Water transport in pigmented waterborne coatings studied with NMR

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Summary

A critical feature of a waterborne coating is its sensitivity to water that may affect its durability. At the Eindhoven University of Technology, the group Transport in Permeable Media (TPM) focuses on water uptake by coatings and the influence of the substrate on the uptake process. Water uptake in coatings, applied on various substrates, is monitored with nuclear magnetic resonance (NMR) and compared with wet-cup and DVS measurements. This gives the possibility to study real-time and non-destructively water migration inside a sample.

The key question for water uptake by coatings is: which substance of a coating promotes the uptake of water? With help of NMR imaging and relaxometry, we found that the dispersant of the pigment is the most important factor according to water uptake in waterborne coatings.

So, if the dispersant of pigments is important, what is the relation between permeability and pigmentation? We found that the dispersant creates a layer around pigments which facilitates water transport. The effect of this layer is much stronger in case of smaller pigments compared to larger ones, if in both cases a similar pigment to volume concentration (PVC) is used.

As coating layers are meant to protect an underlying substrate, the effect of a coating layer on the water uptake characteristics of a substrate is also studied. The experiments with coatings on wood show that a waterborne coating keeps liquid water out of a wood substrate, but water can still penetrate the substrate by diffusion through cell walls. The uptake rate decreases with the time between application and the experiment. This time period can take several months.
1 Protection against water

Coatings are widely used for protection of substrates and to improve their aesthetic appearance. In many applications, functional particles, such as pigments, fillers and corrosion inhibitors, are added. These particles are generally impermeable for water and affect the properties of the coating. In waterborne coatings solid particles are stabilized in-can using dispersants that are inherently hydrophilic in nature. As these particles introduce ‘hydrophilic’ interfaces due to the dispersants present at the particle boundaries, this can increase the water permeability of the dry formed coating layer. In literature there are many reports on the effect of the pigment to volume concentration on permeability. Until now, an exact description between the relation of PVC and pigment particle concentrations and the permeability of the coating is not made. Because changing the PVC and particle size is difficult experimentally, the effects cannot be easily investigated and quantified. Consequently, this limits the research generally to a more theoretical approach. For instance it is well known that above a certain critical pigment to volume concentration (CPVC) the stacked solid particles introduce porosity (depending on particle morphology), since there is not sufficient binder filling the gaps between the particles.

Another not well studied topic is the effect in permeability in case a coating is applied on a substrate, e.g. wood. This is caused by the fact that measurement of transport through coated substrates with high resolution ~5 μm is challenging, and only few opportunities exists. For example one could use X-ray tomography or weighing. The latter does not provide spatial resolution, neither do other techniques, such as AFM, electrochemical impedance spectroscopy and Fourier transform infrared spectroscopy (FTIR). Fortunately, X-ray tomography provides a spatial resolution but it provides only limited information on the state in which water is present. A useful technique to measure the moisture contents in coating and substrate is nuclear magnetic resonance (NMR). Additionally NMR can give information of the state of water. Research has shown in wood with NMR that different populations of water exist. One can distinguish between bound water in the cell walls and free water in the lumen of wood. This indicates that NMR is a valuable tool to investigate the protection of coatings of an underlying substrate. In our research the permeability of coatings applied on wood was investigated. Allowing us to investigate how water enters the wood in presence of a coating.

In this paper we discuss the permeability of water in coatings and its relation with the presence of pigments and the accompanied dispersants. The key questions for water uptake by coatings addressed are: Which substance present in the coating formulation influence the uptake of water? How does pigmentation (level and size) effect the water permeability of a coating? What is the barrier effect when applied on a porous substrate, in our case wood? And finally, what is the effect of age and weathering on the protective properties of a coating on wood?
2 Probing inside materials with magnetic resonance

