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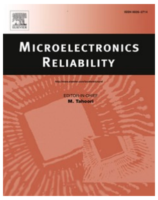

Interphase effect on the effective moisture diffusion in epoxy–SiO_2 composites

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ABSTRACT

Epoxy Mold Compounds (EMC) are used to protect integrated circuits (IC) from environmental influences, with one of these influences being moisture ingress, causing corrosion. To obtain the needed thermal and mechanical properties EMCs require a high loading of (silica) fillers, introducing a large amount of interface. While silane coupling agents promote good binding, they have shown to introduce an interphase volume that exhibits a faster moisture transport between epoxy and SiO_2 in glass fiber filled epoxy. In this work, we investigate if such an interphase volume is also introduced by the filler particles in EMC and if it influences the moisture diffusion coefficient of the composite. We compare moisture uptake measurements performed by dynamic vapor sorption (DVS) with predictions from effective medium theory, as well as with numerical simulations based on micro-CT scans of our samples for a model epoxy system containing different filler levels and commercial EMC samples with two different filler levels. From the measured DVS data, we observe an effective diffusion coefficient, that is higher than predicted for an absence of any interphase for both the EMC and the model system. This suggests that an interphase layer should be present.

1. Introduction

The ingress of moisture is a well-known factor that might cause failure in integrated circuits (IC) [1,2]. Epoxy Mold Compound (EMC) is often used to encapsulate the IC, because it acts as a barrier against environmental influences such as moisture and gasses. Inert SiO_2 filler particles are added to the EMC for balancing the thermal expansion coefficient. As a side effect, they also improve the moisture resistance [3].

A good binding between the epoxy matrix and the SiO_2 particles is a key factor for protection against moisture uptake and transport. Otherwise, delamination and even crack formation may occur at the SiO_2-EMC interfaces due to stresses originated from thermal and moisture related expansion. These interfacial damage modes facilitate (further) moisture ingress and flow along interfaces [1,4]. To ensure a strong connection between the particles and epoxy matrix, silane coupling agents are normally added. One side of these molecules binds to the SiO_2 particle, while the other side crosslinks with the epoxy matrix [5], thus changing the structure of the composite at the interface. A simplified schematic of the coupling agent in the system can be seen in Fig. 1.

Now the question rises; do the coupling agents cause a change in structure influencing the properties of the EMC? During mechanical testing performed on (non-aged) silane containing EMC [6] crack formation was observed through the epoxy matrix, instead of along the epoxy/SiO_2 interfaces, showing that the interfaces are stronger than bulk epoxy matrix. Also in other epoxy composites (e.g. with TiO_2 nanoparticles or glass fibers), differences in mechanical properties between a layer at the interface between the fillers and the epoxy matrix and the bulk epoxy have been observed. We will refer to this layer at the interface as the interphase layer in this publication, clarifying that we

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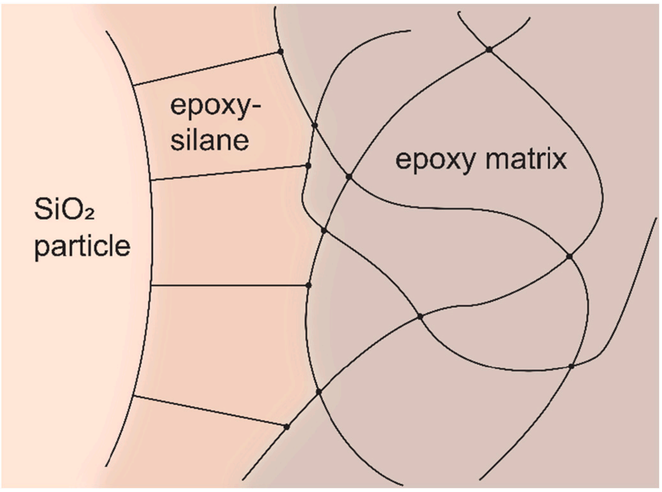

Fig. 1. Simplified schematic of interphase structure (not to scale). Epoxy silane molecules bind to the SiO_2 on one end and the epoxy matrix on the other end.

refer to a volume between the particles and the bulk matrix rather than the two-dimensional surface where particles and matrix touch. Li et al. [7] reported that upon adding SiO_2 nanoparticles and silane coupling agents to an epoxy matrix the glass transition temperature (T_g) of the composite decreases. Wang et al. [8] on the other hand, observed a significant increase of T_g after adding TiO_2 nanoparticles to an epoxy matrix, which they attribute to the restricted movement of molecular chains in the interphase, which they estimate to be a few tens of nanometers wide. In studies on composites of epoxy and glass fiber, the interphase region is generally found to be softer than the bulk epoxy [9,10]. Griswold et al. [9] measured the thickness of the interphase by means of AFM. They coated different amounts of silane coupling agent onto glass fibers and embedded them into epoxy. While they could not observe any interphase without added silane, an increase in silane concentration caused an increase in the interphase thickness to up to 880 nm (measured by AFM-phase imaging). Joliff et al. [10] found effects of an interphase in an epoxy glass fiber composite to reach about 1 μm by AFM measurement. By means of micro thermal analysis however they could observe differences in the softening temperature to reach as wide as 10 μm from the glass fibers.

Differences in the polymer structure not only affect mechanical properties but also influence moisture transport [11]. As thermal motion of the polymer chains is needed for diffusion of water, soft polymers with more chain mobility exhibit higher diffusion coefficients than more rigid structures. Thus, a softening effect upon adding fillers can be expected to lead to an increased moisture transport. In case of EMC this might imply a reduction in the moisture resistance of the package.

Previous moisture diffusion measurements in an epoxy/glass fiber system by Rocha et al. [12] not only showed a higher effective diffusivity of the composite in the direction parallel to the fibers, compared to perpendicular to them, but even gave a value twice as high as in the unfilled epoxy. Joliff et al. [10] observed the interphase diffusivity to be 5 times the bulk diffusivity. What would this mean for an EMC? With filler fractions as high as 79 vol%, silica particles are packed closely. If the distance between particles is in the range of the interphase region thickness, the interphase region can form a network stretching through the composite that significantly influences the moisture transport properties of the composite. While adding a high amount of SiO_2 filler particles should decrease the effective diffusion by increasing the path length and reducing the epoxy volume, an interphase with increased diffusivity could oppose this effect and (partly) suspend the retarding effect of the fillers on diffusion. Such a network with increased conductivity has already been observed in EMCs. Imperiale et al. [13] report an interphase effect when studying the electric conductivity and charge carrier mobility in EMCs with differing filler volumes. They could see an increase in conductivity with increasing filler content and explain it with an increase in charge carrier mobility around the interfaces, forming a network with increased mobility at high filler fractions. A high conductivity in EMCs is problematic, as it might lead to product failure. Several studies connect the moisture content in EMC with the conductivity measured in electric measurements [14,15]. An increase in conductivity by a factor of up to 18 between a wet and a dry EMC has been reported [14]. A direct connection between the transport of moisture and the difference in electric properties around the interface is not clear from the studies. Ahn et al. [16] used a modeling approach (without taking interface effects into account) to describe data for both moisture diffusion and electric conduction for EMCs with filler levels ranging from 60 vol% to 84 vol%. In this work, we test the possibility of an increased moisture diffusivity through the interphases between SiO_2 filler particles and epoxy matrix in mold compounds that might reduce the protective property of the EMC. For this, we measured the effective diffusion on two sets of samples — a commercial mound compound with two different filler levels and an epoxy model system, which we prepared unfilled as well as containing two different filler levels. The advantage of the model system is the ability to attribute changes in the effective diffusion between the samples to the interphase uniquely, as no other additives are present. However, reaching filler levels as high as in the commercial EMC was not attainable with our available equipment. Filled epoxies are known to show anomalous moisture uptake behavior, with a fast uptake visible in the initial stages of diffusion following a Fickian behavior and a slower uptake process in later stages of the process [17–19]. In this publication we focus on the initial stages of moisture uptake. To draw conclusions on the interphase diffusivity, we compare the measured values, obtained by gravimetric moisture uptake measurements with dynamic vapor sorption (DVS), with the effective medium theory (for the low filled model system) as well as with numeric simulations (EMC samples) based on micro-CT scans of the EMC samples.

2. Materials and methods

2.1. Materials used and sample preparation

Two types of samples were used for the experiments: a commercial epoxy mold compound with two different filler volume fractions (60 and 79 vol%), and a model system consisting of epoxy with differing amounts of SiO_2 filler coated with an epoxy silane (filler content 0 vol%, 20 vol% and 30 vol%). While the commercial EMC contains many additives of unknown concentration (e.g. flame retardant, carbon black, wax, ion trappers) that might impact test results, the model system only contains epoxy and silane modified SiO_2 fillers, which makes the attribution of measured effects to the interphase between fillers and bulk matrix easier. It was mixed from Novolac Epoxy (EPN1180), Bisphenol A (BPA) as hardener and Triphenylphosphine (TPP) as catalyst. Per 100 g of epoxy, 64.95 g of BPA and 4 g of TPP were used. The mixing was done in 2 steps. First, the BPA and the catalyst were separately mixed with the Novolac epoxy in two beakers, creating 2 components. In the second step these two components were mixed at 90 °C and subsequently cooled down rapidly to −32 °C to stop the curing reaction. For the batches containing filler particles, these were added in step 1 together with the BPA. At 90 °C, part of the BPA was added to (part of) the Novolac epoxy before slowly mixing in the particles. BPA has a melting temperature of 158 °C, so that at 90 °C the grains are still solid and help obtaining a good dispersion of the SiO_2 particles. After all SiO_2 particles were mixed in, the rest of the BPA was added and the temperature was slowly increased to 160 °C to fully melt the BPA. After cooling down to 90 °C, the other component (Novolac Epoxy + catalyst) was added. The SiO_2 with a particle size distribution of 2 μm to 12 μm (data sheet: median diameter of 2.9 μm) were obtained from Denka. For the sample preparation, the mixture was heated up again and cast onto an aluminum foil at 110 °C and subsequently cured for 3 h at 175 °C. The samples with a filler volume fraction of 20% became thicker as the casting temperature slightly lower and thus the viscosity at the time of casting was higher. The aluminum foil was left attached to the samples, as removing the foil could easily cause damages to the samples and leaving it attached would not have an impact on the measurement.

