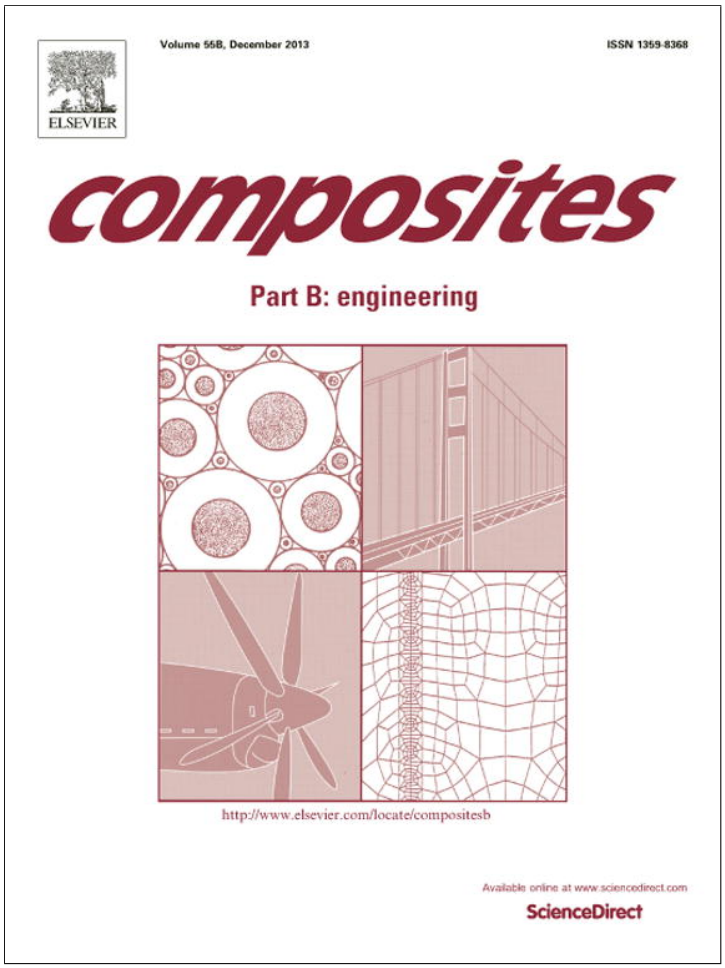

Composites: Part B 55 (2013) 203–207

Contents lists available at SciVerse ScienceDirect

Composites: Part B

journal homepage: www.elsevier.com/locate/compositesb

Self-healing mortars based on hollow glass tubes and epoxy–amine systems

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ARTICLE INFO

Article history:
Received 25 May 2012
Received in revised form 31 May 2013
Accepted 12 June 2013
Available online 24 June 2013

Keywords:
Self-healing
Repair
Hollow glass tubes
Epoxy system

ABSTRACT

In the present work key parameters of different epoxy systems (such as viscosity and gel time) were evaluated to be used as healing agents when were included in a cement matrix. Epoxy systems were encapsulated in hollow glass tubes and were introduced in a mortar matrix. Samples were preloaded under three point bending in order to create a crack and release the healing system. After that, they were loaded to measure the residual strength and estimate the healing efficiency. The influence of temperature and the volume of the glass tubes were examined. Regarding the healing efficiency, a higher temperature led to an improvement of autogenous healing of the mortar matrix and a higher degree of crosslinking of the healing agent. For the studied systems, the use of glass tubes with smaller diameter containing the healing system seemed to be better in order to maintain the mechanical properties of the mortar-based composite.

1. Introduction

Concrete can bear high compressive stresses; however, its tensile strength is limited. In the tension zone, concrete will always exhibit cracks. In the initial stage, this causes no problems relating to the load bearing capacity but it does potentially generate durability problems. Aggressive liquids and gasses may enter these cracks and they may cause concrete degradation. Because of such cracking, aggressive substances may reach the steel reinforcement and induce corrosion that may lead to further concrete damage and possibly structural failure.

The development of self-healing cementitious composites is a relatively new area of research. It is based on the natural ability of hydrates to heal cracks over time (autogenic) and by an artificial means of crack repair that are man-made inclusions (autonomic) [1].

A distinction was made between self-healing and self-sealing. In the former the original strength of the concrete is completely recovered, in contrast to the latter where leaking cracks are closed but no strength recovery is obtained.

