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Predicting water transport in multilayer coatings

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ABSTRACT

Water transport in polymer coatings is a key process in their failure. Mostly, such systems are composed of multiple layers to meet the required specifications. Understanding water transport requires a model that relates the kinetics with the properties of the layers. In this article a theoretical model for water transport in two-layered coatings is formulated and verified. The model considers systems consisting of a hydrophobic top coat and a hydrophilic base coat. It describes the process on the basis of the top coat permeability and the base coat sorption isotherm, which define the timescale and the driving force of transport. The systems of interest had a base coat sorption isotherm, which indicated that sorption is a process of clustering of water. The non-linear isotherm shape resulted a timescale for uptake and drying of days and hours, respectively. The model is verified with NMR imaging of water transport and gravimetry. Practically, the results mean that it is sufficient to measure the top coat permeability and the base coat sorption isotherm to understand water transport kinetics in such systems.

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1. Introduction

When water is present in a coating, it can promote deterioration of the coated substrate and affect the performance of the coating. Regarding multilayer coatings, the distinct physical and chemical properties of the different layers and sometimes complex nature of the individual layers make understanding the water transport in multilayer films challenging. Only a few studies are dedicated to water uptake in multilayer films [1–6]. Carbonini et al. [1] studied the effects of the chemical composition of the constituent layers on the water uptake in a multilayer system. It was shown that water absorption and degradation of the multilayered systems depend on the chemical characteristics of each layer and on the layer position in the system [2]. Allahar et al. [3] pointed out that the layer interface can play an important role in transport of water in multilayer coatings. De Rosa et al. [4] simulated water transport in two-layered coating as Fickian diffusion in each layer and discussed the influence of ordering of more and less permeable layers.

Recently we have used high resolution NMR imaging to study water uptake in two-layer coatings [5,6]. The coatings consisted of a hydrophilic waterborne base coat and a hydrophobic solventborne top coat. The ingress of water into a waterborne base coat through a protective top coat was visualized [5]. Identification of polymer phases and water in the base coat, plasticization of the polymer phases and evaluation of water mobility in the base coat were performed with relaxation analysis of NMR signal [6]. It was found that water in a saturated base coat is highly mobile and is more weakly bonded to the polymer matrix than in a partially saturated base coat.

These two studies have provided a strong empirical basis for understanding water uptake in the multilayered systems. The next step in investigation of water transport in multilayer coatings is understanding relationships between water transport and properties of the layers in such systems. This will allow to get insight into the driving force of the process and to provide knowledge, which is necessary for further developments of multilayer systems in terms of resistance to water. This requires a valid theoretical model, based on the key properties of layers in multilayer coatings.

This paper aims to find a relationship between water transport in two-layered coatings and the layers properties. The coatings consist of a hydrophilic base coat and a hydrophobic top coat. In general, such systems are representative to multilayer coatings, where the top layer acts as a barrier and one or more layers under the top coat have a hydrophilic character. This is actually the case in many automotive systems. A theoretical model for the process is formulated and verified for this purpose. The process is described...
as Fickian transport with a constant diffusivity through the top coat with an instantaneous redistribution in the base coat. According to the model, the barrier properties of the top coat, i.e. thickness and permeability, define the timescale of the process and the sorption isotherm of the base coat defines the driving force for transport. The model is verified experimentally with NMR measurements of water transport and gravimetric measurements of the base coat sorption isotherm and the top coat permeability. The model is further validated by a comparison of NMR measurements of water transport with the analytical predictions of the model based on the base coat sorption isotherm and the top coat permeability.

