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Changes in microstructures and physical properties of polymer-modified mortars during wet storage

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Abstract

The decrease in strength of tile adhesive mortars during wet storage was investigated. In a first approach, the water resistance of the polymer phases was tested on structures isolated from the mortar and in situ. It was observed that cellulose ether and polyvinyl alcohol structures are water-soluble. Subsequent investigations on polymer mobility within the mortar showed that the migrating pore water transports cellulose ether and polyvinyl alcohol during periods of water intrusion and drying. This leads to enrichments at the mortar–substrate interface. In contrast, latices interacting with the cement are water-resistant, and therefore, immobile in the mortar. Further experiments revealed that the mortar underwent considerable volume changes depending on the storage condition. Cracking occurred mainly close to the mortar–tile interface, cement hydrates grew within these shrinkage or expansion cracks. Test results revealed that the strength decrease of wet stored tile adhesives is caused by different mechanisms related to cement hydration, volume changes of the mortar, and reversible swelling of latex films.

Keywords: Mortar (E); Microstructure (B); Polymers (D); Wet storage; Shrinkage (C)

1. Introduction

Polymer-modification is widespread in cementitious applications to improve the physical properties of building materials. As many of these materials are exposed to wet conditions during service life, numerous studies investigated the influence of water storage on their physical properties.

Tile adhesives are commonly modified with cellulose ether (CE) and redispersible powder (RP), the latter containing latex and polyvinyl alcohol (PVA; for mortar formulation see Table 1). Each of these polymers fulfils different tasks during the mortar evolution [1]. CE thickens the fresh mortar, entrains air during mixing and retains water. RPs mainly provide flexibility and tensile strength in the hardened mortar. In contrast to concrete applications, such tile adhesive mortars are prepared with a high w/c (water/cement ratio) of approximately 0.8 and characterised by high air void contents of more than 20 vol.%, and low degrees of cement hydration (sometimes less than 50%, [1]).

The influence of water contact on the mechanical properties of polymer-modified cementitious products, were studied extensively [2–5]. The investigations of Tubbesing [6] include a microstructural characterisation of wet stored polymer-modified mortars. Based on scanning electron microscopy (SEM) images of fracture surfaces, Schulze and Killermann [5] concluded that latex morphology undergoes no structural changes, even after 10 years of outdoor exposure. Other studies focussed on changing pore size distributions due to water contact (e.g., [7–9]). Water intrusion and shrinkage/expansion of mortars were rarely investigated [10], but more frequently in the field of concrete (e.g., [11–14]). Mortar-specific aspects like hydro-

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Table 1
Formulations used for ceramic tile adhesives

[wt.%] of dry mix	Component	Details
35.0	Ordinary portland cement	CEM I 52.5 R, Jura Cement Fabriken, Wildegg, CH
40.0	Quartz sand	0.1–0.3 mm, Zimmerli Mineralwerke AG, Zürich, CH
22.5	Carbonate powder	Durcal 65, average grain size 57.5 μm, Omya AG, Oftringen, CH
0.5	Cellulose ether	MHEC 15000 PFF, Aqualon GmbH, Düsseldorf, D
2.0	Redispersible powder	Noncommercial powders with different latex compositions, whereof three types were tested: — VC (vinyl-acetate/ethylene/vinyl-chloride co-polymer) — SA (styrene/acrylic co-polymer) — EVA (ethylene/vinyl-acetate co-polymer) All containing PVA, mean particle size in dispersion $d(0.5)$ of about 1 μm, Elotex AG, Sempach Station, CH
25.5	Water	Deionised

Note that the percentages relate to 100 wt.% of the dry mix. In lab mortars with only one or two polymer types, mineral filler replaced the omitted polymers.

phobicity (discussed in Ref. [15]) and the increased importance of the mortar's interface [16,17] have to be considered. Beeldens [18] showed different drying rates of films from alkaline and non-alkaline latex dispersions, but did not investigate differences in other film properties.

In this study, we focus on polymer-related microstructures and on their changes during wet storage. Mechanisms like water intrusion, polymer mobilisation and redistribution, cement hydration and dimensional changes influence strength and were investigated by a variety of different analytical techniques.

2. Materials and methods

2.1. Light microscopy

To investigate the water resistance of polymer films, experiments on the individual polymers were performed. For this purpose, polymer powders were redispersed (RP) or dissolved (CE/PVA) in water, e.g. with an ionic composition representative of the pore water during early cement hydration. In this context, three different types of aqueous phases were used: (a) deionised water, (b) filtered cement water, and (c) synthetic cement water (Table 2). The filtered cement water derived from the same cement paste used in all experiments of this study. This filtered water may deviate from the true pore solution in the fresh mortar and therefore synthetic cement water was used also, which is assumed to represent a more realistic pore solution [19]. In case of RP containing ethylene/vinyl-acetate latex (EVA), further experiments in aqueous solution of NaOH, CaO, and $CaCl_2$ were performed. The amounts of NaOH and $Ca(OH)_2$ were chosen such that a pH value of 12.5 resulted, whereas the $CaCl_2$ concentration was adjusted to gain the same Ca^{2+} concentration as in the $Ca(OH)_2$ solution. The polymer concentrations in these deionised or cementitious waters were 10% for the RP dispersion, 2% for the CE solution, and 2.2% for the PVA solution. Dispersion or dissolution of the polymers was achieved by ultrasonic treatment at 25 kHz/50 W for 2 min. A metal grid of 86 μm sized square voids was dipped into the polymer solution or dispersion immediately to avoid gravitational fractionation (Fig. 1a). Evaporation of the water under room conditions increased the polymer concentration and caused the formation of polymer films in the voids of the grid. The amount of each polymer used was carefully evaluated in advance to promote formation of polymer films with a hole in the centre, which characterises very thin films. This situation is, in terms of film dimensions, similar to polymer films observed in air voids of real mortars (Fig. 2a). After storage for at least 2 weeks under room conditions, the films were exposed to deionised or synthetic cement water between two glass slides, for time intervals ranging from 10 min up to 2 months (Fig. 1b). Water induced changes in the film structure were observed by transmitted light microscopy and qualitatively rated on a scale between 0 (complete disintegration, Fig. 2a and b) and 1 (no major changes of the film morphology, Fig. 2c and d).

The size of these artificial polymer films corresponds to the polymer films in air voids (>10 μm) of real mortars. However, care is required for extrapolating these experimental results to the real mortar system. Cement–polymer interaction is not restricted to the pore solution, but also occurs at various solid–liquid interfaces, which can induce intergrowth of minerals and polymers. Therefore, we also performed in situ studies on polymer films in water stored mortars using an environmental scanning electron microscope (ESEM).

