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Durability of epoxy resin-based materials for the repair of damaged cementitious composites

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Abstract

The behaviour of an epoxy resin to be used for the repair of cementitious damaged structures is evaluated with respect to its adhesion properties and durability. The epoxy resin is used as a primer to link an unmodified repair mortar to a substrate and/or as modifier of the repair mortar. The behaviour and durability of the system when exposed to thermal and environmental stresses are investigated and compared to unmodified materials. The data so far collected outline reliable behaviour of the materials.

Keywords: Adhesion; Epoxy resins; Repair mortars; Durability

The search for reliable, long-lasting repair materials for damaged concrete structures is becoming more intensive [1]. These materials must satisfy simultaneously a set of chemical, physical, and mechanical properties, which have been described in detail [2,3]. Polymers frequently are used in the formulation of repair mortars because of particular characteristics (higher adhesion to the substrate, lower shrinkage and permeability) they can provide, if properly dosed. At present, the most widely used polymers in repair materials are thermoplastics in the form of lattices [4,5]. Less common is the use of thermosetting because of the problems associated with the mixing operation; however, thermoset resins show improved mechanical properties and, being cross-linked polymers, are less affected by the "brittle to ductile transition" that takes place around the glass transition temperature.

The aims of the present research were to 1) investigate the performance of the adhesion layer (primer) obtained by mixing a water-dispersible bicomponent epoxy resin with cement, which links the substrate to a repair mortar, 2) evaluate further the difference in behaviour of the system when using either an unmodified or an epoxy-modified repair mortar, and 3) examine the effect of thermal stresses, as polymeric materials show higher coefficients of thermal expansion than plain cementitious materials, and eventually the effect of carbonation on the performance of the different systems.

1. Experimental

1.1. Materials

1.1.1. Epoxy system

The epoxy system used was a water-dispersible, bicomponent epoxy (weight per epoxy equivalent: 170 to 180 g; viscosity: 800 to 1200 cPoise at 25°C), aliphatic amine hardener as curing agent (API Spa, Mignanego, Italy). The hardener contains 36 wt% of water; when used in the bonding layer, fillers (talc, TiO_2) are added. Cement used was 42.5 Portland, type I (Italcementi, Bergamo). Sand used was siliceous, normalized sand (SISA, Torre del Lago) according to Italian standards [6]. Pastes were polymer modified, obtained by mixing the proper amounts of base and hardener and adding 60% wt of cement. Addition of cement eliminates the excess water in the resin and reduces the differences in the coefficient of thermal expansion between the resin and the cement-based materials without decreasing the adhesion properties of the system. At the same time, it further reduces the softening effect of temperature. Table 1 lists the coefficients of thermal expansion (determined by a Perkin Elmer TMA7) of the resin itself and of pastes containing 40 and 60 wt% of cement, in the temperature range from 25 to 150°C and the glass transition temperatures, Tg, determined by differential scanning calorimetry (Perkin

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Table 1
Tg temperatures and coefficients of thermal expansion below and above Tg

Sample	α below Tg	α above Tg	Tg (°C)
Resin	70×10^{-6}	160×10^{-6}	58
Resin + 40% weight cement	50×10^{-6}	100×10^{-6}	67
Resin + 60% weight cement	45×10^{-6}	95×10^{-6}	72

Table 3
Type II samples: Slant indirect shear (MPa)

I	R	28 days	90 days	CO_2	TC1	TC2
UN	UN	7.4	9.9	9.4	10.2	7.8
EP	UN	23.4	29.1	29.0	28.0	28.2
EP	EP	23.2	29.7	28.8	28.7	28.3

Elmer DSC7, heating rate 20°C/min). Unmodified: obtained from mixing Portland cement and water (w/c ratio: 0.32) to be used as primer.

1.1.2. Mortars

Normal mortars (CS), obtained according to Italian standards [6], with a water-to-cement (w/c) ratio of 0.5 and aggregate-to-cement ratio of 3 were used as substrates for all tests after being cured in water (28 days) to favour hydration reactions. This should provide a sound substrate with good mechanical properties, dissimilar from those of damaged concretes. However. the choice was made to try to minimize cohesive failure on the substrate, thus focusing attention on the behaviour of the adhesion layer toward the substrate but also toward the repair mortar. Polymer-modified mortars (PCM) used as repair mortars were prepared by admixing 10 wt% of resin (on cement weight), a ratio chosen based on previous investigations [7]. The w/c ratio was reduced to 0.4 to obtain close workabilities (850 for CS, 800 for epoxy modified, according to UNI 7044), on account of the plasticizing effect of the polymer. The aggregate-to-cement ratio was the same as in normal mortars. The resin was dispersed in the cement-water paste, and mixing procedures were as close as possible to the standards.

