crack growth is dominated by different effects depending on the level of loading. At lower load levels, cracking is most influenced by chemical reactions. At moderate load levels, cracking is most affected by diffusion. At higher load levels, stress-assisted corrosion controls crack growth [146]. The rate of mechanical performance degradation of epoxy-based composites has been observed to be directly correlated with the rate of moisture absorption [147]. Moisture is attracted to areas of air entrainment such as voids and delaminations. Thus, these areas can collect water over time [148]. Cracks and voids, even the microscopic ones, allow for easier penetration of water into the composite system via capillary action and diffusion. Therefore, a generous application of epoxy resin can potentially render moisture-related effects negligible. After an initial period of seeking out and filling cracks and voids, moisture begins to swell the composite. One study observed a linear relationship between strain and water uptake from the beginning of swelling [149]. Notably, water has been shown to diffuse more slowly through epoxy composites than through polyester composites, to give an example [150].

Water uptake results in microcrack formation in the bulk of the epoxy and in the amplified voids, which tend to become linked together, generating paths, which promotes further penetration of water in the epoxy depth. The absorbed water may prove damaging to installed wraps. The tendency of composite materials to suffer damage when operating in harsh humidity environments shows that the humidity issue for epoxy-based composites should not be underestimated. It needs, instead, a rigorous and deep study to evaluate the impact on the system performance and assess the reduction in the operative life.

The moisture history of the composite is important. Both the maximum load at failure and the fracture toughness have been observed to decrease linearly as the time of moisture exposure increases. A higher average moisture content over the life of the material will result in a higher level of damage, and desorption appears to be more destructive than absorption. Additionally, wet–dry cycling has been observed to decrease the ultimate load of various epoxy-based composites. Typically, glass-fiber-reinforced composites suffer much more than carbon-fiber-reinforced composites.

Epoxy matrices are the primary victims of moisture absorption. If unchecked, moisture absorption by the resin will result in plasticization, swelling, hydrolysis, and fiber debonding from the matrix [45]. By plasticizing the polymer and lowering the glass transition temperature, moisture can soften a polymer and increase creep effects. This is typically reversible with drying. The hydrolysis of the epoxy resin, however, is irreversible, and can change both the stiffness and the strength of the polymer. Degradation is substantially slowed if the resin is fully cured prior to exposure [7]. Additionally, water-resistant epoxies have been shown to increase the reliability of glass-fiber-reinforced epoxy composites by 200%–300%. Moisture absorption is known to encourage fibers to debond from the surrounding matrix. Matrix cracking allows further paths for moisture penetration, thus accelerating damage growth. Additionally, fluid ingress can result in swelling, which can cause stresses between the fibers and the matrix and deteriorate the bond between them, resulting in tiny debondings. Epoxy resin swelling and osmotic pressure due to moisture uptake can cause debonding stresses between the fibers and resin.

5. Conclusions

This review discusses water uptake in epoxy thermosets and its effect on their physical properties. The absorption of water strongly affects the exploitation characteristics of epoxy coatings and their lifecycles. The models used for describing water absorption to a polymer matrix involve many parameters that can adequately describe the process with parameter tuning. However, when using multiple variable parameters, the physical essence of absorption can be obscured. Hence, one of the promising directions in this field is the development of new models with fixed physically transparent parameters, which will adequately describe the water uptake process in epoxy resins.

Another challenge is the development of experimental techniques that would determine the water state in an epoxy matrix in a straightforward and unambiguous manner. Conventional and amply used experimental methods (IR and NMR spectroscopies) do not appear to address this issue directly because the interpretation of the data obtained is based on spectra simulation. Hence, the models underlying the calculation predetermine the results.

Therefore, new investigations are required to understand the mechanisms of water uptake for advanced epoxy materials or any incidental effects related to it. Like all polymer materials, epoxy resins are expected to become recyclable or reusable. As they are used in sophisticated technological devices, self-healing and recyclable materials have to be readily accessible. The controlled water uptake can be considered for this challenge. Epoxy resins offer an excellent platform for materials and systems that integrate stimuli-responsive motives to obtain life-like and intelligent materials with dynamically adaptive and interactive functions.

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