Available online at www.sciencedirect.com
ScienceDirect
Cement & Concrete Composites 29 (2007) 146–156
Cement & Concrete Composites
www.elsevier.com/locate/cemconcomp

Petrographic and mechanical aspects of accelerated ageing of polymeric mortars

Manuel A.G. Silva [a,*], Zenaide C.G. Silva [b], Joaquim Simão [b]

[a] UNIC, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[b] CEG, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

Received 1 February 2006; received in revised form 2 August 2006; accepted 21 August 2006
Available online 16 October 2006

Abstract

An educated estimate of changes of mechanical properties of polymeric mortars under environmental actions requires further knowledge since data are insufficient and the understanding of alterations incomplete. An experimental program to generate information on those aspects for artificially aged coupons of polyester and epoxy mortars is described. At pre-established temporal stages, flexural tensile bending and compression strength of coupons was determined and compared. Environmental conditioning consisted of cycles of (i) temperature; (ii) humidity and (iii) salt fogging, emphasis being, herein, placed on the effects of the temperature and humidity cycles. Thin lamellae of the tested coupons were cut along the ageing process and observed under petrographic microscope. Changes on the aspect of air voids and textures are reported. A systematic SEM study of the mineralogical and textural aspects is also presented that qualitatively contributes to the interpretation of the results. Higher degradation was detected in the samples submitted to the temperature and salt fogging cycles selected in the study and seen to intensify past 3000 h of accelerated environmental action.

Keywords: Environmental degradation; Mortar artificial ageing; Epoxy and polyester mortar; Temperature cycles; Salt fogging

1. Environmental effects on polymeric mortars

Extended use of polymeric mortars and concrete is recent and besides the current applications on pre-cast panels, pools, overlays on pavements and the strengthening of the anchorage of structural cables, it has involved the fast growing market of strengthening and repair of buildings, monuments and structures. The question of the evolution of their properties under environmental aggression poses doubts given their relatively recent application and has technical and economical importance since they may experience, e.g., either successive conditions of dry–wet environment or cyclic changes of temperature or the synergetic effects of these and other conditions. The modifications of the properties depend, e.g., on the composition of the polymeric mortars, on the amplitude, mean value, duration and type of cycles and such dependence increases the need for a large number of tests to shorten the existing gap of knowledge on the durability of these materials. Porosity and the effects of size and shape of aggregates on the development of strength and deformability have been established and the influence of curing temperature, additives and fillers on the performance and durability of epoxy mortars shown [1]. These authors show that the plastification of an epoxy mortar is essentially due to the binding properties of the resins and these change with temperature increase, since it raises the mobility of the molecular and segmental polymeric chain and lowers the binding viscosity. They advise the presence of a mineral filler that is a cheaper component to reduce those effects. The recommendations of the chemical industry have consequences on durability and on mechanical performance and require careful weighing by design engineers. The influence of the porosity of the mortar, as well as of the size and shape of

* Corresponding author. Fax: +35 2 21 294 8398.
E-mail address: mgs@fct.unl.pt (M.A.G. Silva).

0958-9465/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2006.08.003

Nomenclature

RH	relative humidity	σ_{ult}	ultimate stress
SEM	scanning electronic microscope	$y_{L/2}$	mid-span bending deflection

the aggregates have also been examined and, e.g., a comparative study of two types of polyester mortars, made with isophtalic and ortophtalic resins, respectively, showed that the mechanical strength, porosity and interface matrix–aggregates are linked [2]. Mebarkia and Vipulanandan [3] and Ohama et al. [4] measured the effects on the compressive strength of a polymeric concrete of one-month immersion in chemical solutions of different pH levels. Results showed that the strength decreased with the increase in pH and a fairly satisfactory behavior after direct exposure to tap water, alkali, salts, kerosene and rapeseed oil. Chawalwala [5] showed that the degradation rate of the vinyl and polyester polymer concrete wear surface of a bridge deck was associated with the performance of the interface aggregate–matrix. The effects of exposure to water and chemical solutions on the flexural strength of polyester and epoxy concretes have also been reported though corresponding to relatively short periods [6].

The physical characteristics of polymeric binders are of great importance in predicting the properties of polymeric mortars and different physical methods may provide data to estimate the effects of artificial ageing on the properties of the resins [7]. The authors establish that the after cure effects come to an end at heating around 80–85 °C, no changes in the material structure being observed for a further rise in temperature and repeated heating. This temperature is higher than that used in the tests to be described in this article. Their moisture tests led to the conclusion that the decrease in T_g is explained by the plasticizing action of moisture. By X-ray diffraction, moisture sorption was shown to cause structural changes. The study was made for different factors and a specific resin, but the conclusions appear of importance for further studies.

A major problem of polymeric mortars derives from the viscoelastic properties of the resins, highly sensitive to temperature [8,9]. At the same time, the mechanical properties of the mortars are known to change under variation of temperature, especially near the glass transition temperature that, for many resins used in polymeric mortars, varies from 50 to 80°C, approximately, i.e. glass transition may occur during service lifetime [10]. Studies on the mechanical behavior of a polyester polymer concrete at 23, 40 and 60 °C showed that higher temperatures caused a small decrease in the compressive strength, a relatively large decrease in bending strength and a very large increase in creep deformation [11].

The temporal evolution of properties during the lifetime of a system with polymeric mortars has also been analyzed [12]. The author, in connection with creep phenomena and based on a relation due to Findley, proposed plots of deformation versus time in a log–log scale in a manner that is believed to be adequate for extrapolation to predict future deformation. The generalization of similar procedures for effects of environmental aggression appears of enormous interest and still to be made.

Pardo et al. [13] compared the influence of temperature on the mechanical strength for three different polymer concretes tested in bending and compression, after conditioning at different temperatures (from 20 to 200 °C). Results showed that the specimens tested at room temperature experienced no important reduction of strength, whereas, when tested at the ageing temperature, a significant decrease of both flexural and compressive strength was found.

Oshima et al. [14] tested temperature-dependent mechanical properties such as the creep coefficient, compressive and flexural strengths and determined the inflexion points at which temperature dependency becomes dominant. The results indicated that those inflexion points are related to the heat distortion temperature (HDT) of the resins used and were not affected by the resin content, HDT being defined as the temperature at which an applied load causes a test bar of the resin to deflect 0.25 mm, according to ASTM D 648.

