Shrinkage properties of polymer-modified cement mortars (PCM)

Kay A. Bode[a], Andrea Dimmig-Osburg[b]

Bauhaus-Universität Weimar, Department of Civil Engineering, F. A. Finger-Institute of Building Material Science, Coudraystraße 11, D-99421 Weimar, Germany

[a] kay-andre.bode@uni-weimar.de, [b] andrea.dimmig-osburg@uni-weimar.de

Keywords: shrinkage, PCC, PCM, polymer modified, cement stone, adhesive bond, longitudinal change behaviour, shrinkage stress, porosity

Abstract. The main difference between normal mortar and polymer modified mortar is the micro-structure. Whereas cement is the only binder in normal concrete, the binder of PCM contains cement and polymer. It is known, that these polymer modified cementious matrixes show a higher shrinkage than the non-modified ones. But it is also known, that the PCMs show fewer cracks due to shrinkage. A lot of different investigations have been carried out to find the reason for this contradiction. The measurement of shrinkage of PCMs and polymer modified cement stones will be presented in this paper. The prisms were stored under various climate conditions and show a varying shrinkage accordingly. Taking these results into account it becomes obvious that the shrinkage of PCMs depends considerably on the hydration shrinkage, to a lesser extent on the drying shrinkage. Furthermore, a model experiment as to the adhesive bond of cement stones compared to natural stones was introduced.

Materials and storages

The investigations were carried out using 2 polymers (Polymer 1 – redispersible powder with a film formation temperature of 5 °C, Polymer 2 – dispersion with a film formation temperature of 30 °C). Both based on styren-acrylic ester copolymer.

Used cements: CEM I 42.5 R and CEM III 42.5.
Maximum grain size: 2 mm.
Used additives: superplasticizer and a defoamer.

The mixtures based on a mortar mixture according to DIN EN 196-1. The cement was 450 g, the sand was 1350 g. The w/c-ratio was 0.40, different from DIN EN 196-1.
The water content of the polymer dispersion and the superplasticizer was charged to the w/c-ratio. The p/c-ratio varied from 0.05 to 0.15.
The workability of the mixtures should be equal. Therefore the flow table measurement was defined between 150 cm and 180 cm and adjusted by means of superplasticizer.

Specimens were stored under various conditions:

condition A storage under water
condition B storage under normal climate (20 °C and 65 % relative humidity)
condition C storage up to 7 days under water, then under normal climate

Storage A improved the hydration of the cement. In terms of film formation storage B is the best. Storage C is a mix of both conditions and should improve a good cement hydration and a subsequent film formation.

Classic shrinkage with measurement pins

The determination as to expanding and shrinkage was carried out on PCC- mortar prisms by means of measurement pins (type 1) according to DIN 52450 up to the 90th day.

