

可再分散聚合物粉末改性的瓷砖胶 –  
在新拌和硬化状态下微结构的发展及其与宏观性能的联系

**Tile adhesives modified by redispersible polymer powder –  
Microstructural evolution and resulting macro properties in both fresh and hardened states**

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**Abstract**

This paper describes the new methods developed to quantitatively investigate microstructures in redispersible polymer powder modified mortars and the resulting properties in both, fresh and hardened states.

A combination of fluorescence light and electron microscopy allowed the visualisation of different mortar components such as specific polymer components, air voids, cement phases, and mineral fillers. The results show that the mortar fractionated during application and hardening, inducing a variety of phase enrichments and depletions. The occurrence of these microstructural heterogeneities explains the major influence that the microstructure has on the physical properties of the mortar. The ability of the redispersible polymer powder to resist fractionation explains the homogeneity in strength properties, including cohesion, adhesion and flexibility.

**Introduction**

The ease in application and gain in premium material properties are the main technical reasons for the strongly growing Chinese market of dry mortars. Dry mortars describe a wide variety of ready to use dry mixes which are subdivided into so-called bulk dry mortars and special dry mortars. The latter contain a significant amount of polymeric additives to provide the special technical requirements.

In this paper we focus on the most dominant species of special dry mortars, namely tile adhesives mortars which are designed for fixing ceramic tiles onto walls and floors.

Optimised workability of the freshly mixed mortar and final adhesion of the tile are the main requirements of such mortars. This study investigates the different mechanisms behind these properties and how they are influenced by the redispersible polymer powder (RPP).

## Materials and methods

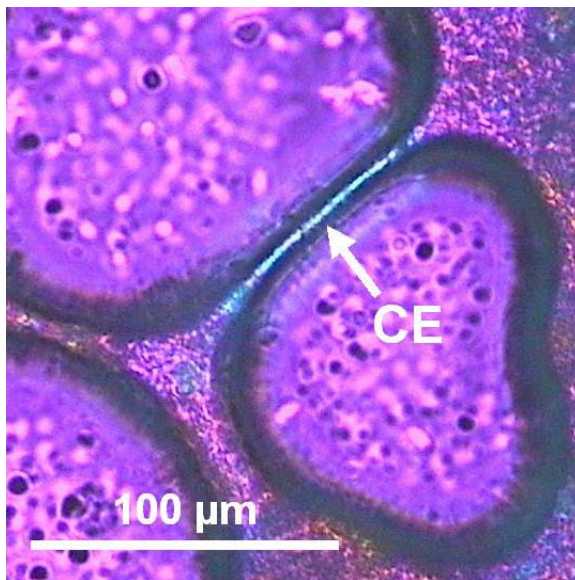
The authors followed a multi-method structural analysis approach which allows to resolve the evolution of microstructures and various polymer-cement interaction mechanisms in time and space. The biggest challenge was the development of quantitative methods, especially for the two main additives, cellulose ether (CE) and RPP. In case of the RPP we used a vinyl-chlorine containing copolymer which allowed to detect the polymer by the mapping of chlorine by means of electron microscopy. CE was stained prior to mortar mixing by a fluorescence dye to visualize it later on by fluorescence light microscopy. The tile adhesive mortar was applied and stored under dry conditions (23°C/50%r.h.) according to standard EN 1348. Samples were cut, impregnated and polished to gain representative sections for quantitative microstructural analysis of hardened samples.

To cover the early evolution of microstructures during the fresh mortar stage (prior to cement setting) in-situ microscopy on fresh mixes were performed.

All methods are described in details in Jenni et al. (2003).