2.2. Environmental scanning electron microscopy

The ESEM allowed in situ observation of microstructures before and after water contact. The behaviour of the polymeric microstructures during such water immersion experiments revealed their water resistance.

Table 2
Composition and pH of filtered and synthetic cement waters used for synthesis of the polymer films in the model experiments

Production	Filtered cement water	Synthetic cement water
	Filtering of a 5 min old Portland cement paste ($w/c=1$)	Mixing of pure components
Na	540 mg/l	870 mg/l
K	7800 mg/l	9000 mg/l
Ca	400 mg/l	150 mg/l
SO_4	8400 mg/l	9700 mg/l
Cl	140 mg/l	0 mg/l
pH	13.1	12.7

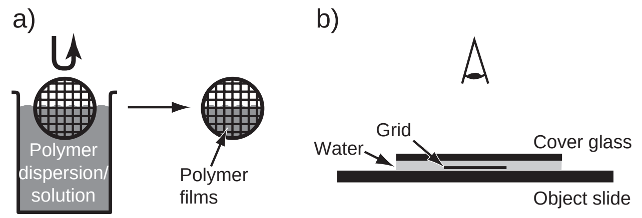

Fig. 1. (a) Polymer films with thicknesses of about 1 μm generated by dipping a grid into polymer dispersions or solutions. The polymer films form in grid meshes during evaporation of the water. (b) Water resistance experiment: a grid with polymer films is placed between two glass slides and immersed in water. Morphological changes can be monitored by light microscopy.

First, three lab mortars containing a single polymer type (latex, PVA, or CE) were analysed. In a second step, more realistic mortars with two or all three polymer types were investigated. In addition, different latices were used (formulation details see Table 1). This comparative study allowed the development of characteristic morphological criteria for the identification of the individual polymer types. The criteria were used to detect different types of polymer films in real mortars containing all three polymeric additives.

Based on standard EN1348, the mortars were applied in two steps on a concrete plate (10 × 40 × 3 cm, Gehwegplatte, Gebr. Müller AG, Triengen, Switzerland; water uptake is approximately 3 wt.%): (1) A first contact layer with a thickness corresponding to the coarsest grain size (approximately 0.3 mm) and (2) in a ripple and groove pattern induced by a toothed trowel (teeth 6 × 6 × 6 mm) on top of the first contact layer. After 5 min of air exposure (referred to as Open Time), fully vitrified ceramic tiles (5 × 5 × 0.5 cm; Winkelmanns weiss unglasiert lose, SABAG Bauhandel AG, Rothenburg, Switzerland) were laid in. They were loaded with 2 kg for 30 s, creating a 1–2 mm thick continuous mortar layer between concrete substrate and tile. A more detailed description is available in Ref. [20]. After 28 days of dry storage (23 °C and 50% relative humidity), the sample was crushed, and a mortar fragment smaller than 3 mm was sampled and studied in a Philips ESEM-FEG XL30 equipped with a gaseous secondary electron detector and a Peltier cooling stage. Polymer domains were located, imaged and their coordinates were stored. By changing the sample temperature and the water gas pressure, water condensed on the sample, which was consequently wetted completely. After 30 min of water exposure, all water was evaporated by changing temperature and pressure conditions. During the whole experiment, the temperature was in the range of 1–10 °C. The polymer domains were imaged again and qualitatively compared with the microstructures documented before watering.

2.3. Quantitative scanning microscopy

Two specific methods were developed to quantify the latex, CE, and PVA distribution within mortars with compositions according to Table 1 and prepared as described above. The visualisation and quantification of the latex from the RP containing vinyl-acetate/ethylene/vinyl-chloride (VC) was based on wavelength-dispersive spectrometric (WDX) Cl mappings of a 1.5 mm wide section in the centre of the mortar bed (electron microprobe Cameca SX-50).

CE and PVA were stained with a fluorescent dye prior to mortar mixing. Their occurrence in the mortar bed was visualized with a laser scanning microscope (LSM) on impregnated and polished sections across the half-length mortar bed. In a second step, the spatial distributions of VC, CE, and PVA were measured using quantitative image analysis [20]. The polymer concentrations in horizontal stripes were stacked to generate vertical concentration profiles across the 1.1–1.4 mm thick mortar bed. Due to large differences in grain size between the coarse sand fraction and the fines, which comprise the cement-polymer matrix, the interstitial matrix phase is enriched at the relatively flat interfaces to tile and substrate. In order to avoid this geometric effect on calculations of distributions within the matrix, and to investigate potential polymer fractionations within the matrix, all its constituents are normalised to the volume percentage of the cement-polymer matrix. Following Ref. [21], we define the cement-polymer matrix as the sum of all fines including cement phases, gel pores (<10 nm), capillary pores (10 nm–10 μm), fine-grained mineral filler, and all polymer phases. The mortar consists therefore of air voids, sand grains, and the cement-polymer

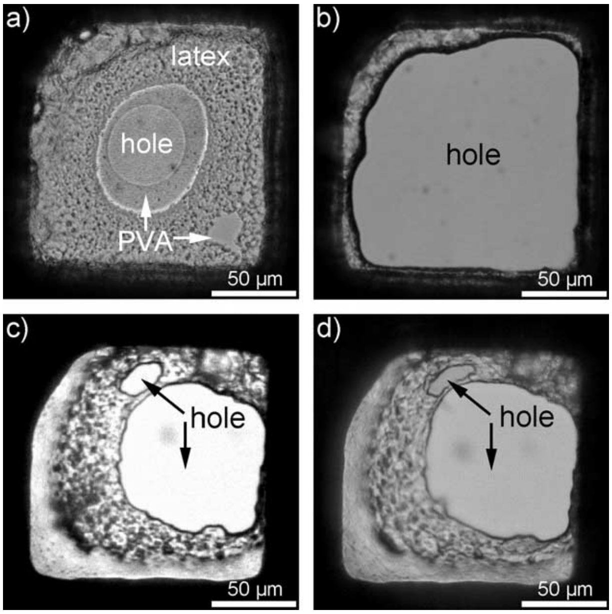

Fig. 2. (a) A composite polymer film consisting of PVA and latex formed from RP redispersed in deionised water. This structure is representative of all investigated RPs. (b) Disintegration of composite film due to water exposure. (c) Polymer film of the same redispersible powder, but redispersed in filtered cement water. Only one polymer film is developed that is water-resistant (d). Even after several weeks of water contact, only minor morphological changes like swelling are visible.

matrix. As mortar components may be fractionated across the mortar bed, the distribution patterns were depicted in cross-sections perpendicular to the mortar bed and the trowelling direction. An extended description of sample preparation, image acquisition, analysis, and quantification of polymer-modified mortars is available in [20]. The samples were subjected either to dry storage (28 days at 23 °C and 50% relative humidity) or wet storage (7 days at 23 °C and 50% relative humidity + 21 days completely immersed in water, followed by at least 28 days under room conditions before impregnation). The obtained data provide the basis (a) for the detection of various microstructure modifying processes during wet storage, and (b) for a comparison between microstructures and physical properties.

