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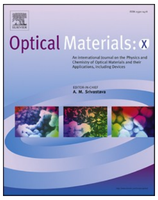

The influence of phosphor particles on the water transport in optical silicones for LEDs

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ABSTRACT

The reliability of LEDs decreases in moist environments. One potential gateway of moisture ingress, reducing the product lifetime is the lens. In white LEDs, phosphor particles are embedded into the optical silicone of the lens to convert the blue light emitted by the diode down in frequency and achieve a light output that appears white.

In this study, the influence of these phosphor particles on the moisture sorption, permeation and diffusion in optical silicones is investigated by comparing two silicone resins that are commonly used in LEDs, both with and without the addition of phosphor particles. The results of two methods are compared: the wet-cup method and a gravimetric approach of dynamic vapour sorption (DVS). Diffusion coefficients between 20 and 75 °C are reported as well as sorption isotherms, activation energy and sorption enthalpy.

It is concluded that the addition of phosphor particles only has a very small impact on the moisture transport properties of the silicones.

1. Introduction

Much research is conducted to detect, understand and reduce causes of product failures in LED technology. Moisture has been found to be an important factor in accelerating the degradation of not only LEDs, but electronic systems in general and is a key component in product lifetime testing [1–3].

Packages of white LEDs usually consist of the light emitting diode itself, mounted on a silver coated lead frame, reflecting stray light through a silicone lens. Around this, there is a housing that can be made of e.g. epoxy moulding compound. To achieve a white light output, the blue light from the diode is converted into a lower frequency by phosphor particles that are embedded in the silicone. A cross section image of an LED is seen in Fig. 1. This example shows that a large part of phosphor particles is agglomerated at the bottom of the silicone lens (f), building a layer on top of the lead frame (a) and the diode (e). However, there are still particles in the bulk silicone.

Silicone is commonly used as a lens material in LEDs, because of its good chemical and thermal resistance, which gives rise to less degradation in light transmittance over time than other possible lens materials, e.g. epoxy. A downside of the material is its high permeability to gases and moisture [4–6], which makes it a possible pathway for moisture ingress towards the interior micro-electronics and the silver reflector.

The water transport behaviour in silicones has been studied before for both LED- and other applications [5,7–9]. Also, it has been shown that exposure to humid environments has a negative impact on the conversion efficiency of the silicone-phosphor composite [3]. Some moisture uptake and diffusivity and characterization has been done for a silicone phosphor mix before [10,11]. Hoque et al. found a significant decrease of moisture uptake as well as diffusivity at 60 °C after the addition of 9 wt% phosphor particles to optical silicone.

In this paper the transport properties of optical silicones, containing phosphor particles is compared with previous results [9], where the

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resins where measured without phosphor particles. The aim is to obtain knowledge about how the phosphor particles influence the sorption, permeation and thus diffusion of water vapour in the silicones. For that, measurements have not only been performed at room temperature, but also at other temperatures to obtain activation energies and sorption enthalpies.

The measurements were performed by a wet-cup permeation experiment and by a gravimetric method using dynamic vapour sorption (DVS). The results at room temperature of both techniques are compared. Measurements at higher temperatures for activation energy and sorption enthalpy evaluation were only done with DVS.

2. Materials and methods

2.1. Materials

For this study commercially available silicone resins, OE-6650 & OE-7662[1], of optical grade silicone with high refractive index were used. In contrast to low refractive index silicones, which are made up of pure PDMS (polydimethylsiloxane, commonly referred to as silicone rubber), these resins contain a high amount of phenyl groups, which increase the refractive index of the silicone (1.41 in pure poly-dimethyl-siloxane resins (PDMS) vs. 1.55 in poly-methyl-phenyl siloxane resins) [4,6]. Also, phenyl groups are known to decrease the water permeability of the silicone [5,6]. The resins OE-6650 & OE-7662 have refractive indices of 1.54 and 1.55. There are also differences in the glass transition temperature ($Tg^{6650} = 30\ ^{\circ}C$, $Tg^{7662} = 50\ ^{\circ}C$), shore D hardness (6650: 52 vs. resin 7662: 62 at 25 °C) and storage modulus (6650: $2.2 \cdot 10^{7}$ Pa vs. 7662: $1.6 \cdot 10^{8}$ Pa at 25 °C) between the two resins.

A mass of 6 wt% of phosphor particles with a size distribution of 3–9 µm, as typically used in LEDs, was mixed into the resin to investigate possible changes to the water uptake and transport properties. Their density is 4.65 g/mL at 25 °C. In this paper, the samples containing phosphor particles will be referred to with the letter 'P', while samples without phosphor particles will be referred to as clear with the letter 'C'.

2.2. Sample preparation

Both silicone resins consist of 2 components. These were mixed, following the weight ratios given by the manufacturer. After the mixing, a degassing step was necessary to remove small air bubbles. Thin films of silicone resin were obtained by spin coating the uncured resin on an ECTFE (ethylene chlorotrifluoroethylene) surface, resulting in films of 90–200 µm (depending on resin type and spin speed). Thicker films for the DVS experiments, were obtained by applying the resin on the ECTFE surface without any spreading step. The films were subsequently cured in an oven at 150 °C for 1 h.