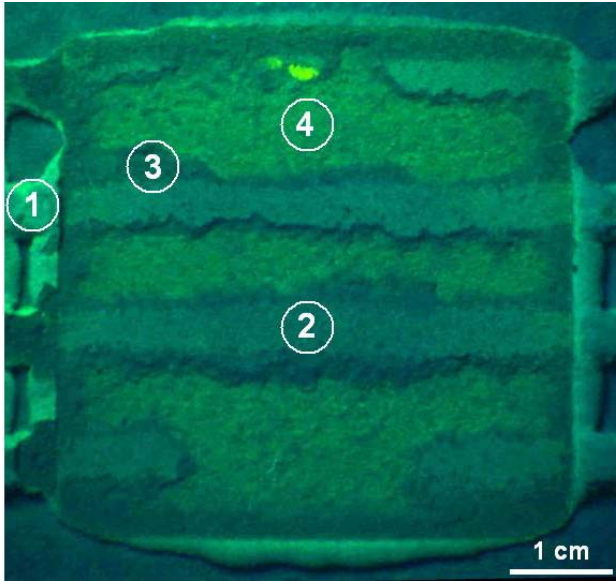
## Discussion of results

In-situ experiments (Fig. 1) revealed that CE is stabilising air voids by film formation. These CE films form probably already during mixing or right afterwards. The driving mechanism for this is interpreted to be the surface activity of CE. As the air is physically entrained by the stirrer CE suddenly occupies the air-slurry interfaces to form films. These films are still wet and, thus, highly flexible and squeezable, but the polarizing effect clearly proves their molecular ordering. Later, under the scanning electron microscope these CE films can be found along the air voids.



*Fig. 1: The freshly mixed paste was prepared between two glass slides and immediately imaged by polarised light. The micrograph shows a polarising film of CE between two air pores in a 15 minutes old paste.*

The same mechanism is thought to explain part of the enrichment of CE at the mortar surface. But as the free mortar water evaporates from the mortar surface there is a second mechanism for CE enrichment (see figure 2).



*Fig. 2: UV-light photograph of the failure surface after adhesion test (28 days storage at 23°C/50% r.h.). Cellulose ether was stained by a fluorescent dye prior to mortar mixing. Bright greenish spots indicate locations of enrichment of cellulose ether. (For explanations of the numbers see text below.)*

Figure 2 shows an adhesive mortar after the pull-out test (tile was removed). The failure mode is mainly of the adhesion type. Where the mortar was not covered by the tile (1) evaporation at the mortar surface caused a strong enrichment of the cellulose ether. During Open Time (5 minutes between mortar application and tiling) cellulose ether supported the formation of a skin. This skin caused the mortar to fail 28 days later at the tile interface (2). In between the mortar ripples the tile was wetted properly resulting in a mixed cohesion (3)/adhesion (4) failure. Adhesion failure (4) is located near to the contact to the porous concrete substrate where cellulose ether was strongly enriched by the migrating pore water.

The fractionation mechanisms mentioned above occur within the first minutes to hours after mortar application. Even though the example shown in figure 2 is not representing the general case (usually, failure mode is strongly dominated by adhesion failure at the tile-mortar interface) it is a nice case example which demonstrates how early formation of microstructures can influence final physical properties.

In contrast to CE, the latex particles of the redispersible powder are homogeneously distributed throughout the cement matrix (between air pores and sand grains; see figure 3). The reasons that the latex is homogeneously distributed is (a) that it is a particle of about 1  $\mu\text{m}$  which cannot pass the smallest capillary pore, (b) most lattices have an affinity to the cement and, therefore, tend to adsorb onto the cement grains. The latter is also thought to be the mechanism for the mutual intergrowth of cement phases with latex film on a microscopic scale.

The homogeneous distribution of the redispersible powders throughout the entire mortar bed improves everywhere cohesion between the mortar components and adhesion to the tile.

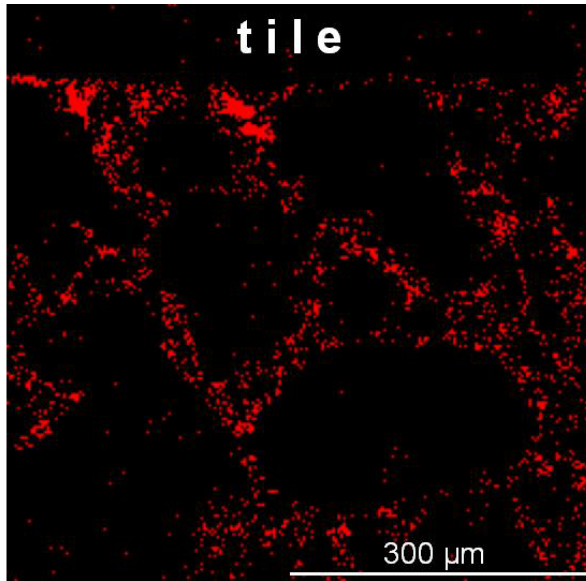


Fig. 3: Chlorine distribution map of a tile adhesive mortar modified by a vinyl-chlorine containing redispersible powder (red). The redispersible powder is homogeneously distributed in the cement matrix. Black holes are air voids and sand grains enclosed by the cement matrix.