2.4. Testing of mechanical properties

The adhesive strength was measured by a standard tensile test according to EN 1348. Shear strength and flexibility were evaluated by a test in which, in contrast to the tensile test, the deformation apparatus was run in compressive mode pushing the ceramic tile (50 × 50 mm), which overlapped the substrate plate by 10 mm. Both, applied force and shear displacement were continuously monitored. In order to obtain the shear strength, the measured force was divided by the mortar–tile contact area (2000 mm^2). This simple method provides information about both, shear strength and flexibility (shear stress and deformation at break, respectively). Five strength tests were performed on each sample and the mean value was then calculated. Note that the mechanical properties of wet stored samples were measured in the wet stage immediately after withdrawal from the water tank.

Alternating storage consists of dry–wet cycles including 7 days of dry storage (23 °C and 50% relative humidity) and 21 days of wet storage (completely immersed in water). The tests described above were performed immediately after each storage period.

Shrinkage and expansion were measured on 1 × 4 × 16 cm mortar prisms, which were demoulded after 24 h for a zero reference measurement. The prisms were then stored under dry or wet storage conditions and prism length was measured at selected time intervals.

2.5. Examination of failure surface

The failure mode was examined macroscopically and classified into adhesion failure (failure occurs between tile and mortar), cohesion failure (failure occurs within the mortar), or mixed failure, as described in Ref. [1].

Furthermore, SEM was used to study the fracture morphology. For this purpose failure surfaces were coated with a 300 nm thick carbon layer (Balzers carbon coater) and examined in a CamScan CS4 SEM equipped with a Robinson back-scattered electron (BSE) detector and a Voyager 4 digital image acquisition system.

3. Results

3.1. Model system

During water storage there is a significant loss in adhesion strength. In order to understand the role of the polymer during water contact, we performed model experiments where the behaviour of polymer films was microscopically investigated during water immersion (item 2.1).

Fig. 2a shows RP after film formation in deionised water. The transparent PVA film in the centre is clearly distinguishable from the textured rim, as described in Ref. [24]. The film identification is based on film morphology, which was compared with monophase latex or PVA systems and was also confirmed by element dispersive spectroscopy. During water exposure, both phases disintegrated within minutes (Fig. 2b). In contrast, a film formed from RP redispersed in cement water (Fig. 2c) was water-resistant even after several weeks of water immersion (Fig. 2d). Note that macroscopic polymer films synthesised from deionised and cement water behaved in a similar manner when exposed to water.

Different types of RP, CE, and PVA films produced from redispersions/solutions made of deionised, synthetic cement, and filtered cement water were rewetted by deionised water (Fig. 3). All RP films showed a remarkable increase in water resistance when produced from a redispersion made of cement water instead of deionised water. In particular, a large increase in water resistance of the EVA was observed in the presence of cementitious ions. In general, RP films made from filtered cement water were more water-resistant than RP films made from synthetic cement water. NaOH seems to have a more pronounced influence on water resistance than Ca salts. In contrast, CE and PVA redissolved instantaneously, independent of the composition of the aqueous phase used for film synthesis.

To check for a potential influence of cement water (a situation that is closer to a real wet stored mortar system), all

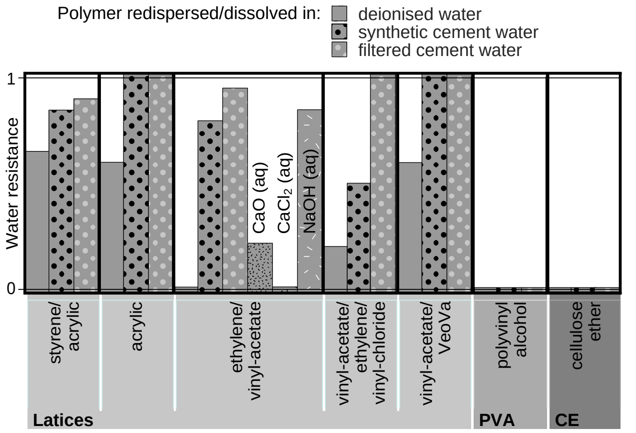

Fig. 3. Qualitative observation of the water resistance of different polymers synthesised from deionised, filtered, and synthetic cement water. Vertical axis: 0 = virtually complete disintegration (shown in Fig. 2b), 1 = no changes during water contact (shown in Fig. 2d).

films were also exposed to cement water. However, no difference in polymer behaviour was observed with exposure to cement water, relative to deionised water.

3.2. In situ watering

To investigate the behaviour of polymers in a real mortar exposed to water, mortar samples containing only one polymer type were monitored before and after wetting within the ESEM sample chamber (method description in item 2.2, data in Fig. 4). The images represent typical examples from an extensive image database.

The latex film depicted in Fig. 4a survives the wetting period without major changes (Fig. 4b), and only the film surface tends to change from a smooth to a more structured morphology. In contrast, CE structures (arrows in Fig. 4c) dissolve completely during wet storage (Fig. 4d). Fig. 4e shows the base of an air void with no polymer microstructures. After water immersion, PVA films precipitated out of the evaporating water (Fig. 4f), clearly indicating the mobility of PVA.

These results are consistent with qualitative SEM investigations on fractured mortar samples after water storage. There, latex films are present and partly overgrown with cement hydrates, whereas the typical CE membranes of dry stored mortars are absent after water storage [25].