2. Tests

Three different tests were carried out on different types of samples to evaluate bonding effectiveness:

1. Type I according to the “Adhesion test in flexure” (RILEM Standards, PC-9 [8]). Substrates were obtained by sawing 4 × 4 × 16 cm CS mortar prisms;
2. Type II, recalling the Arizona Test, ASTM 882/87 and BS 6319 [5], with substrates obtained as before; and
3. Type III, according to the Adhesion in tension/Core pull-off test (CEN TC104) [9]; substrates obtained from direct casting of CS mortars.

In all samples, a layer (about 250 μm thick) of modified or unmodified paste was brushed on the water-saturated surfaces (relative humidity 96%) of the substrates. Smooth surfaces (obtained by cutting with a diamond saw) were used on type I and II samples. No treatment (sandblasting, hammering, etc.) was applied except for air blowing to remove dust particles. Substrate surfaces of type III samples were sandpapered. The fresh repair mortars were cast after no more than 30 min. After restoration, samples were stored in air at 21 ± 2°C and 60 ± 10% UR until testing at 28 and 90 days. Thus, three kinds of systems were prepared, subsequently referred as: UN/UN (unmodified primer/unmodified mortar), EP/UN (modified primer, unmodified mortar), and EP/EP (modified primer/modified mortar).

To evaluate the durability of the adhesion, reconstructed samples, cured for 28 days, were submitted to two types of thermal cycles:

1. from 20 to 80°C, leaving samples at both temperatures for 5 hours, hereafter referred to as cycle 1. In this way, the samples reach a temperature above the Tg of the resin;
2. similar to that described by other authors [10]: 6 h at −25°C, 4 h at 60°C, and 14 h in water at 19°C, hereafter referred to as cycle 2.

Microstructural observations were carried out on surfaces obtained by fracturing type I, II, or III samples by means of a steel wedge or directly on the fracture surfaces using a scanning electron microscope (Philips 501).

Specimens were stored, again after 28 days of curing, in a carbonation chamber (15% volume CO_2 and 70% relative humidity). All measurements performed on samples submitted to either thermal cycles or carbonation were carried out after 90 days from casting.

Table 2
Type I samples: Flexural strength (MPa)

I	R	28 days	90 days	CO_2	TC1	TC2
UN	UN	2.0	2.3	2.1	2.1	1.7
EP	UN	7.2	8.2	8.0	6.4	5.8
EP	EP	7.0	8.1	8.0	6.2	6.3

I, primer; R, repair mortar; UN, unmodified, EP, epoxy modified; CO_2, carbonated; TC1, thermal cycle 1; TC2, thermal cycle 2.

Table 4
Type III samples: Bond resistance (MPa)

I	R	28 days	90 days	CO_2	TC1	TC2
UN	UN	1.1	1.3	1.2	1.4	1.1
EP	UN	2.3	2.4	2.2	1.9	1.2
EP	EP	2.8	2.9	2.7	2.6	1.2

Table 5
Prevailing zone of failure in type III samples

I	R	28 days	90 days	CO_2	TC1	TC2
UN	UN	B	A	B	B	C
EP	UN	C	C	C	A	C
EP	EP	C	C	C	C	C

A, repair mortar; B, adhesive bond; C, substrate.

3. Results and discussion

Tables 2, 3, and 4 list the results of the mechanical tests for the different samples.

The modified paste used as primer (EP/UN and EP/EP systems) exerts a good bonding effect, whereas the unmodified primer (UN/UN) shows lower bonding efficiency, which is contrary to what has been reported elsewhere in repaired concretes [11]. This may be ascribed to the lower porosity of mortars and to the smoothness of the substrate surfaces, which allows reduced mechanical interlocking of hydration products. Thermal cycles reduce flexural strength in EP/UN and EP/EP, whereas bond adhesion remains almost unchanged, underlining the severity of the former test. When the resin is used both in the primer and in the repair mortar, slightly higher resistance to thermal cycles is found. The same effect is observed for thermal cycles involving freezing and thawing. UN/UN samples improve their properties when submitted to TC1 and are slightly affected by TC2. The carbonation process does not induce changes in all the investigated properties of all systems. Tables 4 and 5 confirm the observation drawn before: the modified primer provides good adhesion to the substrate, always leading to a cohesive fracture in the substrate. The EP/EP system gives increased results, especially when submitted to TC1, whereas the EP/UN system gives cohesive fracture in the repair mortar. Freeze and thaw cycles mainly affect the tensile strength of the substrate, where all samples fail (Table 5), thus leveling bond resistance values. However, the result is still to be considered as positive. The unmodified primer provides lower bonding resistance, being almost unaffected by thermal cycles. Figs. 1 and 2 depict the substrate and adhesive primer for unmodified and modified repair mortar, respectively. Good continuity is gained in both cases, and few porosities induced by air bubbles are found. When unmodified repair mortars are used (EP/UN), a zone containing well-developed hydration products is found, just close to the epoxy primer (Fig. 3). This microstructure is not found in UN/UN and EP/EP samples. The same phenomenon was described by other authors on lattice-modified repair mortars [12]. Well-developed hydration products may be related to the presence of a zone that presents higher po-