Dispersing the phosphor particles proved challenging since normal stirring did not lead to a proper wetting. In our previous study [9], the amount of phosphor particles that could be mixed in was negligible. For this study, the mixing was done with a high speed mixer, so that a particle concentration of 6 wt% could be achieved. The phosphor particles were added in three portions to one part of the resin. After each addition the beaker was placed in the high speed mixer at 2000 rpm twice, with a 30 s duration. After all phosphor particles were added, part two of the resin was added to the mixture and again stirred at 2000 rpm for 2 times 30 s. Since the particles initially agglomerated during the curing process, the casted films were later left to settle at room temperature over night, before curing them. For making thin films of about 150 µm from these batches of samples, the resin was casted on a tin foil, which was dissolved in a mercury bath after the curing of the films. A microscope image in Fig. 2 shows the dispersion of the particles in the silicone.

2.3. DVS

For studying the vapour sorption, a TA Q5000 SA was used. Samples of about 1 mm thickness were cut in disks of 9 mm diameter, fitting the 9 mm flat Platinum DVS pans. Even though the sides of these disks were not covered by the pan and the samples are just layed in the pan, the evaluation of the diffusivity started from the assumption that only one side of the sample is exposed. To check the validity of this simplification, the results of the DVS analysis are compared to the results from the wet cup experiments at 20 °C. To obtain information about the temperature dependence of the sorption process, the measurement was repeated at 20, 30, 45, 60 and 75 °C.

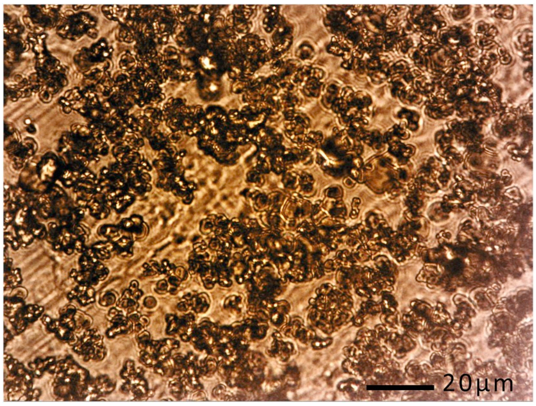

Fig. 2. Microscope image of sample 6650 P shows even dispersion of phosphor particles with some agglomeration.

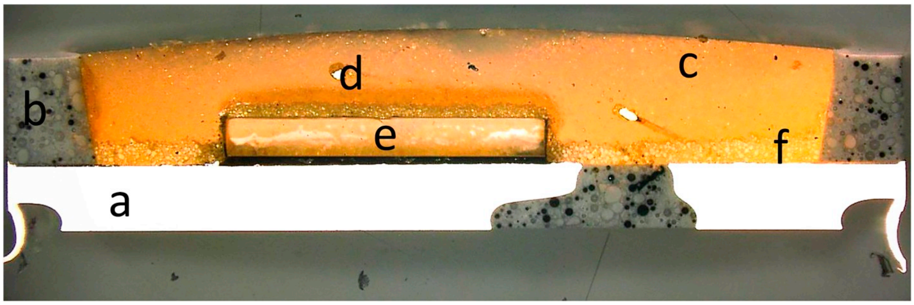

Fig. 1. Cross section of an LED; a – lead frame, b – housing, c – silicone lens, d – gold wire, e – die with diode, f phosphor particles, many of them segregated at the bottom. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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[1] Both supplied by Dow Corning Corporation in 2016, now Dow Silicones for the experiments reported in this paper. Currently available from DuPont.

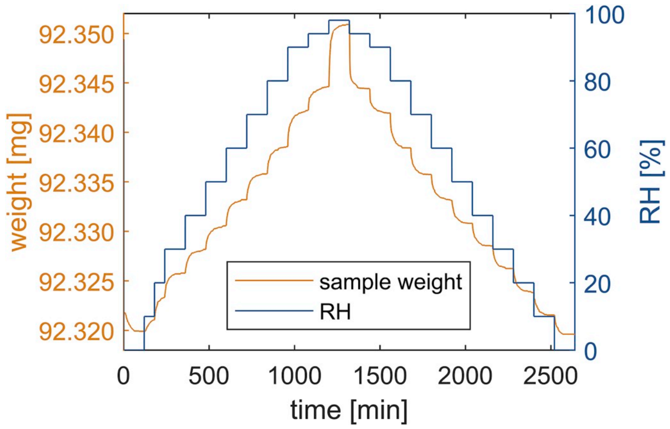

Fig. 3. Example of a DVS measurement cycle; relative humidity (blue) is set while the weight of the sample (green) is measured over time; T = 20 °C, sample 6650C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

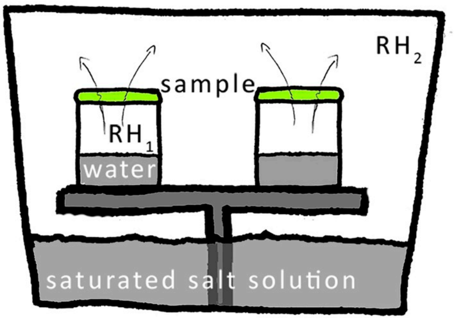

Fig. 4. Schematic of wet cup setup: The samples (green) are glued to the top of a water containing vial. The difference in RH between the inside of the vial and the RH in the deciccator acts as driving force for moisture permeation through the sample. The weight of the vials is measured in regular intervals to monitor the amount of water that passed through the samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The measurement sequence consisted of a first drying step, after which the relative humidity (RH) was raised to 90% in steps of 10%, then in steps of 4%–98%. After that, the same sequence of steps was taken to return reversely to a RH of 0%. The criterion for taking the next RH step was based on the sample's weight change: less than 0.001% change over 60 min entailed the next step. In Fig. 3, a typical measurement cycle is depicted together with the measured weight over time.