The limit values laid down in [1] relating to the longitudinal change (0.9 mm/m shrinkage or 0.3 mm/m expansion after 28 days were exceeded by two recipes only (CEM I, PCC 1, p/c=0.15, storage B and CEM III, PCC 2, p/c=0.15, storages A and B) (Fig. 1). The limit values of 1.2 mm/m according to [2] and [3] after 90 days, however, were sometimes significantly exceeded by several recipes. Especially dry storage (storage B) which offers the worst hydration conditions for the cement stone, led to enormous shrinkage in the case of PCC no matter if their p/c ratio was high or low. Most recipes did not reach their final shrinkage measure after 90 days. This result illustrates that a shrinkage determination after 28 days can only produce approximate values. General statements as to the development of the shrinkage behaviour and thus as to the possibly occurring stresses within the PCCs are not possible after this period of time. In case of PCCs it generally makes sense to determine shrinkage at least up to the 90th day.
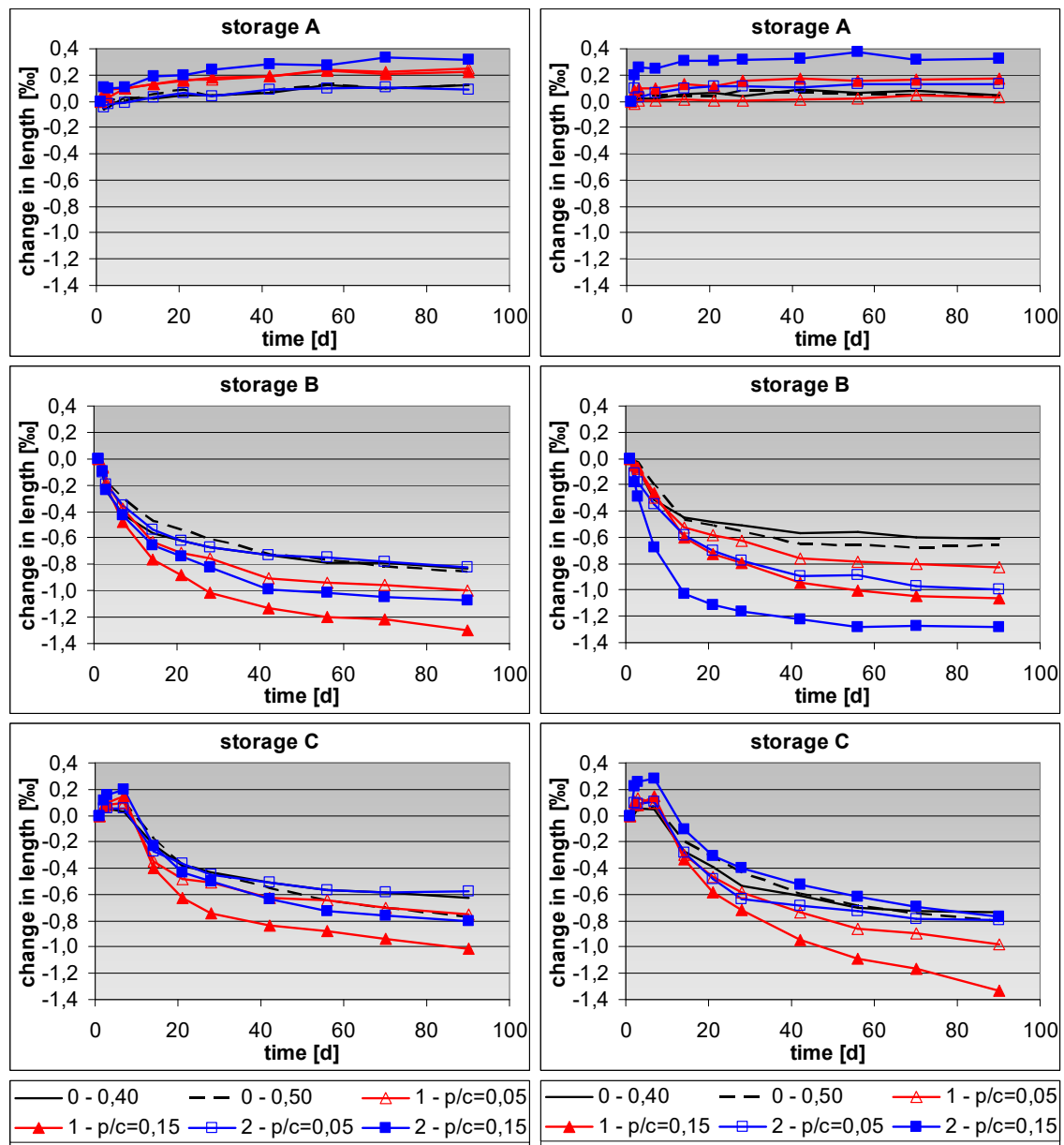

Fig. 1: Graphs of change in length: left side - CEM I - mortars; right side - CEM III - mortars

When comparing both recipes it becomes obvious that both mixtures show an almost identical shrinkage behaviour although they differ in the w/c ratio. The PCCs with the same polymer only differing in their p/c ratio, however, show a diverging shrinkage behaviour. The PCC with the higher p/c ratio shows a more pronounced longitudinal change than the same PCCs having a lower p/c ratio.

