

Drying and film formation's first steps in polymer dispersions – Insights from a parallel gravimetric experiment and profile NMR study



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ABSTRACT

Understanding the microscopic mechanisms of film formation in polymer dispersions is a complex analytical and physical challenge. In this contribution, we present results from parallel gravimetric and NMR profiling experiments along with a semiempirical model approach to establish a systematic relation between both data sets. As a result of the semiempirical model, a critical water content at which rotation dynamics of the polymer particles changes can be determined. Furthermore, it is shown that the addition of film-forming agents to the dispersion shifts the critical water content to higher values.

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1. Introduction

One-dimensional (1D) NMR profiling studies on drying solutions or dispersions of polymers and associated effects such as film formation have been studied by 1D NMR imaging methods for quite some time [1–3]. While these first studies involved rather bulky and heavy magnet systems, the introduction of the NMR profiling, MOUSE[®] [4] has brought a much smaller and more accessible version of a 1D NMR imaging setup. This experimental system (or setup or device) has become available and has been in the meantime applied to profiling studies of several drying polymer systems [5,6]. One has to be aware that the NMR signal is influenced by several parameters, which are often hard to disentangle given the rather low signal/noise ratio typical for such experiments.

Considering this challenge, combining data from NMR and other techniques seems to be a reasonable way to extract further information from the profiling data. In order to obtain such data under comparable conditions, a sample cell system was developed that can be used on the measuring table of the profile MOUSE as well as on other experimental setups such as a balance or an inverse microscope [7]. For the present study, profiling NMR and gravimetric experiments were run in parallel using two drying cells situated right next to each other. Film-formation of two dispersions for

wall-paint applications was studied with and without addition of a film-forming or coalescing agent [8]. Such co-solvents are added to many water-based coating formulations to promote better film-formation in the drying process.

2. Materials and methods

NMR profiling measurements were conducted using an ACT profiler MOUSE[®] with a magnetic field of 0.48 T and a gradient of 22 T/m and a Bruker minispec mq20 console. The profiler MOUSE[®] consists of an unilateral magnet with a thin, slice-like sensitive volume [4] which can be moved into different positions relative to the sample using an electrical lifting stage. The electrical lift is controlled from the spectrometer console and time-sequences of profiles can be acquired like this. Via the length of the excitation pulse, the slice thickness can be chosen between 100 μm and 10 μm . In order to allow optimal sensitivity and acceptable length of the profiling cycles, a slice thickness of 100 μm was used in all experiments described here. Conventional transverse relaxation time measurements on the fresh dispersion samples were conducted on a standard Bruker minispec mq20 using a pulse sequence with a solid echo followed by a CPMG pulse train [9]. Profiling experiments were done with a CPMG train with 512 echoes and an echo time of 57 μs .

On the measurement table of the profiling system, the drying cell sketched in Fig. 1 was mounted. In this closed cell, reproducible drying conditions can be obtained by inserting the same amount of drying agent (in our experiments, 50 g of silica gel were used). The drying rate can further be controlled by inserting

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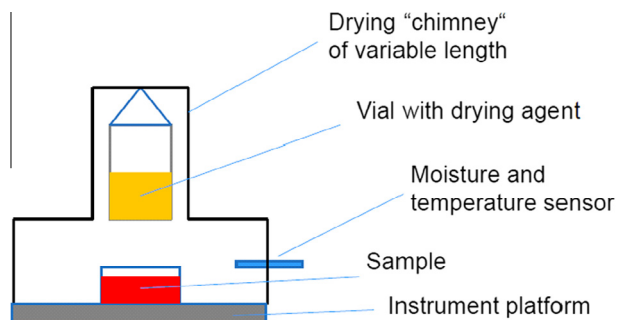


Fig. 1. Schematic representation of the measurement cell used for profiling and gravimetric experiments.

“chimneys” of different length into the cell (the cell was built in a way that ordinary 10 cm PE wastewater tubes can be used for this). For the experiments presented here, the shortest possible “chimney” length of about 15 cm was used. An identical cell was also built to house and was fitted to a balance (Precisa PREMIUM 321 LX), which was connected to the PC using the BALINT program provided by the manufacturer. With such a combination of analytical devices, parallel experiments in profile NMR and gravimetric drying could be performed. So as to control the experimental conditions, both cells were equipped with sensors to monitor real-time moisture and temperature.