3.3. Distribution patterns before and after wet storage

By combining WDX, fluorescence microscopy and the appropriate image analysis techniques, the spatial distributions of the polymer phases were determined. The comparison of the distribution diagrams before and after wet

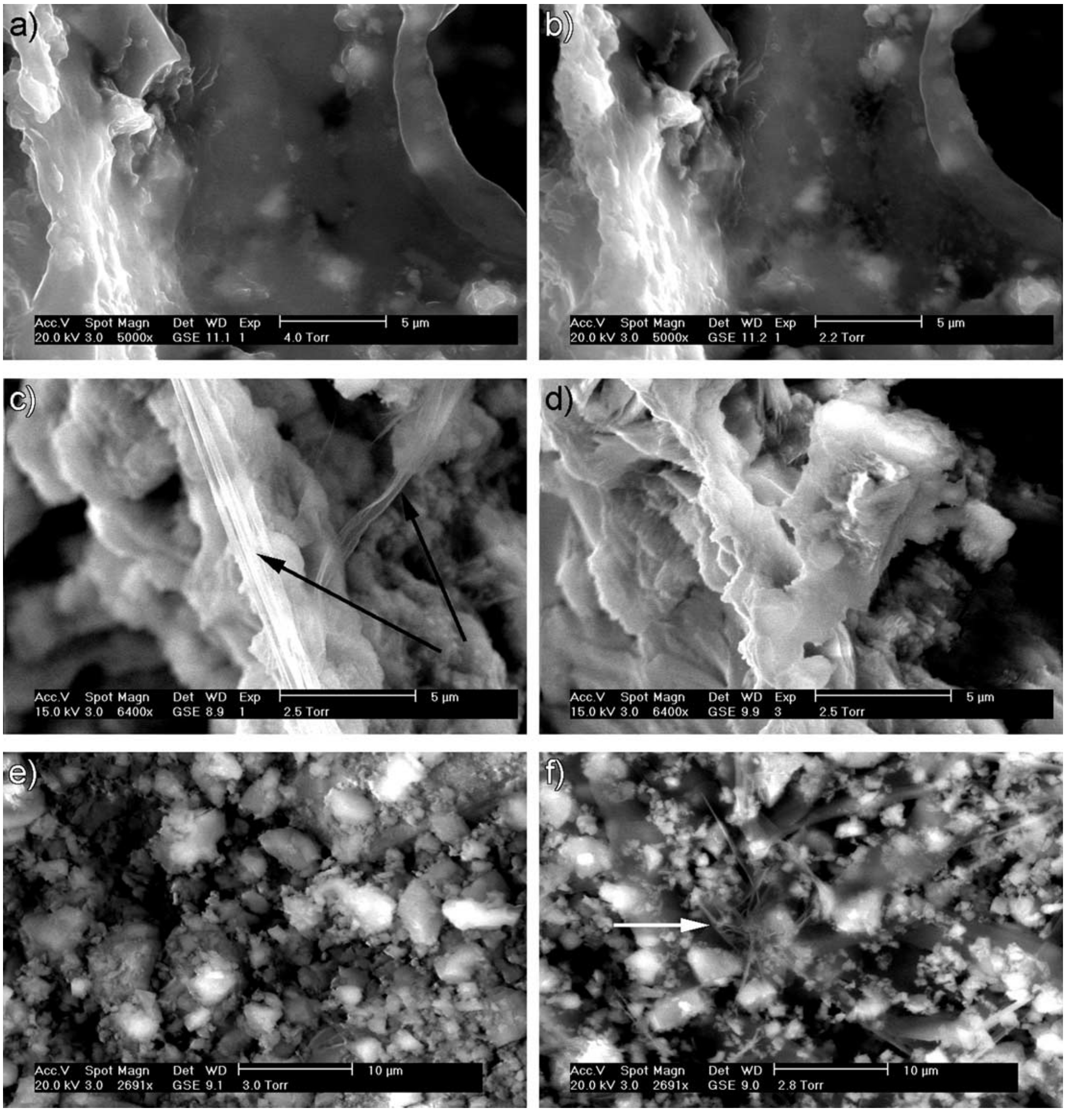

Fig. 4. In situ polymeric microstructures in mortar before (left column) and after wetting experiment (right column) in the ESEM sample chamber. Each pair of pictures shows the same location in the microstructure. VC latex film (a, b) and CE films (c, d). PVA structures could not be found in the mortar before wetting (e), but PVA films form as the water front retreats during redrying (f).

storage indicates what type of polymer is mobilised, to what extent and in which direction.

Fig. 5 shows a representative VC latex distribution in the cement-polymer matrix before (a) and after (b) wet storage. The mortar bed is subdivided into layers parallel to the mortar–tile interface and for each layer, the latex concentration in the cement-polymer matrix is depicted. Apparently, there are no changes in latex concentration and distribution during wet storage. To date, no methods exist to visualise and quantify other latices within the microstructure.

Analogously, Fig. 5c and g show the CE distributions in a VC-/CE-modified and a SA-/CE-modified dry stored mortar, respectively. After wet storage, the corresponding CE distributions are shown in Fig. 5d and h. Both wet stored mortars show a pronounced CE increase from tile to first contact layer. The enrichment at the contact layer surface after dry storage increased significantly, and there is also a significant enrichment directly above the substrate.

The PVA distributions in the same two dry and wet stored mortars are depicted in Fig. 5e, f, i, and j. In both mortars, the PVA enrichment at the substrate surface is more intense after wet storage. Otherwise, the distribution patterns after dry and wet storage are identical for both VC- and SA-modified mortars.

3.4. Mechanical properties

Dry and wet stored mortar samples were subjected to adhesive strength tests to compare their mechanical properties (Fig. 6a, first cycle). All wet stored samples show a decrease in adhesive strength compared to their dry stored equivalents. Mortars without CE were not tested because they are not applicable as tile adhesives. However, modification of the mortar with RP reduces the strength decrease remarkably (Fig. 6a).

In addition, an alternating dry and wet storage were applied to a mortar modified with RP (EVA) and CE. Adhesive strength, flexibility and shear strength were measured immediately at the end of each storage period. In general, the adhesive strength increased with each new dry–wet cycle (Fig. 6a). Fig. 6b shows the corresponding flexibility and shear strength values. After the initial dry storage, the following wet storage causes a decrease of both, flexibility and shear strength. After the second dry storage period, the flexibility recovers and reaches the value of the initial sample, whereas the shear strength increases. In the following wet–dry storage cycles shear strength increases with each cycle. With respect to flexibility, a slight decrease occurs with each cycle.

Fig. 6c shows the evolution of pore size distribution (mercury intrusion porosimetry) and portlandite content (measured according to Ref. [26]) as a function of the wet storage duration. The total porosity decreases with ongoing wet storage and the pore size distribution shifts towards smaller pore sizes (gel pores). Simultaneously, the portlandite content, which is an indicator for the degree of hydration, increases (data taken from Ref. [35]).

