Water mobility during drying of hard and soft type latex

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Water mobility during drying of hard and soft type latex: Systematic GARField $^1$H NMR relaxometry studies

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ABSTRACT

GARField $^1$H NMR relaxometry experiments were done to study the drying process of two latices with different polymer $T_g$ and to elucidate water mobility behavior during this process. It was found that the hard type latex, with a polymer $T_g$ above room temperature, dries faster than the soft type latex, with a polymer $T_g$ below room temperature. Diffusion measurements by means of echo time variations at different moments in the drying process show that water auto-diffusion decreases with increasing solid content of the latex independent of particle $T_g$. Two pools of protons with different mobilities were observed based on transversal relaxation times $T_2$. Determination of the long $T_{2,\text{long}}$'s and short $T_{2,\text{short}}$'s of both latex dispersions and their respective proton densities during drying at 80% RH showed evidence of particle deformation for the soft type latex and the absence thereof for the hard type latex. Additional drying of the resulting coatings with anhydrous CaCl$_2$ showed a higher porosity for the hard type coating based on the proton distribution profile width. Moreover, two domains with different polymer proton mobilities are found for both coatings that are both plasticized by water at 80% RH. This is more apparent for the hard type coating, suggesting that a more hydrophilic polymer gives a higher degree of plasticization.

1. Introduction

Paints are probably the most abundantly used form of coating materials in the world. Apart from the aesthetic value, it can provide substrates with the necessary protection against external influences. Examples are the prevention of wood rot and metal corrosion due to the continued exposure to weather phenomena, such as rain, wind, and UV-light.

In the past decades, innovations in paint technology have been focused on the switch from solventborne to waterborne coatings, mainly driven by regulatory laws. Over the years, this development has lead to the complete elimination on the use of organic solvents for paints. The development of latex was mainly enabling this switch to waterborne coatings, mainly focused on the switch from solventborne to waterborne coatings, mainly driven by regulatory laws. Over the years, this development led to the complete elimination on the use of organic solvents for paints. The development of latex was mainly enabling this switch to waterborne paints [1].

Latex is an aqueous dispersion of polymer particles, generally submicrometer sized, that upon drying form a network and give the coating its mechanical, chemical and physical properties. This film formation process takes place in a sequence of stages. First, particles are concentrated through the evaporation of water and colloidal stability by repulsion is overcome [2]. Next, particle deformation occurs decreasing the void volume between the particles [3]. Finally, the formation of a coherent coating is driven by the interdiffusion of individual polymer chains.

Studies on polymer interdiffusion are rather limited and are mostly done by the use of the fluorescence resonance energy transfer technique (FRET), often applied by Winnik and co-workers. With this, many factors that can influence the interdiffusion process, such as polymer $T_g$, are investigated [4-6].

The polymer $T_g$ is directly related to its mobility. To study this, only a few techniques are available. The aforementioned FRET technique gives information on the polymer interdiffusion, but lacks the possibility to study polymer mobility changes during a drying process. Another technique used is the quartz crystal microbalance (QCM) to probe viscoelastic properties of cross-linking alkyd resins [7]. This technique could be used to study $T_g$ and polymer mobility decrease. A major limitation of QCM, however, is the limited thickness of the applied coating (≤ 2 µm).

GARField $^1$H NMR can be used to study coatings up to 400 µm thickness and has been used previously to study the drying behavior of latices [8,9]. In a recent study, it was used to investigate the drying.
behavior of latices with various particle $T_g$'s, showing the effect of skin formation on the drying rate of latex [10]. It is an ideal technique to study water distributions and the drying rate of thin wet films. In addition, using an Ostroff–Waugh pulse sequence, information is provided on the transversal relaxation ($T_2$ relaxation) of water and polymer, which is directly linked to the mobility of both phases. Erich et al. [11] successfully used GARField $^1$H NMR to show the decrease in $T_2$ relaxation of alkyd resins due to cross-linking of the fatty acids. For latex, where film formation occurs due to interdiffusion of polymers rather than cross-linking, such mobility studies have not been done before. Although water distributions in drying latex dispersions have been studied extensively before with GARField $^1$H NMR [7,8,10,12,13] no systematic study has been done before on the mobility of water in such systems. In the present study the drying behavior of two acrylic latices with $T_g$'s lower (soft type) and higher (hard type) than room

Table 1
Monomer compositions (wt.%) of the latices used for this study.