Several types of healing agents have already been tested in research on self-healing of concrete, but to our knowledge no resin system especially designed for this type of application (i.e., low viscosity, insensitivity to mix ratio, rapid cure under ambient conditions and unlimited shelf-life) has been reported.

Dry and McMillan [2] have used a three-part methylmethacrylate release system to repair cracks in concrete. Van Tittelboom et al. [3] tested a two-component polyurethane foam as a healing agent, which had commercial applications in making cracks watertight and cutting off running water. Nishiwaki et al. [4] used a low viscosity epoxy resin filled organic film pipe that melts at temperatures indicative of a high gauge strain to create a self-healing system.

Several types of reservoir suitable for a healing agent have been used: microcapsules [5], ceramic tubes [3], hollow porous fibers and hollow glass tubes [6,7] It is important to consider the geometry, dimension and concentration of this reservoir in order to minimize their effects on the mechanical properties of the matrix. According to Li et al. [7] the crack width of the matrix should be limited to less than the inner diameter of the glass fiber for effective actuation. So, it is critical that the tensile crack width be controlled, and it must be limited to tens of micrometers. Otherwise, very large hollow glass tubes will be needed, which in turn will affect negatively the mechanical properties of the composite. Hunger et al. [8] studied the direct mixing of microencapsulated polymers with concrete and its influence on the material properties. They found that the porosity of the samples was increased with increasing capsules content and, consequently, a significant loss of compressive strength was observed with a capsule content up to 3 wt.%.

There are different methods of measuring self- healing, which makes quantifying the extent of healing within the material and comparing it with other systems rather difficult. Zhong and Yao

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1359-8368/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compositesb.2013.06.023

[9] estimated the damage degree by the decrease in ultrasonic pulse velocity (UPV) before and after loading, and the self-healing effect was deduced from the strength increment after self-healing. Several works have measured the regain in mechanical properties to estimate the self healing properties [5,10], while others focused on the decrease in water permeability or on the results of ultrasonic measurements [11].

The present work is divided into two parts. First, the properties of different healing agents were analyzed in order to get key parameters for healing properties. In particular, a systematic study of the chemical system being used as the healing agent was performed taking into account the gel time and viscosity. The second part was accomplished using the best candidate healing agent from the first part via examining the self-healing of a cementitious matrix under three point bending. Hollow glass tubes with two different volumes and different storage temperatures were investigated.

2. Experimental

2.1. Healing agent

Different epoxy resins were tested as healing agents. Considering that the healing agent will be stored for a long time, a two component epoxy which is chemically stable along the time was chosen.

Three types of commercial epoxy resins with different chemical structures were considered as healing agent: diglycidyl ether of bisphenol A (DGEBA GY250 from Ciba Geigy), with an aromatic structure and equivalent weight of 189.9 g/eq; Araldite CY 184, with a cyclo-aliphatic structure and equivalent weight of 161.5 g/eq; butanodiol diglycidyl ether (BDGE, from Distraltec S.R.L.), with an aliphatic structure and equivalent weight of 114 g/eq. Triethylentetramine was used for all of the epoxies as the curing agent (from Distraltec S.R.L. and equivalent weight of 34.5 g/eq). Fig. 1 shows the structure of each component.

Epoxy resins were characterized through Differential Scanning Calorimeter (DSC – Perkin Elmer Pyris 1). For dynamic DSC scans, samples (5–8 mg) were sealed in aluminum pans, and heating up to 300 °C from room temperature at 10 °C/min under nitrogen atmosphere. It was repeated three times for each sample and the reported results and the average values were reported.

The viscosity measurements were carried out using a rotation viscosimeter (NiRun Instruments – Shanghai Technology Co. SNB-2) at a constant shear rate of 4 Hz. The measurements were done in a thermostatic cell at a constant temperature (15 ± 0.1 °C). It was repeated 5 times for each sample and the average values were reported.

Gel times were determined by submerging a glass container with a small sample (50 mg) into a controlled thermostatic bath at different temperatures. It was repeated three times by each condition and the reported results are the average values.

2.2. Self-healing properties

Hollow glass tubes were used to carry the healing agent. Glass tubes possess a high brittleness, so they easily break whenever cracks appear in the mortar matrix. Hollow glass tubes with two different volumes were evaluated. An overview of the tubes dimensions is given in Table 1.