Fig. 6d documents changes of the mortar volume during wet and dry storage. Dry stored mortars shrink within the first 7 days. The following wet storage induces a rapid expansion during the first 2 days. Surprisingly, redrying of this wet stored sample induces shrinkage that is twice as intense as the initial drying shrinkage.

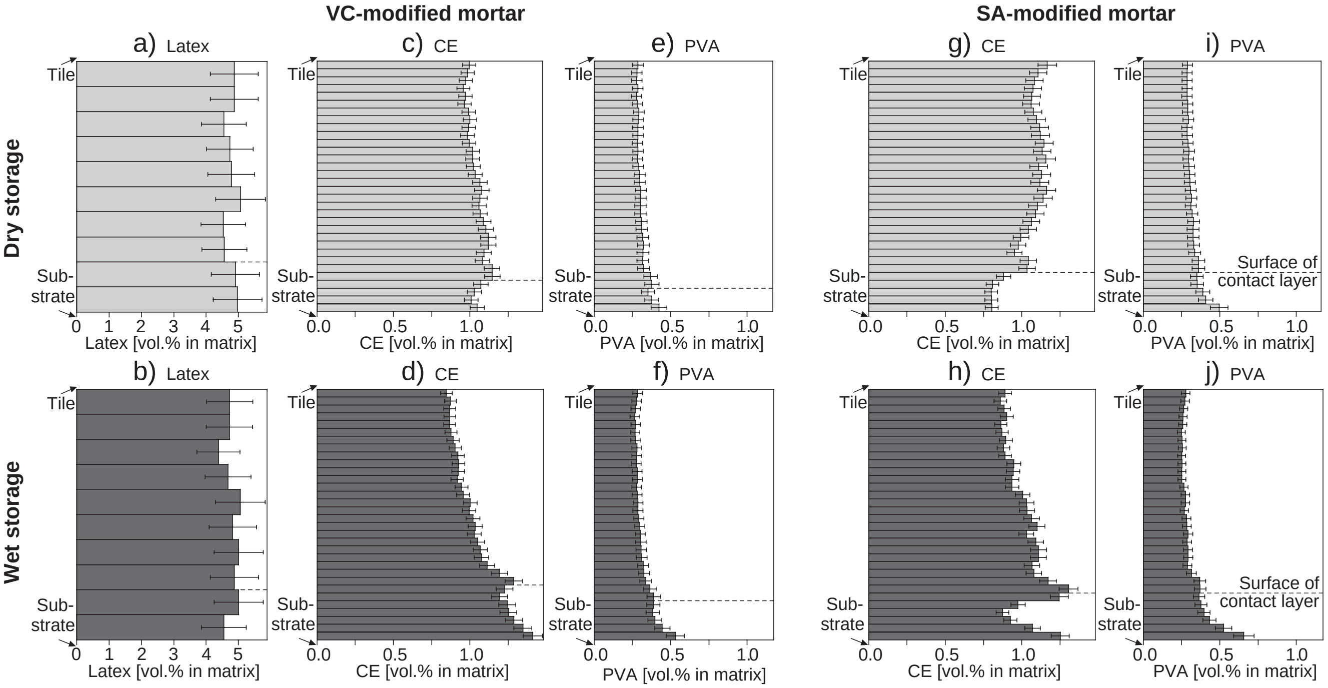

Fig. 5. Quantitative distribution diagrams of VC latex, CE and PVA across the mortar bed for dry and wet stored samples.

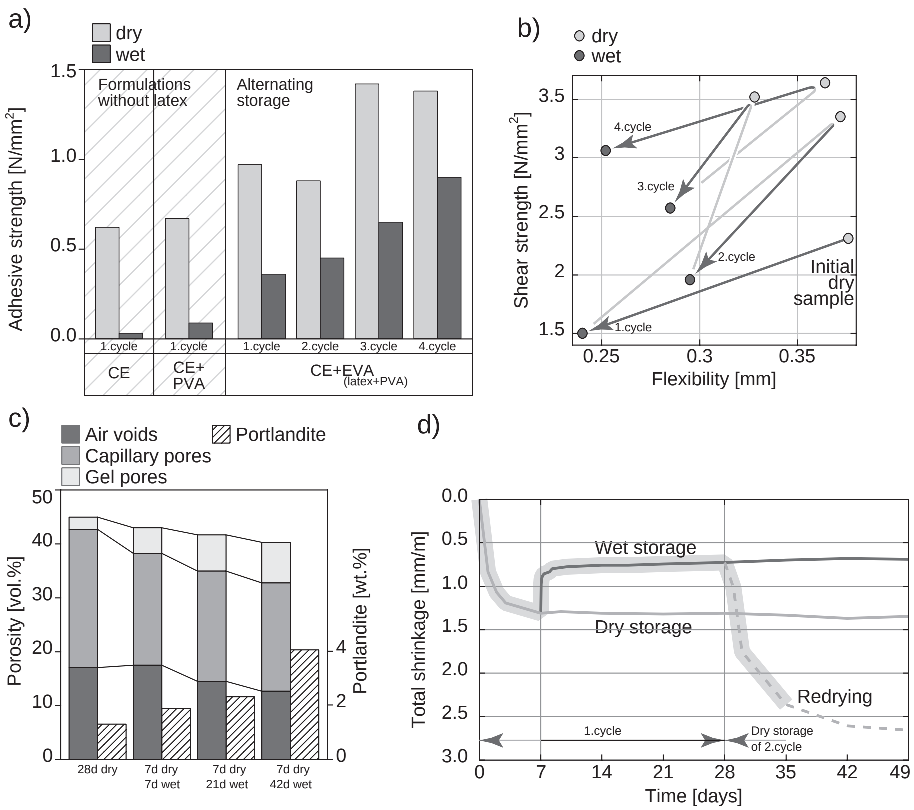

Fig. 6. (a) Adhesive strength of different mortar formulations (see Table 1). (b) Evolution of shear strength and deformation during four cycles of dry–wet storage applied to the tile adhesive modified with CE and RP (EVA) measured in (a). (c) Pore size distribution and amount of portlandite after dry and wet storage. (d) Shrinkage and expansion during dry and wet storage, and during redrying of a mortar prism.