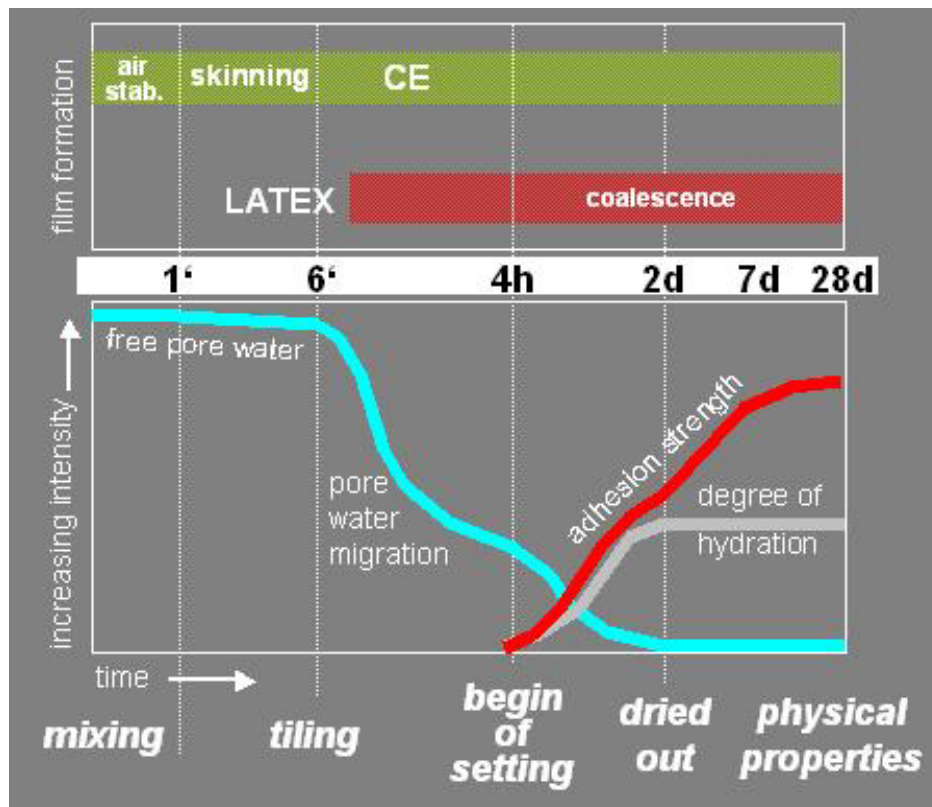


Fig. 4: Evolutionary diagram for simultaneous film formation (cellulose ether in green and redispersible powder, referred to as latex, in red), free water content (blue curve), cement hydration (grey curve) and strength development (red curve) as a function of time (x-axis).

Figure 4 shows a synthesis of the dynamic evolution of the key mechanisms and related microstructures and the resulting physical properties. Most critical is the amount of free pore water. It controls film formation, as well as cement hydration. The moment when the mortar dried out represents an important milestone in the evolution of strength properties. While cement hydration virtually stops, adhesion strength is still increasing over the following days. This is a general phenomena of mortars modified by redispersible powders, but cannot be observed in unmodified cement mortars. The explanation is that the redispersible powder undergoes different stages of latex film formation (Keddie, 1996). The early stages of coagulation and deformation are mainly driven by evaporation and, thus, occur during drying of the mortar, simultaneously with cement hydration. At the moment when all free pore water is consumed cement hydration stops. This is proven by experiments with unmodified cement mortars where strength increase is coeval with drying of the mortar. Not so in case of mortars modified by redispersible powders: after the mortar is dried out the already formed latex films coalesce (final stage of latex film formation) and the mortar continues to gain in cohesion and adhesion strength. Our investigations have shown that the cementitious environment (high pH and ionic strength of the pore water) is an important factor for the latex particles to coalescence.