We obtained the EMC as molded sheets of 0.6 mm thickness. Fig. 2 shows a SEM image of the EMC sample with 79 vol% of fillers. The SiO_2 particles are tightly packed, with only as much as 0.5 to 2 μm of space between them. The amount of filler particles in the EMC samples was verified by TGA measurements where the epoxy was burned off by heating the samples to 600 °C while monitoring the weight change. In this measurement, the SiO_2 weight fractions from the data sheet could be reproduced (The EMC with 60 vol% SiO_2, containing 74 wt% according to the data sheet showed a filler fraction of 76 wt% in the experiment and the EMC with 79 vol% containing 87.5 wt% in data sheet vs. 87.4 wt % in experiment).

For measuring the weight gain with moisture exposure in the DVS, disks of 9 mm diameter were cut from the sheets. The thickness of the commercial EMC samples was 0.6 mm, while the thickness of the samples from the model component varied between the samples (0.15–0.4 mm), where the samples of the unfilled and the 30 vol% filled model component had approximately the same thickness, while the samples of the 20 vol% filled model component were about twice as thick.

2.1.1. Dynamic vapor sorption (DVS)

The DVS is a thermogravimetric measurement: samples are exposed to a certain, well-defined step in relative humidity (RH) at fixed temperature and the weight gain or loss is measured over time. This weight gain or loss represents the amount of ab- and desorbed moisture at the designated condition. For a well-defined sample geometry (most commonly thin sheets are used) it is possible to not only obtain the moisture saturation level, but also the diffusion coefficient by fitting the measured weight gain over time. In this study, the TA Q5000 SA was used. Before the measurement, the samples were pre-dried in the oven for 24 h at 130 °C. The sample weight was not monitored during the drying, but the measurement sequence included a drying step to desorb moisture that might have been absorbed during the time between removing the samples from the oven and starting the DVS measurement. This initial period at 0% RH also ensured that it could be checked if the samples were fully dried before the absorption step started. After the drying, a step in RH to 60% followed. This measurement was performed at 4 different temperatures (30 °C, 45 °C, 60 °C and 75 °C). For each run, a new sample was used, as subsequent sorption experiments might influence the diffusion coefficient [20]. The baseline drift for a measurement without sample was below 0.5 μg, while weight changes due to water uptake in the samples were in the range of about 70 to 130 μg.

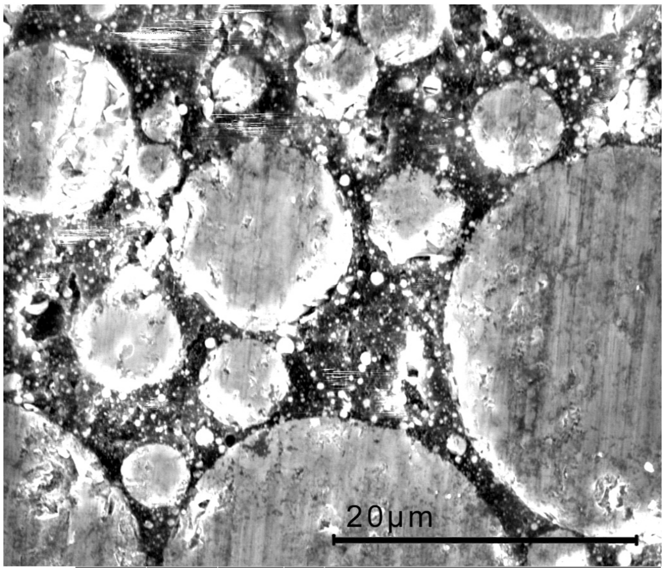

Fig. 2. SEM micrograph of commercial EMC with 79 vol% of SiO_2 filler. HV = 10 kV; WD = 10.2 mm.

2.1.2. Moisture transport evaluation

For evaluating the diffusion coefficients from the measured weight gain, the obtained data needs to be fitted. Starting from Fick's first law of diffusion

$$J = -D\frac{\partial c}{\partial x}, \tag{1}$$

with J [mol/m^{2}s] being the diffusive flux, D [m^2/s] the diffusion coefficient and c [mol/m^3] the moisture concentration, both the diffusion coefficient and the moisture concentration in the sample are needed to characterize the amount of moisture transported through a material. While the diffusion coefficient contains information on the dynamics of the process (how long it takes for the first diffusing species to reach a certain depth), the moisture concentration comprehends the information on the amount of species transported. For the moisture concentration, the saturation level in the material at a certain environmental condition (RH and temperature) is the determining factor. When adding impermeable fillers to a polymer, the moisture uptake of the composite decreases with increasing filler level and thus the flux of moisture will reduce. At the same time, the filler particles act as barriers, increasing the path length of the water molecules, slowing down the transport (reducing D and thus also J). Changes in the structure of a polymer (without changing the nature of the polymer) are known to only have small influence on the saturation levels in the polymer compared to the effect on diffusion coefficients [11]. As the effect on the diffusion coefficient is expected to have larger influence on the total changes in transport, we focus on the evaluation on the diffusion coefficients. Epoxies tend to show anomalous uptake behavior, with a fast uptake dominating the initial stages of diffusion and a second slower uptake process, that becomes visible in later stages [17–19]. When fitting the data of the whole uptake process with the assumption of a single Fickian process, the measured corves are not fully represented. When fitting only the initial parts of the uptake with the assumption of a Fickian process on the other hand, the fit describes the data well, as the initial uptake behaves as Fickian. For this study we focus on the dynamics of the initial uptake, as this describes the minimum time it takes for water molecules to travel through the material. Thus, the fitting is done for the first stages of diffusion only, where the measured weight gain M_t over time (t) is less then half of the (estimated) saturation uptake M_∞ $\left(M_t < \frac{1}{2}M_\infty\right)$. The diffusion coefficient (D) can be fitted using the following relation [21]

$$\frac{M_t}{M_\infty} = \sqrt{16\frac{Dt}{\pi L^2}}, \tag{2}$$

where M_∞ represents the final mass uptake and L the sample thickness. This formula is valid for z-directional moisture exposure from both sides. In our experiment, the samples from the model system were measured with Al foil on one side (see Section 2.1). Here the sample thickness changes to $L_{eff} = 2L$. Due to the dual stage nature of the moisture uptake, the value for final mass uptake (M_∞) cannot be determined without containing an error, which has a large impact on the accuracy of the diffusion coefficient. For the evaluation, the highest measured value from the uptake experiment was used as M_∞. This is a simplification, as the value partially contains moisture uptake from the second process. An evaluation fitting two processes to the data is beyond the scope of this paper and will be addressed in future work. In this study we decided to use the last measured value as M_∞ and estimate the error as approx. 5%.

At low temperatures (low values for the diffusion coefficients) an error of 5% in M_∞ gives rise to 18.4% error in D. For the samples of the model component, an additional error needs to be added to the error evaluation. The sample thickness L shows some variations of up to 4%. The thickness of all samples was measured at three points and the sample thickness as well as error was noted and later used in the evaluation for each sample individually. The error in D is thus evaluated using error propagation with errors from both M_∞ and L and the error from the linear fit through the data (M_t over t). For each condition (temperature, sample type), one sample was measured.

2.2. *Modelling — effective medium theory and COMSOL*

From the experimental data alone, it is not possible to make statements on the interphase effect. While fillers have a retarding effect on the diffusivity due to extending the path length, the effect of the interphase depends on the specific (molecular) nature of the interphase region. In case of a lower diffusivity through interphase compared to the bulk matrix, the retarding effect of fillers will be enhanced, thus the effective, measured D will be lower than without interphase effect. If on the other hand the interphase diffusivity is higher than the bulk diffusivity, the retarding effect of the fillers will be counteracted and possibly even outbalanced.

To be able to quantify the effect of the interphase, it is thus necessary to compare the measured data to a model that can distinguish the effect of the fillers on the effective diffusivity from the effect of the interphase. We use 2 models: The model epoxy contains up to 30 vol% of fillers. For this evaluation the effective medium theory is suitable. However, it is not suitable to model the highly filled EMC systems. For that, we model the moisture ingress with an explicit FEM model based on micro-CT scans of the commercial EMC samples. Both effective medium theory and numerical modeling has been used before to study the effect of filler particles on the effective conductivity and diffusivity in EMCs [13,16,22,23]. Ahn et al. [16] for example, evaluated data from EMCs with filler levels ranging from 60 vol% to 84 vol% with a generalized effective medium and solubility (GEMS) Langmuir model. In our evaluations, the focus is on studying a possible interphase effect.