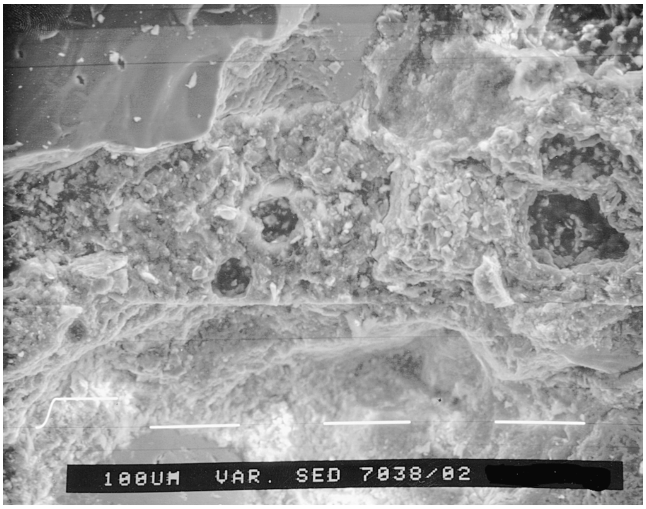

Fig. 1. Microstructure of the EP/UN system: substrate (bottom) and repair mortar (top).

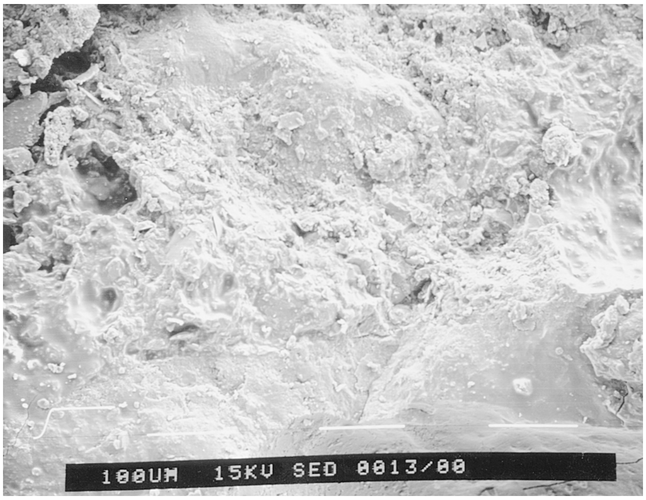

Fig. 2. Microstructure of the EP/EP system: substrate (bottom) and repair mortar (top).

Fig. 3. Hydration products near the primer layer in EP/UN samples.

rosity. Experiments carried out on water-unsaturated substrates showed the same microstructure, a feature that rules out the effect of water content on the substrate; indeed, the primer has proved to form a rather impermeable mean, unlike the unmodified primer. According to what has been found by other authors [13], impermeability can lead to moisture accumulation near the primer boundary, thus creating a higher w/c ratio zone. This does not take place when using the epoxy-modified repair mortar, probably because of the lower w/c ratio (0.4) of the mortar and from possible chemical linking of the resin in the primer and in the repair mortar. The use of low-water cement repair mortars thus should be recommended. Fig. 4 shows the interface between the primer and the substrate of sample EP/UN submitted to cycle 2. According to mechanical results (Tables 4 and 5), structural damages can be observed in the substrate (upper part of Fig. 4), but not at the interfaces between the primer and the substrate. No particular microstructures are found in carbonated samples.

Fig. 4. Microcracks in the substrate of an EP/UN sample submitted to thermal cycle 2.

4. Conclusions

The following conclusions can be drawn:

- The epoxy-modified paste is able to provide good adhesion to smooth and low-porous substrates because of its chemical structure.
- Mechanical stresses induced by the different coefficients of thermal expansion do not compromise the efficiency of the repair system.
- Freeze and thaw cycles mainly affect the tensile properties of the substrate, thus avoiding cohesive failure in the primer or adhesive failure at the interfaces between primer and substrate and primer and repair mortar.
- Carbonation does not alter the properties of all the investigated systems.
- Epoxy-modified repair mortars used together with epoxy-modified primer provide higher durability and bonding strength because of more homogeneous microstructure.

Acknowledgments

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