The comparison between both cements used clearly marks the influence of the polymers. Whereas in case of storage A (water storage) a clear trend can be observed (increasing expansion with the polymer content increasing), it is impossible to make general statements on the storages with drying possibility.
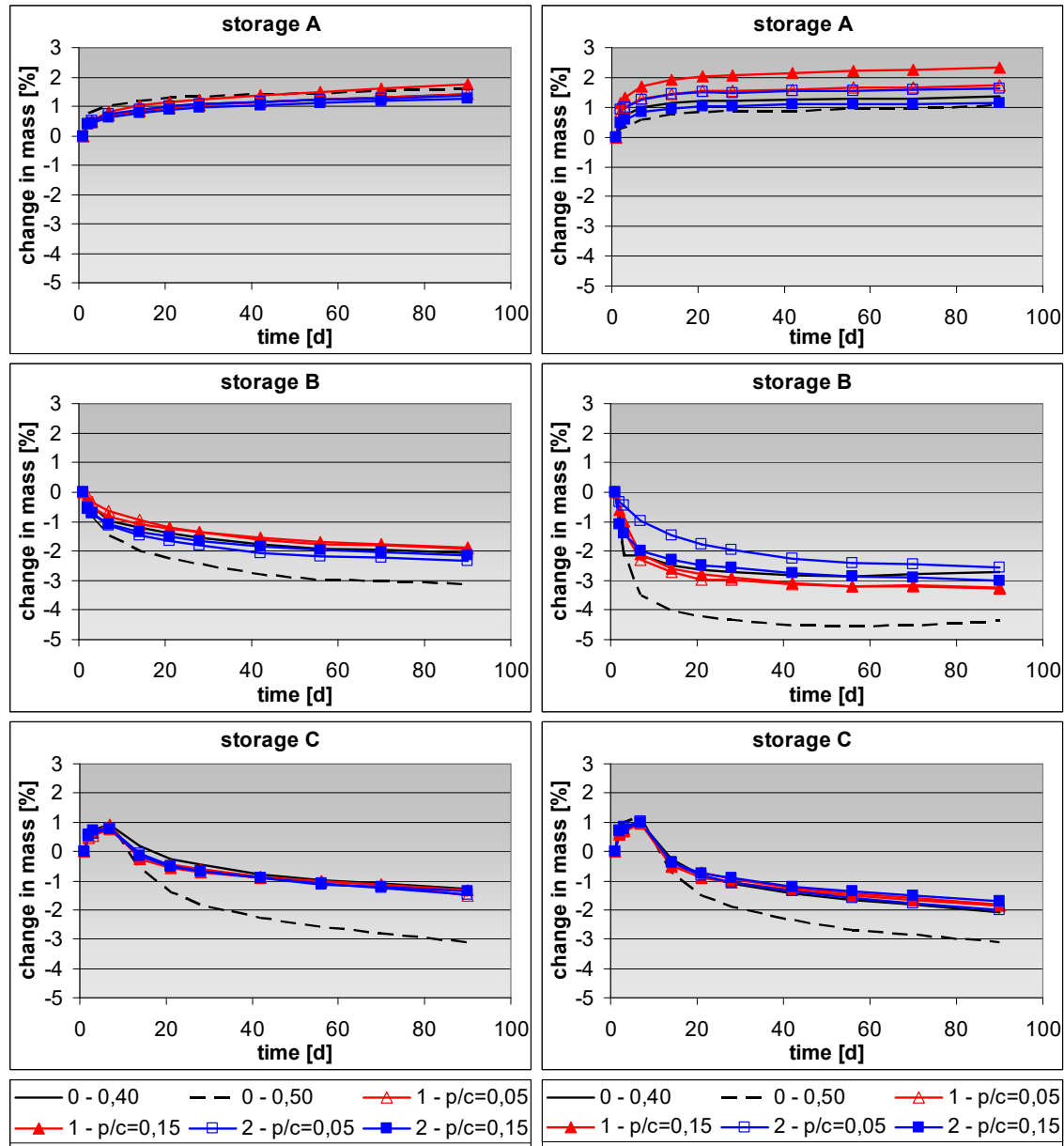