2.2.1. *Effective medium theory (EMT)*

With help of the EMT it is possible to get a theoretical indication on the influence of an interphase layer between impermeable, spherical particles and a (polymer) matrix on the effective diffusion coefficient of the composite. The theory was first developed by Landauer in 1952 [24] for estimating the effective conductivity of metals containing two phases with different conductivities and later modified to describe diffusion. The system is simplified to a model which consists of spherical particles in a matrix. In the model, all particles have the same radius. Donkers et al. [25] transferred the EMT from conductivity to diffusivity in a polymer system with impermeable particles and also added a third phase – an interface layer covering the particles. This model is valid for dilute mixtures, where particles do not interact with each other. The theoretical percolation limit for equally sized spheres in a “Swiss cheese” model is $\phi \approx 0.29$ [26]. A simplified representation of the effective medium, containing only one particle (radius r_s) surrounded by an interphase layer (thickness d_i), is shown in Fig. 3. The effective D diffusivity (D_{eff}) of the medium can be calculated by [25]

$$D_{eff} = \frac{1}{4(Q+2)}\left[2D_i(Q-1)(3\phi_b-2)+D_b(Q+2)(2-3\phi_s)\right]+\frac{1}{4(Q+2)}\sqrt{16D_iD_b(Q+2)(1-Q)+\left\{2D_i(1-Q)(3\phi_b-2)+D_b(Q+2)(3\phi_s-2)\right\}^2}, \tag{3}$$

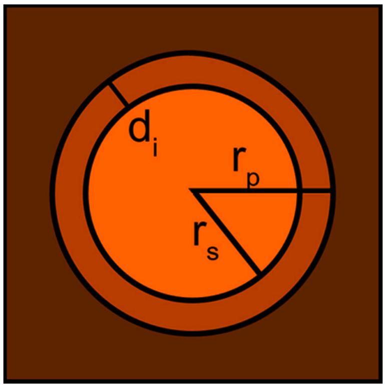

Fig. 3. Simplified representation the system described by the effective medium theory: The effective medium consists of the polymer matrix, the solid particle with radius r_s and an interphase layer of thickness d_i.

with

$$Q = \frac{r_s^3}{r_p^3}.$$

and D_i [m^2/s] being the interface diffusivity, ϕ_b the volume fraction of the bulk polymer, D_b the diffusivity of bulk polymer, r_p the radius of the particle including the interphase and ϕ_s the volume fraction of the solid particles.

2.2.2. *Explicit modelling by FEM diffusion model*

As explained in the previous section, the effective medium theory can only describe the effective diffusion at low filler fractions. The filler level in the EMC samples is as high as 79 vol%. In order to understand the effect of interphase at these high packed EMC's, we need to move to realistic three-dimensional (3D) description of these interface layers. This can be achieved through means of numerical simulations, with a mesh based on a realistic model structure. In earlier work performed by Joliff et al. [10] on epoxy–glass fiber systems, a simplified geometry could not correctly mimic the real system. To accurately model the effects of interfaces, we need to describe these structures through realistic 3D meshes. To obtain this realistic structure, the distribution of particles, interface and polymer distribution should be known. Only few techniques exist to unravel these distributions. On a scale from 0.5 μm onwards, this can be achieved by micro-CT imaging. For the EMC a higher resolution is desirable as not all features can be captured (see description of step 1 below). To finally obtain a full model we developed a three-step process: (i) Measurement of the sample in 3D by using micro-CT, (ii) Use of Synopsis Simpleware software to generate a 3D mesh structure and (iii) Use of COMSOL to solve diffusion process in 3D.

2.2.2.1. Step 1: Micro-CT measurements. A slice of the micro-CT image of the EMC sample containing 79 vol% of fillers is shown in Fig. 4(a). In the histogram (b), two peaks in the number of pixels having a certain brightness are visible. SiO_2 has a higher density than epoxy and thus absorbs more photons. In Fig. 4(a), the filler particles thus appear brighter. When ascribing a black value to the pixels present the lower and broader peak in the histogram (Fig. 4(c)), it can clearly be seen that epoxy and SiO_2 particles are represented by the two peaks in the histogram. Also, it becomes obvious that the lower peak represents the

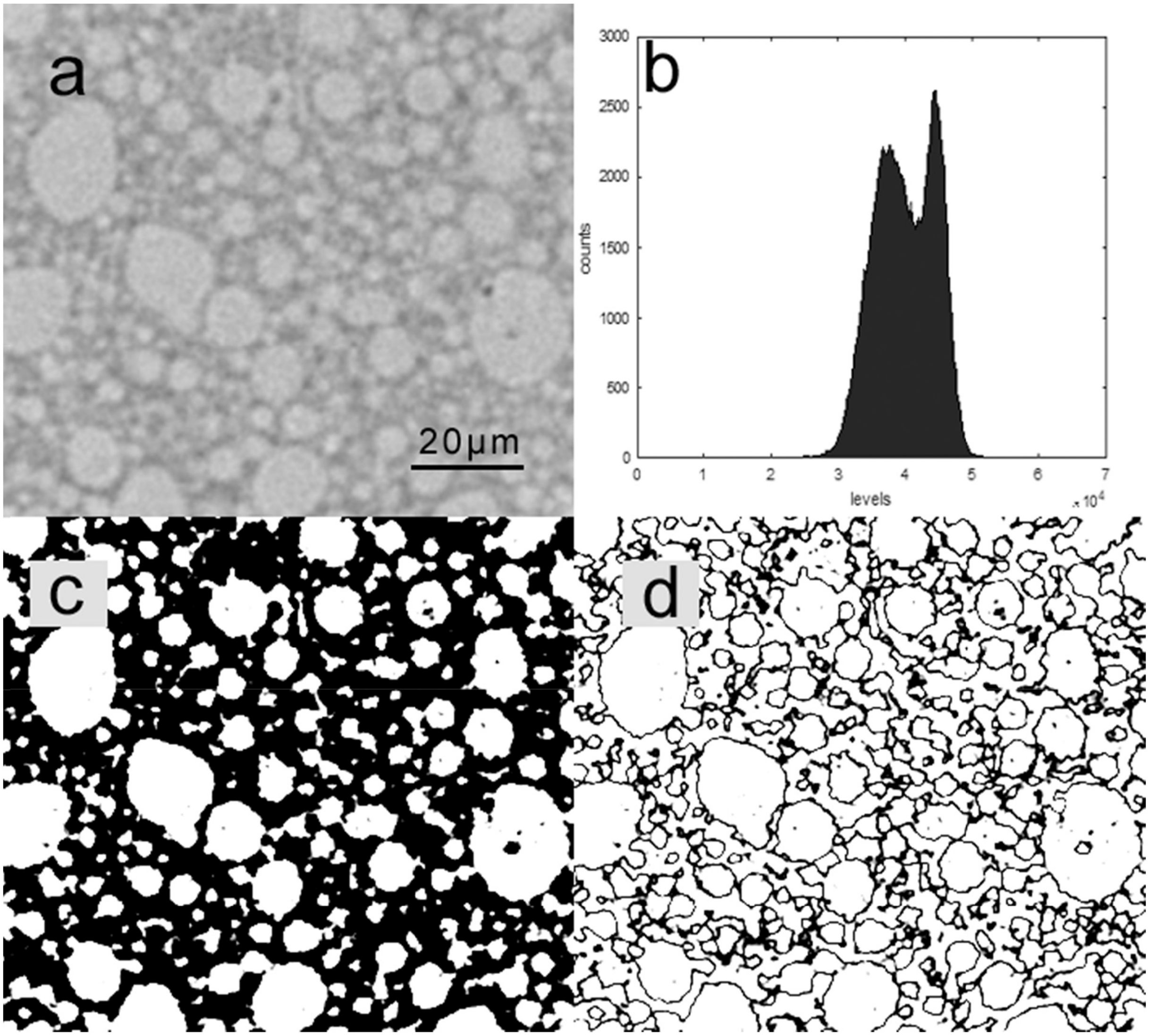

Fig. 4. Micro-CT image (1 slice) of EMC sample (79 vol%). (a) Image as obtained from the micro-CT scan, SiO_2 particles appear brighter than epoxy matrix. (b) Histogram of this image. (c) Pixels of lower peak in histogram (levels of $2 * 10^4$ to $4 * 10^4$) are ascribed a black value. (d) Pixels from max of epoxy peak to the minimum between the peaks are ascribed a black value.

epoxy. However, the white areas in Fig. 4c take up less than the expected 79%, which is the filler volume fraction of the imaged sample. It seems that some information from the SiO_2 particles overlaps in brightness with the part of the histogram corresponding to the epoxy peak. Part (d) of Fig. 4 assigns a black colour to the pixels with a level between the maximum of the epoxy peak and the minimum between the two peaks in the histogram. Although on first sight, it might seem that the edges of the particles or maybe even an interphase become visible. In fact, this stems from the resolution of the micro-CT scan. The smallest measurable voxel size has an edge length of 1 µm. This is larger than our estimate on the interphase thickness of about 250 nm (see Section 3.2). Voxels on the edges partly absorbed X-rays from SiO_2, epoxy and interphase at the same time. The value for the voxel is then the average absorption of this region (the so-called partial volume effect). In the figure, it can be seen that the features giving an intermediate density in the scan are in the length scale of the voxel size, thus we do not observe an interphase region here, but rather a blurring effect stemming from the fact that the resolution of the imaging is in the range of our feature size. To create a mesh for the simulation, it is necessary to choose the threshold for distinguishing particles from epoxy matrix (pixels with which brightness should be regarded as particles). As described above, choosing the minimum in the levels graph will lead to an underestimation of the filler volume. Instead, we chose the threshold to give a correct representation of the filler volume fraction in the sample.

2.2.2.2. Step 2: Simpleware mesh generation/interface generation. The 3D image obtained from the micro-CT scan was masked using Synopsis Simpleware Scan IP P-2019.09. The threshold level was chosen based on the histogram and the knowledge of the sample's filler level as described in the previous section. The EMC used in this study contained a filler fraction of 60 vol% and 79 vol%. The volume fractions in the final meshes were 58.7 vol% and 81.7 vol%.