## Conclusions

The study showed that the polymers in a tile adhesive mortar act by different mechanisms during the different stages of mixing, application and hardening. Thereby, the role of the redispersible polymer powder is key in terms of (a) redispersion, (b) interaction with cement phases and (c) film formation.

- (a) Redispersion: A fast and complete redispersion during mixing generates an initial, fine and homogeneous distribution of the latex particles.
- (b) The finely distributed latex interacts with the cement in a specific way, not to disturb hydration, but to form an intensively intergrown polymer-cement matrix which, later on, provides the unique material properties, such as cohesion and flexibility.
- (c) The study has shown that the cementitious environment helps the latex to coalesce. This latex coalescence is continued long after cement hydration virtually stopped due to drying out. This explains the continued increase in adhesion strength days after the degree of cement hydration became stabilized (Fig. 4). Latex film formation at the tile-mortar interface is the primary mechanism for adhesion.

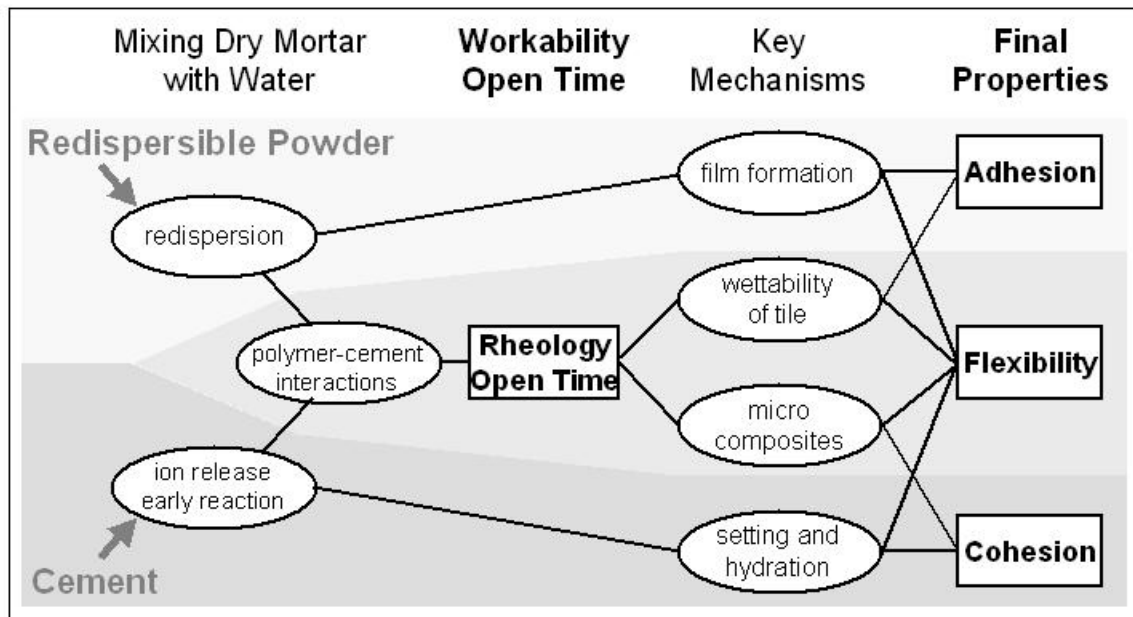


Fig. 5: Scheme of functionality, mechanisms and resulting properties of polymer-modified tile adhesive mortars.

The following main conclusions can be made (see Fig. 5):

- (1) The cement alone primarily provides cohesion, but not necessarily adhesion and definitely no flexibility properties.
- (2) The ability of the RPP to form strong and flexible films at the mortar-tile interface is the main mechanism for adhesion. Especially, in case of trendy, densified and vitrified ceramic tile materials, scanning electron microstructural studies show that there is no porosity for mechanical intergrowth, and, thus, polymer adhesion becomes the key mechanism for adhesion.
- (3) A well balanced interaction of the RPP with the cement phases (a) provides the right workability properties (viscosity, shear strength), (b) prolongs Open Time (ability to wet properly the tile), and (c) leads to the formation of micron-sized polymer-cement composite structures with unique material properties for strength and flexibility.

### Acknowledgements

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### References

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