2. Experimental details

2.1. Samples

The investigated polymeric systems are two-layered base coat/top coat systems. For a detailed description of the samples we refer to a previous paper [6]. Such systems are representative to multilayer coatings, which consist of a top layer that acts as a barrier and more hydrophilic layers under the top layer. Here, we briefly summarize the sample composition and the sample preparation for the experiments. The base coats are waterborne physically dried systems which consists of 40% w/w acrylic particles, 20% w/w polyurethane (PUR) particles, 30% w/w DPP (di-keto-pyrrolo-pyrrrole) pigment particles and 10% w/w polymeric dispersant in the sample. The acrylic particles have the glass transition temperature of ca. 25 °C and the glass transition temperature of the PUR particles is approximately equal to 0 °C. The top coat is a 2-component solvent borne polyurethane coating which comprises polyacrylic polyl, polyester polyl and an isocyanate crosslinker. The glass transition temperature of the top coat equals approximately 60 °C.

The coatings were prepared on glass slides of 18 × 18 mm² and had various base coat and top coat thicknesses. The list of studied samples is shown in Table 1. BC means base coat and TC means top coat and the numbers after BC or TC refer to layer thicknesses in μm.

To measure water distributions during water transport in coatings, depth profiles of ²H were recorded with NMR imaging based on the GARField approach [7]. The NMR signal was obtained with an Ostroff-Waugh-like pulse sequence $\alpha_s - t_e/2 - [\alpha_y - t_e/2 - echo - t_e/2,\alpha_y]_n$ with a nominally equal to 90° [8,9]. As a result a train of so-called spin-echoes is obtained, of which the first one is used for imaging purpose. In the case of N distinct ²H pools the signal of the n-th spin echo $S_n(x)$ reads

$$S_n(x) = \frac{N}{n_{ref}}\rho_k(x)\exp(-nt_e/T_{2k}(x)).$$

where $\rho_k(x)\left[g/cm^3\right]$ is the density of ²H nuclei in the k-th pool and $n_{ref}$ is the density of ²H nuclei in a reference sample. $T_{2k}[s]$ is a so-called transverse relaxation time which is related to the molecular mobility and diffusivity of the measured species. $t_e[s]$ is echo time during measurements. In order to calibrate the signal, aqueous CuSO₄ solution with a concentration of 0.01 M was used as a reference. Thus, the density of ¹H in the reference equals to the density of ¹H in pure water. Finally, it has to be mentioned that all water transport measurements were performed with $t_e = 0.1$ ms and 2048 averages with a repetition time of 0.5 s.

The $T_2$ relaxation time of water contains important information about the dynamics of water. For mobile species the $T_2$ time reads

$$T_2^{-1} = T_{2D}^{-1} + T_{2S}^{-1},$$

where $T_{2D}[s]$ is the relaxation time due to self-diffusion in a field gradient and $T_{2S}[s]$ describes the relaxation time associated with the dipole–dipole interactions of the measured species.

The relaxation due to self-diffusion in the field gradient is given by the following equation

$$T_{2D}^{-1} = \gamma^2 g^2 D_r t_e$$

where $D_r[m^2/s]$ is a self-diffusion coefficient of the measured nuclei, $t_e[s]$ is an echo time [6]. The parameter $\gamma$ was estimated from the reference $T_2$ and self-diffusion constant and equals 5 [6]. The self-diffusion coefficient of water in the base coat can be estimated via investigation the echo time dependency of relaxation time of water.

During NMR measurements of water transport, signal profiles in the samples were obtained. The total amount of water in the base coat was estimated by integration over the base coat of water distribution profiles. Water transport was measured as a function of the water activity in the environment. To vary the water activity experiments were performed with water, dry air and PEG (polyethylene glycol) aqueous solutions. With PEG the water activity of an aqueous solution can be regulated very accurately according to Ninni [10]. In case of pure liquid water, the water activity equals one, whereas with PEG solutions it can be set to lower values. For dry air, the water activity equals zero. Additionally, the dependency of water self-diffusion coefficient on the water activity was measured with NMR diffusometry.