It has been observed that polymer concrete and mortars have lower coefficients of thermal expansion at lower temperatures, while strain versus temperature curves are often bilinear, indicating a sharp change in the coefficient of thermal expansion. To determine how this discontinuity changes, Ribeiro et al. [15] concentrated their work on the variation of the coefficient of thermal expansion of two specific binder formulations of epoxy and unsaturated polyester mortars, specimens being tested for several temperature ranges from 20 to 60 °C. The authors concluded that the variation of thermal expansion with temperature follows a parabolic law rather than a bilinear law.

Diamond [16] addressed, qualitatively, his studies to the internal structures of hydrated cement pastes to correct inadequate background of engineers in this field, with strong ties to the study of property changes of polymeric mortars. He used backscatter SEM recognizing its various limitations resulting from magnification and observations made on a two-dimensional surface. Additionally only a small portion of the surface exposed is documented with micrographs, i.e. the selection of the areas to be documented and the interpretation may vary and require extensive experience. This paper and the companion papers in the same issue of Cement and Concrete Composites support the decision previously taken of associating SEM and petrographic techniques to the study of polymeric mortars.

A more exhaustive search would find more contributions, but still show need for additional research to allow generalization of results for engineering purposes. This study attempts to provide a partial contribution to that objective.

2. Materials and tests

Polymer mortars comprise three material phases, namely inorganic (essentially quartz sand), organic (thermosetting resin) and inert (air inherent to the porosity due to the mixing process). A brief description of the sands and resins used in the studies follows.

The distribution of the grain size of the sand and its chemical composition is briefly characterized in Table 1. The sand is siliceous, of quasi-uniform grains with an average diameter $d_{50} = 342$ μm.

Mortars were produced either with epoxy or polyester resin, in a 20% proportion by weight. Mixing of the mortars was made in accordance with [17]. The main properties of the epoxy and polyester resins are summarized in Table 2. The selection of the resins was based on the fact that they were used in industrial applications and in previous research projects. The orthophtalic polyester resin (NESTE-S226E) was pre-accelerated by methyl ethyl ketone peroxide catalyst with 2% by mass. The low viscosity epoxy resin (EPOSIL-551) was based on a diglycidil ether of bisphenol mixed with an aliphatic amina hardener on a proportion of 2/3 resin, 1/3 hardener.

Table 1
Distribution of grain size of sand

Average grain size distribution		Chemical composition	
Size (μm)	Average (%)		
		SiO_2	99.0 min
$850 < d < 1000$	0.05	Fe_2O_3	0.07 max
$425 < d < 850$	1.05	Al_2O_3	0.40 max
$300 < d < 425$	24.30	TiO_2	0.10 max
$212 < d < 300$	57.00	CaO	0.03 max
$150 < d < 212$	15.00	MgO	0.03 max
$75 < d < 150$	2.80	Na_2O	0.05 max
$d < 75$	0.10	K_2O	0.07 max

Table 2
Properties of resins

	Units	Value
Epoxy		
Hardness	Shore D	85
Specific mass	g/cc	1.18
Vitreous transition Tg (TMA) [ISO 6721-5]	°C	54
HDT [ISO 75A]	°C	34
Gelification time	min	27
Tensile strength [ISO 527]	MPa	40 ± 5
Flexural strength [ISO 178]	MPa	70 ± 5
Elasticity modulus [ISO 178]	MPa	2200 ± 200
Polyester		
Hardness	Barcol	45–50
Specific mass	g/cc	1.08
Vitreous transition Tg (TMA) [ISO 6721-5]	°C	87
HDT [ISO 75A]	°C	50
Gelification time	min	25
Tensile strength [ISO 527]	MPa	58
Flexural strength [ISO 178]	MPa	119
Elasticity modulus [ISO 178]	MPa	4100

Batches of $160 \times 40 \times 40$ mm prisms of polymeric mortar were cast and cured for one day at room temperature and, then, for 3 h (post-cure treatment) at 80 °C as was the case with polymeric mortars studied by other authors as, e.g., in [18]. Afterwards, they were artificially aged in adequate chambers, except for the reference specimens, and tested for flexural and compressive strength at pre-established times throughout the process of accelerated ageing. Observations of the coupons, prior and after mechanical tests, were made by different means, comprising surface stereoscopic imaging, thin sections through petrographic microscopy and scanning electronic microscopy (SEM) images.

Flexural characteristics were determined by standard three point bending tests that also provided data on the deflection of the specimens at mid-point, three coupons being loaded to failure for each aging condition. The two halves on which the prismatic coupons split due to flexural failure were used to obtain the compressive strength with a standard device.

Loading was applied, in the three point bending tests, at a rate corresponding to 0.2 mm/min and in the case of compressive tests at a rate of 0.01 mm/min. The tests on compression strength presented smaller scattering than those on bending strength. In percentage, the ratio of standard deviation by average value of strength ranged from 0.7 to 5.1%, being in most cases around 2.5%.

Sorption or water uptake affects the mechanical strength, both due to absorption and adsorption. Absorption relates to capillary uptake by air voids existing in the mortar. Adsorption relates to the process of formation of a solution that causes temperature changes and swelling of the composite and it is a major cause of water uptake for polymers free of voids and air bubbles. The diffusion of water molecules into a polymeric binder weaken the interaction among the molecules and cause plasticization, that may occur with simultaneous dissolution and removal of components into the water. Studies of gain of mass were made and reported elsewhere by the senior author [19].

Accelerated ageing was implemented through cycles of different relative humidity, salt fogging and temperature as well as simulation of solar rays incidence. Coupons were subjected to a continuous sequence of cycles and records were kept up to 10 000 h of conditioning.

Ageing of the standard prisms for 3-point bending tests took place in commercial chambers. Humidity cycles were imposed at a constant temperature of 40 °C and the relative humidity (RH) was changed every 12 h from 20% to 90%. Aging by means of temperature cycles was imposed keeping the relative humidity RH, in the chamber, set at 80%, while temperature was changed every 12 h from 20 °C to 50 °C.

Salt fog cycles, on the same prisms of $160 \times 40 \times 40$ mm, were defined by 8 h of salt fog (98% humidity) followed by 16 h drying, at 35 °C, and lasted for 10 000 h. Salinity was imposed at 50 g of NaCl per litre of water and two commercial salt fog chambers were utilized.