Measurements above 90% RH showed artefacts from condensation in the initial stages of uptake and were thus not used for diffusivity evaluation. A measurement of an empty pan showed a baseline drift of below 0.5 μg for the steps below 90% RH and a mass increase of about 1 μg in the steps between 90% and 98% due to moisture condensation.

2.4. *Wet cup*

For the wet cup measurement, thin films of both clear resins and resins containing phosphor particles were glued on top of glass vials (DIN 18; 5 ml volume), containing approximately 2.5 ml of water. The so-prepared vials were placed into desiccators with saturated salt solutions in the bottom, giving a defined relative humidity (from 12% to 85%). Fig. 4 gives a schematic picture of this. Several (8 for clear samples and 5 for samples containing phosphor particles) of these desiccators were prepared, each with different RH. Every 72 and 96 h the weight of the vials was measured with an analytical microbalance.

3. Results and discussion

In this section, we first show the results of the DVS and wet-cup measurements. After the results of the two methods are presented, the obtained diffusion coefficients will be compared. To be able to make further assumptions on the binding properties of the water molecules to the silicone matrix, the diffusion process and a possible change in these due to the addition of phosphor particles, we subsequently calculate the sorption enthalpy and activation energy from the data.

3.1. *DVS analysis*

The DVS measurements can be used to calculate the sorption as a function of relative humidity and temperature. Additionally, the diffusion constant for water can be calculated in case of a well-defined sample geometry, as e.g. a disk.

3.1.1. *Sorption*

A typical example of a measured curve from DVS is already shown in Fig. 3. It can be seen that the measured weight changes with every step in relative humidity. The positive and negative weight change represents the ab- and desorbed moisture. From the equilibrated mass at each RH step, sorption isotherms were obtained. These are shown for 3 temperatures in Fig. 5. The x-axis, shows the relative humidity (RH), while the saturated moisture content is depicted on the y-axis. For better visibility, Fig. 5 is divided in two subgraphs. Fig. 5a depicts the comparison of resin 7662 with and without phosphor particles, while Fig. 5b gives the same comparison for resin 6650. For these graphs, only the silicone volume fraction is taken into account as we assume that the phosphor particles do not take up water. By doing this, effects of possible changes to the silicone matrix caused by the phosphor particles become more visible. For further calculations however, the whole composite was evaluated as they are used in the actual LED product.

From the graphs, it can be seen that the moisture absorption in both resins follows Henry's law up to a relative humidity of about 90%, giving a linear increase in solubility with increasing water vapour pressure. The amount of absorbed water increases with an increase of temperature, pointing to an endothermic process. The influence of the phosphor particles visible in the graphs is close to the measurement's error, which can be expected as the actual volume fraction of the resins filled with 6 wt% of phosphor fillers is below 2 vol%. However it seems that the phosphor particles cause a slightly reduced water uptake in resin 7662 at all temperatures and relative humidity levels, while resin 6650 seems unaffected below 75 °C. This is in contrast with the 50% reduction in uptake upon the addition of 9 wt% phosphor particles as Hoque et al. [10] found. This difference in observation might be caused by a difference in silicone composition.

To obtain the solubility of water (s), the slopes of the isotherms (of the complete composite) were fitted from 0 to 90% RH using Henry's law:

$$\rho = s \cdot a, \tag{1}$$

with ρ being the water concentration [g_{water}/g_{sample}] and a the activity ($a = \%RH/100$). The obtained values for the solubility for all temperatures measured are presented in Fig. 6. The error bars give the confidence bounds of the fit with 95% confidence level. It can be seen, as before, that under saturated moisture conditions ($a = 1$), the saturation increases with temperature. Both resins take up about the same amount of water. As before, the difference observed between the clear resins and the composite of resin and phosphor particles is very close to the measurement's error. However small differences in solubility can be seen for some temperatures, where solubility is a bit lower for the samples containing phosphor particles. But overall, there is no large effect from