<table>
<thead>
<tr>
<th>Latex</th>
<th>Butylacrylate</th>
<th>Methyl methacrylate</th>
<th>Methacrylic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard type</td>
<td>25</td>
<td>70</td>
<td>5</td>
</tr>
<tr>
<td>Soft type</td>
<td>54.5</td>
<td>40.5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2
Physical characteristics of the latices. $Z_{av}$ is the average particle diameter, $D$ the polydispersity index of the size distribution and $T_g$ the glass transition temperature of the latex.

<table>
<thead>
<tr>
<th>Latex</th>
<th>$Z_{av}$ (nm)</th>
<th>$D$</th>
<th>$T_g$ (°C)</th>
<th>Solids fraction (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard type</td>
<td>47.3</td>
<td>0.118</td>
<td>75.3</td>
<td>37.0</td>
</tr>
<tr>
<td>Soft type</td>
<td>57.0</td>
<td>0.253</td>
<td>18.6</td>
<td>37.0</td>
</tr>
</tbody>
</table>

Fig. 1. Proton distribution profiles of soft type (top) and hard type (bottom) latex. The profiles at $t_{drying} = 0$ was obtained using an average of 256 measurements. During drying at 80% RH, the first 20 drying profiles and the subsequent 10 drying profiles were obtained using averages of 64 and 256 measurements respectively. To reduce noise further, a moving average of 4 drying profiles was used. As a consequence the slope of the drying fronts increase. Arrows indicate the final maximum signals $S_{max}$ and thicknesses $d$ of the coatings.
temperature, respectively, is discussed. This provides insight into the influence of the polymer particle packing morphology and deformation ability, governed by the particle $T_g$, on the mobility of water including free auto-diffusion, enclosed water evaporating through a polymer matrix and water that is physically bound to the polymer material. This will ultimately support research on the influence of water on the latex film formation process and how this can be used to develop latex dispersions that are fully plasticizable with water.

2. Materials and methods

2.1. Latex synthesis

The latices used for this study were supplied by DSM Coating Resins and were prepared via an emulsion copolymerization of $n$-butyl acrylate, methyl methacrylate, and methacrylic acid. The $T_g$ of the latices could be varied by adjusting the ratio of butyl acrylate and methyl methacrylate. In Table 1, monomer compositions of two latices used are shown. The monomer amounts used in the synthetic procedure described below are those of the hard type latex.

A 2L flask equipped with a thermometer, $N_2$ inlet and overhead stirrer was charged with water (858.7 g) and sodium lauryl sulphate (41.3 g; 30 wt.% solution in water) and heated to 85 °C, while stirring under nitrogen atmosphere. At 82 °C a solution of ammonium
persulphate (2.7 g) in demineralized water (8.1 g) was added to the flask. Next, 5 wt.% of a mixture of methyl methacrylate (MMA; 376.5 g), n-butyl acrylate (n-BA; 135.5 g) and methacrylic acid (MAA; 27.0 g) was added to the flask and the temperature was allowed to increase to 85 °C. At 83–87 °C the remainder of the monomer mixture was added to the flask over 90 min. Subsequently, the funnel was rinsed with demineralized water (7.3 g), which was added to the flask. The flask was kept at 85 °C for 45 min, after which the temperature was decreased to 60 °C. During cooling, a solution of ammonia (7.9 g; 25 wt % in water) in demineralized water (16.0 g) was added. After addition of the ammonia solution, the mixture was allowed to cool down to room temperature. Finally, ProxelUltra10 (6.0 g) was added, followed by demineralized water (13.0 g). The resulting latex was filtered using a filter cloth to remove any coagulated material. The average particle diameter ($D_{pp}$) and polydispersity index (PDI) were determined by dynamic light scattering (Malvern Zetasizer Nano ZS) at 25 °C. The midpoint $T_D$ of the dried latex materials was determined by DSC (TA Instruments Q2000) under a nitrogen atmosphere at a heating rate of 20 °C. The solid weight fractions were determined gravimetrically.