Nuclear Magnetic Resonance Imaging (NMR/MRI) is well known as a technique to image the inside of the human body. Its principle is based on the fact that magnetic nuclei (for instance hydrogen nuclei) located in a magnetic field have a specific resonance frequency \( f \), which depends linearly on the magnitude of the applied magnetic field \( B \) according to \( f = \gamma |\vec{B}| \), where \( \gamma \) is the gyromagnetic ratio (for hydrogen nuclei \( \gamma = 42.58 \) MHz/T). After exciting the nuclei by a radio frequent pulse at the resonance frequency, the nuclei start emitting their own signals which can be recorded by a receiver coil. In general the signal is related to the density of the nuclei (in this paper hydrogen), but additionally the signal decay rate provides valuable information. The signal decay is due to dipolar interaction between the nuclei, these interactions change due to their mobility. As a consequence the signal \( S \) decay can be described by:

\[
S = \rho e^{-t/T_2},
\]

where \( \rho \) the density, \( t \) the time, and \( T_2 \) the typical relaxation time, of which actually multiple can be present. This signal decay can be related to pore size distributions\(^{14}\), coating components\(^{11}\) or state of water\(^{11}\). The relaxation time of free water is generally one or more orders of magnitude larger than that of bound water\(^{15-18}\). This allows to distinguish water in the cell walls (bound water) from water in lumina and vessels (free water). In the latter case, the size of the lumina and vessels can be determined.

In case of coating, the challenge is to obtain a sufficiently high resolution to obtain spatial resolved information of that coating. In the presented research, two setups were used to investigate the moisture transport through the coatings and into wood. The highest one is a 4.7 T NMR scanner, which allows for 3D imaging with a resolution of 78 µm. The second is a high resolution NMR setup which allows one dimensional imaging within coatings with a resolution of 5 µm, based on the so called GARField concept\(^{23}\).
3 Dispersants attract water

Many coatings contain solid particles that have to add functionality: filler particles, pigments, etc. In water based systems these particles easily flocculate in the pot in case that they are not stabilized. Systems can be made stable by adding molecules that bind to the surfaces of those solid particles and change the surface properties such that particle start to repel each other. As water is the main solvent in waterborne coatings, these dispersant molecules have generally big hydrophilic moieties (ionic and/or nonionic). As these dispersant molecules are not volatile they remain in the coating after application and create spots in the coating where water could bind. In a series of studies we have investigated two-layer coatings that are representative for typical automotive multi-layer systems\textsuperscript{19,20,21}. The top coat was a solventborne and highly crosslinked layer. The base coat was a waterbased coating consisting of different polymeric compounds and containing pigments. This two-layer system was applied on glass substrates for experimental reasons. For details about the coating systems and the followed NMR procedure we refer to the papers related with that studies\textsuperscript{19}.

Two-layer coatings were subjected to water and the water ingress was monitored with NMR based on the so-called GARField method\textsuperscript{22}. In Figure 1 the time evolution of the depth profiles is shown for two-layer system consisting of 102 \( \mu \)m thick top coat and a 52 \( \mu \)m thick base coat. Hardly any water is seen in the top coat. However a strong response is observed in the base coat. A striking feature of the base coat is that the water seems to be homogeneously distributed in the base coat from the start on. This indicates that the diffusivity of water in the base coat much higher than in the top coat. As soon as water has been able to reach the base coat is quickly redistributes in that layer. This enabled us to formulate a model that has the top coat permeability and the sorption isotherm of the base coat as input\textsuperscript{21}. This model proved to be predictive and enabled us to simulate the response of coatings on humidity fluctuations as experienced in weathering tests\textsuperscript{23}.

![Figure 1: NMR signal profiles during water uptake by a coating with a 102 \( \mu \)m thick top coat and a 50 \( \mu \)m thick base coat. The base coat is in contact with the glass substrate. Water is put on top of the top coat and ingresses via the top coat into the base coat.](image-url)
Simultaneously with measuring the water redistribution through the two-layer coatings we were also able to measure on every spot the NMR signal relaxation\textsuperscript{30}. By doing a $T_2$ analysis we obtained relaxation spectra of the base coat that showed the different components contributing to the NMR signal: latex particles, water and pigment dispersants. In Figure 2 relaxation spectra are shown of a base coat in different states: dry, saturated with water ($\text{H}_2\text{O}$) and saturated with heavy water ($\text{D}_2\text{O}$). As the used NMR set-up can only measure $^1\text{H}$ nuclei, in the system saturated with heavy water only hydrogen atoms of the coatings are visualized and not the ones of water itself. By doing so one can more easily detect which components strongly interact with water. By introducing both water and heavy water in the coating, components with a long $T_2$ (relaxation time) appear in the spectra. These are either water and/or polymeric components significantly mobilized by the water. Note that the $T_2$ of a component becomes longer when its mobility increases. By comparing the spectra of the water and heavy water saturated coatings, we could assign the relaxation peak with the longest relaxation time to the polymeric dispersant. This proved that the dispersant is strongly interacting with the water that gets into the coating, suggesting that indeed the hydrophilic nature of the dispersant in this particular system is the important factor driving water uptake.