The comparison of the values obtained for the artificially aged specimens is reported, taking as reference values found at zero ageing hours. Part of the changes, however, is due to the normal process of ageing that would take place without the artificially accelerated process. Testing specimens naturally aged and of the same age (and batch) as those subjected to the humidity cycles led to results that show little discrepancy, in terms of trends, to those resulting from comparisons with the data obtained at zero hours.

It has been recognized that the main reason for irreversible loss of strength of polymer mortars subjected to humid environments is the localization of water at the resin–aggregates interface [20]. The water, once arrived at the contact surfaces, lowers the adhesive bonds and plasticizes the polymer in the vicinity owing to the normally lower degree of polymerization of the resin in that region, an effect that depends also on the mineralogical composition of the mortar.

After each ageing cycle, macroscopic observations were made by using hand lenses and a Olympus SZ51 stereoscope; microscopic analyses were performed on thin sections taken from the interior of the coupons with a petrographic microscope Olympus VANOX AHMT3. After the experimental cycles, slices taken from the interior of the coupons were coated with gold and analyzed with a scanning electron microscope (SEM), a JEOL 330A (0.6 A, 20 kV) associated to TRACOR (EDS) microprobe. These analyses were performed on the surface of the slices, allowing enlarged views of the specific features to be interpreted and compared. The macroscopic observations helped, in all cases, to estimate the spatial phases distribution, the relationship among them, the air voids shapes and to detect very small textural features on both types of mortars. The most striking feature is the identification of a thin line contouring the border of the air voids and the changes of its configuration. The petrographic microscope allowed the interpretation of some of these particularities and the identification of grain compositions, be it a simple quartz grain or eventual mica flakes, not so uncommonly present as traces within the aggregates (sand grains). The air voids can be easily recognized, since under crossed nicols they remain dark; the contour border line, mentioned earlier, is better detected at this point, due to its lower refractive index as compared to the bulk mortar phase, as will be discussed.

3. Polyester mortar

3.1. Humidity cycles at fixed temperature

The average values of the bending stress at failure, as well as the mid-point maximum deflection at the onset of the brittle rupture recorded in three point standard bending tests are shown in Table 3.

Some initial fluctuation of the values of ultimate bending strength was observed, tending to a slight decrease at the latest stage of the cycles. The average values of compressive strength and ultimate compressive strain, after the humidity cycles, as well as the values of the same quantities obtained from coupons of the same age that underwent no accelerated process are seen in Table 4. The decrease of strength, due to the humidity cycles, becomes detectable only past 5000 h, while the ultimate strain after the humidity cycles is considerably smaller than on coupons naturally aged. The fact that the temperature of 40 °C is well below the HDT of the polyester resin used accounted also for the relatively small differences detected.

The cause of the fluctuations is not established, and they appear to take place independently of any physical or chemical change due to the humidity cycles. The statistical scatter of the 10 sets of three results of the tests may account for the recorded changes, but some additional studies are thought necessary to ascertain if some of the changes are associated with further curing of the resin along time.

Under the stereoscope, Fig. 1a the samples exhibit a good definition of their components and all three elements are well identified; the mineral grains are dispersed through the polyester resin where the pore spaces show a round contour. At 1000 h, ''signs'' of an eventual modification of the resin consistency are observed; a thin line delineates the inner contour of the pore; at 3000 h this ''border line'' is a very distinct feature. When thin sections of the coupons are observed under the petrographic microscope, Fig. 1b, grains are identified, as in any rock, but the resin which behaves as an isotropic material (dark under crossed

Table 3
Three point bending tests after humidity cycles – polyester mortar

Ageing (h)	Failure bending strength (MPa)	Midpoint deflection (mm)
0	20.0	0.87
1000	18.4	0.77
3000	19.7	1.04
5000	17.0	0.73
10 000	18.8	0.86

Table 4
Compressive strength and strain after humidity cycles compared with values found on coupons of same natural age

Polyester mortar				
Time (h)	Strength (MPa)		Strain	
	Artificial	Natural	Artificial	Natural
0	76.6	76.6	0.0292	0.0292
1000	76.1	76.1	0.0278	0.0278
3000	78.8	76.6	0.0261	0.0277
5000	78.3	77.2	0.0263	0.0323
10 000	72.0	76.0	0.0288	0.0301

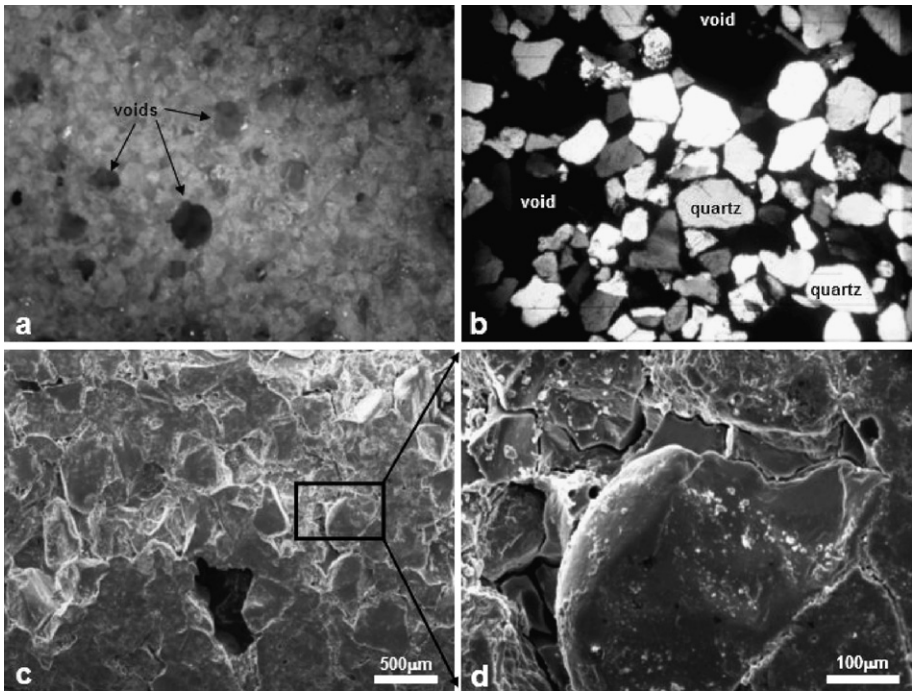

Fig. 1. Images of polyester mortars after 3000 h humidity cycles; (a) stereoscopic, (b) microphotography (x-nicols), (c) and (d) SEM images (35× and 200×, respectively).

nicols) shows clearly that the thin contour line observed in the inner part of the air voids is visible and suggests to represent a stage of plasticity of the resin, causing the material to change its density and as consequence, its refractive index.