Results of the analyses are listed in Table 2.

### 2.2. GARField $^1$H NMR

GARField $^1$H NMR imaging is a useful tool to describe drying of thin films and its design and principles have first been described by Glover et al. [14]. The magnetic field strength of the equipment used for this study was 1.5 T and the static gradient was 42.2 ± 0.2 T/m. From the signal decays of an Ostroff–Waugh [15] pulse sequence ($90^\circ_r-\tau-[90^\circ_r-\tau-\text{echo}-\tau_{ee}]$), $T_2$ relaxation times of both water and polymer are obtained. Unless stated otherwise, the echo time $\tau_e = 2\tau$ used for this study is 40 μs with an acquisition time $\tau_{acq}$ of 35 μs, resulting in a spatial resolution of 14 μm. The long delay $\tau_d$ was set at 1.7 s and the number of echoes $n$ at 128. To reduce the signal-to-noise ratio, signal decays were obtained by averaging multiple measurements as follows: 20 decays of 64 averages, 10 decays of 256 averages, and 20 decays of 1024 averages. The results were normalized with a reference signal, obtained by a measurement on an aqueous 0.025 M CuSO$_4$ solution, with $\tau_c = 40\mu$s, $\tau_{acq} = 35\mu$s, $\tau_d = 0.3\, s$, $n = 2048$ and 4096 averages.

To control the evaporation rate of the latex, the NMR set-up is equipped with a temperature and humidity controlled chamber in which the sample is placed directly onto the RF coil. This sample holder is a 140 μm thick cover glass covered with a microscope object glass having a circular hole with a 10 mm diameter. Herein, 37 μL of latex was placed using a 100 μL volumetric pipette, resulting in a wet coating of about 300 μm thickness. Initially, the sample holder is closed with a silicone stopper to perform a measurement without any drying. Subsequently, the cover is removed and sequential drying measurements are performed.

The Ostroff–Waugh signal decays of latex at a certain position in the film can be fitted with an exponential decay function,

$$S_t(x) = P_t(x) \sum_{k=1}^{N} A_k(x) \exp\left(\frac{-Nt}{T_{2,k}(x)}\right) + S_0$$

(1)

where $S_t(x)$ is the total signal at time $t = n\tau_c$ [s], $T_{2,k}(x)$ [s] is the transversal relaxation time of the kth proton pool of the sample with amplitude $A_k(x)$, and $S_0$ is the signal noise level. $P_t(x)$ is a weighing factor necessary to correct for heterogeneities in the coil profile and echo modulations introduced by the Ostroff–Waugh sequence. $P_t(x)$ is obtained using an aqueous 0.025 M CuSO$_4$ solution. For details, we refer to [16]. With this, Eq. (1) can be re-written as

$$I_t(x) = \sum_{k=1}^{N} A_k(x) \exp\left(\frac{-Nt}{T_{2,k}(x)}\right) + \sum_{k=1}^{N} \rho_k(x) \exp\left(\frac{-Nt}{T_{ld,k}(x)}\right)$$

(2)

where $I_t(x)$ is the relative signal intensity and $\rho_k(x)$ the relative proton density of the kth proton pool with respect to water. $A_{ref}(x)$ is the signal amplitude obtained with a reference measurement of the 0.025 M CuSO$_4$ solution. The $T_2$ describes the relaxation processes of protons due to mobility [17–19] and diffusion [20,21].