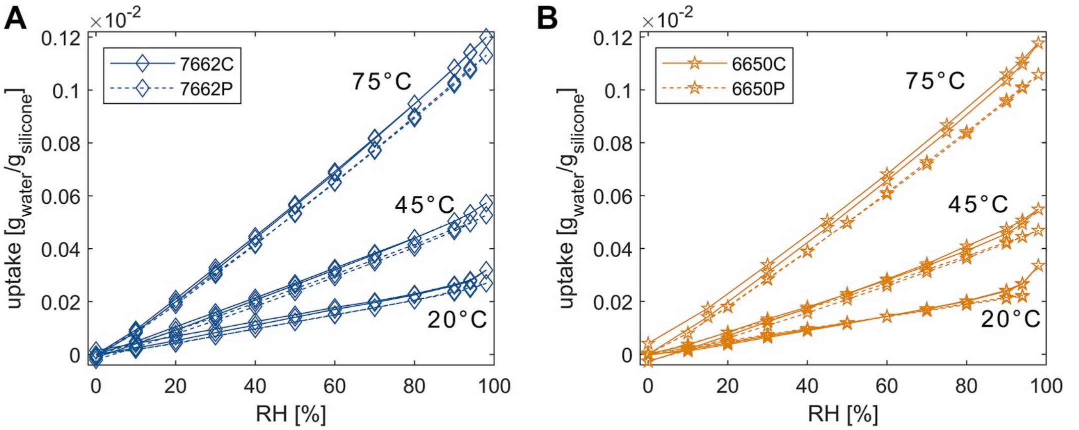

Fig. 5. Sorption isotherms at 20 °C, 45 °C & 75 °C; comparison of resin a) 7662 and b) 6650 with phosphor particles ‘P’ and clear resin ‘C’, considering only the silicone volume fraction.

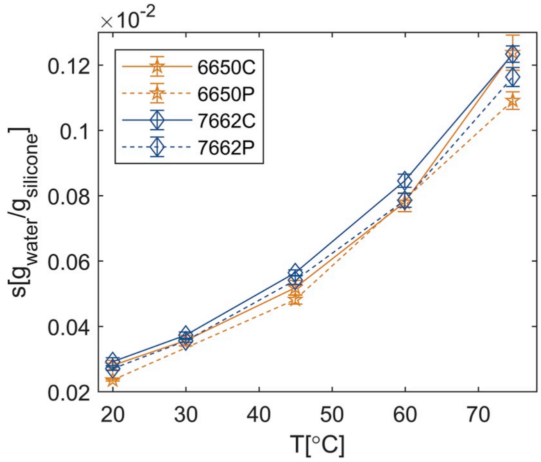

Fig. 6. Saturation level of water vapour in the samples at different temperatures obtained from fitting the sorption isotherms from the DVS analysis using equation 1.

the interfaces that significantly changes the moisture uptake of the composite.

3.1.2. DVS diffusivity analysis

To obtain the diffusion coefficient from the DVS data, each step in relative humidity was fitted using the assumption of 1D transport, following Fick’s second law:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{2}$$

with c being the moisture concentration, t the time, D the diffusion coefficient and x the sample dimension. After solving the partial differential equation for a sample of thickness L, considered to be infinitely wide and initially dry ($c(t=0)=0$ for $0<x<L$), that is exposed to moisture of constant concentration $c1$ at both sides at $t>0$ the concentration profile over time becomes [12]:

$$C(x,t) = C_{sat}\left[1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}e^{\left[-\frac{(2n+1)^2\pi^2 D}{L^2}t\right]}\cdot\cos\frac{(2n+1)\pi}{L}x\right]. \tag{3}$$

In case of penetration from only one side of the sample, the solution slightly changes in the way that the sample thickness L needs to be changed to an effective thickness of $L_e = 2L$. Integration of this concentration dependency over the sample thickness, gives the weight change over time [12]:

$$w(t) = (w_2 - w_1)*\left(1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}e^{-((2n+1)\pi)^2\frac{Dt}{L^2}}\right), \tag{4}$$

where $w_{1,2}$ is the sample weight before and after the step of RH change and n a counting variable. Also here, in case of penetration from only one side, the sample thickness L needs to be replaced by the effective thickness $L_e = 2L$. In Fig. 7, an example of the fitting using equation (4) is shown for the step from 20% RH to 30% RH.

The fitting was performed for each step, both going up and down in relative humidity. No significant difference in diffusivity was observed between the uptake and the drying. For the evaluation, only the steps between 10% RH and 90% RH were used, because the other steps at the high and low end of measured humidity levels contained artefacts from e.g. condensation in most measurements, affecting the initial phases of the uptake and thus gave problems with the fitting. To obtain a final value for D, a mean value from the fitted results was used.

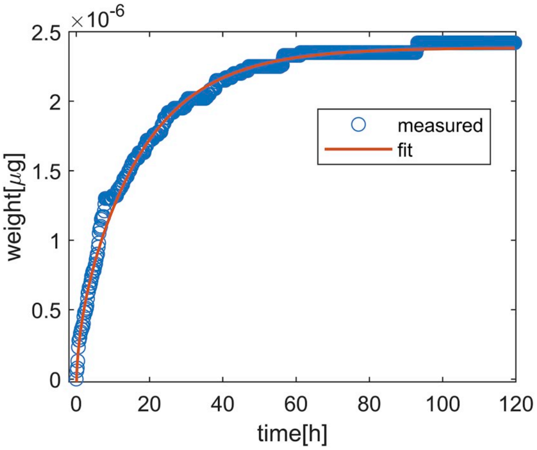

Fig. 7. Fitting example (using equation (4)) of resin 6650C at 20 °C, step from 20% RH to 30% RH, weight change over time; circles: measured points, line: fitting.