Fig. 2: Graphs of change in mass: left side - CEM I - mortars; right side - CEM III - mortars

The course of the graphs in case of the modified CEM I recipes are almost identical for storages B and C. In case of storage C the shrinkage measure is aprox. 0.25 ‰ lower than in storage B. This roughly equals the relation of the unmodified reference mixtures in the respective storages and can thus be ascribed to the better hydration conditions during the first 7 days in water storage. The CEM III – recipes show a completely different behaviour. The initial water storage here seems to be disadvantageous. The shrinkage measures of the reference mixtures as well as of the PPC 1 at storage B are approx. 0.20 ‰ higher than at storage C. The PCC 2, however, show a significant decrease in

their shrinkage measures in consequence of the initial water storage – the higher the polymer content, the stronger the decrease. There is no difference in shrinkage behaviour between PCC 2 and the reference mixture.

The mass change analysis (Fig. 2) shows that the polymers have no (CEM I) or only marginal (CEM III) influence on the drying behaviour of the mortars. Whereas in the case of storages B and C the influence of the different w/c ratio of the reference mixtures becomes obvious, the course of the graphs of all mortars with a w/c ratio of 0.40 is almost identical. That means that polymer modification has hardly any influence on the drying shrinkage of a mortar. The longitudinal change behaviour is mostly a result of an influence on the hydration shrinkage. As documented in literature (e.g.) polymers have a retarding effect on cement hydration. Thus, and in conjunction with the generally improved water retentivity, the hydration process is shifted in time. As a result the effects of hydration shrinkage are also retarded.

Determination of shrinkage on polymer-modified cement stones

After the investigations on PCCs in modified shrinkage channels had not led to the expected results, the aim was to verify the gained findings by means of experiments on polymer-modified cement stones (Fig. 3). CEM I – cement stone recipes were used. The water requirement of the stone granulation as to its w/c ratio was taken into account.

After 24 hours the shrinkage channel samples were demoulded (which had been covered since that point of time) up to the end faces. They were rested on rollers in the shrinkage channels (void of stress), so that they were exposed to the environmental conditions from all sides. Due to the strongly liquidizing influence of the polymers it was not possible to move the movable plastic block by means of an early loosening of the locking screw. That is why the measuring of all samples was started 24 h after mixture production, i.e. after the relocation on the rollers. On the basis of the mortar investigation results on early longitudinal change it was assumed that during the first 24 h no significant structure-changing deformations would occur. The longitudinal changes of the samples were continuously measured over 14 days. They were stored under normal climate conditions.
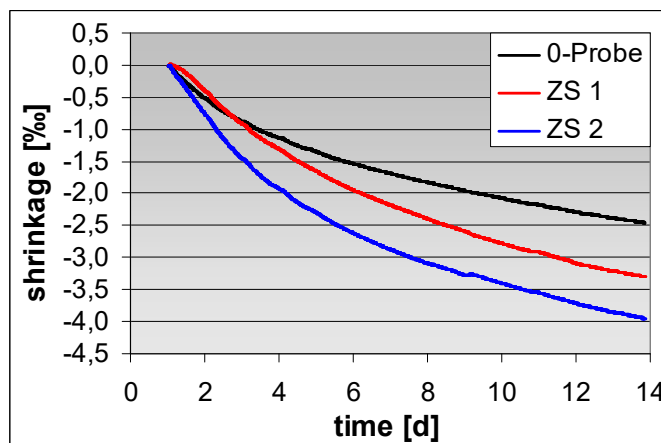