The transversal relaxation time $T_2$ can be split in a dipole effect $T_{2,dp}$ [s], related to the local molecular mobility, and a diffusion part $T_{2,diff}$ [s] according to:

$$\frac{1}{T_2} = \frac{1}{T_{2,dp}} + \frac{1}{T_{2,diff}}$$

(3)

The self-diffusion $D$ [m$^2$/s] of water in latex is determined by acquisition of $T_2$ relaxation times at various $\tau_c$. The $T_2$ dependence on $\tau_c$ is given by the following relation,

$$T_{2,diff}^{-1} = \alpha \gamma^2 G^2 D^2$$

(4)

where $\alpha$ is a constant, which is determined experimentally, $G$ [T/m] the field gradient, and $\gamma$ [Hz/T] the gyromagnetic constant for proton atoms [22,23]. By determining the $T_2$ relaxations of an aqueous 0.025 M CuSO$_4$ reference solution at various $\tau_c$, Eq. (4) can be used to determine $D$ for both latex dispersions taking $D = 2.3 \times 10^{-9}$ m$^2$/s for Ref. [24].

$T_{2,dp}$ can be approximated by

$$T_{2,dp}^{-1} \sim (\omega^2)\tau_c$$

(5)

where $\tau_c$ is the correlation time of the local molecular motions and $\langle \omega^2 \rangle$
is the second moment associated with residual interactions [25,26,18]. If $\tau_c \ll \tau_e$ Eq. (5) holds. For more detailed discussion we refer to [16]. Therefore, using various echo times $-T_2,\text{diff}_1$ and $-T_2,\text{di}_1$ can be determined.

### 2.3. Atomic force microscopy

After drying a latex film, the resulting coating was glued onto a metal disc and mounted on the sample stage of the AFM. AFM images were obtained under ambient conditions in tapping mode (NanoScope V multimode atomic force microscope, Bruker Nano Surfaces) using silicon cantilevers (TESP, Bruker Nano surfaces) with resonance frequencies of 300–400 kHz. Height scale and scan area are shown next to the AFM images.

### 3. Results

#### 3.1. Proton distributions during drying

The drying of the latex dispersions can result in a heterogeneous distribution of water and polymer particles, which affects the drying rate and final coating structure. Therefore, it is important to study the proton distributions during drying. With GARField $^1$H NMR proton distribution profiles during drying of latex can be obtained.

Drying experiments of the soft and hard type latex dispersions were done using GARField $^1$H NMR as described in Section 2.2 (Exp. I). Fig. 1 shows the normalized proton distribution profiles of both the hard and soft type latex during drying at 80% RH. The drying shows the well-known two-step drying behavior.

First, a receding front is observed, indicating shrinkage of the layer due to evaporation of water and concomitant packing of the latex particles. It should be noted that the increased slope of the drying fronts is an effect of the averaging of drying profiles used to reduce noise. To compare water evaporation rates, Fig. 2 shows coating thicknesses $d$ and maximum signal intensities $I_{\text{max}}$ during drying. The sharper decrease of the hard latex thickness $d_{\text{hard}}$ and signal intensity $I_{\text{max,hard}}$ refers to a higher drying rate for the hard type latex.

Second, $d$ and $I_{\text{max}}$ are leveling off to more constant values. The leveling of the soft latex thickness $d_{\text{soft}}$ and signal intensity $I_{\text{max,soft}}$ appear to more or less coincide at approximately 40 min drying. The leveling of $d_{\text{signal}}$ at approximately 20 min, however, does not coincide with the leveling of $I_{\text{max,hard}}$ at approximately 40 min, which suggests continuation of bulk water evaporation for this latex dispersion while...
latex particles are fixed in position and cannot deform and interdiffuse. This is in line with expectations for latex containing non-deformable and non-coalescing particles, which upon drying forms a brittle and porous network [1]. $I_{\text{max,hard}}$ after drying is also significantly lower than $I_{\text{max,soft}}$. This could be a result of the presence of empty pores and, therefore, less water in the hard coating, and different $T_2$ relaxation behavior may play a role. Additional relaxation analyses as discussed in Sections 3.2 and 3.3 are necessary for clarification.