![Figure 2: The $T_2$ spectra of the base coat (a) saturated with H$_2$O, (b) saturated with D$_2$O and (c) in a dry state. The bars mark the spectral positions of the peaks and their intensities. The bar intensities are shown by the left scale and the raw spectra intensities are quantified by the right scale. The blue oval and red ovals respectively highlight the water and mobilized dispersant peaks.](image-url)
4 Pigments pave the way for water

The influence of the pigment concentration and size on the rate of water penetration in a coating is discussed in this section. For a detailed discussion of the work summarized in this section and the model developed to describe the effect of pigmentation we refer to our paper\textsuperscript{2}. Water uptake by a waterborne acrylic coating on an inert substrate has been studied. As the focus was on the role of the pigment, we added spherical non-functionalized SiO\textsubscript{2} particles. We added a dispersant for stability reasons and because we were interested to see how the presence of this dispersant on the particle/polymer interface would facilitate water transport. The coatings were applied on an inert substrate (glass). Both the volume fraction of particles (PVC values) and their size was varied.

The permeability of the coatings was studied by wet-cup and NMR experiments. The results of the wet-cup experiments are shown in Figure 3. It shows the effective diffusion coefficient of the as measured with wet-cup experiments. It clearly shows two trends. Firstly, increasing the pigment concentration leads to an increase of the water permeability. Secondly, at fixed particle loading the permeability dramatically increases with a decrease in particle size. Given a certain volume fraction of the coating occupied by particles the total area $A$ of the particle/polymer interface dramatically increases with a decrease in the particle diameter $d$: $A$ is proportional to $1/d^2$.

![Figure 3: The effective diffusion coefficient of a waterborne acrylic coating as a function of the loading with SiO\textsubscript{2} particles. The permeability was determined with wet-cup experiments. Every data point is average of five experiments. Three different particle diameters were used: 0.1, 1 and 10 \textmu m.](image)

Furthermore water uptake experiments have been performed and monitored with the GARField NMR. These coatings were applied on an (inert) glass substrate. In Figure 4 profiles during uptake in an unpigmented coating are shown. The initial and final profiles are plotted with a thick line. The water is located on the left side in the profile, while the inert substrate is placed on the right side of the coating. During uptake, the water ingress is more or less homogeneous over the whole sample and the coating swells (25 \textmu m). Homogeneous uptake indicates a fast redistribution of the water, compared to the water uptake rate at the water-coating boundary.
Figure 4: The signal profiles during water uptake in an unpigmented coating. The time between each plotted profile is 38 minutes for the first 12 h. The saturated profile is measured at equilibrium after 48 hours.

To compare the different coating systems, the averaged signal intensities of the coatings divided by the polymer content are plotted against the time. The results of the experiments are plotted in Figure 5. In Figure 5a only the PVC is varied, while the pigment size is kept constant. It shows that by increasing the PVC, water is transported faster through the coating layer. In a second set of experiments the PVC was kept constant, but the size of the pigments varied. In Figure 5b it is shown that the water uptake rate increases with decreasing particle size.

Figure 5: The increase of NMR signal divided by the fraction polymers during water uptake in coatings for different compositions. In figure 3a the PVC is varied while the particle size is kept constant at 1 µm, while in figure 3b the PVC is kept constant and the particle size is varied between 0.1, 1 and 10 µm.

These observations could be modeled with a modified effective medium theory that assumes the existence of a “conductive” around the pigments. This layer facilitates the water better in case of smaller pigments or larger pigment concentrations. This layer mimics the effect of the dispersant present at the particle/polymer interface.
A fresh applied coating only partly blocks water uptake by wood

A first study was performed on water transport through a coating into wood\textsuperscript{24}. A waterborne acrylic and solventborne alkyd were compared. The main question to be solved was the protective properties of these commercial systems of wood. In Figure 6 the water uptake curves are plotted for meranti. In the inset you see typical moisture profiles observed every 140 minutes for a 100 µm acrylic coating on meranti. In order to compare the influence of the coatings on the water uptake, the average moisture content (MC) in a layer at the wood coating interface with a thickness of 1 mm is determined and plotted against time. One observes that in case of meranti the acrylic coating does not provide a barrier for moisture uptake, since the uptake with and without a coating is comparable. Additionally, we see that the moisture content does not surpass the Fiber Saturation Point (FSP). This is the point in which the cell walls of the wood are fully saturated, but the lumen and voids are not filled by water. In case of the alkyd layers water uptake is prevented and moisture is not entering the wood at all.