The methodology employed to prepare the healing system was as follows: First, the hollow tubes were sealed with an adhesive at one end. Then, half of the tubes were filled with epoxy resin and the other half with the curing agent and acetone (to complete

Table 1
Dimensions of the tubes used for encapsulation of the healing agent.

Code of tube	Internal diameter (mm)	Length (mm)	Volume (mm^3)	Wall thickness (mm)
V_1	1.2	75	84	0.3
V_2	2.0	75	235	0.7

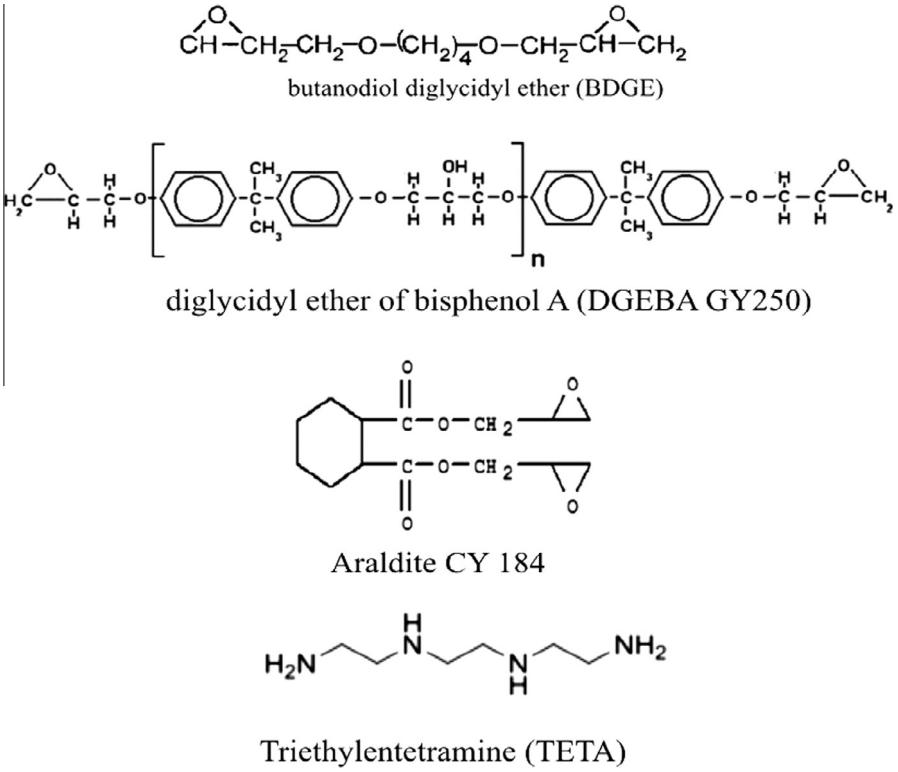

Fig. 1. Scheme of the compound chemical structure.

the volume), injected via a syringe with a needle. After that, the other end was sealed with an adhesive. The two tubes (one with epoxy and the other with the curing agent) were bonded with polymethylmethacrylate, finalizing the preparation of the healing system.

Mortar with a water to cement ratio of 0.5 and a sand to cement ratio of 3 was made by using ordinary Portland cement. It was necessary to include a plasticizer (Pozzolith 390N, supplied by BASF S.R.L.) in order to have adequate workability. Prismatic moulds of 40 mm × 40 mm × 160 mm were used. First, 10 mm of mortar layer was poured into the moulds. When this layer was compacted by means of vibration, three reinforcement bars (Wirand® FF3, from Maccaferri) and two pairs of the healing systems (with one tube of each couple filled with the epoxy resin and the other tube filled with the curing agent) were placed on top of it. Afterwards, the moulds were completely filled with mortar and revibrated. After casting, all moulds were placed in an air-conditioned room with a temperature of 20 ± 2 °C and a relative humidity of 90 ± 10% for a period of 24 h. After demoulding, the specimens were stored in the same conditions for 6 subsequent days.

The reference samples (R) and self-healed samples (SH) were prepared in the same way as described above. The unique difference between them was that the reference sample had the hollow tubes without the healing agent. The sample configuration is schematically presented in Fig. 2.