3.5. Failure mode and related microstructures

Two types of failures can be distinguished: adhesion failure occurs at the mortar–tile interface, whereas cohesion failure is localised within the mortar bed. Comparing failure modes after dry and wet storage indicates that dry storage causes mixed failure (adhesive failure above ripples and cohesive failure above grooves, see Fig. 11 in Ref. [1]), whereas wet storage predominantly induces pure adhesion failure. In this context, the mechanism of interfacial water intrusion and the consequences for mineral growth is of special interest. Therefore, the migration of the waterfront at the mortar–tile interface was observed through a transparent glass tile (Fig. 7a). The capillary waterfront can be recognised as an abrupt change from bright (dry) to dark grey (wet). In terms of water migration the following observations were made by mapping the waterfront at different times: (a) The migration rate of the water front slows down in mortars with increasing amounts of latex, and also depends on the latex hydrophobicity. (b) Water intrusion in the mortar bed starts at the rim of the tile and progresses continuously towards the centre. Additional SEM investigations showed that in the rim regions, both portlandite and ettringite are found, whereas ettringite predominates towards the centre. This difference in mineralogy is attributed to the variable time interval during which water is present at the rim and at the centre. Note that this variation is found close to the tile–mortar interface as well as in the mortar bed itself.

At the interface, ettringite grows in pores and in shrinkage/expansion cracks, which opened during water storage (Fig. 7c and d). Ettringite needles grown in these cracks rarely touch the opposite crack side and therefore did not induce cracking. Instead they rather seem to fill the created cavity. It is important to note that these cracks do not occur in dry stored mortars. No ettringite grows across interfacial cracks, i.e., between mortar and tile. In contrast, portlandite plates grow parallel and perpendicular to the interface, and even grow onto the ceramic tile (Fig. 7e).

Phenolphthalein applied to the failure surface of a dry stored mortar sample shows a carbonation front that advanced from the grout (peripheral part of mortar bed) towards the centre (Fig. 7b) [27].

4. Discussion

The mechanisms which occur from the time the fresh mortar is mixed until hardening, and the resulting microstructures are extensively discussed in Ref. [1]. One of the major findings was that the migrating pore water causes CE and PVA to segregate across the mortar bed. The resulting

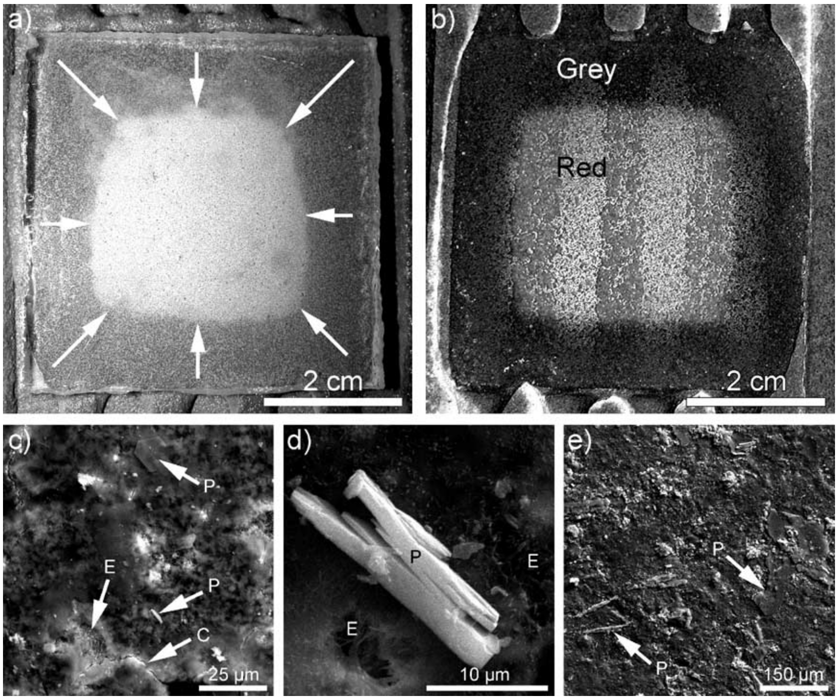

Fig. 7. Microstructures at the mortar–tile interface. (a) Glass tiles allow tracing of the intruding water front. Situation after 2 days of water immersion. (b) Phenolphthalein applied to mortar bed of dry stored mortar after tearing off the tile. (c, d) SEM images: Ettringite (E), micro-cracks (C), and portlandite (P) on the failure surface of a wet stored VC-modified mortar. (e) Tile part of the mortar–tile interface after adhesive strength test, opposite side from sample shown in c).

microstructural heterogeneities have a major influence on type of failure mode and bulk strength. As water intrusion during wet storage also induces water fluxes, further phase migrations can be expected. In the following, we focus on the relationship between microstructural changes and related physical properties of tile adhesives during water immersion. The mechanisms detected are valid for the chosen mortar formulation and sample configuration (e.g., material and dimensions of substrate and tile), and may change for deviating set-ups. Three major topics are discussed: (1) the mobility of pore water and polymers, (2) volumetric changes, and (3) reinitiated hydration of the cement.

4.1. Influence of water intrusion and related mobilisation of polymers on mechanical properties

Because of the interconnected pore network, water intrusion during wet storage is a 3D-problem. Based on sections parallel and perpendicular to the tile–mortar–substrate interfaces (Figs. 5 and 7), we can detect the 3D water flow and study the related microstructural changes. In top view, the water front moves from the grout towards the centre of the mortar bed (Fig. 7a). Perpendicular to the mortar bed, the water usually first intrudes the mortar, and from there the underlying concrete plate, creating a water flux through the mortar towards the substrate. The more hydrophobic the redispersible powder is, and the higher its quantity, the lower the intrusion rate. As the polymers seal the pores, they reduce the degree of connectivity of the pores and also the intrusion rate. Such pore structure alterations also result in a reduced carbonation depth prior to water immersion (Fig. 7b). Ohama [21] has already demonstrated that latex-modification decreases the total porosity and the carbonation depth.

In the case of wet storage, questions about the behaviour of the polymers during water exposure arise. The water resistance depends on the latex type: Beeldens [18] measured a good water resistance of macroscopic polymer films made from dispersions without cement ions (polymer types: styrene acrylic acid ester, carboxylated styrene–butadiene, acrylic emulsion, styrene–acrylic emulsion, styrene–butadiene, vinyl co-polymers). In the present study, model experiments and ESEM investigations under wet conditions show a significant difference in water resistance between latex and solution polymers (CE and PVA; Figs. 3 and 4). Water dissolves CE and PVA films immediately, independent of the initial ion concentration of the polymer solution. In contrast, all tested latices show an increased water resistance if cementitious ions were present during film formation. In case of the EVA powder, enhanced water resistance in the presence of sodium ions suggests a close relationship between film properties and type of ion.