### 3.2. Proton mobilities during drying

As a consequence of polymer particle compaction during drying, the water mobility in latex will be restricted. The auto-diffusion $D$ and $T_2$ relaxation of water will decrease and interdiffusion of particles, and thus particle $T_{sp}$, is expected to be of influence. Water protons and polymer protons of the latex dispersions have different $T_2$ relaxations. This $T_2$ is a measure of proton mobility, which can be determined by fitting an Ostroff–Waugh signal decay using Eq. (2). The solid and dashed lines indicate the points at which the soft type and hard type latex dispersions reach their closest packing of particles, as shown in Fig. 2. Values for $p$ are taken at a position in the bulk, i.e. as close as possible to the bottom of the sample.

In Fig. 7, the relative proton densities with respect to $0.025 \text{ M CuSO}_4$ of the long ($\rho_{\text{long}}$; top) and short ($\rho_{\text{short}}$; bottom) relaxations obtained by a double exponential fit of the Ostroff–Waugh signal decays using Eq. (2). The solid and dashed lines indicate the points at which the soft type and hard type latex dispersions reach their closest packing of particles, as shown in Fig. 2. Values for $p$ are taken at a position in the bulk, i.e. as close as possible to the bottom of the sample.

Fig. 7. Relative proton densities with respect to $0.025 \text{ M CuSO}_4$ of the long ($\rho_{\text{long}}$; top) and short ($\rho_{\text{short}}$; bottom) relaxations obtained by a double exponential fit of the Ostroff–Waugh signal decays using Eq. (2). The solid and dashed lines indicate the points at which the soft type and hard type latex dispersions reach their closest packing of particles, as shown in Fig. 2. Values for $p$ are taken at a position in the bulk, i.e. as close as possible to the bottom of the sample.

### 3.3. Water content

As a consequence of polymer particle compaction during drying, the water mobility in latex will be restricted. The auto-diffusion $D$ and $T_2$ relaxation of water will decrease and interdiffusion of particles, and thus particle $T_{sp}$, is expected to be of influence. Water protons and polymer protons of the latex dispersions have different $T_2$ relaxations. This $T_2$ is a measure of proton mobility, which can be determined by fitting an Ostroff–Waugh signal decay using Eq. (2). The solid and dashed lines indicate the points at which the soft type and hard type latex dispersions reach their closest packing of particles, as shown in Fig. 2. Values for $p$ are taken at a position in the bulk, i.e. as close as possible to the bottom of the sample.

During drying, water protons and polymer protons of the latex dispersions have different $T_2$ relaxations. This $T_2$ is a measure of proton mobility, which can be determined by fitting an Ostroff–Waugh signal decay using Eq. (2) using $k = 2$, thus assuming two proton pools with different mobilities. Using an Ostroff–Waugh pulse sequence, measurements were done on both latex dispersions (Exp. II). The sample cups were closed to prevent evaporation of water. In Fig. 3 the resulting Ostroff–Waugh decays are shown. A short $T_{2,\text{short}}$ and long $T_{2,\text{long}}$ relaxation time can be identified for both latices, each corresponding to proton atoms with a different mobility.

As was mentioned in Section 2.2, $T_2$ relaxations can consist of a diffusion part ($T_{2,\text{diff}}$) and a dipolar part ($T_{2,\text{dip}}$). The contributions of $T_{2,\text{diff}}$ and $T_{2,\text{dip}}$ can be investigated by determining $D$ of water during the drying process on the basis of $t_c$ variation measurements. For this, drying experiments (Exp. III) were done similar to those discussed in Section 3.1, but the drying process was stopped by closing the sample cup. Subsequently, $t_c$ variation measurements were done. For each data point, a separate experiment was done and stopped at a different drying time. Fig. 4 shows examples of the results of these experiments at different solid contents, derived from the coating thicknesses $d$, during the drying process for both the soft and hard type latex using the $T_{2,\text{long}}$ relaxations. The $T_{2,\text{short}}$ relaxations do not vary with $t_c$ and are therefore not used to determine $D$ of water. From the slope of the curves in Fig. 4, $D$ is determined using Eq. (4) and $T_{2,\text{short}}$ is determined with the inverse of the intercept of the curves. In Fig. 5 $D$ and $T_{2,\text{short}}$ during drying of both latex dispersions are shown.