Figure 3: Modified shrinkage channel

Figure 4: Shrinkage of cement stone, with polymer 1 modified cement stone (ZS1) and with polymer 2 modified cement stone (ZS2)

As expected, an enormous shrinkage of all cement stone samples occurred (Fig. 4). The shrinkage measure of the reference mixture was the lowest after 14 days, whereas it was significantly higher as far as the modified samples are concerned. Interesting enough is the fact that the dispersion–modified samples (ZS2) showed the highest shrinkage measure. The mortar investigations according to DIN 52450 showed the exact opposite. The main reason for this is the lacking of stone granulation. Stone granulation has a shrinkage-reducing effect in the mortar by disrupting the cement stone matrix, and by having a stress-relieving effect, it thus obstructs the spreading of microcracks. In addition, the volume share of the shrinking cement stone in the test piece is drastically reduced and evenly distributed in the test piece's volume. In the case of pure cement stone samples this impact is completely absent. Only the forming pores can replace the shrinkage-reducing effect of stone granulation at least in part. Since the redispersable powder (Polymer 1) produces more and especially bigger pores than when dispersion 2 is used it could be expected that the cement stone modified with Polymer 2 (ZS2) would show a higher shrinkage measure than the one modified with Polymer 1 (ZS1) (Fig. 5).
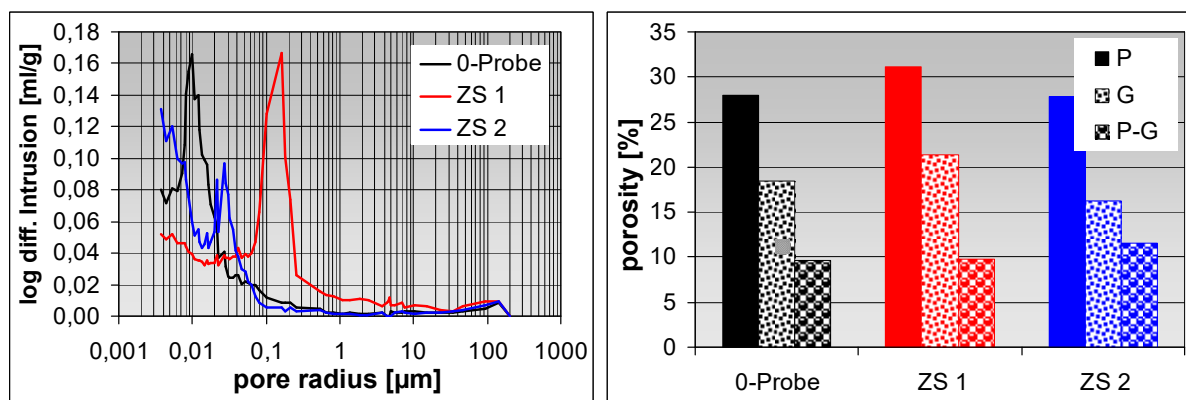

Figure 5: Pore radius distribution; distribution of total porosity (P), open porosity (G) and closed porosity (P-G)

Far more interesting is the finding, however, that the influence on the shrinkage measure by means of polymer modification is only to be seen after the 2nd – 4th day. This confirms the investigations on the PCCs. The early longitudinal change of the polymer-modified mortars shows no big difference compared to unmodified reference mixtures. Thus, it can be assumed that the resulting shrinkage stresses can be taken without causing damage because of the higher tensile strength – in spite of the retarded hydration and consequently lower compressive strength in the first days. That means on the other hand that the increased shrinkage deformations will manifest themselves even stronger in a later stage of hardening. Should at this point the tensile strength of the modified mortars not be significantly higher than the tensile strength of the unmodified ones it could come to an exceeding of the tensile strength caused by the high shrinkage stresses. The PCCs would then lose cohesion which would manifest itself in the formation of cracks.