All investigated dispersions and redispersible powders contain PVA, which is assumed to form the shell of the latex particles or even exists as an interstitial phase between them. According to Ref. [28], saponification generally is enhanced by a higher alkali (Na^+ and K^+) concentration. Transferred to our system, saponification of PVA is promoted by the sodium hydroxide. This hydrolysed PVA is supposed to hinder latex interdiffusion to a smaller extent. Consequently, sodium hydroxide favours coalescence of latex particles resulting in an increase in water resistance. This assumption is in agreement with findings of Chevalier et al. [29].

Du Chesne et al. [30] describe the addition of ionic surfactants to improve the water resistance of latex films. In this case, interaction with the surfactant leads to imperfect PVA membranes that are no longer able to prevent latex interdiffusion (coalescence). Presumably, cementitious ions might have a similar effect leading to PVA accumulations in interstitial pools and PVA immobilisation. In this context, different ions might play different roles. While alkali and hydroxyl ions increase the degree of hydrolysis of the PVA, which in turn reduces its cold water solubility, divalent cations may cause a bridging of the accumulated PVA polymers.

Beside these inferences about the mechanisms that improve latex interdiffusion, we have microscopic evidence that the degree of film formation is more advanced in cementitious systems. The SEM morphology study [24] revealed that the surfaces of latex films made from a cementitious redispersion are smoother, while latex films made from deionised water redispersions predominantly show particle structures. According to Ref. [31] the film surface flattens with advanced film formation. Therefore, we interpret the reduced film relief as a progressed stage of film formation of these “cementitious” latex films. Latex films in real mortars rarely show relicts of the initial particle structure (Fig. 4 a and b; [1]). This suggests that latex film formation in mortars usually reaches the final stage of coalescence, which is also concluded in Ref. [18].

In the case of acrylic co-polymers, divalent calcium ions might induce an additional mechanism to increase water resistance, called cross-linking [2,32]. Because carboxylate groups can also link onto cationic sites on mineral surfaces, this involves a latex–cement interaction mechanism. Often, such interactions occur too early in the fresh mortar stage and cause coagulation and bad workability properties, which in turn reduce proper wetting of the tiles and, thus, lower final adhesion properties.

Because latex structures in mortars are water-resistant, they are also immobile during water storage. This is confirmed in Fig. 5a and b where a homogeneous latex distribution after dry and wet storage are shown.

In contrast, CE and PVA films in the mortar dissolve during water exposure (Fig. 4c to f). Although the distribution patterns of CE prior to water immersion in mortars with different latices (VC versus SA) vary due to the different CE–latex interaction mechanisms [1], water intrusion changes the CE distribution in both mortars in a similar way and via the same mechanism (Fig. 5c, d, g, and h). Water intrusion from the grout induces water migration through the mortar bed towards the underlying concrete substrate. Simultaneously, the dissolved CE is transported downwards through the capillary pores, but accumulates at the contact layer and substrate surface, which act as micro-filters (Fig. 5 d and h). This filtering is interpreted to result from a locally reduced pore size. The pore size reduction at the upper horizon (top of contact layer within the mortar bed) results from trowelling by the tool whereby this temporary surface is smoothed and superficial pores are closed [1]. Fig. 8a illustrates an example of reduced porosity at the surface of the mortar versus the internal porosity (inset). The local porosity is further reduced by the CE enrichments at surfaces. This can be seen by comparing the frames in Fig. 8a and b. The filtering effect at the mortar–substrate interface can be explained by a drastic change in porosity between the high-porous mortar and the dense concrete substrate. The carbonated surface of the concrete plate also helps to reduce the porosity. The few CE occurrences found in the substrate are all located in micro-cracks.

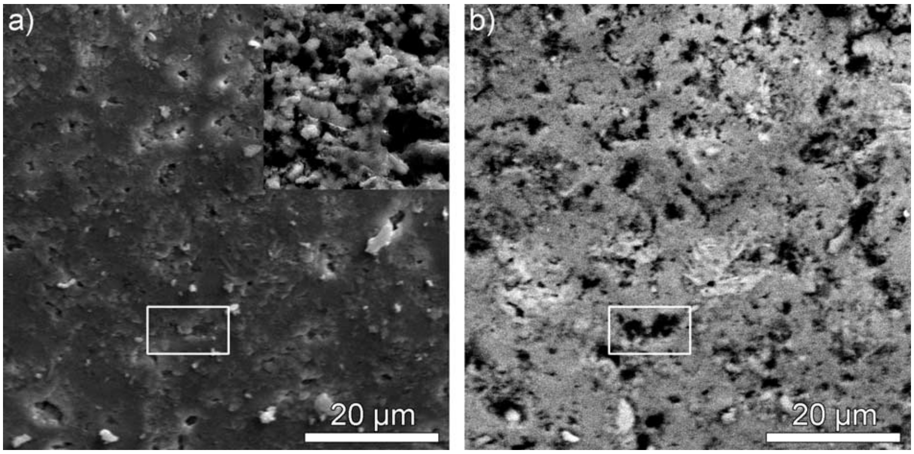

Fig. 8. (a) SEM secondary electron image of the uncovered mortar surface that underwent skinning (dry stored, EVA-modified mortar). The inset (same scale) shows the microstructure of a cohesive failure across the cement-polymer matrix. (b) The same mortar surface as in a) in back-scattered electron mode where polymers become transparent and only mineral structures are visible. Compare the boxes in a) and b).

Although exactly the same segregation mechanisms as described above can be expected for PVA, the water flux during wet storage stage influences the PVA distribution to a much lower extent. This can be attributed to the reduced cold water solubility of a fully hydrolysed PVA, and to the fact that the smaller polymer size allows PVA to occur in smaller capillary pores. As a consequence, PVA is intergrown with cement hydrates on a smaller scale.

Even though redispersible powders increase tensile adhesion strength after both dry and wet storage, there is a significant loss in wet strength (difference between dry and wet strength in Fig. 6a). The same is observed for adhesive shear strength and flexibility (Fig. 6b). In spite of these reductions, however, further drying of the samples yields the same or even higher strengths than those of the initial sample. This reversible behaviour can be explained by water uptake and softening of the latex microstructures during water immersion followed by redrying and related strengthening of the same microstructures. Enhanced latex interdiffusion in a swollen stage of latex during water immersion, resulting in an increased coalescence of the latex film, represents an explanation for the overstepping in strength compared to the initial dry stored sample (compare Ref. [33]). Additional effects of water storage and their influence on the mortar strength are discussed below.