SEM images, Fig. 1c and d allow a better observation of the traces detected through other techniques as described above. At 1000 h no special feature is observed, but at 3000 h there is more definition of the contour grains and the border of air voids, as illustrated in Fig. 1a–d. SEM images are shown at different scales.

3.2. Thermal cycles at fixed relative humidity

The effects of ageing due to selected cycles of temperature, partially reported [19], are reproduced here to allow correlation with their petrographic and SEM studies reported in this paper. The average effects on bending and compressive strength are depicted in Fig. 2. The compressive strength of the polyester mortar decreased 13.6% by 10 000 h, after experiencing almost negligible changes at the previous times of measurement. Nonetheless, the trend is one of initial increase of strength, until approximately 3000 h and decrease after 5000 h. The bending strength was little affected until 5000 h, oscillating around 24 MPa, reaching a slightly higher value at 5000 h, when it started to decrease to a value of about 22% less at 10 000 h.

Samples submitted to temperature cycles present slight differences. The three elements are well defined, grains, matrix (resin) and air voids; the distinct thin border line

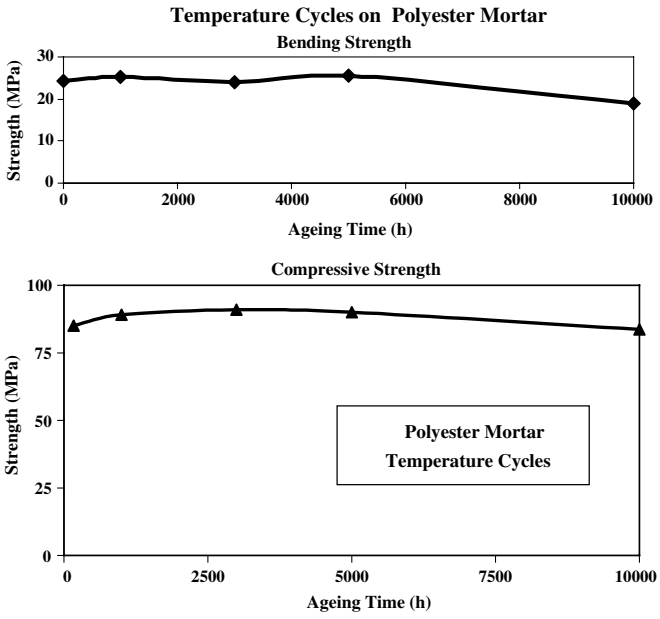

Fig. 2. Effects of temperature cycles (12 h at 20 °C, followed by 12 h at 50 °C) on bending strength and compressive strength of polyester mortar.

on the air voids is visible at 1000 h and becomes a striking feature (a wider line) at 3000 h cycles, mainly when the observation is made through the stereoscope. At 3000 h, voids are partially filled with small non-identified particles, possibly due to ''cracking'' of the void rim on the surface exposed to high temperature. The borders are delineated, both features being well defined under the SEM observations; under the petrographic microscope no specific

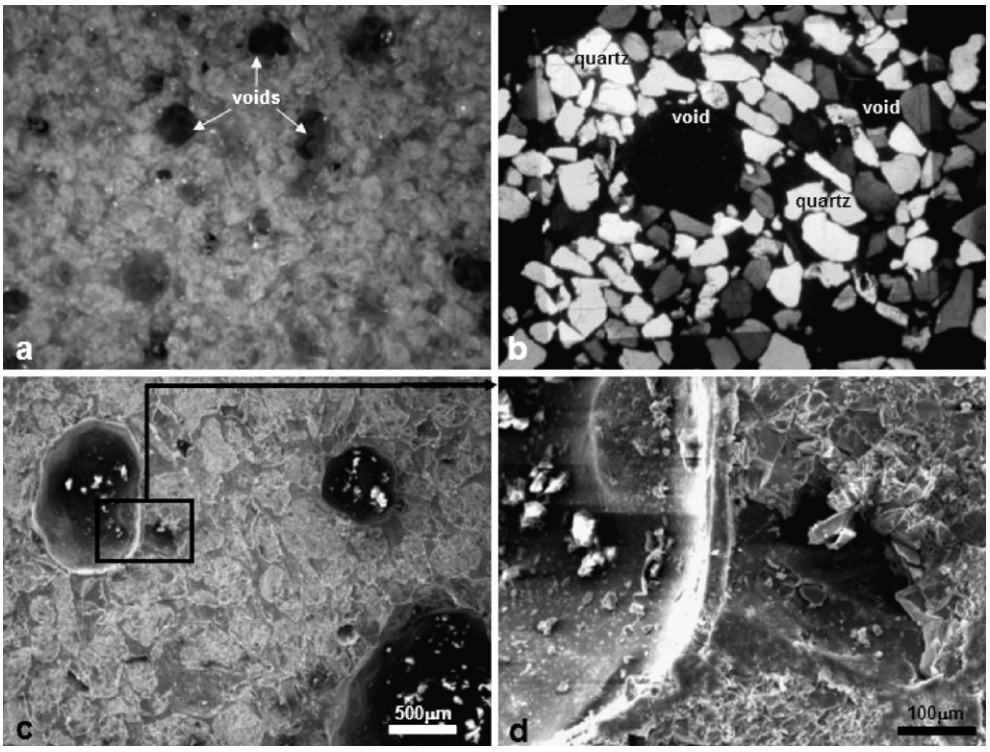

Fig. 3. Polyester mortar effects of temperature cycles at 3000 h. (a) Stereoscopic image; (b) microphotography (x-nicols); (c) and (d) SEM images (35× and 200×, respectively).

feature is detected. Fig. 3a–d illustrates these textural observations.