3. Theory

3.1. Model

This section introduces a model for water transport in twolayered base coat/top coat systems, where the hydrophobic top coat has a barrier function and the hydrophilic base coat is an instantaneous reservoir. The latter means that water redistributes instantaneously in the base coat upon entering the layer. A schematic picture of the system is shown in Fig. 2.
The state of water can be described in terms of the chemical potential $\mu$ [J/mol] and the activity $a$, which are related as $\mu = \mu^\circ + RT \ln a$, (4)

where $\mu^\circ$ [J/mol] is the standard chemical potential of pure liquid water. The description of the state of water requires knowledge of chemical potentials and activities in the environment $a_{ex}$ in the top coat $a_{TC}$ and in the base coat $a_{BC}$. Water in the environment can be present as liquid, i.e. either pure water ($a = 1$) or an aqueous solution ($a < 1$), or as vapour ($a < 1$). In the case of a vapour phase the activity is directly linked to the relative humidity: $RH = a \times 100$.

The top coat will act as a barrier only when it absorbs water in negligible quantities and when diffusion constant of water is low in the top coat. In case that water in the top coat is diluted, it behaves ideally and the chemical potential of water $\mu_{TC}(x)[J/mol]$ at depth $x$ [m] in the top coat can be related to its concentration $\rho(x)[mol/m^3]$ by the following expression

$$\mu_{TC}(x) = \mu^\circ + RT \ln \rho(x)/\rho_S.$$ (5)

where $\rho_S[mol/m^3]$ is the maximal concentration of water in the top coat, when it is in contact with pure liquid water. Therefore, the activity of water in the top coat reads

$$a_{TC}(x) = \rho(x)/\rho_S.$$ (6)

As water behaves ideally, the water flux [J/mol-m^2-s] is described by Fick’s law with a constant diffusivity of water in the top coat. Thus, the flux of water through the top coat reads $[5,12]$

$$J = -D \frac{\partial \rho}{\partial x} = \frac{D_d}{L} \left( \rho(0) - \rho(L) \right).$$ (7)

With Eq. (6) the flux, Eq. (7), can be rewritten as

$$J = -\frac{D_d}{L} \left[ a_{TC}(0) - a_{TC}(L) \right].$$ (8)

When the base coat acts as an instantaneous reservoir the water concentration and the water activity in the base coat are homogeneous during the water transport. This implies that the water activity is a unique function of the total water content in the base coat

$$a_{BC} = a_{BC}(\theta).$$ (9)

where $\theta = n/n_{max}$ is the water content, $n[mol]$ and $n_{max}[mol]$ are the total amount of water and the maximal water uptake of the base coat, respectively. We assume that water instantaneously equilibrates at the interfaces. This implies the following boundary conditions: $a_{TC}(0) = a_{ex}$ for the TC/environment interface and $a_{BC}(L) = a_{BC}(\theta)$ for the BC/TC interface.

The rate of change in the total amount of water in the base coat follows from the conservation law

$$\frac{dn}{dt} = AJ,$$ (10)

where $A [m^2]$ is the area of penetration. The combination of Eq. (8) and Eq. (10) results in the equation for water content in the base coat during water transport

$$\frac{d\theta}{dt} = \frac{1}{\tau} \left( a_{ex} - a_{BC}(\theta) \right),$$ (11)

where the timescale $\tau$ assimilates both characteristics of the top coat ($D, \rho_S, L$) and the base coat ($n_{max}$)

$$\tau = \frac{ln_{max}}{AD_d\rho_S}.$$ (12)

Note, that $\rho_S$ equals the permeability [11] of the top coat to water.

According to the model, water uptake in the systems of interest is governed by two system-related parameters: the timescale $\tau$, which is determined by the barrier properties of the top coat and the maximal water uptake by the base coat (Eq. (12)) and the inverse sorption isotherm of the base coat $a_{BC}(\theta)$. The way, how the parameter $\tau$ is present in the transport equation (Eq. (11)), implies that it defines the timescale of the process. The inverse isotherm $a_{BC}(\theta)$ defines the transport process kinetics (i.e. time dependency of the water content $n(t)/\tau$), in particular the sorption and desorption kinetics.