For the two sets of simulations, two types of meshes needed to be generated using the FE module of Synopsis simpleware. First, a mesh for each filler fraction for analyzing the effective diffusion constant without an interphase was generated. These are shown in Fig. 5. We masked as described above to obtain the proper filler content and subsequently, cropped it to 200 × 200 × 200 voxels of 0.97 µm resolution. The masks amount up to 9.2 and 6.7 M triangles in total. Afterwards, using the FE module, a mesh was generated, which is importable by COMSOL Multiphysics 5.5. As can be seen from Fig. 5. As already mentioned in the description of the CT images, the resolution is too low to correctly image

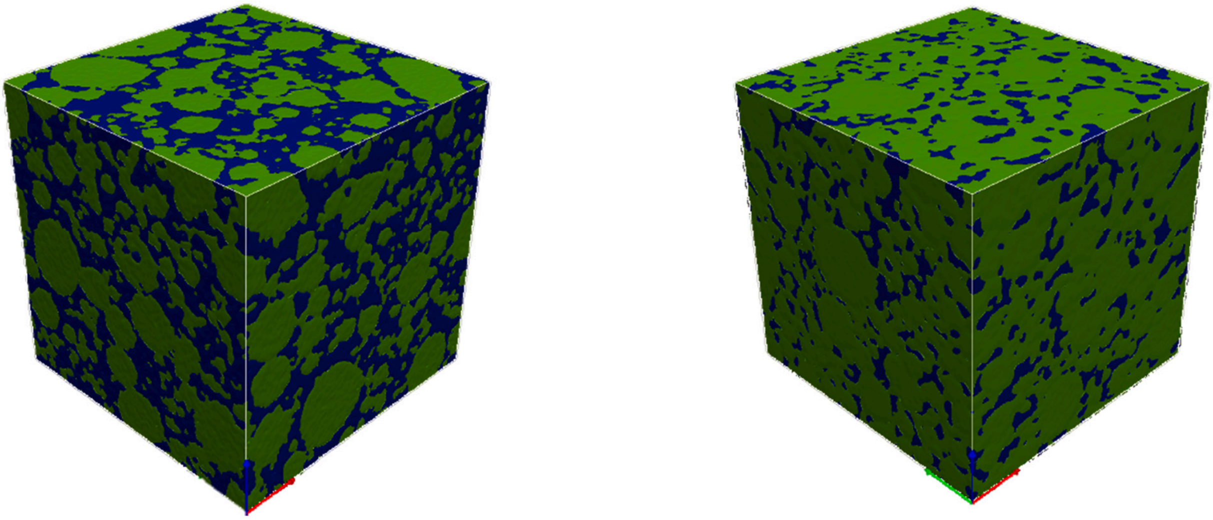

Fig. 5. Synopsis Simpleware masks of CT scan with 60 vol% (left) and 79 vol% (right) fillers. Green shows the SiO_2 filler, while blue depicts the epoxy. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

all features of the sample. Very small grains are not imaged and/or "melted together" with other/larger filler particles. This is both visible in Fig. 4 and Fig. 5. In the final simulation these two artefacts can lead to errors both increasing and decreasing the diffusion coefficient. The lack of small particles can increase the diffusion coefficient, as there is less hindrance to the moisture transport, while the melting together of the particles can cause a decrease in diffusivity, creating more hindrance to the moisture diffusion than in the real sample.

For the second simulation, a mesh for studying the interphase effect was created for the 79 vol% filler level. We resampled (enhanced) the masks to 500 × 500 × 500 voxels of 250 nm resolution to be able to obtain an interphase layer of 250 nm. It was also necessary to choose a smaller volume of the sample, as the computing power needed to solve the simulation increased with this resampling and exceeded the capabilities of our hardware without decreasing the sample size. The thickness through which the diffusion is simulated is 190 μm in the case of the EMC without interphase and 125 μm for the simulation of the EMC with interphase. Subsequently we eroded the whole mesh by 1 pixel, thus taking away a 250 nm thick layer of the epoxy at all interfaces. This mesh was used as mask for the bulk epoxy. To obtain a mask for the interphase, this new mask of the bulk was subtracted from the previous (uneroded) mesh. The interface consists of a 250 nm thick outer surface covering the whole bulk mask. As previously, a mesh was generated, that was subsequently imported in COMSOL Multiphysics 5.5. The masks of the epoxy and interphase amount to 37 M triangles in total. Fig. 6 depicts the mesh. The interphase (green in the figure) covers the entire bulk epoxy form in a network of interphase volume. In the figure, the bulk epoxy can thus only be seen on the sides of the simulation mesh. Although the mesh does not capture all small features, we do not expect a large error in the simulation of the interphase effect, as small variations on the filler particle size only have a minor impact of the total interphase volume. Additionally, we used the actual filler volume fraction of the samples in the thresholding to obtain meshes with the correct volume fraction of filler particles. The final volume fractions in the mesh is 79.9 vol%, which is almost identical to the EMC volume fraction.

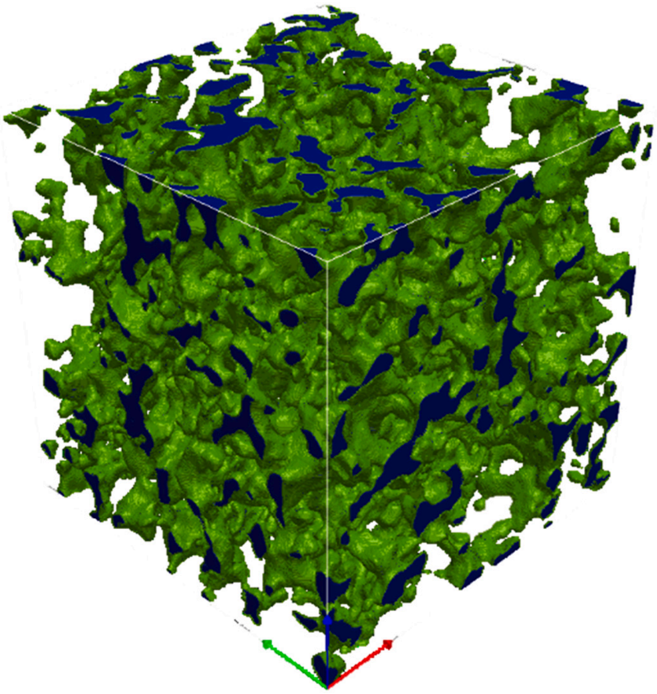

Fig. 6. Synopsis Simpleware masks of CT scan with 79 vol% fillers and 250 nm interface layer. Green shows the interphase, while the bulk epoxy is colored in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2.2.3. Step 3: Solving a diffusion equation in COMSOL Multiphysics 5.5.

The exported files were directly imported as mesh in COMSOL. Fick's second law

$$\frac{\partial c}{\partial t} = -\nabla J = D\nabla^2 c, \tag{4}$$

was implemented with the following boundary conditions: We simulate a cubic box with length L as shown in Fig. 7. The moisture ingress is from one side of this cube (showing red in the figure) with $c = c_0$, at $x = 0$. At the boundaries ($y = 0$, L and $z = 0$, L) boundaries the flux is zero $J = 0$. With the saturation level of the epoxy set to $s_0 = 0.8 \bullet 10^{-2}\ g_{H20}/g_{epoxy}$ (measured values from the model epoxy), the epoxy density of $\rho_{epoxy} = 1.2\ kg/dm^3$ and the molar mass of water $M_w = 18$ g/mol, the concentration c_0 becomes:

$$c_0 = s_0 \frac{\rho_{epoxy}}{M_w}. \tag{5}$$

A time dependent study was performed simulating 20 h at 10 min intervals. Subsequently, the data on the moisture concentration in the

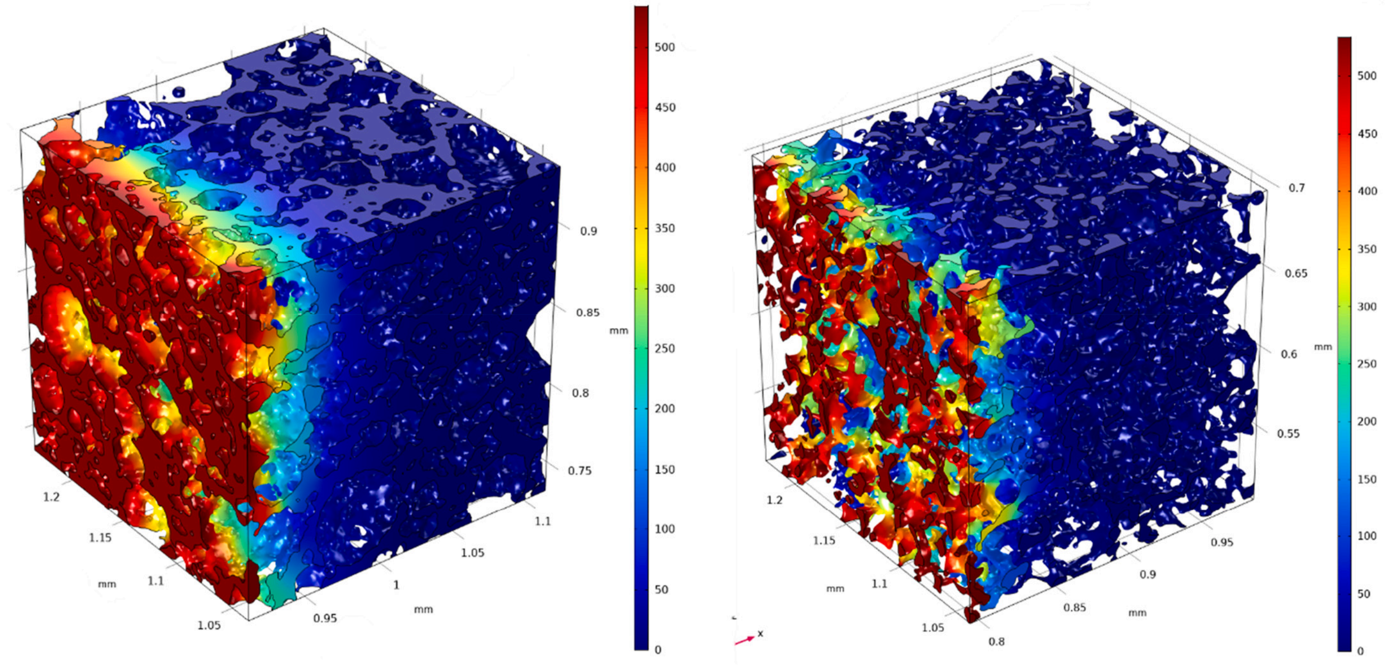

Fig. 7. COMSOL simulation mesh of 60 vol% and 79 vol% EMC sample, moisture ingress from one side (red); the SiO_2 fillers show as gaps in the simulation. Time = 600 s; Moisture concentration in [mol/m^3]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

simulation model was exported to a text file and fitted in the same way as the experimental data. For the first simulation without interphase effect, the total calculation took about 5 h with file sizes of up to 16 Gb. The COMSOL simulations on the mesh with interface, took about 67 h to complete, requiring the full 64 Gb memory of the computer producing save files of 80 Gb. Simulations were run on an 8 cores Intel Xenon E5-1620 v3 processor with 64 Gb internal memory.