Each mortar prisms were preloaded under three point bending (following EN standard 196-1:2005 recommendations) until the load had suddenly dropped 50%. The first peak load was taken as the preloading peak, F_p (Fig. 3A). After that, a small crack has been observed in the sample. Then, samples were stored at two conditions for 48 h: 20 °C and 60 °C. After that, all prisms were loaded until the samples were separated into two halves. The load–displacement curve can be divided in two parts: the first one presents a linear increasing until a peak value is reached, F_l (Fig. 3B). After that, the load decrease until a low and approximately constant value was reached with an important increase of the displacement. The last part of the curve is associated with the pull out of the steel fibers. The residual strength (R_s) was defined as the ratio between F_l and F_p (Eq. (1)).

$$R_S = \frac{F_1}{F_p} \tag{1}$$

The healing efficiency (HE) was defined as:

$$HE = \frac{R_S^{SH} - R_S^R}{R_S^R} \tag{2}$$

where R_s^{SH} and R_s^R are the residual strength of the self-healed samples (SH) and the reference samples (R), respectively.

The following code was used to identify the different samples: the first two characters indicated the glass tube volume (V_1 or V_2), the next number indicated the temperature at which it was stored after preloading (20 °C or 60 °C), and the last letters were either R or SH, depending on whether it was a Reference sample or a self-healing sample. Five samples for each condition were tested; and the average values were reported.

3. Results and discussion

3.1. Healing agent

Each epoxy resin was mixed with the curing agent in the stoichiometric ratio. Fig. 4 shows the results of non-isothermal DSC analysis for the different chemical systems studied.

There are two important features in these curves: BDGE, the aliphatic epoxy displayed the higher exothermic reaction (area under the peak curve). Considering the onset temperature of the reaction peak, the BDGE presented the lower value. Both characteristics are shown in Table 2.

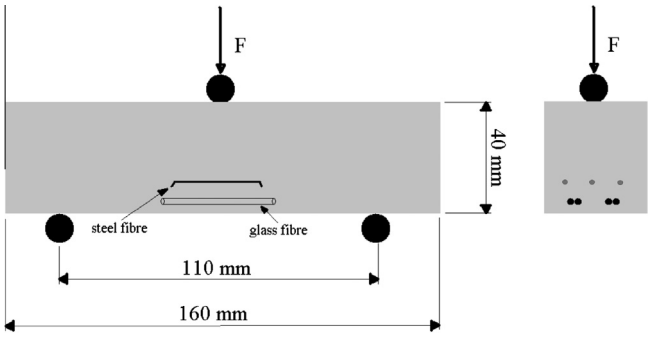

Fig. 2. Scheme of the configuration used for the self-healing process.

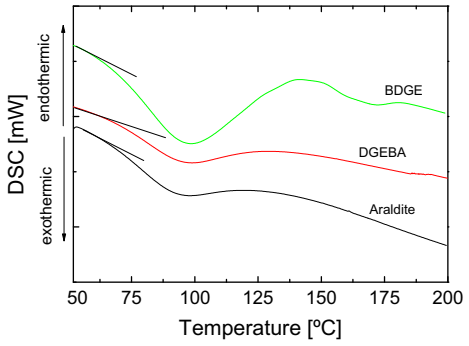

Fig. 4. DSC of the different system in stoichiometry ratio.

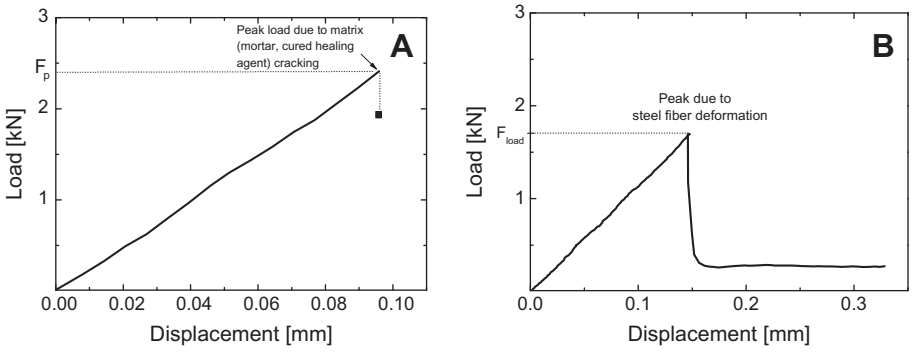

Fig. 3. Typical load–displacement curves obtained during the self-healing test. (A) preloading curve, (B) loading curve.

Table 2
Heat reaction from non-isothermal DSC studies.