In Fig. 8 the results of the diffusivity evaluation for the clear silicone resins and the resins containing phosphor particles are shown. The error

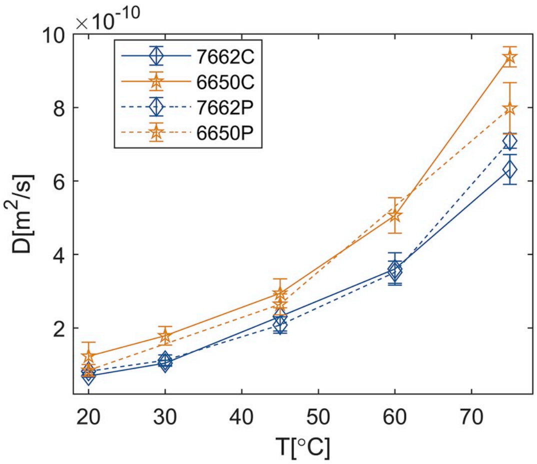

Fig. 8. Diffusivities obtained as mean values from the fitting the steps between 10-90% RH; 20–75 °C; error bars give standard error with 95% confidence bounds.

bars give the standard error with 95% confidence bounds[2]. Due to the low water uptake of the silicone, only small changes in sample weight occur introducing this measurement error. A difference in diffusion coefficient between the clear resin compared to the resin containing phosphor particles cannot be seen. However, there is a difference in diffusivity between the two resins, with resin 7662 showing a lower diffusivity at all temperatures.

3.2. *Wet-cup analysis*

From the wet cup experiment, the flux through the samples was calculated, by fitting the measured weight over time using:

$$J = \frac{\Delta m}{\Delta t \cdot AM} \tag{5}$$

with A being the sample area [m^2], M the molar mass of water [g/mol], Δm the mass change of the vials [g], and t the time [s]. The flux through the samples is shown in Fig. 9 as a function of water activity difference between up- and downstream of the silicone films.

It can be clearly seen that the flux increases linearly with an increase in Δa, meaning that a higher difference in water activity level on the different sides of the films give a higher moisture flux. This linear behaviour, as well as the linear sorption isotherms and low solubility levels points to the absence of strong interactions of water molecules with the silicone matrix or other water molecules. From the measurement data, we to obtain the diffusion coefficient with the help of Fick's first law, using the fact that the concentration c is given by $\Delta\rho$ in our case, and the fact that coordinate x can be replaced by our sample thickness ($L[m]$):

$$J = -D\frac{\partial c}{\partial x} = -D\frac{\Delta\rho}{L} \tag{6}$$

Inserting equation (1), which describes the water content as a function of water activity, results in:

$$J = -Ds\frac{\Delta a}{L} = -P\frac{\Delta a}{L}, \tag{7}$$

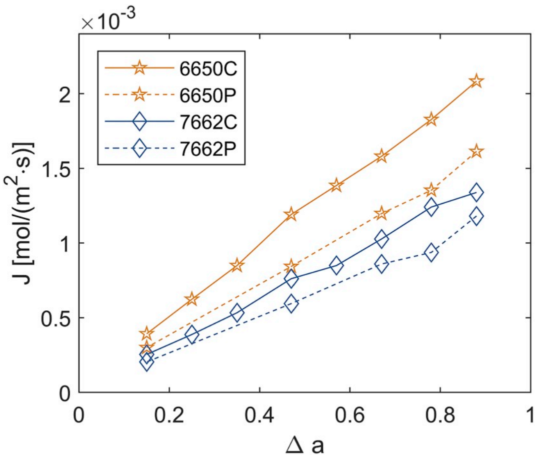

Fig. 9. Flux of moisture through the films (normalized to 1 μm film thickness) at various differences in up-to downstream water activity (Δa) of the silicone films measured by wet cup, at 20 °C.

where we used the well-known definition of permeability of diffusion times solubility: $P \equiv D \cdot s$. The fitting was done for every Δa, using the measured values of mass change Δm over time t (equations (1) and (5)):

$$P = Ds = -\frac{\Delta m \cdot L}{\Delta t \cdot AM \cdot \Delta a} \tag{8}$$

For the permeability, the mean values over all measured Δa are presented in Table 1.

As the solubility s was obtained in the DVS analysis using equation (1), we can now calculate the diffusion constant. The results are shown in Fig. 10. Here the error bars mark the standard deviation, while the dashed line gives the mean value. It can be seen what is already expected from the linear relationship of the flux to Δa – the diffusivity is independent of relative humidity. The diffusion coefficient between the two resins differs by a factor of 2, which is in line with the difference in cross link density that can be assumed from the shore D hardness values (resin 6650: 52 vs. resin 7662: 62 at 25 °C), which give a measure for the resistance of the materials to an indentation. The higher the value, the harder a material is. Also resin OE-7662 has more phenyl groups (hence a higher refractive index than 6650), which plays a key role in reducing the gas permeability in addition to the effect of crosslink density.

Comparing the clear resin with the resin containing phosphor particles, a small difference in the transport is observed. The mean values together with standard error in 95% confidence bounds (see footnote 2) are given in Table 3. For both resins, the diffusion coefficient of the resin containing phosphor particles is smaller than the diffusion coefficient of the clear resin by a factor of 0.89. A filling of 6 *wt*% represents a filling in volume of the resins of 1.49 (6650) and 1.62 (7662) vol%. Based on these values not much difference in transport properties would be expected.

To see how much difference in diffusivity can be expected due to an increased diffusion path length, it is sensible to find a model that comes close to the conditions in the sample. A suitable model for estimating the influence of impermeable fillers of circular shape on the diffusion

Table 1
Permeabilities as obtained by the wet cup experiment (equations (5)–(7)) at 20 °C.