3.3. Humidity and temperature versus salt spray

Salt fog spray, with salinity provided by 50 g of NaCl per litre of water, i.e. approximately twice the actual sea salinity, was cyclically imposed on the prisms (8 h at 98% humidity followed by 16 h drying, at 35 °C) in order to accelerate the visibility of the effects and results were recorded for 10 000 h as described before. The same type of salt fog spray cycles led to mechanical strength results described in [21] and partially excerpted in Table 5 to allow comparison of the effects of relative humidity and temperature cycles. Not unlike previous trends, under salt fogging the bending strength of polyester mortar shows an initial gain, followed by a decrease until 10 000 h, when the deterioration exceeds 30%, a decrease much more pronounced than due to the previous type of cycles. The compressive strength displays early fluctuation of values, a 7% decrease at 3000 h and a slight recovery thereafter.

Textural differences exhibited in polyester mortar during humidity, temperature and salt spray cycles are displayed in Fig. 4a–c. The individualization of the components is more noticeable on the humidity and temperature cycles, while mortar and sand grains contours appear as a quite homogeneous matrix in the salt fog cycles. The "dust" deposit on the interior of air voids which appear on the temperature cycle, as mentioned before, is distinct on the image of Fig. 4b.

Table 5
Effects of salt spray cycles on bending and compressive strength polyester mortar

Time (h)	Compression (Mpa)	Bending (Mpa)
0	85.2	24.2
168	94.9	26.6
1000	95.6	25.0
1344	96.4	23.2
3000	89.0	22.7
5000	89.7	17.1
10 000	90.5	16.5

4. Epoxy mortar

4.1. Humidity cycles at fixed temperature

The modifications recorded on the compressive failure strength and ultimate strain of the epoxy mortar under the same cycles of moisture is shown in Tables 6 and 7. The tabulated values contrast the mechanical characteristics of artificially aged prisms with those of prisms maintained at room temperature (22 °C) and humidity (RH60%) and of the same age.

Naturally aged specimens do not show great variations of strength, with an average of 85.3 MPa, and a maximum deviation of 2%. Artificially aged specimens show an initial

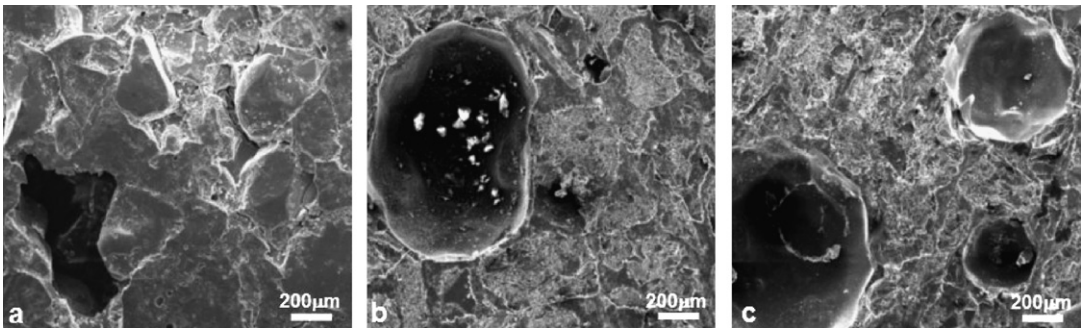

Fig. 4. SEM images (75×) of polyester mortar. (a) Humidity and (b) temperature cycles at 3000 h. (c) Salt fog cycles at 1000 h.

Table 6
Average bending characteristics after humidity cycles – epoxy mortar

Aging time (h)	Failure strength (MPa)	Midpoint deflection (mm)
0	33.6	0.86
1000	33.3	1.12
3000	31.8	1.00
5000	27.8	0.72
10 000	23.6	1.55

Table 7
Compression characteristics after humidity cycles – epoxy mortar

Ageing time (h)	Strength (MPa)		Strain	
	Artificially aged	Naturally aged	Artificially aged	Naturally aged
0	85.3	85.3	0.0182	0.0182
1000	85.6	–	0.0179	0.0236
3000	88.5	83.4	0.0205	0.0191
5000	84.3	87.0	0.0179	0.0182
10 000	61.4	85.5	0.0174	0.0173

growth of strength, perhaps due to post-curing at 40 °C and plasticization of the resin matrix caused by moisture transport, followed by accentuated degradation of compressive strength when those initial, beneficial aspects disappeared.

Data on changes of bending characteristics of the epoxy mortar are summarized in Table 6. The results, graphically displayed in Fig. 5 for both quantities, show an accentuated degradation of bending tensile strength for the epoxy mortar at the later stages, with a decrease that reaches 30% at 10 000 h, almost doubling the loss of 18% verified at 5000 h. Failure load at 10 000 h is approximately 70% of the failure load at zero hours, but the ultimate deflection is almost double revealing an important decrease of *bending stiffness*.

Average compressive strength did not show appreciable changes until 5000 h, but there was significant reduction from 5000 to 10 000 h.

Compression testing specimens naturally and artificially aged (of the same batch) showed, in this case, an almost constant compressive strength for the unaged coupons, thereby leading to comparisons that show little discrepancy

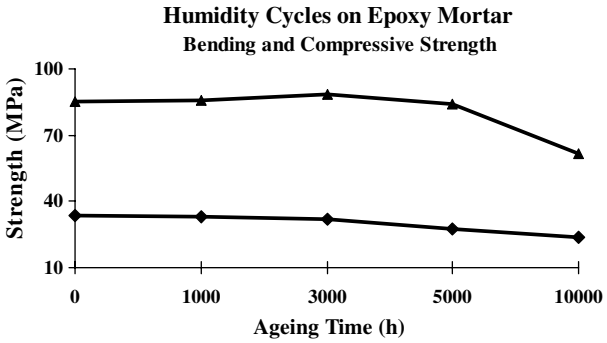

Fig. 5. Effects of humidity cycles on bending (♦) and compressive strength (▲) of epoxy mortar.

if made with the data obtained at zero hours or at the same age as the artificially treated.