Before drying, both values for $D_{\text{soft}}$ and $D_{\text{hard}}$ are similar and in the same order of that of free water. Therefore, it is concluded that the long $T_2$ component represents the latex water phase. As expected $D$ decreases during drying. At approximately 30 min drying, this is at latex solid contents above 67%, $D$ could not be measured anymore.

$T_{2,\text{dip}}$ of both latex dispersions also decreases. This can be explained with the increasing surface-to-volume ratio of latex particles and water during drying, which increases the interaction of water with the latex particle surface.

Although after approximately 30 min drying there is no measurable $D$ of water anymore, significant amounts of water are still present in between the closer packed particles. Continued drying of the latex dispersions can still reduce $T_2$ relaxations and, therefore, water mobilities. Fig. 6 shows short and long $T_2$ relaxation times obtained from experiment I at a position in the bulk, i.e. as close as possible to the bottom of the sample holder. As expected, the long $T_2$ relaxation time decreases during drying due to limitations in proton mobility by an increased interaction of water molecules with the latex particles. Initially, $T_{2,\text{long}}$ is higher for the soft type latex, which suggests more
mobile water-polymer interaction affecting $T_2,\text{short}$. During the first 20 min drying, $T_2,\text{long}$ of the soft type latex appears to remain more constant and decreases rapidly for the hard type latex. After 20 min drying, $T_2,\text{long}$ of the hard type latex decreases at a similar rate, but decreases more rapidly for the soft type latex. After approximately 40 min drying, the $T_2,\text{long}$'s of both latex dispersions level off to an equilibrium value. The final $T_2,\text{long}$ of the soft type latex is higher than that of the hard type latex. To explain this phenomenon, more information on the state of the residual water is necessary.

The $T_2,\text{short}$'s for both latex dispersions remain constant at approximately 0.1 ms during drying. Evidently, both latex dispersions have proton pools with similar mobilities that do not change as a result of the evaporation of bulk water. These relaxations are therefore attributed to protons embedded in the latex particles, which are not affected by the evaporation of water. The relative proton density changes during drying are shown in Fig. 7. The proton densities of the $T_2,\text{long}$ ($\rho_{\text{long}}$) decrease during drying for both latex dispersions. Again, $\rho_{\text{long}}$ for both latex dispersions levels off at approximately 40 min, which coincides with the results for the soft type latex shown in Fig. 2 but not for the hard type latex. The proton densities for $T_2,\text{short}$ ($\rho_{\text{short}}$), however, show an increase for the soft type latex, but appears constant for the hard type latex, which suggests further concentrating of the latex polymer phase for the soft type latex.

### Table 3

$T_2$'s of the hard and soft type coatings after drying at 80% RH for 24 h and after additional drying with anhydrous CaCl$_2$ for 48 h.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Drying condition</th>
<th>$T_2,\text{short}$ (ms)</th>
<th>$T_2,\text{long}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard type</td>
<td>80% RH</td>
<td>0.06</td>
<td>0.69</td>
</tr>
<tr>
<td>Hard type</td>
<td>$+\text{CaCl}_2$</td>
<td>0.04</td>
<td>0.17</td>
</tr>
<tr>
<td>Soft type</td>
<td>80% RH</td>
<td>0.07</td>
<td>0.39</td>
</tr>
<tr>
<td>Soft type</td>
<td>$+\text{CaCl}_2$</td>
<td>0.04</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Fig. 10. Ostroff–Waugh decays of the soft and hard type coatings saturated at 80% RH and after additional drying for 48 h with anhydrous CaCl$_2$.

3.3. Coating structure and proton mobility

In a coating, water can be present either in pores or pockets in a liquid state, or in a state of physically bound to the polymer matrix. Both states influence the coating physical and mechanical properties in their own way, and as such it is necessary to know how water is distributed in a coating. As was mentioned in Section 2.2, Eq. (2) can be used to provide insight into the proton densities of the latices. For a dry coating, proton densities of both polymer and residual water can be determined. Using proton balance equations, the absence of signal is an indication for air-filled voids, pores, or cracks. Here an assumption is
made that between the excitation pulse and the first echo, no decay of a rigid group of protons occurs. Since, $T_{2,\text{long}}$ is successfully used to determine $D$ for water, its presence after drying of latex can be an indication of water-filled voids or physically bound water.