	P [mol/(m·s)]
6650C	$2.6 \cdot 10^{-9}$
6650P	$1.8 \cdot 10^{-9}$
7662C	$1.6 \cdot 10^{-9}$
7662P	$1.3 \cdot 10^{-9}$

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[2] Calculations of standard errors (SE) were done from the standard deviations (SD) using the relation $SE = SD/\sqrt{N}$, with N being the number of observations. To gain 95% a confidence level the Student's t distribution was used, multiplying the corresponding t factor, so that the confidence bound final value $\overline{X}$ becomes.$\overline{X} \pm t_{0.95,N-1} \cdot SD_{\overline{X}}/\sqrt{N}$

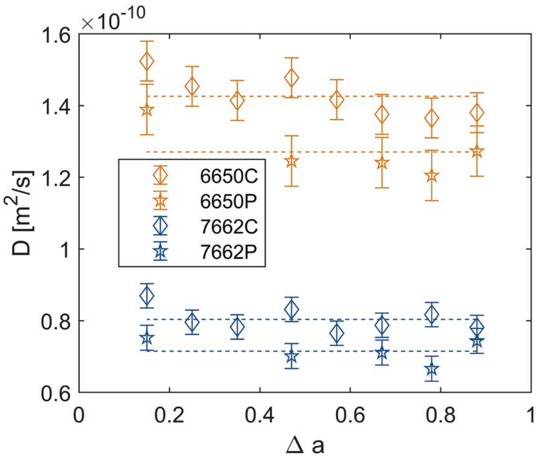

Fig. 10. Diffusion coefficients obtained from wet cup at various differences in up-to downstream water activity (Δa), measured at 20 °C.

Table 2
Ratios of diffusivities of composite/clear resin and theoretical values from Maxwell model.

	$^{D_P}/_{D_C}$ Measured	$^{D_F}/_{D_0}$ Maxwell
7662	0.89	0.992
6650	0.89	0.993

Table 3
Comparison of diffusion coefficient obtained in wet-cup and DVS at 20 °C.

	D (20 °C) $[m^2/s]/10^{-10}$ (wet-cup)	D (20 °C) $[m^2/s]/10^{-10}$ (DVS)
6650C	1.43 ± 0.05	1.2 ±0.4
7662C	0.80 ± 0.03	0.69 ± 0.03
6650P	1.27 ± 0.09	0.8 ± 0.2
7662P	0.71 ± 0.05	0.82±0.03

coefficient (D) for low filler contents up to a filler volume fraction of 0.3 is the Maxwell Model [13]:

$$\frac{D_{Filled}}{D_0} = \frac{1}{1 + \Phi/2}, \tag{9}$$

where Φ = filler fraction, D_0 = the diffusivity of the unfilled system and D_{filled} = the diffusivity of the filled system. This model considers the particles as well distributed and impermeable, possessing no interface region between them and the polymer matrix. As can be seen in Table 2, the measured difference in diffusivity is larger than the theoretical one.

A possible reason for this difference between model and measured values is that the system is not well represented by the model. This could be due to bad dispersion of the particles, e.g. if a large amount of them are sunk to the bottom of the film during sample making building a dense layer at the bottom. However we do not see that in our samples. What we see is some amount of agglomeration of the particles, forming larger particles, which are still well distributed in the matrix, so that the assumption of spherical particles might not be totally correct. A microscope image of sample 6650 with phosphor particles is shown in Fig. 2. Another reason could be an interface region between the fillers and the silicone matrix with different density or binding properties to water, causing a lower amount of transport. This difference might be visible when looking at the activation energy of diffusion and the sorption enthalpy (see section 3.4).

Table 4
Sorption enthalpy, and activation energy of diffusion.

	ΔH [kJ/mol]	Ea [kJ/mol]
6650C	21 ± 4	31 ± 5
7662C	22 ± 2	34 ± 5
6650P	24 ± 11	35 ± 5
7662P	22 ± 2	33 ± 4

3.3. *Comparison of DVS & wet-cup*

The initial evaluation of the diffusion coefficient from the DVS measurement assumes moisture ingress only from the top side of the sample. When comparing the fitted values with the values obtained from the wet cup experiment, the DVS results are higher by a factor of about 4. If we assume moisture ingress from both the top and the bottom side of the sample, the values of both techniques are in the same range (see Table 3). In an additional test, we measured a sample in a round pan where both sides were well exposed to moisture and found the same value for D (within error margins) as for the same sample measured in a flat pan. It can be concluded that there also is transport from the bottom side even if samples are placed in flat pans, applying some pressure to expel air from between pan and sample. A partially reduced uptake from the bottom side of the samples can also explain the relatively large error of the DVS analysis we found compared to the wet-cup experiment. In future experiments, samples should be either placed so that moisture exposure from both side is guaranteed or sealed from the bottom side.

3.4. *Binding properties of water*

Quantifying the sorption enthalpy and the activation energy of the diffusion gives the possibility to draw conclusions on the binding properties of water to the matrix.