Similarly to what was analyzed for the polyester mortar, observations were carried out on the samples surfaces and also through petrographic microscopy. The stereoscope images define air voids with more irregular contours and showed that the resolution of grains is fair at 1000 h, but well delineated at 3000 h; at 5000 h this definition is not so visible; on the contrary, petrographic microscopy provides better images of the border line defining the voids, since they start appearing at 1000 h and become very striking at 3000 and 5000 h (Fig. 6a and b). SEM images (Fig. 6c and d) show that the resolution between contour grains and the mortar is not clear until 3000 h, but some pore spaces get linked, as shown in Fig. 6c; at 5000 h air voids borders are better defined.

4.2. Thermal cycles at fixed relative humidity

The results for bending and compressive strength are displayed in Fig. 7. The compressive strength showed alternating slight changes until 5000 h that can hardly be explained by scatter that, for 1000, 3000, 5000, 10 000 h was respectively 2.8%, 1.9%, 1.2% and 2.4% of the average values. A subsequent marked decrease, over 30%, at 10 000 h is noticed. The bending strength showed a marked initial decline of strength from 0 to 1000 h, kept fairly

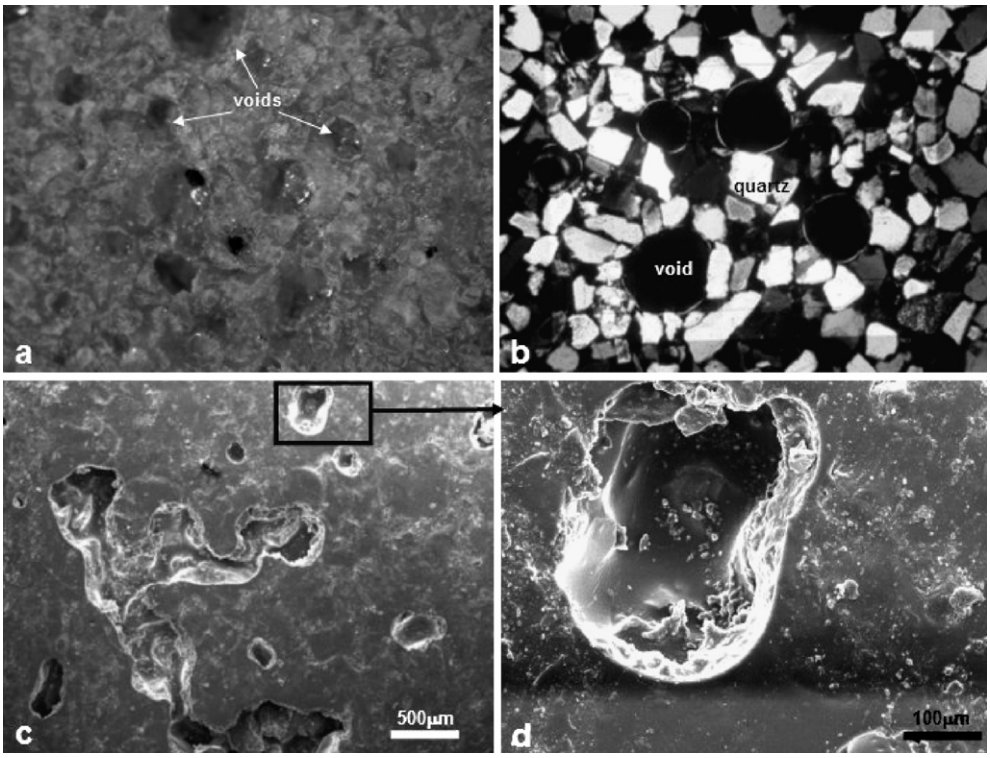

Fig. 6. Images of epoxy mortars after 3000 h humidity cycles; (a) stereoscopic, (b) microphotography (x-nicols), (c) and (d) SEM images (35× and 200×, respectively).

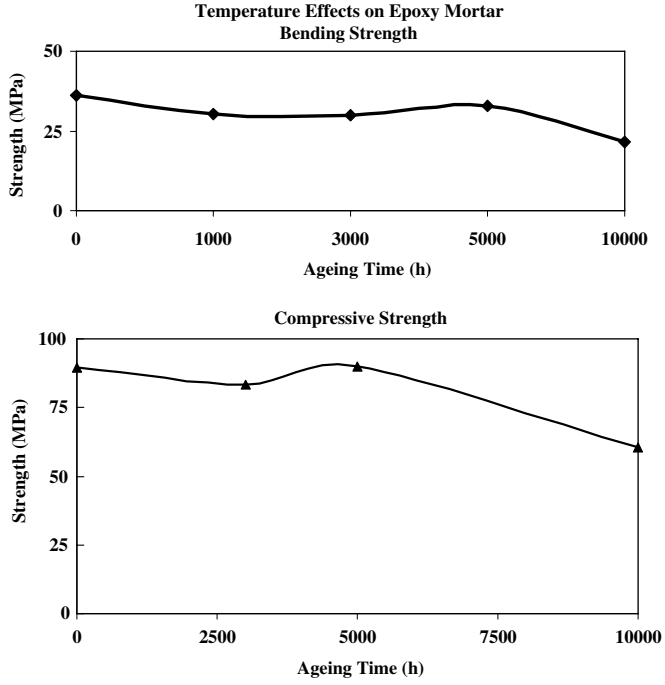

Fig. 7. Epoxy mortar. Effects of temperature cycles on average compressive and bending strength.

constant until 3000 h, to increase slightly till 5000 h and show accentuated downgrade of about 40% at 10 000 h.

Observations on sample surfaces showed irregular pore contours as if crystals grew inside the air voids; after 3000 h the slight thin line could be observed on thin sections through the petrographic analyses; the contour line turns more visible after 5000 and 10 000 h. Fig. 8 are illustrations of these textural features at 3000 h cycles. SEM images allow a better view of the irregularities displayed on the border and inside the voids.

4.3. Humidity and temperature versus salt spray

Average values from mechanical tests on the epoxy coupons, after the predefined salt spray cycles, are summarized, both for the compressive and bending strength, in Table 8.

The results show that this type of weathering requires particular attention and, possibly, a change of composition of epoxy mortar for structural applications likely to undergo similar conditions, due to the substantial loss of tensile bending strength recorded. Unlike the bending strength of polyester mortar, no initial gain of strength was recorded, possibly because the initial post-curing at 80 °C was more effective for the epoxy mortar that has a lower heat distortion temperature [18]. Actually, the epoxy mortar exhibited a monotonically decrease of strength that reached more than 50% at 10 000 h.