3. Results and discussion

In order to understand the impact of interphase diffusion on the effective diffusion, it is necessary to compare the measured values with models, which help distinguish the effect of adding inert particles to the polymer from the effect of an interphase layer with different moisture transport properties than the bulk. In this section, we first present the measured results for the effective diffusion coefficients of the model epoxy and the EMC, to give an overview of the data. Subsequently, we compare this data with the appropriate models as introduced in the previous section.

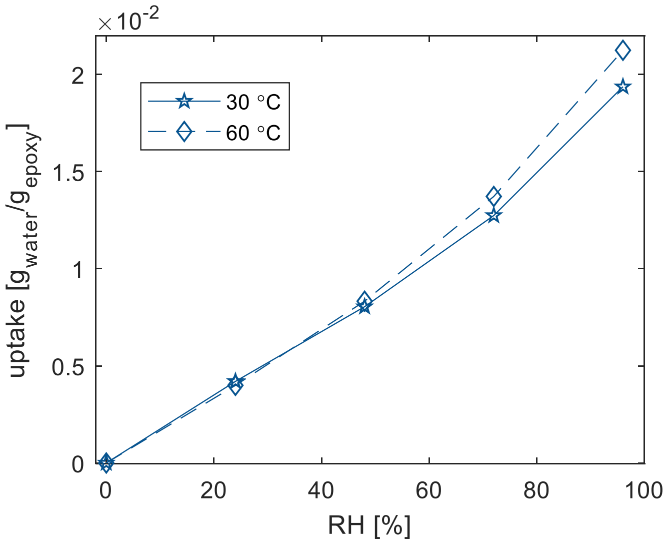

Fig. 8. Sorption isotherm illustrating the moisture uptake in the unfilled model epoxy system at 30 °C and 60 °C.

3.1. Moisture diffusion measurements

3.1.1. Sorption characteristics

The sorption of the unfilled model system was characterised over a wide range of RH by exposing a previously dry sample to subsequent steps in RH of 24% to a maximum of 96%. Fig. 8 shows the resulting sorption isotherms at both 30 °C and 60 °C. It can be seen that the sorption isotherms are linear up to a relative humidity of approximately 60%. From this, we can assume that it is reasonable to assume Fickian diffusion for measuring steps in RH from 0 to 60%. Further it can be seen that the moisture uptake in this RH range is independent of temperature, showing that the moisture sorption in this system is enthropy driven.

Looking at the moisture sorption for the uptake measurements used in the diffusivity evaluation (with one step in RH from 0 to 60%) (Table 1), the amount of absorbed moisture per gram of epoxy (thus without taking the filler particles into account) for the model component showed no significant difference between the unfilled material and a

Table 1
Moisture content (for 60% RH) of the epoxy weight fraction [g_{water}/g_{epoxy} * 100%] of the composites in wt%, error estimated to 5% (except for *, where error is approx. 15%, due to too short measurements).

T [°C]	Moisture content [%]				
	Model epoxy $\phi = 0$	Model epoxy $\phi = 0.2$	Model epoxy $\phi = 0.3$	EMC $\phi = 0.6$	EMC $\phi = 0.79$
30	1.0	0.82*	0.93	0.55	0.84
45	0.99	0.87	0.91	0.60	0.73
60	1.0	0.91	1.1	0.56	0.77
75	1.1	0.94*	1.1	0.65	0.92

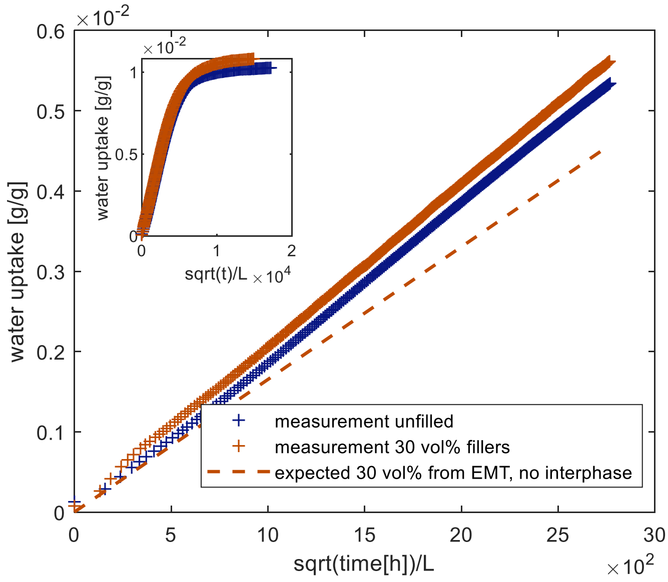

Fig. 9. Uptake data of unfilled model component and model component with 30 vol% filler level measured at 60 °C, normalized to only take the epoxy weight fraction into account. X-axis is normalized to cancel out the sample thickness difference. Dashed line marks the expected uptake dynamics of the 30 vol% filled sample assuming no interphase effect, according to EMT.

filler level of 30 vol%. Fig. 9 gives the measured data for a comparison of these two at 60 °C, with the inset showing the full uptake measurement). The samples with 20 vol% on the other hand show a lower uptake. As the unfilled and the 30 vol% filled model component were significantly thinner than the samples of the 20 vol% filled model component, this deviation in the moisture uptake might be due to a thickness effect (as previously described in literature [27–30]) rather than to an interphase effect. Studies on moisture sorption in EMCs showed a linear relation between the filler volume fraction and the moisture uptake, with a decrease in moisture uptake with increasing filler level [14,16]. This indicated that there is no large amount of uptake to interphase volumes and is in line with the observations on the model component with comparable thickness. Adding fillers does not seem to introduce an interphase volume with largely differing moisture uptake properties compared to the bulk epoxy for this system. However, the EMC in our measurements showed an increased moisture uptake of the epoxy volume fraction (including a possible interphase) at the higher volume fraction at all temperatures.

3.1.2. *The influence of filler addition on the dynamics as measured*

In order to gain information on the dynamics of the uptake process, the diffusion coefficient of both the commercial EMC and the model system was evaluated at four different temperatures, by fitting the measured uptake (with a measurement step going from 0 to 60% in relative humidity) with Eq. 2. A comparison of the uptake data between the unfilled model component and the model component filled with 30 vol% is presented in Fig. 9. The measured moisture uptake over time is normalized to only account for moisture uptake to the epoxy fraction, as the fillers are impermeable to moisture. Further, the time axis is normalized to account for the difference in sample thickness. The inset shows the entire measured uptake process, while the main graph shows only the initial uptake phase. It can be seen that the uptake is linear with the square root over time, following a Fickian dynamic. Additional to the measured uptake, a prediction on the dynamics of a sample containing 30 vol% of fillers without any interphase effect is presented. This prediction is based on the EMT as described in Section 2.2.1. The predicted uptake is slower than the actual measured uptake. This means that the addition of the particles does not slow down the diffusion to the extent that the model predicts, pointing to a phenomenon accelerating the uptake.

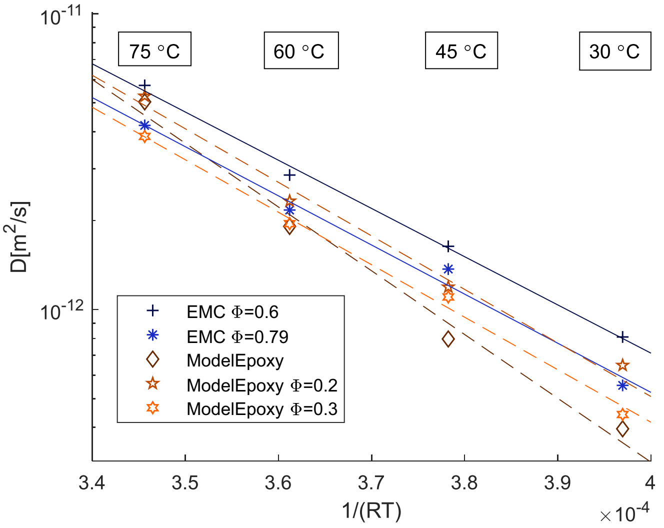

Fig. 10. Arrhenius plot of effective diffusivity as measured in DVS for a step in RH from 0 to 60%. The markers represent the measured values, while the lines show the Arrhenius fit; ϕ is the filler level of the sample; error bars are lacking for better visibility, errors are 10%–20%, with exception of the model epoxy at $\phi = 0,3$, which has errors of about 30% for 30 °C and 45°°C.