3.4.1. *Sorption enthalpy*

The sorption enthalpy gives the heat change during a sorption process. In an endothermic process $\Delta H>0$, heat is absorbed while in an exothermic process ($\Delta H<0$) heat evolves. In physisorption, where the species forming bonds are held by weak interactions as Van-der-Waals interactions or hydrogen bonding, the change in enthalpy ranges around 20 kJ/mol. In chemisorption on the other hand, where species form chemical bonds, the enthalpy change is much higher (≈200 kJ/mol) [14]. So, by knowing the sorption enthalpy of the water vapour sorption to our samples, we can draw conclusions on the kind of bonds the water molecules form or break in the polymer network to insert a water molecule. An evaluation of the sorption enthalpy can be obtained

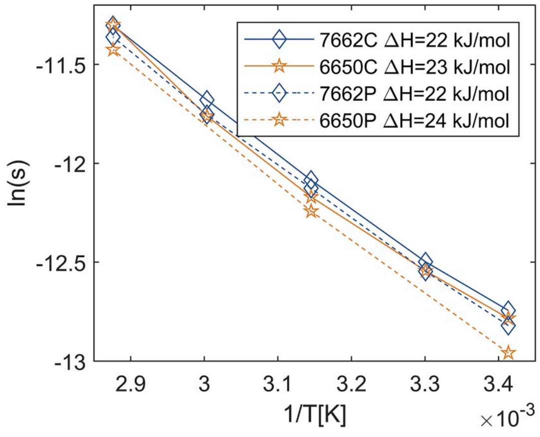

Fig. 11. Evaluation of sorption enthalpy, by using a Van't Hoff plot of the solubility of water vapour at different temperatures; not corrected for phosphor content.

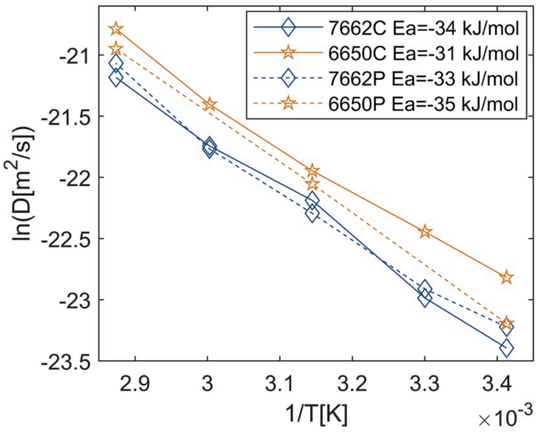

Fig. 12. Arrhenius plot of Diffusion coefficients, used for the evaluation of the activation energy of diffusion.

from the solubility at different temperatures, which were obtained by fitting the slopes in the sorption isotherms as described above. Since the sorption is an equilibrium constant, the Van't Hoff equation can be used for the evaluation [14,15] giving rise to the relation:

$$s = s_0 \cdot e^{-\frac{\Delta H}{RT}}, \tag{10}$$

where ΔH represents the sorption enthalpy, R the gas constant, and T the temperature. The obtained sorption enthalpies are about 22 kJ/mol (see Table 4). Comparing the resin with and without phosphor particles, no difference in the sorption enthalpy can be seen, indicating that the particles do not change the process of water molecules binding to the matrix. The fact that the value is positive (more absorbed species at higher temperature) is remarkable, as adsorption of water in polymers is more commonly an exothermic process. In polymers below the glass transition temperature T_g however, it is also common to see an endothermic process [12]. In our experiments we did not see a change in sorption characteristics when crossing T_g; the plots of ln*(s)* over *1/T* are straight for both resins (see Fig. 11. Evaluation of sorption enthalpy, by using a Van't Hoff plot of the solubility of water vapour at different temperatures; not corrected for phosphor content). In literature, both negative and positive sorption enthalpies are reported for silicones: Comyn et al. found a not further specified negative value in a silica reinforced crosslinked PDMS system [8], while Khalilullah et al. found a positive value ΔH between 8 and 11 kJ/mol in a system containing phosphors [11]. Unfortunately, the amount of phosphors was not given in the study. In previous publications there was a discussion on a possible water cluster formation in silicones, where Comyn and DeBuyl suggest clustering, while Watson and Baron see no clustering and suggest the sorption of water in the silicone to be an entropy driven process [7,8].

Silicone has hydrophobic nature, so when observing water absorption one could assume a clustering of the water molecules to reduce the contact area between the silicone and the adsorbed water. When comparing the concentration of water vapour in air with the concentration we found the silicones, it shows that the concentration in air is 5–20 times higher than in the silicone (5 times at 20 °C, increasing up to 20 times at 75 °C). This shows that the absorption is indeed very low. As we also see straight sorption isotherms and the independency of D upon relative humidity, water clusters do not seem a likely hypothesis.

Even though 22 kJ/mol is in the range of Hydrogen bonding$O - H \cdots H_2O$, we see an endothermic process, while the formation of hydrogen bonds is an exothermic process. So, what we observe is not binding of the water to side groups present in the silicone or to other water molecules, but rather a breaking of bonds, rearranging the silicone matrix to accommodate for the water molecules. This would mean that the sorption should be regarded as an entropy driven process. We can calculate the energy to open the polymer matrix and generate voids in which water molecules can reside by using [7].

$$E = RT \ln\frac{N-n}{n},$$

where N is the number of possible sites (For PDMS $N = 10^4$ [7] [mol/m^3], n is the number of actual absorbed molecules [mol/m^3], T the temperature [K] and R the universal gas constant [J/(K*mol)]. Using this, we get a value of (26.6 ± 0.3) kJ/mol for both tested resins with and without the addition of phosphor particles. This value is very similar to measured sorption enthalpy, suggesting that the sorption we see is indeed entropy driven.