### 3.2. Influence of sorption isotherms on water transport

To explore how the shape of the sorption isotherms influences the transport kinetics, typical isotherms for polymeric materials, were used to simulate uptake ($a_{ex} = 1$) and drying ($a_{ex} = 0$): linear, Type II and Type III isotherms. Linear isotherms indicate that water—water interactions can be neglected and are usually observed for hydrophobic polymers with a low absorption capacity. Type II isotherm indicate that some water is bonded by hydrophilic sites at low activities, i.e. polar groups, with a subsequent formation of water clusters at higher activities. Type III isotherms indicate that sorption is mainly due to formation of water clusters in the polymer. For a detailed discussion of the backgrounds of the isotherms we refer to reviews on water in polymers [14] and coatings [15]. Eq.
was integrated numerically to obtain \( n/n_{\text{max}} \) as a function of \( t/\tau \) for each isotherm (Fig. 3).

In the ideal case, Henry’s law, the sorption and desorption kinetics are symmetric. Type II and III isotherms result in slow uptake and fast drying. The drying process for system with Type II isotherm features a slow rate later stage, which is absent in Type III systems. This is due to the fact that in case of Type II isotherm drying is slow at low water activities as the shape of the isotherm at low activities results in a much smaller driving force then for Type III isotherm.

The slow uptake rates in Type II and Type III systems are a result of the low driving force at high water activities combined with the large amount of water that still has to be absorbed. The fast drying rate is caused by the fact that high driving force is maintained during a major part of the drying process. Hydrophilic polymers usually have Type II or Type III isotherms [14].

3.3. Measuring the barrier: D\(_2\)O/H\(_2\)O exchange

The permeability of the top coat in a two-layered system can be measured with a D\(_2\)O/H\(_2\)O exchange experiment [5]. The amount of water can be measured with NMR. Due to the fact that protons and deuterons have significantly different NMR frequencies, only water is probed in such experiment. This section discusses the theory behind this experiment, based on the model.

In D\(_2\)O/H\(_2\)O exchange experiment a sample is saturated with water and then placed in a liquid environment with heavy water. The water exchanges with heavy water through the top coat between. When Fickian diffusion with a constant diffusivity of water in the top coat is assumed, this process can described with Eq. (11). If water and heavy water behave identically in the base coat, the energy of water molecules in the mixture is independent on proportions of H\(_2\)O and D\(_2\)O. This means that H\(_2\)O/D\(_2\)O mixture in the base coat is an ideal mixture [16]. As a result, the water activity in this mixture is linear with water content: \( a_{BC} = \theta \).

As the environment considered to be an infinite reservoir of heavy water, its water activity \( a_{\text{ex}} = 0 \). Thus, the solution of Eq. (11) for the system, initially saturated by water \( (n(0) = n_{\text{max}}) \) and subsequently exposed to heavy water, reads

\[
\theta = \exp \left( -\frac{t}{\tau} \right)
\]

where \( \tau \) is the timescale for water transport, see Eq. (12).

4. Results

4.1. Visualization of water uptake

First of all, understanding water transport in two-layered coatings requires knowledge of water redistribution in the sample. To study this, NMR signal profiles of the samples during uptake were measured.

First, one particular sample, BC50TC64, is investigated in detail. The signal profiles during water uptake are shown in Fig. 4. There are 20 min between subsequent profiles for the first 10 profiles and 200 min for the later profiles. Signal increase and swelling are...
observed during water uptake. The signal increase is proportional to the amount of water [5]. An important observation is that there is signal increase near the base coat/glass interface already in the first profiles, indicating that water quickly equilibrates in the base coat. Therefore, the rate of water transport is limited by permeation through the top coat and not by water redistribution in the base coat.

To evaluate the kinetics of water uptake, NMR measurements were performed on all samples. From the profiles the total amounts of water in the base coats were calculated. In Fig. 5 the amounts of absorbed water are shown as a function of time for all samples (for explanation of the labels, see Table 1). In all cases a decreasing water uptake rate as a function of time is observed. The maximal amount of absorbed water varies for each sample, see Table 2.

### 4.2. Barrier properties of the top coat

Understanding water transport in the top coat requires knowledge about the effect of the top coat properties on water diffusion in the film. In this section water permeation through the top coat and the barrier properties of the top coat is investigated at room temperature.