A first order approximation of the coating porosity can be made by studying the thickness of a wet latex layer and the resulting coating after drying. Thicknesses of wet latex layers were measured by determination of the width of the first echo profile obtained with an Ostroff–Waugh pulse sequence with $t_e = 100 \mu s$, $t_w = 90 \mu s$, $n = 256$, and 256 averages. The increase of $t_e$ and $t_w$ with respect to the procedure described in Section 2.2 was necessary to improve the spatial resolution and thus the accuracy of the measurements. After 24 h drying at 80% RH an additional drying step was introduced by placing the sample cups in a closed vessel containing anhydrous CaCl₂ for 48 h to ensure full evaporation of water. The thicknesses of the dry coatings were assessed using the same procedure that was used to determine the thicknesses of the wet latex layers. Fig. 8 shows proton distribution profiles of layers of the hard and soft type latex, both for the initial, wet situation and the resulting coatings after drying are shown.

Taking both front positions and sample bottom positions at $S = 0.5S_{\text{max}}$, the thickness of the wet layers and dried coating can be determined. The void fraction $\phi_0$ of the coating can be calculated, $\phi_0 = \frac{V_0}{V_{\text{coat}}} = 1 - \frac{H_{\text{pol}}}{H_{\text{coat}}}$ (6) with $V_0$ and $V_{\text{coat}}$ the volume of the void space and the total coating volume, respectively. $V_0$ is either taken up by water or air present in the coating. $H_{\text{pol}}$ is the theoretical thickness of the coating when film formation is complete and no air or water is present in the coating, and $H_{\text{coat}}$ is the actual thickness of the coating. This can be re-written as $\phi_0 = 1 - \phi_{\text{pol}} \frac{H_{\text{wet}}}{H_{\text{coat}}}$ (7) where $H_{\text{wet}}$ is the thickness of the wet latex layer and $\phi_{\text{pol}}$ is the polymer volume fraction in the latex. On the basis of this, void volume fractions are estimated at 0.37 and 0.08 for the hard type coating ($\phi_{\text{void}}$) and soft type coating ($\phi_{\text{void}}$), respectively. AFM was used to analyze the surfaces of both hard and soft type coatings and to reflect on the void volume fraction results. In Fig. 9, images show a featureless soft type coating surface, whereas the hard type coating shows packed un-coalesced particles.

Fig. 10 shows Ostroff–Waugh decays of the coatings after 24 h drying of the latex at 80% RH and after the additional drying step with anhydrous CaCl₂, of which the first echo profiles are shown in Fig. 8. Both coatings at 80% RH show a clear double exponential decay, which could indicate residual water present in the coating. After the additional drying step the decays shorten, but the fit of the curves still show the presence of two proton pools. In Table 3, $T_2$ values obtained from fits of the Ostroff–Waugh decays are listed. $T_{2,\text{long}}$ and $T_{2,\text{short}}$ of both coatings decrease after 48 h drying with CaCl₂.

It is possible that the $T_2$ relaxations in the coatings are mixed polymer and water signals. Calculating “residual curves” by subtracting the post-dried decays from the 80% RH decays could provide decays for the residual water in the 80% RH coatings. These results in Fig. 11 can be fit with single exponential decay functions, indicating a single pool of protons for both coatings, which can be attributed to water. The hard type coating appears be more affected by the presence of water at 80% RH.

3.4. Discussion

In the previous sections different stages of the drying process have been discussed in which the mobility of water changes from free to pore water and water that is physically bound to the polymer matrix. In this section a comprehensive overview is given. In Fig. 12, a visual representation is given of a plausible drying mechanism of the hard and soft type latex.

