



# Water transport in cement-in-polymer dispersions at variable temperature studied by magnetic resonance imaging

A.M. Olaru, B. Blümich, A. Adams\*

*Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Templergraben 55, D-52056 Aachen, Germany*

## ARTICLE INFO

### Article history:

Received 21 December 2011

Accepted 11 October 2012

### Keywords:

Hydration (A)

Dispersion (A)

Diffusion (A)

NMR

## ABSTRACT

The hydration of recently developed cement-in-polymer dispersions (c/p) containing 30% and 40% poly(vinyl acetate) [PVAc] and 30% poly(vinyl alcohol) [PVA] was monitored on-line at various temperatures using  $^1\text{H}$  Single Point Imaging (SPI). The physical changes undergone by the materials as well as the complex manner in which the absorption process takes place and the evolution of the spin density were characterized and were found to be strongly dependent on the nature and amount of polymer and on the temperature. Based on the results obtained we propose a simple mathematical model which can be used to characterize the behaviour of the c/p dispersions exposed to hydration at variable temperature.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

During the last decades organic–inorganic cementitious materials have been extensively studied due to the continuously expanding demand for high-performance light-weight macro defect-free materials in demanding applications of the nuclear or the oil industry. It has been shown that the addition of organic phases to cementitious pastes contributes to the development of performance properties like flexural strength or pull-out load [1], increases the resistance to mechanical and chemical aging, and decreases the permeability of the material to corrosive fluids [2,3].

Earlier organic additives have been used in small amounts (typically up to 5%) and combined directly with water and a hydraulic cement by high-shear mixing with the purpose of modifying the mixture's rheology and improving the mechanical properties and the porosity of the material. After exposing the mixture to a curing–drying process, the physical interactions and the chemical bonding lead to the formation of an inorganic/organic inter phase which increases the flexural strength and the Young modulus of the material [4,5]. Organic components were also used to modify the properties of glass/steel fibres reinforced cement composites, either in small amounts, to improve the cementitious matrix resistance to chemical agents [3] or in higher amounts, combined with non-hydrated cement, with the purpose of enhancing the penetration of the cementitious paste in the fibre system [1]. It has been shown that in a typical fibre-reinforced cement preparation pore solution is absorbed in between the reinforcing filaments,

while the cement grains cannot penetrate the fibre system due to their particle size. During matrix crystallisation, this leads to a highly inhomogeneous roving penetration and a differentiation into two types of filaments [6]: the outer ones, which are in contact to the unaffected matrix and the inner ones, in contact to pure pore solution, leading to a crystalline material of low density and strength. None of the inner filaments can act as reinforcer since the load transfer is only possible to the outer filaments via the fibre–matrix interface. As a result, the roving fails at values considerably below its nominal tensile strength [7]. To circumvent this situation, reactive cement-in-polymer dispersions (c/p) have been developed as an alternative to the classical cementitious matrix phase. They consist of a water or alkali soluble polymer and non-hydrated cement [7,8] and are used as coating to fill the capillary system of the rovings before being embedded in cement paste. In contact with the aqueous environment of the cement paste, the polymer dissolves and exposes the non-hydrated cement. The reaction of the non-hydrated cement and water locally raises the temperature and triggers the formation of a crystalline matrix between the inner filaments of the roving, significantly increasing the pull-out load [9].

In a previous publication [10], we have presented a detailed study on the influence of the chemical and physical properties of the polymers used to prepare the c/p coating formulation on hydration of the cement matrix. We have shown that the type of polymer used for the preparation of the c/p samples is the key parameter controlling the behaviour of the mixture during hydration. The completely different behaviour of the samples containing polymers with contrasting chemical and physical properties – poly(vinyl alcohol) and poly(vinyl acetate) – was attributed to the competition of the swelling speed, speed of the water ingress, and speed of the hydration of the calcium silicate (CS) phases.

Since in most practical applications the hydration and setting of cement or cementitious composites take place at temperatures

\* Corresponding author.

E-mail addresses: [aolaru@mc.rwth-aachen.de](mailto:aolaru@mc.rwth-aachen.de) (A.M. Olaru), [aadams@mc.rwth-aachen.de](mailto:aadams@mc.rwth-aachen.de) (A. Adams).

different from room temperature, we focus herein on the effect the hydration temperature has on the wetting behaviour of the two types of dispersions, the goal of this study being to establish a set of empirical rules which can predict the evolution of the hydration behaviour as a function of c/p content, relative amount of organic and inorganic phases and hydration conditions. We analyse the aforementioned c/p hydration at temperatures ranging from 293 K to 323 K and focus on the effect of the temperature at which the hydration takes place on the diffusion of water inside the material. Furthermore, since dispersions containing 30% PVAc were previously found to have very good hydration properties [10], we analyse the effect a higher amount of PVAc has on the c/p dispersion reaction to water at variable temperatures.

The observation of the time evolution of the water distribution inside the dispersions can offer valuable insight into the matrix formation and reflects different transport driving processes, related to the release of the excess water due to chemical reactions of the dispersed components and to the continuous changes of the porous matrix. Magnetic resonance imaging spin-echo techniques, combined with pulsed field gradient NMR have been successfully used to study proton distribution and molecular diffusion in porous materials [11–13]. However, due to technical reasons, such methods fail in cases where the fluid inside the material exhibits very small transversal relaxation times ( $\approx 100 \mu\text{s} - 1000 \mu\text{s}$ ) [13]. When the porous medium and the fluid molecules form strong chemical and physical bonds and/or contain paramagnetic impurities, as it is the case in hydrated cementitious materials, the NMR signal decays extremely fast, due to the strong dipolar interactions between the protons and the surrounding environment, difficulties in detecting and acquiring the desired information arises [13,14]. Single Point Imaging (SPI), a pure phase-encoding MRI method, has been proven to overcome such problems and has been by now established as an analysis technique in the field of cementitious composites [15–18].