Further, the fitted diffusion coefficients for all samples are presented in an Arrhenius plot in Fig. 10. The diffusion coefficients increase with temperature for both model epoxy and EMC. The errors in the measurement are rather large (mostly 10%–20%, with exception of the model epoxy at $\phi = 0.2$, which has an error of about 30% for 30 °C and 45 °C), due to inaccuracy in the final moisture uptake value (which we estimate to be 5% as well as sample unevenness in the case of the model component, error estimation in described in Section 2.1.2). When comparing the different filler levels in the EMC, the higher filled samples (79 vol% compared to 60 vol%) show a lower diffusion coefficient at all temperatures. For the model epoxy, there is no trend of diffusion coefficient with filler fraction, the diffusion coefficients are in the same range and not clearly distinguishable within the error margins. Unfortunately, it is not possible to directly compare the model epoxy system with the commercial EMC, as the EMC contains additional additives of unknown concentration, which will influence the diffusion coefficient.

When comparing the diffusion coefficients without further evaluation, the assumption of an interphase effect might seem farfetched as all values are in the same range. However, it is important to remember that adding filler particles to the polymer can have two effects that might oppose each other: Adding the filler particles will slow down diffusion by increasing the path length. At the same time an interphase layer with a higher diffusion coefficient as the bulk polymer will increase the speed of diffusion. This can already be seen in the evaluation of the raw data in Fig. 9, where it becomes obvious that the uptake in the filled sample is faster than expected when only taking the slowing effect of adding fillers into account. Conclusions on the existence of an interphase layer can only be made when both processes are evaluated separately.

The data has been fitted with the Arrhenius relation, giving activation energies for diffusion with values of around (40 ± 10) kJ/mol, the fitted lines are shown in Fig. 10. In literature, activation energies of 30–60 kJ/mol are reported for epoxies as well as EMC [20,31,32]. Soles and Yee describe that there are two main processes important for the activation energy of the diffusion process in epoxies: hydrogen bonding and molecular motions (beta relaxation) of the epoxy matrix [33]. While the hydrogen bonding contributes with 10–30 kJ/mol to the activation energy, the molecular motions account for 20–30 kJ/mol. Changes in the epoxy structure due to an interphase around the fillers might

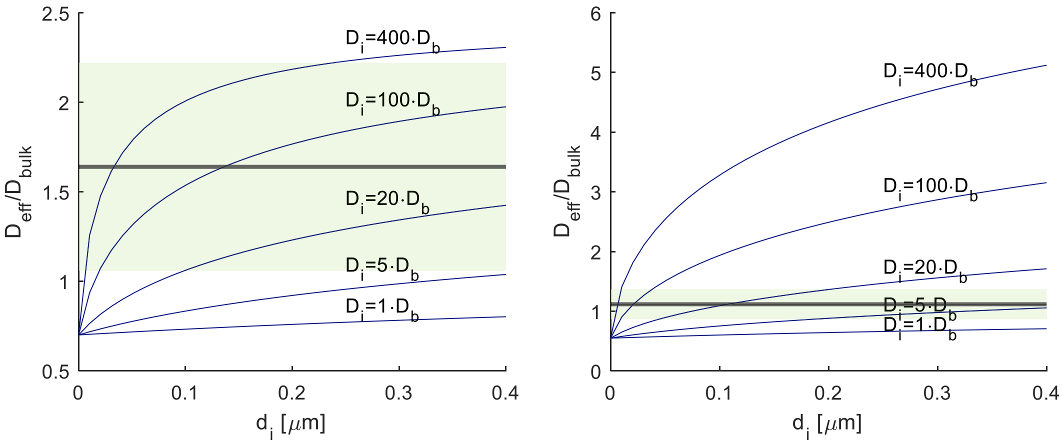

Fig. 11. Effective medium theory predictions for the effective diffusivity normalized by the bulk diffusivity (D_{eff}/D_{bulk}) at different interphase thicknesses(d_i), for a particle size of 2.9 μm, at filler volumes of 0.2 (left) and 0.3 (right); the solid lines mark the measured values at 30 °C. The green shadow gives the error of the measured value with 95% confidence bounds. The blue lines give the results of the EMT for various ratios of interphase diffusion compared to the bulk diffusion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

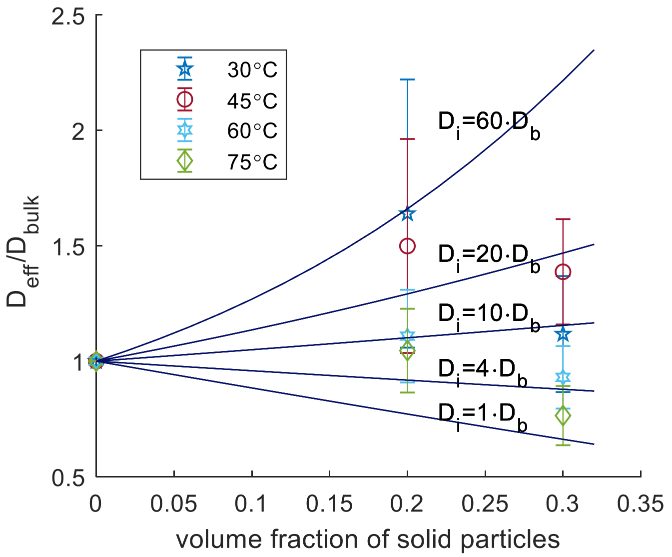

Fig. 12. EMT, effective diffusivity of the medium normalized by the bulk polymer's diffusion (D_{eff}/D_{bulk}) for different filler volume fractions at an interphase thicknesses of 250 nm. Blue lines give theoretical D_{eff}/D_{bulk} (from EMT) for different interphase diffusivities D_i compared with the measured values for the epoxy model component for different temperatures (error bars give 95% confidence interval). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

influence both the molecular motions and the H- bonding in the composite. Concerning our measurements, we unfortunately cannot make statements on a possible change in transport mechanism as the error margins are rather large (up to ±10 kJ/mol).

3.2. EMT — interphase effect in model system

Through comparing measured data with predictions from the EMT, the effect of the fillers (slowing down the transport) can be distinguished from the effect of the interphase (which might either further slow down the transport or increase the transport speed, depending on its diffusional properties).

Fig. 11 and Fig. 12 show several comparisons between the measured data and the predictions of the EMT. The effective diffusivity is normalized by the bulk epoxy's diffusivity to facilitate a comparison. The predictions of the EMT are presented for different interphase diffusivities (D_i) compared to the bulk epoxy diffusivity (D_b) for a particle radius of $r_s = 2.9$ μm, which is the median radius of the filler particles in the model epoxy composite. As we do not know the thickness of the interphase, we also included variations in the interphase thickness d_i into the evaluation. Measurements of the interphase thickness in previous studies [9] showed that d_i is dependent on the amount of silane added to the epoxy. In this study, the silane is not added to the epoxy, but coated on the particles. Consequently, the interphase thickness could be as small as the length of the silane coupling agent's molecule as it connects the SiO_2 particles to the epoxy matrix. The length of these molecules is only about 1 nm. However, it is likely that the effect spans wider, as the binding to the silane also affects the epoxy structure. Effects spanning several orders of magnitude beyond the length of the silane molecules were observed in previous studies on the interphase in filled epoxies [8–10]. In epoxy–glass fiber systems a softer interphase was observed. Joliff et al. [10] observed a lowering of the elastic modulus (measured by AFM) reaching 1 μm into the bulk epoxy, with a high difference in the modulus in the 500 nm closest to the particles.

Fig. 11 includes two graphs, showing how the measured values at 30 °C compare to the predictions of the EMT for an interphase thickness d_i ranging from 1.5 nm to 400 nm at filler volume fractions of 0.2 (left) and 0.3 (right). The measured values are given as (straight) lines in the plots, while the prediction of the EMT for different ratios of interphase to bulk diffusivity is given by blue lines. For all values of interphase thickness considered, the lines marking the experimentally measured effective diffusion (grey lines) are above the effective diffusion coefficient predicted for the case of no interphase effect. This also holds true, when taking the error margins into account. Thus, we can see an increased diffusivity in the interphase (D_i) compared to the bulk (D_b). Further, the actual layer showing increased transport is most likely thicker than the silane molecule length itself, as otherwise the interphase diffusivity would have to be far more than 400 times the bulk diffusivity to explain the effective diffusion we measured. Previous studies on a similar system (glass fibers in epoxy) indicate a factor of 5 times for this difference in diffusion coefficients [10]. Considering this, it seems likely that the interphase effect stretches far beyond the silane molecular length. Assuming an interphase diffusivity between 5 and 20 times the bulk diffusivity, an interphase thickness above 100 nm seems appropriate. Unfortunately, the error margins are rather large in this evaluation, due to the division of two measured values, so it is difficult to come to exact values. Comparing the findings in literature, assuming an interphase thickness of 250 nm seems reasonable.

In Fig. 12, we show the predictions of the EMT for an interphase thickness of 250 nm in comparison with the measured values at different temperatures. Interestingly, the effect of increased interphase diffusion seems to become less pronounced with increasing temperature, as at lower temperatures the interphase and bulk diffusivity differ more than at higher temperatures. It can be speculated that as the temperature increases, the bulk epoxy has a larger potential to soften than the interphase as the chain mobility of the interphase is already higher at low temperatures and cannot increase in the same degree with temperature as the bulk epoxies' chain mobility.

Evaluation of the model compound with a filler fraction of 30 vol% are on the edge of the validity of the EMT model, which can be estimated at a filler fraction of 29 vol%. 29 vol% is the theoretical percolation limit for equally sized spheres in a “Swiss cheese” model [26]. It can thus be expected that above this filler fraction, the filler particles interact with each other and can no longer be regarded as unaffected by the neighbors. The volume fraction of 30 vol% is still reasonably close to this percolation limit, especially considering that in the filler size in this study is not uniform, but distributed, which allows for a more efficient packaging.