![Figure 6: The average moisture content of a 1 mm thick slice directly behind the meranti-coating interface, plotted against time. Coating thicknesses of 100 and 200 µm are shown. The horizontal dashed line indicates the FSP.](image)

Since meranti is a heardwood also a softwood was investigated, in our case pine wood and spruce. The results of pine wood are plotted in Figure 7. Besides plotting the average moisture content the inset shows the relaxation time distribution. This shows that in case of uncoated pine long relaxation components are present, which can be attributed to free water present in lumen and voids. This is to be expected since no coating is present on top, and pine is much more permeable than meranti. The acrylic coating restricts water from entering the lumen and voids, but cannot prevent water been taken up by the wood fibers. This bound water is represented by the blue peak (at 1500 µs) plotted in the inset. Again the solvent borne alkyd totally prevents the water from entering the lumen or cell walls and acts as a perfect barrier.
Figure 7: Average moisture content of a 1 mm thick slice directly behind the pine-coating interface, plotted against time. Coating thicknesses of 100 µm and 200 µm are shown. The horizontal dashed line indicates the FSP. The inset shows the relaxation times corresponding to water found in the wood.
6 Weathering improves initially the barrier properties

To test the influence of ageing on the permeability of a coating on a wood substrate, permeability studies were performed at different moments in time after application. Experiments were done with waterborne acrylic coatings applied on meranti. The experiments were performed with uncoated meranti, a coated sample of respectively one and five months old and one of five months old subjected to accelerated weathering. The weathering was performed by applying two times eight hours UV-radiation at a temperature of 75 °C, while the sample was additionally exposed to two times for two hours rain. The uptake measurements are performed as described in previous section. The results of the uptake experiments are plotted in Figure 8. The uncoated and fresh coated sample have a similar water uptake, while the coatings of 5 months old absorbs less in time. These experiments show that a freshly coated coating has not reached its optimal barrier properties immediate after physical drying. The coating is still changing on molecular level, while on macroscopic scale the appearance of the coating does not change. An improvement of the barrier properties of the coating seems to be a matter of time, but can be accelerated with artificial weathering. By additional experiments it was shown that the applied temperature is the crucial factor for improving the barrier properties of the coating, which points to progressive coalescence of the polymer particles induced by thermal annealing.

Figure 8: The rise in MC in wood is plotted against the time. Four different uptake experiments on a meranti sample are shown. The open squares represent the fresh coated sample, the solid circles the five months old coated sample, the solid triangles a weathered coated sample and the solid diamonds an uncoated sample.
7 Conclusions

NMR is a versatile tool for studying water migration in coatings and its penetration into the underlying substrate. Water distributions can be measured quantitatively in waterborne coatings and wood. In addition NMR can also be used to monitor the interaction of water with the polymeric matrix, which is helpful because it helps to identify the major attractors of water in a coating.

In a study with a two layer coating it was shown that a lot of water migrates into the waterborne base coat in this system. The mobility of water in that layer seems to be high, which can be explained by the fact that water is there in quasi-liquid state. It was shown that the dispersants for solid particles (the pigments in this particular case) strongly interacted with water. Upon water uptake these dispersant molecules become extremely mobile. This suggests that the dispersant is in this particular coating system the main component driving water uptake.

With help of experiments on coatings with artificial pigments it is shown that the surface area of the pigments is crucial in the water transport through a coating. More surface area results in a higher permeability of the coating. This is probably a result of the clustering of the dispersants at the surface of the pigments and as explained before these dispersants strongly interact with water.

The differences between the behaviour of various wood coating combinations can be summarized as follows. In case of all wood types investigated the low water uptake of the alkyd prevents water uptake by diffusion into the wood. In case of pine the acrylic coating prevents water uptake in the lumen, but does not prevent water to diffuse into the solid matrix of the wood.

Finally, it is shown that a freshly applied waterborne acrylic coating does not prevent moisture uptake in a meranti sample. This does not mean that the acrylic coating does not act as a barrier at all. Over time the barrier properties improve. This can be boosted by a short heating period.

With help of this study, water transport in waterborne coatings is better understood. In future, the focus of the studies should be on accelerated leaching of dispersants, because these molecules strongly influence the water permeability of a coating.

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