Experiments on the longitudinal change behaviour of polymer-modified cement stones on the adhesive bond

In the experiments carried out so far, it was shown that the longitudinal change behaviour of mortars is negatively influenced by polymer modification. In order to draw conclusions what kind of effect this has as far as cohesion in the PCCs is concerned, model tests were carried out on stone samples which were coated on both sides with modified cement paste. In preliminary works before, the development of the dynamic E-modulus as well as of the tensile strength of the cement stones had been investigated.

The stresses caused longitudinal changes in mortars must be taken and forwarded by the matrix. Therefore, it is crucial how stable the cohesive bond within the cement stone matrix is. Furthermore, the bond of cement stone matrix and stone granulation is also very important. In order to simulate this bond makroscopically and to analyse it under defined conditions stone slices with exact dimensions (4 x 4,5 x 1 cm³) were coated with cement paste in a defined thickness of 1 cm (Fig. 6). The used stones were a Seeberger sand stone (SS) and a limestone (Oberdorlaer Muschelkalk - MK). Both stones have a relatively low but significantly different tensile strength. (SS 1.30 N/mm²; MK 2.31 N/mm²). In addition, they have a different water absorption capacity (SS 4.18 %; MK   2.0 %) which could influence the adhesive bond. The coating was applied on both sides in order to have the same conditions on both test piece sides for the subsequent tensile test. In doing so, the embedding of stone grains in the cement stone matrix could be simulated.

The applying was carried out by means of a form which had been produced for this purpose, in order to achieve constant layer thicknesses. The stone slices were pre-wetted to achieve an as good as possible adhesive bond. After 24 h the samples were demoulded and stored in normal climate. After 28 days steel testing stamps were applied on both sides of the samples by means of a PMMA-adhesive. The samples then underwent a tensile test by means of the universal testing device TIRAtest 28100. The samples were fixed lateral-force-free. The testing speed was 100 N/s. A testing series consisted of 4 individual samples.

In the course of analysing the fracture force was determined and the fracture pattern was judged.
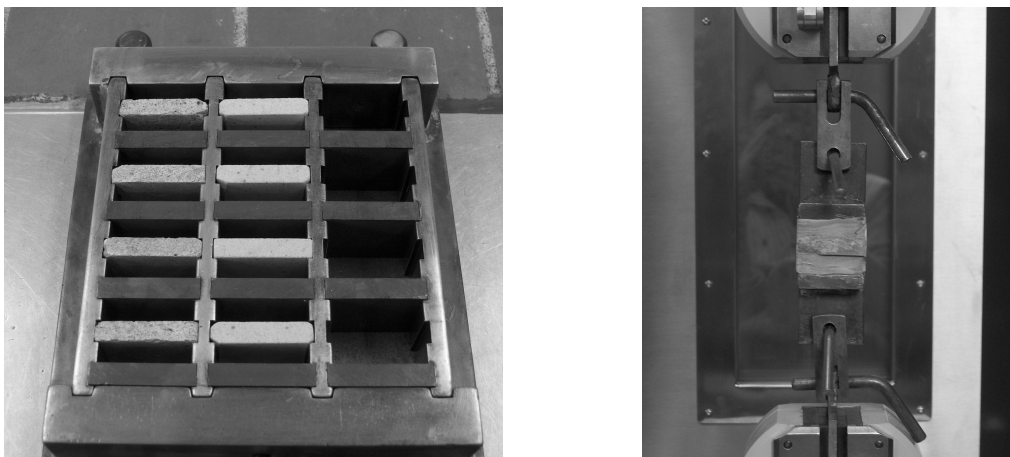

Figure 6 Left-form for preparing the model-specimen; right–fixed specimen in the testing machine

The result shows that the determined values for the tensile adhesion strength are extremely low. The tensile adhesion strengths of all cement stone samples are significantly lower than the tensile strengths of both stones and the cement stones themselves. When judging the fracture pattern it could be observed that above all it had come to a cohesion failure of the stones. The examination of the test pieces before test start showed a pre-damage on all samples which had not been there on the stone slices after demoulding (Fig. 7).