SEM images illustrate some of the differences that humidity, temperature and salt spray cycles cause in the epoxy mortars, as displayed in Fig. 9a–c. Similarly to what was observed in the polyester mortar, when samples are submitted to the salt fog cycles there is a lower resolution

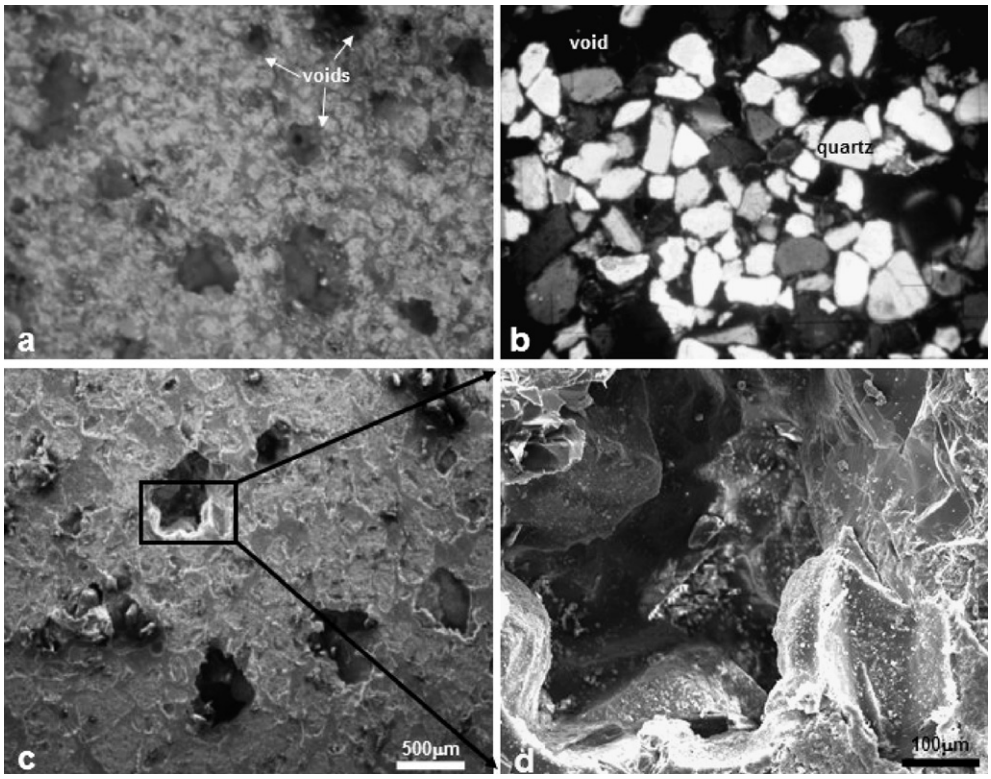

Fig. 8. Epoxy mortar effects of temperature cycles at 3000 h. (a) Stereoscopic image; (b) microphotography (x-nicols); (c) and (d) SEM images (35× and 200× respectively).

Table 8
Effects of salt spray cycles on bending and compressive strength of epoxy mortar

Aging time (h)	Compressive strength (MPa)	Bending strength (MPa)
0	89.5	36.1
168	88.4	33.0
1000	86.9	30.3
1344	85.7	28.6
3000	77.1	26.1
5000	73.1	21.4
10000	67.0	17.3

between the mortar and the sand grains than when exposed to the humidity and temperature cycles. In addition, unlike the case of polyester mortar no "dust" was observed, possibly due to the different behaviour of the epoxy submitted to a temperature comparatively higher than its HDT.

5. Summary and final remarks

The study allowed comparison of bending and compression strength of an epoxy and a polyester mortar made with resins used currently in construction, along a period of 10000 h under artificially imposed severe environmental conditions. Features of the changes that take place at microscopic scale were observed, described and correlated with length of time of their duration and type of artificial ageing (humidity, temperature and salt fogging cycles).

– During the earlier hours of artificial ageing of polyester mortar under humidity ageing, no significant change of

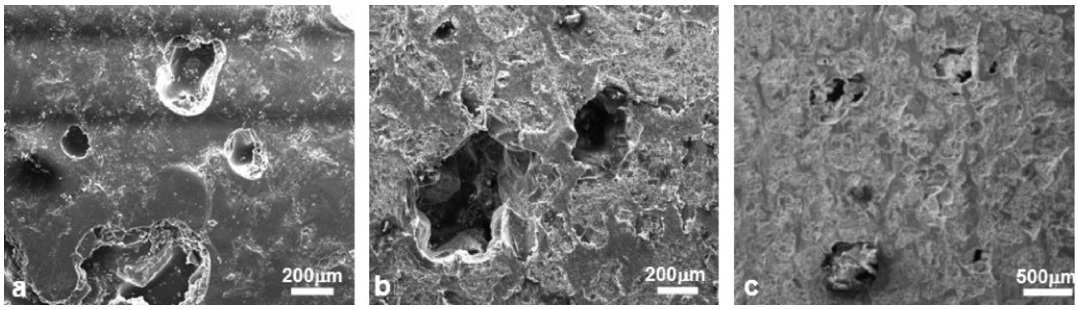

Fig. 9. Epoxy mortar. (a) Humidity, (b) temperature cycles at 3000 h and (c) salt fog cycles at 1000 h.

mechanical strength is apparent when compared with results from naturally aged coupons.
- Textural features observed on the coupons surfaces and on microscopic images of polyester mortars are detectable at 1000 h and accentuated starting at 3000 h, with both humidity and temperature treatment. The same features become pronounced, with the epoxy mortar, at 3000 h and more striking at 5000 h and these data are tentatively correlated, below, with the evolution of the mechanical characteristics. It is worth reminding that in both situations the "starting point" of the reduction in mechanical properties is simultaneous with the appearance and "accentuation" of the "line" or "rim" in the contour of the voids, which could be accounted for a slight change in the mortar viscosity (the rim is detected because there is a change in the mortar refractive index at that place, compared to the other parts of the coupon).

It is thought that cure of the resin is completed in the first part of the process. In addition, some plasticization occurs, induced by temperature and moisture sorption that may lower the vitreous temperature. Those changes explain observed changes of microstructures and counter the process of degradation of mechanical strength, but the latter becomes predominant beyond a time limit that depends on material and type of ageing being imposed.