3.3. *Numeric simulation — interphase effect in EMC*

To simulate the interphase effect of the EMC samples, the EMT cannot be used, as its validity only holds for low filler fractions, below the percolation limit of about 29 vol%. Consequently, we ran numerical simulations in COMSOL based on micro-CT scans of the samples. We ran 2 different simulations. The first simulation has the same goal as the EMT analysis: distinguishing the slowing down effect of the fillers due to a possible interphase effect. For that, we compare the measured effective diffusion through the two samples (with 60 vol% and 79 vol%) filler level with simulations of the effective diffusion without the addition of an interphase layer. The second simulation (of the 79 vol% EMC) includes a 250 nm wide interphase layer. In that case we simulate the effect of different interphase diffusion speeds on the total effective diffusion. These values are compared with the bulk diffusivity to see at which interphase diffusivity the retarding effect of fillers is counterbalanced by an accelerating effect of increased interphase transport.

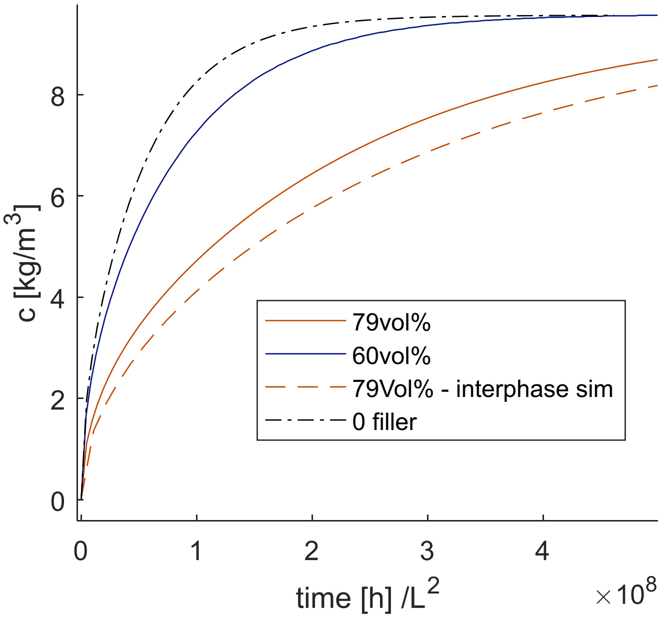

Fig. 13. Uptake simulation of EMC samples with different amount of fillers (water uptake (kg/m^3) on epoxy volume considered for better comparison of uptake dynamics), dashed line: interphase simulation.

3.3.1. *Simulation without interphase effect*

First, calculations have been performed to compare the effective diffusivity of the mold compounds without taking interphase diffusion into account. In this way, the effect of the filler particles on the effective diffusion can be studied. Fig. 7 shows the beginning of the moisture ingress simulation for the 2 meshes (EMC with 60 vol% and 79 vol% filler level) without interphase effect. The moisture can only enter the cube from one side, showing red in the figure. After running the simulation, the data of the moisture concentration was exported and fitted the same way as the experimental data to compare the values for the effective diffusivity.

This can be seen in Fig. 13. We only consider the water uptake on the epoxy weight to facilitate the comparison of the uptake dynamics. The diffusion coefficient in the epoxy phase was set to $2 \bullet 10^{-12}$ m^2/s (dashed line in the figure), which is the value we measured for the unfilled model epoxy system at 60 °C. It must be expected that the bulk diffusivity in the EMC is different from the model component, as it contains a multitude of additives. The value of $2 \bullet 10^{-12}$ m^2/s is thus merely an estimation (so that the simulations are not directly comparable to measured values of diffusivity, see below). The effective diffusion coefficient obtained through the simulation for the 60 vol% filled EMC is $1.4 \bullet 10^{-12}$ m^2/s and $0.56 \bullet 10^{-12}$ m^2/s for the 79 vol% filled EMC. This graph shows that the addition of 60 vol% of fillers only has a small effect on slowing down the moisture diffusion. However, adding (79 vol%) has a large effect on the effective moisture diffusion through the EMC.

What can we learn about interphase diffusion in the EMC? To answer this, we need to compare the simulation results with the measured diffusion coefficients. Even though the exact bulk diffusivity is unknown, it is still possible to draw conclusions. Instead of comparing the values for the effective diffusion, we compare the relative difference of the effective diffusion between the two filler levels. In Table 2, the effective diffusion coefficients as well as a comparison of the ratio between the 2 filler levels is given (the relative difference). There is a clear difference in the retardation effect of the higher filler level between the measurement and the simulation. While the diffusion coefficient at 60 vol% in the measurements was on average 1.33 times larger than at 79 vol% filler level, it was 2.7 times higher in the simulation. Thus, the diffusion measured at the higher filler level is faster than what would be expected in the case of no interphase diffusion. An explanation for this is an increased moisture transport along the interphase. As the volume fraction of the interphase is larger in the higher filled composite (as visualized in Fig. 14), an increased interphase diffusion would have a higher impact on speeding up the effective diffusion in higher filled composites, possibly even forming a connected network with increased transport property. Thus, the retarding effect of the increased filler level is lower than in the simulation (without interphase effect). As already described in Section 2.2, there are some imperfections in the simulation mesh due to the CT-resolution being in the range of the size of the smallest features in the EMC, which might lead to uncertainties in the estimation of the interphase effect. As can be seen in the simulation mesh depicted in Fig. 7, the grains are melted together in some areas where SiO_2 grains are in close proximity to each other, thus creating

Table 2

Comparison of simulation results with measured values of effective diffusivity for the EMC, assuming no interphase diffusion. The measured values for the diffusivity are taken from the 30 °C measurement, while the ratio is the mean value from all measured temperatures. As the real bulk diffusion coefficient is unknown (set to $2 \bullet 10^{-12}$ m^2/s for the simulation), only the relative difference between the effective diffusion of the two filler levels holds information on the impact of the filler level on the effective diffusion.

	D (60 vol%) [m^2/s]	D (79 vol%) [m^2/s]	$D_{60\%}/D_{79\%}$
DVS	$1.6 \bullet 10^{-12}$ (45 ° C)	$1.3 \bullet 10^{-12}$ (45 ° C)	1.33 ± 0.18 (30–75°C)
COMSOL	$1.4 \bullet 10^{-12}$	$0.51 \bullet s10^{-12}$	2.7

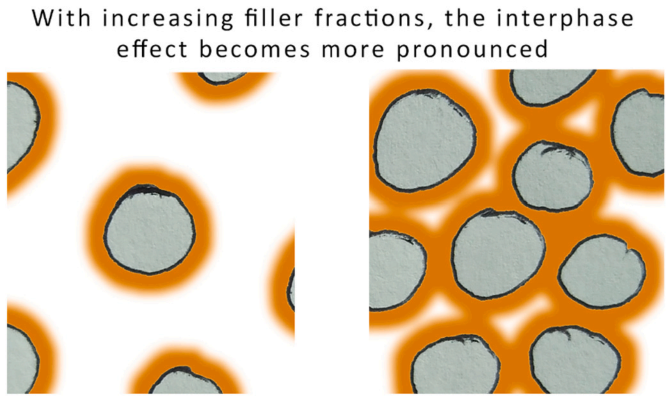

Fig. 14. Simplified schematic showing changes in volume fraction of the interphase with increasing particle density.

more restriction for the water mobility than in the actual sample. On the other hand, some of the smaller particles do not register as particles, but as epoxy matrix leaving more freedom for mobility. Fig. 13 contains a comparison to the simulation containing interphases. This comparison can give an idea of the uncertainty of meshing differences. For the sample containing 79 vol%, two different meshes were made to be able to perform the different simulations (see description in Section 2.2.2.). The simulated uptake of the two simulations (Fig. 13, curves 79 vol% and 79 vol%-interphase simulation, in the interphase simulation interphase and bulk diffusivity set as equal) shows that there are some deviations between the two simulations which are caused by the meshing. The diffusion in the simulation containing the interphase is slightly slower than the simulation through the mesh which does not contain the interphase (with a D of $4.2\bullet10^{-13}$ m^2/s vs. $5.1\bullet10^{-13}$ m^2/s). Calculating the ration of $D_{60\%}/D_{79\%}$ using the interphase mesh, it becomes 3.3, which is an even larger indication for an interphase effect than in the comparison with the mesh without interphase.

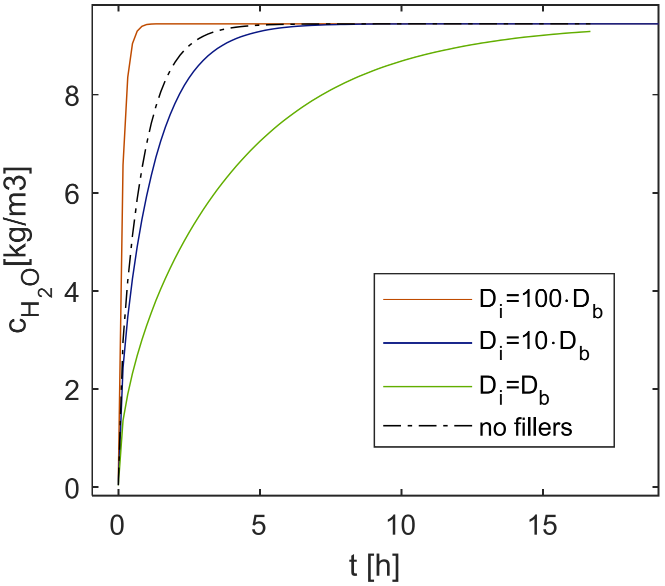

Fig. 16. Water uptake over time for simulations (EMC with 79 vol% filler volume, assuming 250 nm interphase thickness) with differing interphase diffusivity (D_i), compared to the diffusivity of bulk epoxy ($D_b = 2\bullet10^{-12}$ m^2/s) without filler particles.