On the basis of these results it can be assumed that the adhesive bond of all cement stones to their respective stones is very good. The fracture patterns as well as the observations before test start suggest that already during the 28 d storage it came to an exceeding of the tensile strength of the stones. Consequently, the composite strength of the cement stones as well as (as proven) the tensile strength of the cement stones are significantly higher than the stresses caused by shrinkage. That means on the other hand that by shrinkage of the cement stones alone, as a consequence of the hindrance of deformation on compound level, shear stresses > 2,3 N/mm² (= tensile strength MK) were formed. These stresses led to tensile stresses at the free rims, perpendicular to the coating level, which exceeded the tensile strength of the stones. Consequently, it came to a cohesion failure in the stones and to a formation of cracks. These cracks appeared more marked on the sand stones than on the limestone due to the lower tensile strength.
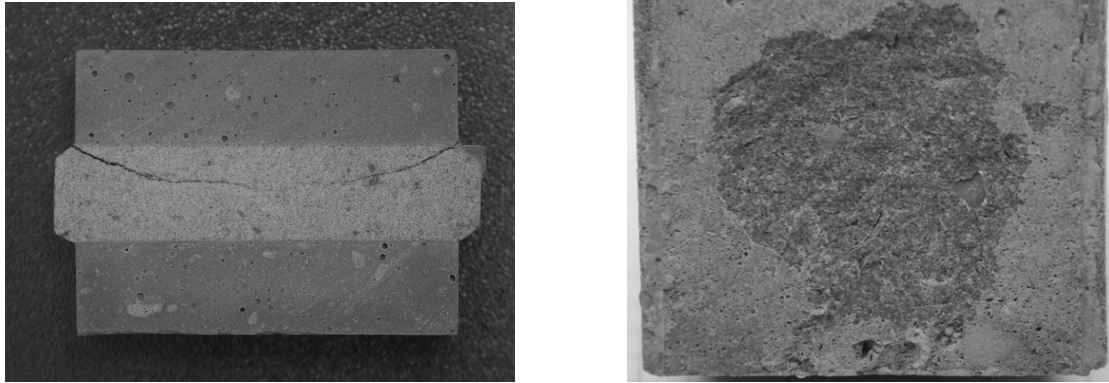
Figure 7 Left:sandstone-specimen after storage, before testing;right:limestone-specimen after testing

In order to illustrate the influence of the polymer modifications on the resulting tensile stresses **δ**, these can be calculated in approximation when the E-modulus **E** and the longitudinal change **ε** are known. The results from the detection of these parameters were set in the following equation:

$$\delta = E \cdot \varepsilon \qquad [N/mm^2] \qquad\qquad (1)$$

The resulting values are strongly abstracted and can only be compared with caution. Unconsidered remains the fact that a major part of the stresses is brought down by plastic deformations of the cement stone, or stresses are reduced by crack formation. Furthermore it has to be said that only the dynamic E-modulus was available for calculations. It differs from the static E-modulus which is usally taken for the stress determination. For these reasons the results from the polymer-modified cement stones were related to those from the not modified ones. In doing so, it becomes possible to make statements by trend as to the influence of polymer modifications.
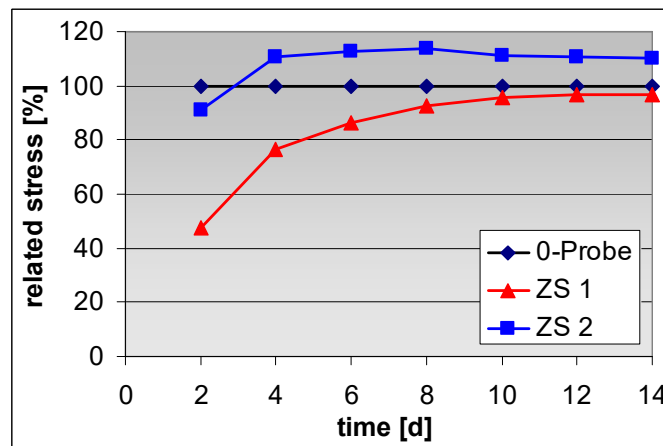