In this study, SPI was used to monitor on line the physical changes of the c/p dispersions during hydration at different temperatures, to quantitatively assess the displacement of the diffusion front and to give an estimate of the diffusion coefficient of water inside the cement samples as a function of the hydration time. As the speed of the water ingress in the samples has, like the swelling process, a major effect on their macroscopic properties, information about how the presence of the polymer inside the cement is modifying the water transport should offer an additional insight into the behaviour of these samples. The sorptivity test – in which one follows the evolution of a water front in a porous sample as a function of time – is usually applied on mature building materials, in which it is assumed that the amount of water consumed by chemical reactions is negligible compared to the total amount absorbed/diffused during the test [19]. When this is not the case, (i.e. for unreacted and/or unsaturated samples like the cement-in-polymer dispersions under study in this work) the displacement of the water front is a consequence of the superposition of several processes: absorption due to capillary forces [19], restricted diffusion [14], the fast evolution of the hydrolysis reaction and the slow hardening of the cement [10]. The amount of water lost and/or gained due to various chemical reactions, as well as the effect of the physical changes which occur during hydration, have to be accounted for in the estimation of the apparent hydraulic diffusivity.

Furthermore, since the NMR signal in SPI depends solely of the transverse effective relaxation time ( $T_2^*$ ) and the proton density inside the sample, the acquisition of SPI- $T_2^*$  maps with sub-millimetre resolution has permitted an evaluation of the spin density inside the pores of the samples and a spatially resolved observation of the water dynamics. The results obtained were used to establish a simple model that predicts the time evolution of the relative water amount in the samples, which indirectly takes into account the influence of the chemical reactions, the nature of the polymer and the temperature at which the hydration takes place.

## 2. Experimental

### 2.1. Materials

Poly(vinyl alcohol) [PVA],  $M_w = 9500$ , saponification number 302, and poly(vinyl acetate) [PVAc],  $M_w = 110,000 - 150,000$  were obtained from Wacker Chemie AG, Burghausen, Germany. A fine-grained Portland cement with a particle size  $d_{95} = 6 \mu\text{m}$  was obtained from Dyckerhoff AG, Neuwied, Germany.

### 2.2. Sample preparation

In a typical preparation of a 70/30 c/p dispersion, 90 g of polymer and 5 ml of n-butyl acetate were placed in an IKA HKD-T 0,6 laboratory kneader and warmed up to 65 °C. When the mixture was soft and appeared homogeneous, a total of 210 g cement was slowly added in ten portions. After the final cement portion was added, kneading was continued for approximately 10 min. The warm mixture was poured onto a Teflon plate and allowed to cool in the fume hood.

When completely solidified, the mass was broken into pieces of approximately 1 mm in size melted at 150 °C and extruded through a round die into 4 mm thick strands. The amounts of polymer and cement were changed to 120 g and 180 g to obtain, following the same procedure, dispersions with a 60/40 cement/polymer ratio.

### 2.3. $^1\text{H}$ NMR imaging experiments

The proton NMR imaging experiments have been performed at variable temperature using a 200 MHz Bruker DSX spectrometer with a standard 10 mm birdcage resonator.

The cylindrical samples have been immobilised inside standard glass tubes (Fig. 2), with an inner diameter of 8 mm, in order to ensure that no movement artefacts generated by gradient ringing affect the image quality. The samples were continuously kept in water up to 96 h while images were acquired using a standard 3D SPI sequence [20]. The use of 3D SPI gives the true picture of the water ingress, provides detailed information about the homogeneity of the samples, and allows for an easy and accurate characterisation of the physical changes that occur upon hydration. The 3D SPI images were obtained by using a pulse length of 3  $\mu\text{s}$  (corresponding to  $\theta = 14^\circ$ ), a phase encoding time  $t_p$  of 41  $\mu\text{s}$  and a maximum gradient strength of 0.93 T/m.

A repetition time of 50 ms allowed the almost complete suppression of the free water signal outside the sample and of the unhydrated polymer inside the sample, ensuring high image contrast. In spite of the high gradient amplitudes which were employed for the experiments, the short encoding time used ensures that the signal loss due to the molecular diffusion in the applied gradient fields is negligible. Fourier transformation of the phase encoded signal produced images with a field-of-view (FOV) of  $10 \times 10 \times 25 \text{ mm}$  and a digital resolution of  $78 \mu\text{m} \times 78 \mu\text{m} \times 195 \mu\text{m}$ . The experiments have been performed at 293 K, 303 K, 313 K and 323 K respectively. The results were evaluated using Prospa 2.2 (Magritek Limited, Wellington, NZ).

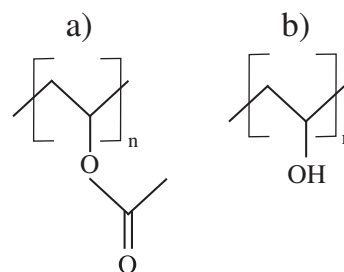


Fig. 1. Chemical structure of the PVAc (a) and PVA (b) molecules.

Download English Version:

<https://daneshyari.com/en/article/1456757>

Download Persian Version:

<https://daneshyari.com/article/1456757>

[Daneshyari.com](https://daneshyari.com)