Reactive system	Average $\Delta H_{reaction}$ (J/g)	Onset temperature (°C)
BDGE	481 ± 13	56
DGEBA	411 ± 12	63
Araldite	354 ± 9	64

In order to get an efficient recovery of the mechanical properties, the healing agent should have the ability to travel the distance between the hollow glass tube and the crack in a short period of time. Having this in mind, the viscosity is a key parameter (which represents the resistance to flow). Table 3 shows the viscosity of the different systems. DGEBA presented the highest viscosity. It was so high that it was difficult to encapsulate this resin within the hollow tubes. While Araldite showed a lower viscosity respect to DGEBA, it was still high as a consequence of its chemical structure and molecular weight. Among the available systems, the best candidate to act as healing agent seemed to be the BDGE system. The low viscosity of BDGE and TETA would favor the diffusion into the crack. Table 3 also includes the equivalent weight of the different systems in order to estimate the theoretical stoichiometry ratio. The highest degree of crosslinking will be reached if one equivalent weight of epoxy reacts with one equivalent weight of H from amine (stoichiometry ratio). It is highly probable that the system does not react with the stoichiometry ratio within the concrete matrix. So, it is important to study the properties of the system when both components are mixed at different proportions.

Table 4 shows the gel time for such different proportions. In both concentrated and diluted conditions of TETA (i.e. 1:1 and 10:1) the gel time remained greater than 24 h, so it was considered that the system did not reach the gel point. The 7:1 relationship resulted in a gel time greater than 15 h. The lower gel times corresponded to samples whose mixing ratios were 2.5:1 and 4:1. The results were expected considering that the stoichiometric ratio can be determined from the relationship of equivalent weights of epoxy and curing agent. Saleh et al. [12] studied the mechanical properties of samples prepared with different curing agent/resin ratios using aliphatic and aromatic amine. They found that Young's modulus was less affected when using aliphatic amines, such a TETA, than when using aromatic amines. This dictated the kind of curing agent chosen for the present investigation.

The heat of reaction for different stoichiometric ratios of the chosen chemical system (BDGE–TETA) was determined by DSC (Table 4). The higher value of heat of reaction corresponds to 4:1 ratio.

Frequently, concrete structures are exposed to wide temperature ranges, so it is necessary to study the dependence of temperature on the kinetics of healing agents. Here, we focused on the influence of temperature and its effect on gel time. The logarithm of the gel time vs. the inverse of the absolute temperature is presented in Fig. 5. A linear dependence corresponding to Arrhenius behavior is observed. The activation energy calculated from this curve is 58 kJ mol^{-1}, which agree with the value obtained by others [13]. Using this equation, it is possible to predict the gel time given a particular temperature. It is clear that the temperature should be high enough in order to have a gel time within the healing time.

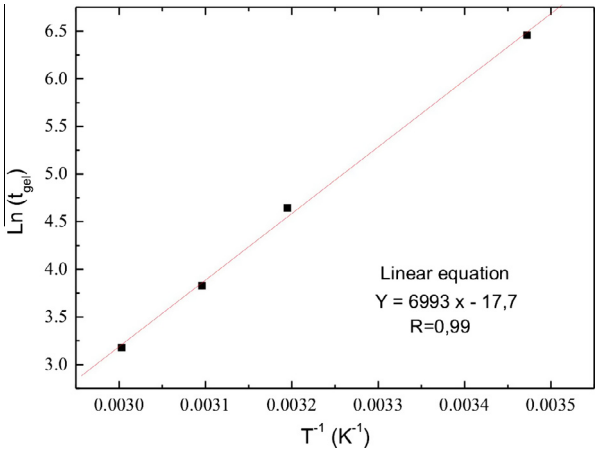

Fig. 5. Dependence of gel time with the temperature.

$$Ln(t_{gel}) = Ln(A) + \frac{E_a}{R}\cdot\frac{1}{T} \quad (3)$$

From the linear regression, the calculated pre-exponential factor A was 1.88×10^{-8} min. The gel time can be approximated by:

$$t_{gel} = 1.88 \times 10^{-8}.e^{\frac{6993}{T(K)}}\,\text{min} \quad (4)$$

3.2. Self-healing in concrete

Regarding our configuration, the residual strength of the reference samples was only due to the pull-out of steel fibers, whereas the residual strength of the self-healed samples was due to the combined effect of pull out of steel fibers and the healing produced by the filled glass tubes.

Fig. 6 shows the average residual strength of the samples containing the glass tubes stored at 20 °C and 60 °C while Fig. 7 shows the calculated healing efficiency.