- A strong deteriorating effect of humidity cycles on the strength of epoxy mortar, reaching 30% at 10 000 h, was identified. The bending deflection almost doubles after those cycles, revealing a significant degradation of the bending *stiffness*.
- Salt fog spraying cycles caused the most severe effects on strength reduction.
- The initial increase of compressive strength, especially in polyester mortar may again be linked to initial further curing of the resin, and to the better distribution of stresses associated with initial plasticization of the matrix that allows better stress distribution among the components of the mortar.

The essence of the results for salt fog cycles can be summarized as follows:

(a) Decrease of the bending strength, reaching 52% in epoxy and 32% in polyester, at 10 000 h.
(b) Initial behavior of the polyester mortar, showing higher strength after enduring 1000 h of salt fog spray cycles is interpreted as above. Fluctuations of ultimate strength took place also under humidity cycles and natural ageing, possibly as a result of further curing and of ±5% scattering present in the results for bending.
(c) Having higher initial strength and lower stiffness, the epoxy mortar showed stronger relative degradation of properties than the polyester mortar.

This fact may be explained by the lower HDT of the epoxy resin (34 °C) compared with polyester resin (50 °C) in line with findings reported in [14], since the environmental temperature for salt fog cycles was 35 °C.

Finally, correlating degradation of mechanical properties with physical and/or chemical changes of these materials is an important step. Analyses of data coupled with microscopic studies appear to be a promising path to pursue.

The composition of the aggregates and the distribution of the size of their grain, the importance of the type of resins, the amplitudes and mean values of the imposed cycles, as well as the consequences of accelerated ageing under imposed stress field are important areas still with unresolved questions that need to be examined in the future.

Acknowledgements

The authors extend thanks to Ms. Cristina Ribeiro, researcher at INEGI (Porto) a partner institution in several projects, who prepared part of the mortar coupons and made several helpful suggestions. Research was partially funded by Fundação para a Ciência e Tecnologia, under Project POCTI/ECM/36113/1999.

References

[1] Proshin AP, Vtorov BB. Polymer mortars for building construction durability increase. Internationale Baustofftagung (14.ibausil), Band2, p. 831–6, Weimar, p. 20–3, September 2000.
[2] San José JT, Vegas I, Ramirez L. Macroscopic properties in relation to polymer concrete internal structure. In: Proceedings of the international conference on composites in construction, Balkema, Porto, Portugal. October 2001. 2001, p. 83–8.
[3] Mebarkia S, Vipulanandan C. Properties and water diffusion in polyester polymer concrete. J Eng Mech 1995;121(12):1359–65.
[4] Ohama Y, Kobayashi K, Takeuchi K, Kawata K. Chemical resistance of polymethyl mehacrylate concrete. Int J Cem Comp Light Mass Concr 1986:86–91.
[5] Chawalwala AF. Material characteristics of polymer concrete. Technical Report, University of Delaware Center of Composite Materials, 1999.
[6] Ribeiro MCS, Tavares CML, Ferreira AJM, Paulo AMC, Silva AG. Mechanical behaviour of degraded polymer concrete. In: Proceedings of international conference on composites in construction, Balkema, Porto, Portugal, 2001. p. 83–8.
[7] Faitel'son EA, Korkhov VP, Aniskevich AN, Starkova OA. Effects of moisture and stresses on the structure and properties of polyester resin. Mech Comp Mater 2004;40(1):57–66.
[8] Tavares CML, Ribeiro MCS, Ferreira AJM, Guedes RJC. Creep behaviour of FRP-reinforced polymer concrete. Compos Struct 2002;57:47–51.
[9] Cano M, San José JT, Ramirez JL. Polyester polymer concrete: fundamental hardened and fresh state. In: Proceedings of the second conference international sur les Matériaux composites in architecture, construction et genie civil – ARQUIMACOM'98, Bordeaux, France, 1998. p. 191–200.
[10] Letsch R. Behaviour of polymers and polymer mortars at constant and changing temperature. In: Proceedings of the 10th international congress on polymers in concrete, Honolulu, Hawaii, 2001.
[11] Letsch R. Polymer concrete with metallic and non-metallic reinforcement. In: 10th International congress on polymers in concrete, Honolulu, Hawaii, May 23–25, 2001.

[12] Letsch R. Polymer concrete properties and structural application. In: International conference on polymers in concretes, Mortars and Asphalts, Porto 9–11 October, 2002, p. 9–14.
[13] Pardo A, Maribona, Urreta J, San José JT, Muguerza A. Influence of dosage and temperature on mechanical properties of polymer concrete. In: Proceedings of the eighth international congress on polymers in concrete, Oostende, Belgium, 1995.
[14] Oshima M, Sato R, Hayashi F, Koyanagi W. 2001. Thermal properties and temperature dependency of mechanical properties of resin concretes for structural use. In: Proceedings of the 10th international congress on polymers in concrete, Honolulu, Hawaii, 2001.
[15] Ribeiro MCS, Reis JML, Ferreira AJM, Marques AT. Thermal expansion of epoxy and polyester polymer mortars—plain mortars and fibre-reinforced mortars. Polym Test 2003;22:849–57.
[16] Diamond S. The microstructure of cement paste and concrete – a visual primer. Cem Concr Comp 2004;26:919–33.
[17] RILEM Technical Committee. Method of making polymer concrete and mortar specimens. In: Symposium on properties and test methods for concrete–polymer composites; proceedings, Oostende-Belgium, TC-113, 1995. PC2, 1995, p. 129–32.
[18] Ribeiro MCS, Nóvoa PR, Ferreira AJM, Marques AT. Flexural performance of polyester and epoxy polymer mortars under severe thermal conditions. Cem Concr Comp 2004;26:803–9.
[19] Silva Manuel AG. Influence of environmental ageing on properties of polymeric mortars. J Mater Civil Eng 2004;16(5):461–8.
[20] Maksimov RD, Jirgens LA, Plume EZ, Jansons JO. Water resistance of polyester polymer concrete. Mech Comp Mater 2003;39(2): 99–109.
[21] Silva Manuel AG, Silva Zenaide CG. Degradation of mechanical characteristics of some polymeric mortars due to ageing, ACI Mater J, in press.