3.4.2. Activation energy of diffusion

The activation energy of diffusion can be interpreted as the minimum energy that is needed to start the process of diffusion. This process is understood as containing three steps: the sorption of the species on one side of the membrane, the transport through the membrane and the desorption at the other side. The activation energy can be obtained by fitting the diffusion constants at different temperatures using the Arrhenius relation:

$$D = D_0 \cdot e^{-\frac{\Delta E_A}{RT}}, \tag{11}$$

where ΔE_A denotes the activation energy and D is the diffusion coefficient measured at a certain temperature. A plot of the evaluation is presented in Fig. 12. It can be seen that, as for the sorption, that the studied process does not seem to differ above or below the glass transition temperature, as the plot of ln(D) over 1/T shows no bend. The fitting gives a value for the activation energy of 33 kJ/mol, which is only slightly higher than the value for the energy needed to generate voids in the silicone (26.6 kJ/mol), calculated in the previous section. From that, we presume that the mechanism for transport is by movement of the water molecules through voids forming in the silicone matrix.

The obtained value is larger than the values presented in previous studies, which are 14 kJ/mol in clear PDMS silicones [7] and 19.3 kJ/mol in silicones containing phosphors [11]. These differences might be due to differences in side groups (phenyl-vs. methyl siloxane) and

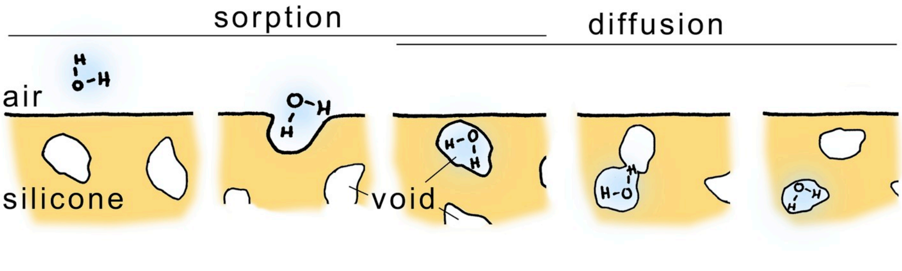

Fig. 13. Schematic of water sorption and diffusion process: Voids (or free volume) form in the silicone due to thermal motion of the chains. Water molecules can get trapped in these voids forming at the surface (activation energy of this process is 22 kJ/mol). When a void forms close enough to another H_2O occupied void for the water to move to the new void, a diffusive transport of the water molecule occurs (with an activation energy of 33 kJ/mol).

cross linking density, which are shown to influence the sorption and permeability in the silicones.

As for the sorption enthalpy, the obtained values for activation energy show no difference between the samples containing phosphor particles and the clear silicone, making it unlikely that there is an interface region with largely different properties than in the silicone matrix.

The results from both the sorption and activation energy are summarized in Table 4.

4. Conclusions

From the results of the measurements, it can be concluded that well dispersed phosphor particles only have very small influence on water vapour transport in high refractive index optical silicones, which will not have an impact on the product lifetime in the LED. A small difference in D at 20 °C measured with wet cup setup, is probably due to an increased path length, as we could not measure a difference in the sorption enthalpy or activation energy of diffusion between the clear resin and the resin containing phosphor particles.

For the transport in the silicone (both the composite and the clear resin) we find very low moisture uptake, which is expected due to the non-polarity of silicone. This uptake is an endothermic process (increases with temperature) giving a sorption enthalpy of 22 kJ/mol, which is similar to the energy needed to open the silicone matrix, creating voids where water molecules can reside in. This indicates that the sorption process is entropy driven. A schematic representation of this process is given in Fig. 13, showing the process of water entering the silicone matrix, by occupying free volume (voids) that form due to thermal motion of the silicone chains. When crossing the glass transition temperature, the enthalpy remains the same, which indicates that there are no changes in the sorption mechanism of the water molecules with the structural changes that happen during glass transition. The sorption isotherms were found to be linear, following Henry's law. The diffusivity was constant over the evaluated range of relative humidity (10–90%) and temperatures, showing an activation energy of water diffusion of ca. 33 kJ/mol. These findings indicate that there is no interaction of water molecules within the silicone matrix, as well as no interaction between water molecules and the silicone matrix.

Author agreement

All authors have seen and approved the final version of the manuscript being submitted. We warrant that the article is the authors' original work, hasn't received prior publication and isn't under consideration for publication elsewhere.

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.

CRediT authorship contribution statement

A. Herrmann: Conceptualization, Formal analysis, Investigation, Writing - original draft. **S.J.F. Erich:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition. **L.G.J.v.d. Ven:** Supervision, Writing - review & editing. **H.P. Huinink:** Supervision, Writing - review & editing. **W.D. van Driel:** Resources, Writing - review & editing. **M. van Soestbergen:** Writing - review & editing. **A. Mavinkurve:** Writing - review & editing. **F. De Buyl:** Resources, Writing - review & editing. **J.M.C. Mol:** Writing - review & editing. **O.C.G. Adan:** Supervision, Writing - review & editing, Supervision, Funding acquisition.

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