First, the water permeability of the single layer top coat is investigated with wet cup measurements on free films. Glass cups with an area $A = 0.95 \text{ cm}^2$ were filled with water and sealed with top coat free films of various thicknesses. The cups were exposed to environments with various water activities $a_w$. Saturated aqueous solutions of various salts were used to create the proper environments with respect to the relative humidity. The mass change $\Delta m$ was measured with a Mettler-Toledo AX205DR analytical balance after exposure of the cups to a specific environment with a duration of $\Delta t$. The typical durations of the exposure $\Delta t$ were in the order of few days. The flux of water $J = \Delta m \Delta t^{-1} A^{-1} m^{-1}$ was measured as a function of difference of water activities over the films (where $M = 18 \text{ g/mol}$ is the molar mass of water). In the case of Fickian permeation through the film with a constant diffusivity, the flux reads

$$ J = \frac{D_p a_w}{L} \Delta a, \quad (14) $$

where $\Delta a$ is the difference of water activity over the film. Note, that $a = 1$ inside the cups.

Fig. 6 shows the measured fluxes through the different free films single layer top coats as a function of the water activity difference in the wet cup experiments. Linear relationships are observed for all samples, proving that water permeates through the top coats via Fickian diffusion with a constant diffusion coefficient. From the slopes of the lines, permeabilities of the top coats can be estimated via Eq. (14): $D_p = 1.2 \pm 0.3 \times 10^{-9} \text{ mol m}^{-1} \text{s}^{-1}$. Note, that coatings, designed to act as a barrier have permeabilities in order of $10^{-9} - 10^{-10} \text{ mol m}^{-1} \text{s}^{-1}$.[3,17]

To investigate how the presence of the base coat influences the top coat properties, the wet cup experiment were also performed on a two-layered BC50TC64 free film, see Fig. 6. The film was fixed with the top coat facing the cup. It is assumed that the base coat permeability is much higher than of the top coat and the flux is determined by the permeability of the top coat. The permeability of the top coat in BC50TC64 $D_p$ equals $5 \times 10^{-9} \text{ mol m}^{-1} \text{s}^{-1}$. Note, that this value is significantly higher than the permeability of free film top coats. This indicates that there is an interaction between the layers, which results in higher permeability of the top coat in two-layered systems compared with single layer top coats.

As water transports in the top coats via Fickian diffusion with a constant diffusivity, the barrier properties and timescale of water transport can also be assessed via $D_2O/H_2O$ exchange experiment [5]. The amount of water in the base coats was measured for every base coat/top coat sample during the exchange.

By fitting the exchange data with Eq. (13), values for $\tau$ and $n_{\text{max}}$ are obtained (Table 2). The ratio $\tau/n_{\text{max}}$ appears to be proportional to $L$, see Fig. 7, which confirms Eq. (12). This means that the permeability of the top coats in two-layered systems does not vary much between the various samples and top coat thicknesses. From

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau$ (h)</th>
<th>$n_{\text{max}}/A$ (mmol/cm²)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC25TC57</td>
<td>1.56</td>
<td>0.031</td>
<td>0.9</td>
</tr>
<tr>
<td>BC50TC23</td>
<td>1.77</td>
<td>0.086</td>
<td>0.96</td>
</tr>
<tr>
<td>BC50TC64</td>
<td>3.38</td>
<td>0.077</td>
<td>0.93</td>
</tr>
<tr>
<td>BC50TC73</td>
<td>3.47</td>
<td>0.068</td>
<td>0.93</td>
</tr>
<tr>
<td>BC50TC102</td>
<td>3.75</td>
<td>0.054</td>
<td>0.88</td>
</tr>
</tbody>
</table>
the linear fit of these values in Fig. 7 the permeability \( D \) is estimated via Eq. (12): \( 3.8 \times 10^{-3} \) mol m\(^{-1}\)s\(^{-1}\). This value is in line with the permeability, estimated from the wet cup experiment with the sample BC50TC64. A clear advantage of the \( D_2O/H_2O \) exchange method over wet cup experiment is the time needed for the experiment: hours for exchange vs. days for the wet cup measurements.