As expected, for all cases the reference samples display lower values of average residual strength than those samples containing the healing agent. Comparing the reference samples stored at different temperatures (V1-20R vs. V1-60R and V2-20R vs. V2-60R), the residual strength of samples stored at 60 °C was higher because a higher temperature accelerated the effect of autogeneous healing [14].

Another feature can be done regarding the samples containing healing agents: the average residual strength of the sample stored at 60 °C was higher than that stored at 20 °C because the healing agent that could get out from the hollow glass tube reached a higher degree of crosslinking when the sample was stored at higher temperature.

Regarding the effect of the volume of the hollow glass fibers, larger volume glass tubes stored a greater quantity of healing agent and this reduced the capillary forces allowing an easier flow of the healing agent to the crack. However, the inclusion of glass tubes of larger volume (larger diameter) would have probably deteriorated the mechanical properties of the matrix. Hence, for the configuration presented in this work, smaller tube diameters seemed to be

Table 3
Properties of the different systems.

Chemical Name	Equivalent weight (g/eq)	Viscosity (15 °C, mPa s)
DGEBA	189.8	4573
BDGE	114.9	21
Araldite	161.5	2350
TETA, 70%	34.5	35

Table 4
Gel time and heat reaction for different weight mixing ratios of BDGE–TETA.

Mixing ratio epoxy:amine (gr:gr)	Heat reaction (J/g)	Gel time (h)
1:1	121 ± 7	28.4 ± 0.1
2.5:1	469 ± 12	10.4 ± 0.1
4:1	481 ± 13	10.7 ± 0.1
7:1	232 ± 6	15.1 ± 0.1
10:1	106 ± 8	29.3 ± 0.1

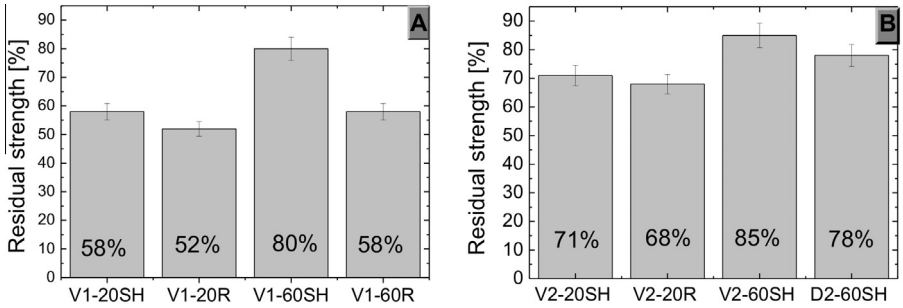

Fig. 6. Residual strength of the tested samples with glass tubes of (a) lower volume and (b) higher volume. Error bars represent standard deviation.

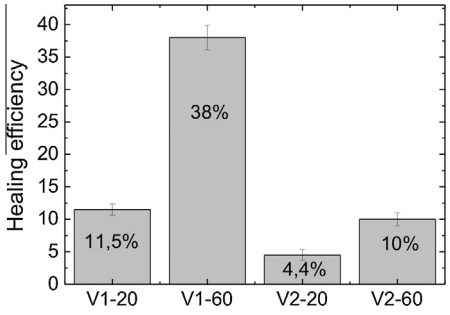

Fig. 7. Healing efficiency of the different systems. Error bars represent standard deviation.

better in order to maintain the mechanical properties of the concrete.

4. Conclusions

In the present publication the key parameters that should be taken into account in order to choose the chemical system such as: viscosity, gel time, heat of reaction, starting temperature of reaction and dependence of the stoichiometric ratio with the heat of reaction were evaluated.

Different epoxy resins were investigated as healing agent: aliphatic, cycloaliphatic and aromatic epoxy.

The aliphatic epoxy resin has found to be the best candidate for this application taking into account the viscosity and reaction temperature. For this resin, the viscosity and the temperature of reaction were the lowest while heat of reaction was the highest.

Steel fibers had to be included into the cement mortar due to the high crack propagation rate that presented the cementitious material. Regarding the healing efficiency, a higher temperature of storage led to an improvement of autogenous healing of the mortar matrix and a higher degree of crosslinking of the healing agent.

Acknowledgement

This work was supported by the Universidad de Buenos Aires, Argentina, the National Research Council of Argentina and the AnPCyT.

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