Capsules changing in brittleness due to leaching of plasticizing agents

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ABSTRACT

Although more and more researchers start to investigate the possibility to obtain autonomous repair of concrete cracks by the internal release of encapsulated healing agents, this technique will only become practically applicable if suitable encapsulation materials are developed. To serve this purpose, encapsulation materials need to be flexible at first to survive the concrete mixing process, while after concrete hardening they need to become brittle so they easily break and release their content upon crack appearance. In the current study, polymeric capsules made from ethyl cellulose were modified by four different plasticizing agents to make them become more flexible. Since the plasticizer will gradually leach out in a moist environment, the capsules will become less flexible in the course of the concrete curing process. Addition of the modified capsules during concrete mixing proved that for increasing percentages of plasticizing agent, the capsules became less fragile and could more easily survive the mixing process. Evaluation of the capsules after exposure to an alkaline solution, demonstrated that the capsules became more brittle after some time due to diffusion and hydrolysis of the plasticizing agent. However, they did not become brittle enough and on top the bond strength between the capsules and the cementitious matrix seemed not high enough to cause capsules breakage upon crack formation. This drawback together with some other shortcomings led to the conclusion that the combination of ethyl cellulose with the proposed plasticizing agents seemed not to be appropriate and will be replaced in the future by other polymeric materials and plasticizers to optimize the proposed idea.

1. INTRODUCTION

Lab-scale proof-of-concept tests have already shown that the incorporation in concrete of glass or ceramic capsules containing a healing agent is a successful technique to heal cracks autonomously [1]. However, a great disadvantage of these brittle capsules is that adding them to the concrete mixture during the mixing process is excluded. To make the process of autonomous healing practically applicable, it will be necessary to develop capsules that can withstand the mixing and casting process on the one hand and on the other hand become brittle later on so that they break and release their content as cracks appear.

2. MATERIALS AND METHODS

The polymer ethyl cellulose (EC) was selected to extrude capsules. Prior to hot-melt extrusion of the hollow tubes, EC was manually mixed with a plasticizer. Four different plasticizers were applied, i.e. triacetin (TAC), triethyl citrate (TEC), polyethylene oxide (PEO) and dibutyl sebacate (DBS). At the beginning of the experiment TAC, TEC and DBS were added to EC in a concentration of 25% w/w. Considering the first results obtained, it was decided to extrude also EC-capsules containing respectively 10% TAC and 10% PEO (w/w). The hot-melt extruded EC-capsules had an inner diameter of approximately 3 mm and an outer diameter of about 5 mm (Figure 1).

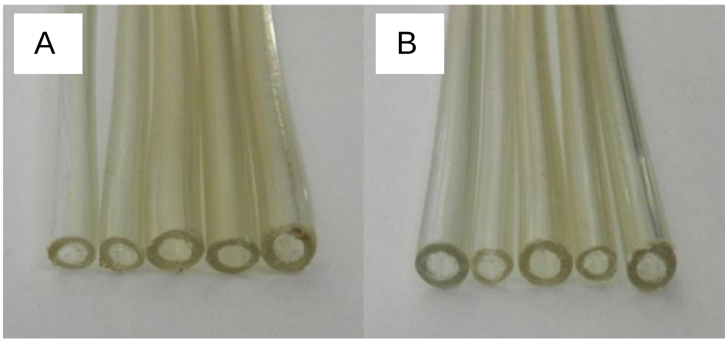

Figure 1: EC-capsules with 25% TEC (A) and EC-capsules with 25% DBS (B).

To evaluate whether the EC-capsules can survive the mixing process, capsules were added during concrete mixing. First, the extruded tubes were cut at a length of 50 mm and sealed at one end. After filling the EC-capsules with water diluted with red pigment, the other end was sealed. Limestone was expected to practice the greatest impact on the EC-capsules and was therefore selected as coarse aggregate for the concrete mixture. Every experiment consisted of ten prepared EC-capsules which were thrown in the concrete mixture during mixing. Afterwards, the concrete was spread and the amount of unbroken capsules was counted. Besides surviving the mixing process, it is obvious that the EC-capsules need to be compatible with the healing agent they will have to store. Based on satisfying results in previous studies [1], a two-component polyurethane-based agent was used. One compound consists of a prepolymer of polyurethane. The second compound is a mixture of accelerator and water that shortens the reaction time. The different types of EC-capsules were filled with these compounds. After 7 days, the EC-capsules were inspected visually. Another important question using this proposed system concerns the fact whether the plasticizer leaches out sufficiently in the concrete environment so that the capsules become brittle enough and will really break when cracking occurs. Therefore, EC-capsules were embedded in mortar prisms (40 mm x 40 mm x 160 mm) which were subjected to crack formation. Each prism contained two 50 mm long EC-capsules which encapsulated respectively the prepolymer and the accelerator of the polyurethane foam. The capsules were positioned 10 mm above the bottom surface. After curing for 7 days, the mortar prisms were cracked by means of a crack width controlled three-point-bending test. Using a linear variable differential transformer, the crack width was increased with a velocity of 1 μm/s until a crack of 0.4 mm was reached. It was then evaluated whether the healing agent filled the crack or not. Furthermore small pieces of the capsule material were subjected to differential scanning calorimetric measurements. Based on the difference between the glass transition temperature of reference capsules stored at room temperature and capsules stored during 7 days in a cementitious material, leaching out of the plasticizer could be examined. The behaviour of capsules embedded in a mortar or concrete specimen which cracks will definitely be influenced by the combination of the bond strength between the capsule and the concrete matrix on the one hand and the tensile strength of the capsules on the other hand. Therefore these values were determined for the EC-capsules and compared to the values of glass or ceramic capsules.