Both the wet cup experiments and the \( D_2O/H_2O \) exchange experiments show that the top coats in two-layered samples have significantly higher permeabilities than the free film top coats. An explanation to this can be that part of the isocyanate in the top coat has been reacted with moisture in the base coat during curing [18]. Another possible reason for the higher permeability of the top coat layers can be a result of crosslinker migration to the base coat [19].

As a result the crosslink density in a free film top coat is higher than in the top coat in the base coat/top coat film, resulting in higher permeability of the latter one.

Important to note, that also the maximal water uptake \( n_{max} \) of the films varies with the top coat thickness, see Fig. 8. This variation is discussed in the next section.

### 4.3. Sorption isotherms of the base coat

Understanding the water transport kinetics requires knowledge of the sorption isotherms of the base coats, see Eq. (11). The shape of the sorption isotherm reflects how water is present in the system. In this section the sorption isotherms of the base coats are studied with the help of gravimetry and NMR uptake measurements.

We start with the sorption isotherm of the base coat in the two-layered system BC50TC64. The sorption isotherm of this sample was obtained gravimetrically, by measuring its mass under equilibrium at various water activities. The measurements were performed with a Mettler-Toledo AX205DR analytical balance. The contribution of water in the top coat to the mass change was neglected, as most of the water is absorbed by the base coat. Fig. 9 shows the desorption and sorption isotherms of BC50TC64. There is no significant hysteresis between sorption and desorption. The shape of the isotherm is typical for Type III isotherms according to the B.E.T. classification [13] and reflects a process of water clusters formation in the base coat. Note, that while the small plateau in the data points at low water activities is typical for Type II isotherms, we do not consider it as significant as it less than the experimental error. Type III isotherms can be described by the so-called Guggenheim-Anderson-De Boer (GAB) expression [20,21]. We adopt the isotherm model under the assumption that there is no difference between initially absorbed water and water in clusters

\[
\theta = \frac{1 - f \cdot q_{BC}}{1 - f \cdot q_{BC}}.
\]  

where \( f \) refers to the difference between clustered water in polymer and liquid water and \( f = \exp[\Delta g/RT] \), where \( \Delta g [\text{J/mol}] \) is difference in the molar free energy of water in clusters present in the polymer and in liquid water. Note, that when \( f = 1 \), the amount of water in the sample diverges at \( \theta = 1 \), resulting in infinite dilution of the base coat. When \( f \) is less than one, water sorption is limited by various
processes, e.g. by swelling stress. In case of stress $D_g = s_v$, where $s$ is the stress generated by a polymer as a response to the creation of extra volume $v$ per mole of water, absorbed by the polymer.

With the sorption isotherm, Eq. (15), analytical expressions for kinetics of water transport can be obtained analytically from Eq. (11). The obtained solution can be used to extract the isotherm parameter $f$ from the uptake data to retrieve the isotherms. The general solution for an arbitrary initial condition $q(0) = q_0$ reads

$$t_s = C_0 \frac{f_1}{C_0 f_aex} \left[ \ln \left( \frac{1}{C_0 q} \right) - \frac{1}{C_0 q_0} \right]$$

For water uptake ($\theta(0) = 0$, $a_{ex} = 1$) the solution reads

$$t = -\frac{1}{f} \left[ f \theta + \ln(1 - \theta) \right]$$

To obtain and compare the sorption isotherms of the various systems, the parameter $f$ is recovered by fitting the solution to the water uptake data (Fig. 5). The isotherm of BC50TC64, obtained via fitting Eq. (17) to the water uptake data, is shown by the solid line in Fig. 9. It is in a good agreement with the gravimetric isotherm. This confirms that the driving force for uptake is determined purely by the sorption isotherm.