4.2. Volume changes and mechanical properties

Physical shrinkage and expansion depend mainly on the porosity, environmental conditions (humidity, e.g., Ref. [12]), and geometric aspects like body dimensions and restraining conditions of juxtaposed materials (tile, concrete substrate, grout). Stress gradients induced by these parameters can occur throughout the mortar layer, which may result in failure, and can therefore be critical. There is little known about the mutual interaction of all these parameters and the resulting internal stresses. In the following section, we will highlight some major findings of the shrinkage/expansion behaviour of tile adhesives.

The w/c of concretes is widely known to be a major factor for drying shrinkage. The higher the w/c, the higher is the capillary porosity, which enhances capillary drying shrinkage. Tile adhesives have a w/c around 0.8 and these mortars are only partly hydrated. Drying shrinkage for dense concrete and high-porous tile adhesive mortars falls within the same range of 1–2 mm/m [11,10]. This indicates that in case of tile adhesive mortars, a major part of drying shrinkage must be accommodated by so-called inner shrinkage (increasing bulk porosity including shrinkage cracks). During water storage of a previously dry-cured mortar, volume changes due to water intrusion and the reinitiated secondary cement hydration can induce cracking (Fig. 7c). The situation can be particularly critical with respect to adhesion strength at the tile–mortar interface, where the highest material contrasts occur.

Of special interest are the irreversible volume changes occurring during alternating dry–wet storage cycles (Fig. 6d). For concrete it is often described that the irreversible part of the initial drying shrinkage increases with higher porosity (e.g., Ref. [11]). In our mortar system, however, we face a different situation of repeated, additional and irreversible drying shrinkage. In case of redrying of wet stored mortars, drying shrinkage can be twice as intense as the expansion during the previous period of water storage. We interpret this behaviour as a consequence of the secondary cement hydration during water immersion. This is confirmed by the fact that both the irreversible drying shrinkage component and the degree of secondary cement hydration, are progressing at similar rates, and terminate as the mortar is close to complete hydration after 5 dry–wet cycles [34]. The link between these two phenomena is interpreted to be the pore size distribution. Air voids, capillary and gel pores change their relative and absolute quantities during ongoing hydration and cause a general shift of pore size distribution towards smaller pores (Fig. 6c). Drying shrinkage is generated by retreating water films along the walls of capillary and gel pores. In this way, the negative capillary pressure causes the cement matrix to shrink (e.g., Ref. [12]). With an increasing number of small-sized pores, the area of pore walls increases as well, lowering the total capillary pressure in the system during retreat of the water films. Consequently, a more intense volume decrease occurs during redrying (Fig. 6d). The reason for the increased irreversible shrinkage during redrying is thus based on the initial low degree of hydration.

Comparing the highly porous mortar, the dense concrete and the ceramic tile, the most pronounced difference in volumetric changes during water intrusion and drying will occur at the mortar–tile interface. As this interface is progressively wetted and dried from rim to centre (Fig. 7a), the lateral variations in volume changes create strong gradients along the interface promoting crack formation. This is a potential explanation for the commonly observed failure localisation at the mortar–tile interface in wet stored mortars.

4.3. Influence of hydration on mechanical properties

As indicated by a strong and progressive increase in the amount of portlandite and gel pores (Fig. 6c), cement hydration, which virtually stopped after 7 days of dry storage, continues during wet storage. Besides polymer film formation, cement hydration is the other major strengthening mechanism. Particularly during water storage when the solution polymers dissolve and the latex films swell and soften, the degree of cement hydration dominates the bulk strength of the mortar. The reinitiated hydration during water immersion is the main reason for an enhanced dry and wet strength with further storage cycles (Fig. 6a and b). As this secondary hydration is considered to create rigid mineral structures, the flexibility, mainly given by latex, is constant or decreases slightly.

The aspect of hydration at the mortar–tile interface is of special interest, because this is the site of failure after wet storage. Fig. 7c to e are typical examples of portlandite crystals, which grew during water storage in cracks at the mortar–tile interface caused by differential volume changes. Because such relatively large portlandite crystals can hinder the reversible opening and closing of cracks during dry–wet cycling, they may induce stress concentration, promoting further crack propagation along the mortar–tile interface during the closing phase (shrinkage during drying). Crystallisation pressure of portlandite might represent an alternative explanation for interfacial cracking and related adhesion failure.

5. Conclusions

In light of polymer film formation, the chemical environment plays a crucial role controlling the final film properties. This is particularly important for experimental simulations of polymer film formation in cementitious systems. In this way, model experiments involving film formation on grids are only realistic when performed under similar chemical conditions (ionic concentration) as present in the mortar. It is important to note that additional parameters like mineral intergrowth do not influence the overall water resistance of the films. Therefore, this type of model experiment represents a fast and easy screening test for the water resistance of polymer films in cementitious environments.

Microstructural changes during wet storage and resulting material properties of tile adhesives can be divided into two principal groups: (a) irreversible changes, and (b) reversible changes.

a) Irreversible changes are mainly related to the low degree of initial cement hydration after dry storage. As the cement continues to hydrate during water immersion, the cement-derived strength component increases. Simultaneously, this secondary hydration during wet storage shifts the pore size distribution towards smaller pore sizes, a process that increases drying shrinkage during the following redrying. In terms of adhesion strength, this additional component of drying shrinkage can be critical, because cracks preferentially form at the mortar–tile interface, where the material contrast is most pronounced. The formation of large portlandite crystals in these cracks is thought to further reduce strength.

Once formed in the cementitious environment, the latex films at least partly reach the coalescence stage, which provides their water resistance. During water immersion, latex interdiffusion can be reactivated promoting further coalescence. This improves the mortar properties after redrying. As a consequence of its immobility, latex cannot enter the newly formed shrinkage cracks to heal these microdefects.

Solution polymers, like CE and PVA, do not form water-resistant microstructures, and have therefore no influence on strength in the wet stage. They redissolve during each water immersion period, are transported by the migrating pore water phase and enriched due to filtering mechanisms. As PVA is fully hydrolysed with time, its solubility is decreased, which lowers the PVA mobility compared to CE.

b) Reversible changes during water storage can be followed in test series over multiple dry–wet cycles. Adhesion strength and flexibility are lost and regained as the sample is wetted and dried, respectively. This can be related mainly to reversible swelling and softening, followed by drying and strengthening of the latex films in the mortar. Shrinkage and expansion are also partly reversible. As RP enhances the flexibility of the bulk system, latex is thought to increase this reversible part of the volume changes.

This study demonstrates that the interplay of all endogenous (mortar components) and exogenous (environmental) parameters determines the evolution of the microstructure and therefore the material properties of polymer-modified mortars during wet storage. The relationships of the various interaction mechanisms have to be taken into account for future research and product development.

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