3. RESULTS

It was observed that mixing in of the EC-capsules with 25% plasticizer (TAC, TEC or DBS) gave good results. In all cases 9/10 EC-capsules survived the process. Nevertheless, the results of the three-point-bending tests were less satisfying. In none of the cases healing agent was detected, filling the created crack. Even when the mortar specimens were completely broken, the majority of the EC-capsules were not broken, but were pulled out of the mortar matrix. Indeed, when comparing the bond strength between the EC-capsules and the cementitious matrix with these of glass or ceramic capsules, the latter showed significant higher values (at least 65% higher for glass and 78% higher for ceramic tubes in comparison to the EC-capsules). When the results of the tensile strength tests were considered, it was noticed that the EC-capsules with 25% plasticizer needed to elongate too much before fracture of the capsules occurred. As a result of this large elongation until fracture, a crack width of 0.4 mm could never lead to rupture of the EC-capsules. Differential scanning calorimetric measurements on the EC-capsules with 25% plasticizer revealed that the glass transition temperature of the encapsulation material increased only slightly after being embedded in a cementitious matrix for 7 days. This indicated that not enough plasticizer leached out from the capsules, and therefore the capsules stayed too flexible. Another problem was noticed while observing the EC-capsules with healing agent after 7 days. The prepolymer which was embedded in the EC-capsules obtained a white colour instead of the light brown colour at the start of the experiment (Figure 2). Breaking open of the EC-capsules confirmed that a polymerization reaction already took place inside the sealed EC-capsules. The accelerator compound was still present in the EC-capsules with 25% plasticizer after 7 days, but half of the initial volume of the accelerator seemed to have disappeared (Figure 2). It may be supposed that a chemical reaction took place between the encapsulation material and the compounds of the healing agent or that the capsule walls were not tight enough to prevent premature hardening of the encapsulated healing agent.

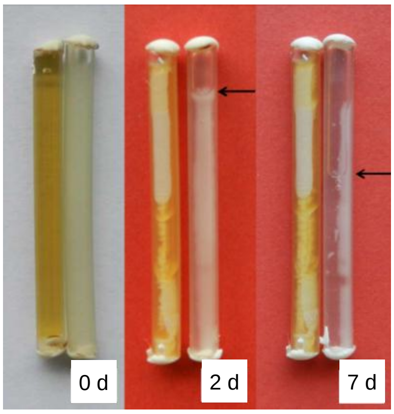

Figure 2: EC-capsules (containing 25% TEC) filled with both compounds of the healing agent in the initial state (0 d) and after 2 (2 d) and 7 days (7 d) storage. The black arrows indicate the level of the accelerator compound at the respective ages.

From these results two conclusions can be drawn. First of all when 25% plasticizer was used, the capsules did not become brittle enough after being stored for 7 days in a cementitious material. Secondly, it seemed that the EC and/or the plasticizers reacted with the compounds of the polyurethane. Therefore, it was decided to extrude new EC-capsules containing only 10% plasticizer. To compare the behaviour between EC-capsules with 25% and 10% plasticizer, TAC was again used as plasticizing agent. On the other hand, another type of plasticizer, i.e. PEO, was introduced. Therefore, also EC-capsules with 10% PEO were extruded. Mixing in the EC-capsules with only 10% plasticizer showed that in some cases more capsules were broken in comparison with the EC-capsules containing 25% plasticizer. But generally 8/10 EC-capsules survived mixing, which is still acceptable. The curves from the tensile strength tests showed clearly that the fracture strains of the EC-capsules with 10% plasticizer did no longer show any significant differences with the values obtained for glass or ceramics. In this way, reducing the amount of plasticizer definitely was a good choice. Despite this positive observation, during crack formation by three-point-bending of prisms with embedded capsules, no indication of capsule breakage and healing was noticed. Moreover, it was observed again that the polymerization reactions of the prepolymer already occurred in the EC-capsules, even when PEO was acting as plasticizer.

4. CONCLUSIONS

The tests done in this research clearly indicated that mixing in of EC-capsules with plasticizer gave satisfying results. In this respect, the proposed idea seems to work. However, in the future different polymeric materials and plasticizing agents will be combined and if necessary multi-layered capsules will be considered in order to combine good bond properties and tightness with flexibility of the capsules.

REFERENCES

[1] Van Tittelboom, K., De Belie, N., Van Loo, D., Jacobs, P. Self-healing efficiency of cementitious materials containing tubular capsules filled with healing agent, Cement & Concrete Composites, 2011