The results of the fit for all other samples are shown by Fig. 10. The $f$ parameter for the isotherms varies between 0.88 and 0.96, which are typical values for water in polymers [22–24]. The parameters are listed in Table 2. It seems that $f$ decreases with increasing top coat thickness. While the accuracy of the fit does not allow to conclude about this trend, the possible explanation can be that bigger stresses are built up in clusters in samples with thicker top coats. This is in line with the observation, that the maximal water uptake of the base coat is dependable on the top coat thickness, see Fig. 8.

To understand the connection between clustering of water and its molecular mobility, the self-diffusion coefficient of water in the base coat of BC50TC64 was estimated. The self-diffusion coefficient is obtained from $T_2$ measurements of water in the base coat via Eq. (3), see Fig. 11. It was measured at several water activities. A significant increase of the diffusivity is observed at $a_{BC} > 0.95$. This indicates that at high water activities ($a > 0.97$) the bonding of water molecules to the polymer matrix decreases and their mobility increases rapidly.

### 4.4. Prediction of water transport

To verify the ability of the model to predict water transport, water transport in the sample BC50TC64 is measured at different external water activities with NMR and compared with the analytical prediction, see Eq. (16).

First, a drying experiment is performed with $a_{ex} = 0$ (RH = 0%). Initially, the base coat is fully saturated. The amount of water in the base coat during drying is shown in Fig. 12a. Clearly the rate of drying is much faster than the uptake rate: a few hours for drying compared to several days for uptake, see Fig. 5. As discussed in the theory section, this asymmetry is due to the non-linear shape of the sorption isotherm, see Fig. 3.

Additionally, the response of the sample on a switch of water activity was measured with NMR imaging and compared with the
analytical solution. The water activity was adjusted by using aqueous PEG solutions. The changes of water activities in the various experiments are shown in Table 3. The results are shown in Fig. 12b–d. The analytical solutions (solid lines) are in good agreement with the experimental data, proving that the model put forward in this article is correct and can predict the transient water content of the base coat under various conditions on the basis of the top coat barrier properties and the base coat sorption isotherm.

5. Conclusions

It was shown in this paper that water transport in two-layered organic coatings, composed of hydrophilic base coats and hydrophobic top coats, can be understood on the basis of the top coat permeability and the base coat sorption isotherms. Generally, this conclusion is applicable for multilayer coatings, consisting of a barrier layer on top of hydrophilic layers, when water transport rate is limited by penetration through the barrier.

A theoretical model for water transport in the considered systems was introduced and verified. The model described the relation between the top coat permeability to water, the base coat sorption isotherm and water transport kinetics. In this model, the top coat permeability determines the transport timescale and the base coat sorption isotherm defines the driving force of transport, and thus the water content in the base coat as function of time.

The model predicted that polymeric systems with a non-linear base coat sorption isotherms will have a faster drying rate than the uptake rate, which was confirmed by the NMR experiments. In contrast, systems with linear sorption isotherms, which obey Henry’s law, show a symmetry between the time dependencies of uptake and drying.

Experiments showed that the interplay between the layers results in increase of the top coat permeability. The permeability to water of the top coat in two-layered systems was approximately 4 times higher that of free film top coats. Additionally, the introduced D$_2$O/H$_2$O experiment proved to be a fast method to estimate the top coat permeabilities.

From the study of sorption isotherms of the base coats in the systems of interest has shown that water absorption is a process of water clustering in the base coats. This conclusion is supported by the concentration dependency of water self-diffusion coefficient in the base coat.

Practically, these findings mean that to understand water transport kinetics in the considered two-layered coating systems, it is sufficient to measure the top coat permeability to water and the sorption isotherm of the system. The introduced model can be used to predict water transport kinetics on the basis of these parameters, which are easy to measure with balance and wet cup experiments. This is an important result, because it enables an efficient screening of the water uptake properties with low tech experimental tools.

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<td>Water activities before and during the experiment.</td>
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<td>Before experiment</td>
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Fig. 12. Amount of water in the base coat of BC50TC64 during desorption processes. The analytical solutions are shown with solid lines, whereas the NMR data is shown by squares.
References

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