Figure 8: Abstracted related stress of modified cement stones

The analysis shows (Fig. 8) that the lower E-modulus has a positive effect on the resulting stresses in the structure. Although the ZS 1 shows a higher shrinkage measure than the reference sample (approx. 34 % more after 14 days) the occurring stresses are roughly equal. When the shrinkage values rise, however, like in the case of ZS 2 (approx. 60 % more after 14 days compared with the 0-sample) the shrinkage stresses exceed those of the reference mixture.This can be compensated, however, by a higher tensile strength. The lower E-modulus has a positive effect especially in the beginning of the hardening process. The ocurring stresses in the first days are sometimes clearly lower than those of the reference mixture – nevertheless the tensile strengths are similar.

Conclusion

The longitudinal change of the PCCs shows a significantly higher dependence of the storage conditions compared to the unmodified reference mixtures. The absolute values of the longitudinal changes increase with the polymer content rising.

The increased longitudinal changes do not result from an increased drying shrinkage. As a consequence of an influence on the hydration caused by the polymers as well as by the increased water retentivity of these mortars, it rather comes to a time-shift in the hydration. Shrinkage stresses are then no longer brought down in the plastic state to a big extent, but in the already hardened mortar and thus can negatively influence the cohesion in the PCCs.

The influence on the shrinkage caused by the polymers is only visible some days after mixing. This could be proven for the mortar as well as for the cement stone by means of experiments in modified shrinkage channels.

In the first days increased stresses in the mortar due to shrinkage can be taken by the increased tensile strength of the PCC.

In the course of hydration – when the increase of the tensile strength of a mortar caused by polymer modification is not so significant and when deformation is hindered – an exceeding of the tensile strength in the mortar matrix can occur, this leads to cohesion failure – cracks are the consequence.

References

[1]   DAfStb-Richtlinie Schutz und Instandsetzen von Betonbauteilen (RILI-SIB) - Teil 4: Prüfverfahren. Ausgabe Oktober 2001

[2]   DAfStb-Richtlinie Schutz und Instandsetzen von Betonbauteilen (RILI-SIB) - Teil 4: Prüfverfahren. Ausgabe November 1992

[3]   Der Bundesminister für Verkehr, Abteilung Straßenbau: Technische Prüfvorschriften für Betonersatzsysteme aus Zementmörtel / Beton mit Kunststoffzusatz (PCC) - TP BE-PCC. Ausgabe 1990

[4]   Schorn, H.: *Betone mit Kunststoffen und andere Instandsetzungsbaustoffe*. Ernst & Sohn-Verlag, Berlin, 1991

[5]   Yamamoto, T.; Osaki, K.; Wakasugi, M.; Sugiura, A.; Sakakibara, H.*: Adhesive Strength of Modified Cement Mortar with Redispersible Polymer Powders*. IX. ICPIC; 14. – 18. September; Bologna (Italien); 1998; S. 255-261

[6]   Justnes, H.; Reynaers, R.; Van Zundert, W.: *The influence of Latices and Redispersible Powders on Hydratation and Strength Development of Polymer Cement Mortars*. IX. ICPIC, 14. – 18. September, Bologna (Italien), 1998, S. 225-238

[7]   Dimmig, A.: *Direkte und indirekte Einflussnahme von Kunststoffmodifizierungen auf die Eigenschaften, insbesondere die Dauerhaftigkeit von Mörtel*. 15. Internationale Baustofftagung - ibausil, 24. - 27. September, Weimar, 2003, S. 2-0331 - 2-0346

[8]   Bode, K. A.; *Aspekte der kohäsiven und adhäsiven Eigenschaften von PCC*. Dissertation, Bauhaus-Universität Weimar, 2009