3.3.2. Simulation of the interphase

In this simulation we used the µCT scan of the 79 vol% filled sample and added a 250 nm thick interphase layer (process described in Section 2.2.2), to study how much an interphase layer influences the effective diffusivity in an EMC. A zoom in of the mesh can be seen in Fig. 15: the filler particles are not visible, the interphase is shown in brown, while the bulk epoxy is green. It can be seen that the interphase forms a network throughout the structure that is only interrupted in few areas. In the figure, the interphase totally covers the epoxy, so that the epoxy itself is only visible at the boundaries of the mesh. In total, the interphase takes up 22% of the total polymer volume and can thus be expected to have a significant influence on the effective diffusivity. Three different values for the ratio of D_i/D_b have been chosen: $D_i = D_b$, $D_i = 10D_b$ and $D_i = 100D_b$. The results are shown in Fig. 16. The data is compared with the uptake dynamics of a non-filled system (dashed line shows D_b). The final concentration is normalized to match the other curves.

The condition $D_i = D_b$ exhibits the slowest uptake, while at 10 times increased interphase diffusivity the uptake speed is comparable with the uptake in an unfilled system. In case of a 100 times higher diffusion

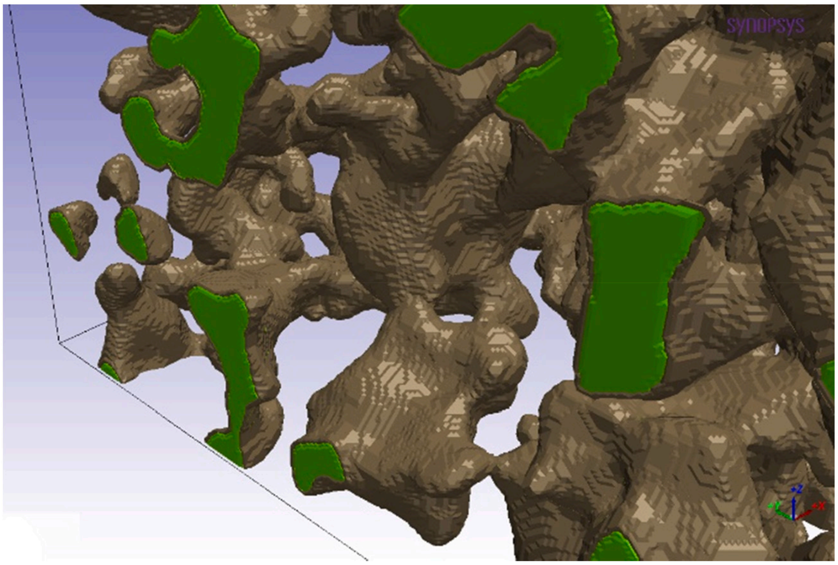

Fig. 15. COMSOL simulation mesh with interphase region; green = epoxy; brown = interphase; fillers transparent. The interphase forms a continuous network. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

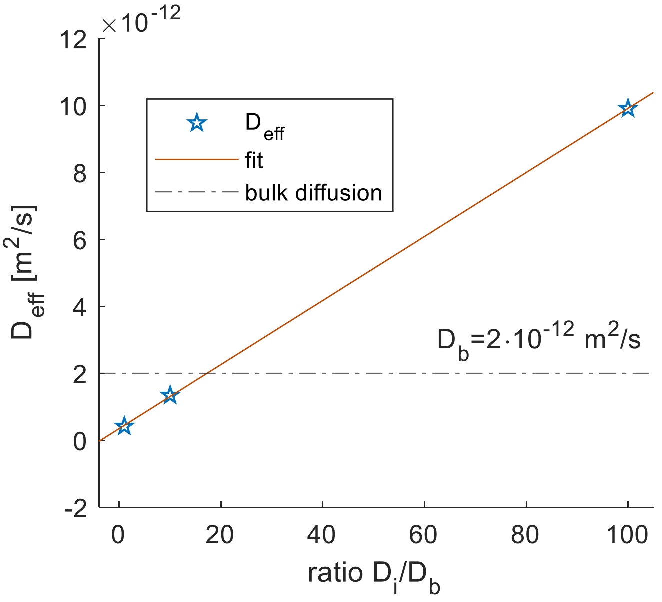

Fig. 17. COMSOL model: effective diffusivity with interface diffusivity change. The dashed line marks the bulk diffusion coefficient, while the stars mark the effective diffusivity for different ratios of interphase to bulk diffusivity. The simulation was done for the EMC with 79 vol% filler volume, assuming 250 nm interphase thickness.

coefficient in the interphase compared to the bulk, the addition of fillers would lead to a faster moisture uptake than in an unfilled system. Fig. 17 presents the effective diffusivity for the three cases. It increases linearly with increasing ratio of D_i/D_b with a slope of $(9.6 \pm 0.8) \cdot 10^{-14}$ m^2/s. In case of a ratio of D_i/D_b above 17, the effective diffusion becomes larger than the bulk epoxy diffusion, thus adding particles to the epoxy would cause no retardation of moisture diffusion. In case of glass fiber filled epoxy [10] a difference of $D_i = 5D_b$ was reported. In this case adding fillers would still have a reducing effect on the effective diffusion. This is in line with our observations from the experiment. The 79 vol% filled sample had a lower diffusion coefficient than the sample with 60 vol% fillers. Reducing filler content in the EMC showed an increase in the effective diffusivity. This is similar to the observation for simulating the interphase effect in a polymer matrix filled with differing volume fractions of impermeable spherical fillers [34]. For high filler fractions, the interphase regions overlap and the effective diffusion coefficient decreases due to a decrease in interphase volume fraction. From comparing our measured values with the COMSOL simulation, we can conclude that the ratio of interphase diffusivity to bulk diffusivity in the EMC is in the range of 1 to 17.

4. Conclusions

In this work we investigated if the interphase volume between the silica particles and the epoxy matrix has an influence on the effective diffusion coefficient of the composite, which might lead to a decrease in the protective properties against moisture ingress. For both the model epoxy as well as the EMC, we found indications of an increased transport through an interphase layer and/or an interphase layer network when comparing the measured results to the model and simulation.

In the case of the model system, the measured diffusion coefficients were higher than the predictions from the EMT for a filled system without interphase effect. Further it showed that the interphase effect stretches beyond the length of the silane coupling agent's molecule. An effect on the epoxy bulk structure stretching further than 100 nm from the SiO_2 fillers surface seems likely in the considered material matrices. Additionally, the effect of the interphase showed to change with temperature, with a larger difference in interphase vs. bulk diffusivity at lower temperatures. As the interphase is softer than the bulk epoxy promoting faster transport, this temperature effect might be explained by a differing potential for further softening as temperature increases. The chain mobility of the interphase is already higher than the bulk's chain mobility at low temperatures and thus might not have the ability to increase in the same degree with temperature.

Also for the EMC, the comparison of the simulated moisture uptake with the measured moisture uptake points to the existence of an interphase layer with an increased diffusivity. The simulation of the moisture uptake without an interphase effect showed that the retarding effect of the increase in filler level from 60 vol% to 79 vol% filler level on the effective diffusion should be larger than the measured values in the samples indicate. In the simulation the effective diffusivity of the lower filled sample was 2.7 times higher than the sample with higher filler level, while it was only 1.33 times in the measurement. When simulating an interphase of 250 nm thickness for the 79 vol% filled EMC, it showed that the interphase formed an interconnected network taking up 56% of the polymer volume. In this example, an increase in diffusion coefficient of 17 times in the interphase compared to the bulk would leave the composite to have the same effective diffusivity as the unfilled epoxy, thus reducing the protective property of the encapsulation. However, the measurements show that the difference in diffusion coefficient between interphase and bulk in the EMC is lower than 17 times. The regular EMC still showed a lower diffusivity than the EMC with reduced filler content. It should be noted that while the increase in effective diffusion coefficient due to adding silane coupling agents is undesirable, cracks caused by a poor binding between particles and epoxy matrix cause a much higher threat to the protective value of the encapsulation, so that the need for coupling agents is not in doubt. However, an increased interphase diffusion is a factor to consider when choosing coupling agents, as the large filling fractions used in EMC lead to such a high interphase volume, that networks of increased moisture transport can form.

While this work shows clear indications for an interphase volume between fillers and the bulk epoxy in EMCs, further studies on the exact properties are desirable. A thorough study with a model component containing a similar amount of filler particles as commercial EMCs would be useful to further study the effect of interactions between the fillers, further researching the impact of a connected network of interphase volumes. Data from such a test would improve the comparability of the model system and the EMC. Additional measurements would also be needed to validate the numerical model. Imaging samples from the model system would facilitate a comparison between measured data and the simulation model, as the bulk diffusivity in the simulation could be matched with the measured sample's diffusivity, making a direct comparison between measured effective diffusion and simulated effective diffusion possible.

CRediT authorship contribution statement

A. Herrmann: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing – original draft, Visualization. **S.J.F. Erich:** Conceptualization, Software, Funding acquisition, Writing – review & editing. **L.G.J. van der Ven:** Supervision, Writing – review & editing. **H.P. Huinink:** Supervision, Writing – review & editing. **W.D. van Driel:** Conceptualization, Writing – review & editing. **M. van Soestbergen:** Resources, Conceptualization, Writing – review & editing. **A. Mavinkurve:** Resources, Conceptualization, Writing – review & editing. **F. De Buyl:** Writing – review & editing. **H.R. Fischer:** Resources, Writing – review & editing. **J.M.C. Mol:** Conceptualization, Writing – review & editing. **O.C.G. Adan:** Supervision, Funding acquisition, Project administration, 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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