Various approaches were used for the evaluation of the profiling NMR data. In order to obtain smooth and clear profiles or maximum signal/noise in the evaluation of diffusion NMR data, the whole CPMG traces obtained in the experiment were integrated. This approach was established already several years ago [4]. The signal intensity S for a component with amplitude f_w and relaxation time T_2 is given as with T denoting the length of the echo trace in time t . It is defined by the equation:

$$S(f_w) = \int_0^T f_w \cdot \exp\left(-\frac{t}{T_2(f_w)}\right) dt$$

$$= f_w \cdot T_2(f_w) \left(1 - \exp\left(-\frac{T}{T_2(f_w)}\right)\right) \quad (1)$$

Two commercial acrylate-based binder dispersions for wall-paint formulations were used in the drying studies. For both dispersions,

a set of experiments was performed with the neat dispersion and a second set of experiments was run on a dispersion with a standard film-forming agent added.

3. Results and discussion

In Fig. 2, results from conventional time-domain (TD) NMR measurements are shown for the dispersion samples used in the study. As one can see from the shading in the graph, most of the signal originating from the polymer component has already decayed within the first echo time, especially for the samples in absence of film-forming agent. We can then expect the signal intensity, according to Eq. (1) for those samples, to be essentially determined by the water fraction. Comparing the signals for the neat dispersion and the dispersion with film forming agent (FFA), the slower decay of the polymer due to the plasticizing action of the film forming agent can be seen. However, even in this case, the relaxation times of the polymer component are sufficiently short to influence only the first few echoes in the profile NMR measurement. And Eq. (1) still gives an appropriate description of the overall signal of the drying film.

The series of signal profiles shown in Fig. 3 is consistent with this understanding: it can be observed that there is a strong decrease in the amplitude of the profile with increasing drying time. In order to compare the data from the profiles in Fig. 3 with the results from the gravimetric drying study, the signal profiles were integrated also over the spatial dimension. The resulting signal intensity value is representative for the overall water content in the drying dispersion sample with a relaxation time weighting factor according to Eq. (1) at the time of each profile.

In Fig. 4, the integrals resulting from this procedure are given for the profiles shown in Fig. 3. The gravimetric water content is plotted as well. The picture shows a much faster decay for the integrated signal intensity than for the gravimetric water content. As the relaxation time of the water content can be expected to decrease with increasing solids content, this observation qualitatively does not come as a real surprise. However, a first naïve attempt to provide a quantitative description of these findings fails quite obviously: The line labelled “naïve” in Fig. 4 corresponds to the assumption that the water phase relaxation is mainly determined by surface relaxation on the particles’ surface A and that

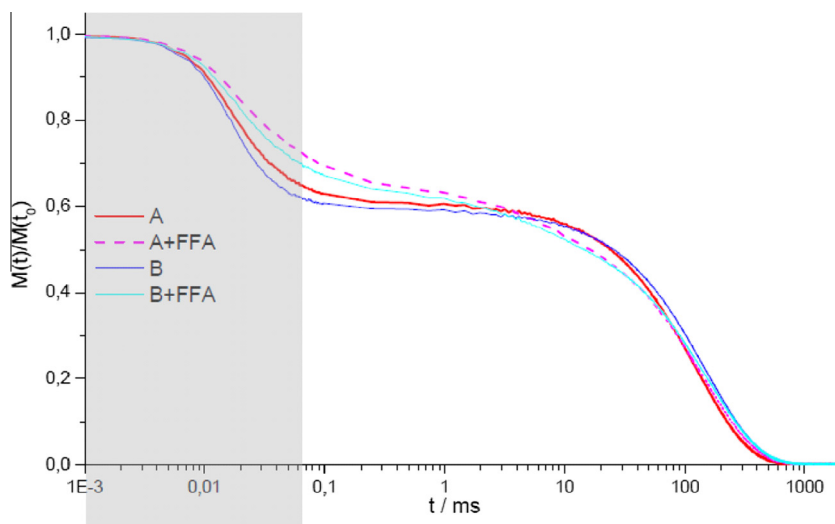


Fig. 2. Signal decay curves obtained in conventional TD-NMR measurements at 20 MHz by means of a solid echo followed by a CPMG sequence [8]. The shaded region corresponds to the CPMG echo time in the profile NMR experiments. As one can see, most of the fast decaying signal from the polymer has already decayed before the first echo of the CPMG train used in the profile NMR experiments.

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