Initially, latex particles and water are able to move freely. Water proton mobility and water diffusion decrease due to an increased interaction with the polymer particle surface, concomitantly decreasing $T_{2,\text{dp}}$ as is shown in Fig. 5. After approximately 20 and 40 min drying at 80% RH for the hard and soft type latex, respectively, the thicknesses of the coatings do not decrease significantly anymore, as shown in Fig. 2. At this point, however, the hard type latex still contains considerable amounts of bulk water, which can evaporate freely through the voids between the non-deformable and non-coalescing particles. This is confirmed by the results in Figs. 2, 6 and 7, which show further decrease of $I_{\text{max,hard}}$, $T_{2,\text{long}}$, and $\rho_{\text{long}}$ between 20 and 40 min for the hard type latex occurring with the proceeding release of water from the coating.

After 24 h drying at 80% RH, Ostroff–Waugh decays still show two proton pools, which can be explained either by the presence of free water in inter-particle voids, or by the presence of water bound to the polymer matrix plasticizing domains with different hardness in the
coating. Fig. 8 indeed shows the presence of void space, in particular for the hard type coating, which could hold water. Further drying under anhydrous CaCl₂ for 48 h shows a definite change in signal in Fig. 10. The Ostroff-Waugh decays still show two proton pools. Two things can be extracted from these results.

First, \( T_{2,\text{short}} \) and \( T_{2,\text{long}} \) found during the entire drying process do not result from the polymer and water protons, respectively, but both are a mix of the polymer and water signals. In the first stage of the drying process, \( T_{2,\text{long}} \) is dominated by \( D \) of water for both latex dispersions, and therefore \( T_{2,\text{diff}} \) as described by Eq. (3). After closer packing of the polymer particles, however, the dipolar component \( T_{2,\text{diff}} \) dominates the relaxation behavior.

Second, since no water is expected to be left in the coatings after the additional drying step with CaCl₂, the presence of two proton pools can be explained by domains in the coatings having different degrees of hardness. The softer domain for the hard type coating appears to be more sensitive to the presence of water, as is shown by the more obvious change in relaxation after post-drying with CaCl₂. Due to the presence of more MMA and less n-BA with respect to the soft type coating, its proton mobility is decreasing more rapidly due to deformation of particles and interdiffusion of polymers. After 24 h drying, water present in the hard and soft coating is plasticized more and therefore, in that stage of drying, \( T_{2} \) relaxations in the coatings are mixed polymer and water signals. Earlier work by Reuvers showed that crystalline and amorphous domains in polyamides were found with water present in the hard and soft type coatings even after post-drying under CaCl₂.

4. Conclusion

The possibility of a latex to form a coherent coating is determined by a number of factors. The polymer particle glass transition temperature \( T_g \) is an important factor as it determines the flexibility of polymer chains and, therefore, influences the ability of particles to deform, which enables polymer interdiffusion. The drying behavior of two acrylic latex types was studied with GARP 1H NMR, with focus on the mobility of water: a hard type latex with a dry polymer \( T_g \) above room temperature (RT) and a soft type latex with a polymer \( T_g \) below RT. Relaxometry measurements were performed at 23°C and 80% relative humidity (RH).

The mobile state of water during drying of the latex dispersions is elucidated. Two pools of protons were found, that appear to be a mix of water and polymer protons. During a first stage of the drying process, the water is diffusing freely and it is shown that the diffusion coefficient \( D \) is dependent on the solid content of the latex. After this first stage, a significant amount of water is still present in both dispersions and the proton mobilities become dependent on the latex particle packing morphology and deformation ability, governed by the particle \( T_g \). For the soft type latex, it was found that proton mobility is decreasing more rapidly due to deformation of particles and interdiffusion of polymers. After 24 h drying, water present in the hard and soft coating is plasticizing two polymer phases with a different degree of hardness. The hard coating is plasticized stronger due to the more hydrophilic nature of the polymer chains.

The drying process of latex dispersions is influenced by additives present in the dispersions. The ionic strength of both latex dispersions should therefore be comparable for both latex dispersions. For future work, studying the influence of sodium dodecyl sulphate (SDS) and other ionic content on the drying behavior of these latex dispersions is recommended.

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