

Summary

Concrete is the most widely used building material on earth. However, concrete structures present several issues that threaten their durability and consequently the safety of their users. One of the major hindrances to the durability of concrete is its susceptibility to cracking. Cracking leads to the reduction of mechanical properties and contributes to create pathways for the penetration of aggressive agents into the bulk material. In order to avoid major durability problems, concrete structures need to be repaired, but repair works can present several issues such as the individuation and access to the damaged zones, the direct cost to realize them, the indirect cost connected to the loss of serviceability, and the environmental impact in terms of carbon dioxide emissions for the production of new cement.

In the last decade, significant advancements have been achieved concerning the enhancement of the longevity of the cementitious structures using preventive repair methods defined as self-healing techniques. These techniques may be implemented based on the autogenous healing mechanisms naturally present in cement-based materials and through strategies aimed to improve it or to built-in new autonomous healing properties. Among these technologies, capsule-based self-healing using macro-encapsulation is being increasingly acknowledged as a promising strategy to improve the durability and resilience of concrete structures.

The focus of this dissertation was the development and characterization of an efficient self-healing system using cementitious capsules filled with a suitable healing agent. The system should be able to provide repair directly at the damage location upon crack occurrence and achieve recovery in both durability-related and mechanical properties, also in presence of large cracks.

The research activities led to the development of a new manufacturing technique, which allowed to produce cementitious capsules with controlled and customizable dimensions using a polymer-modified cement paste. Moreover, the adopted coating and sealing procedures allowed the encapsulation of highly moisture-reactive healing agents. The capsules were used to successfully encapsulate and release several types of healing agents from the main types commonly used for self-healing applications: namely, sodium silicate solutions and water-repellent agents (minerals), highly moisture-reactive polyurethane precursors (polymers), and ureolytic bacterial strain *Bacillus sphaericus* able to precipitate calcium carbonate (bacteria). The

investigation and comparison of the performances of the different healing agents allowed to select the polyurethane precursors as the most promising to realize the desired self-healing system.

Moreover, the cementitious capsules were proven effective in resisting the mixing procedure. This characteristic, combined with their inherent compatibility with the cementitious matrix and the easy customization of the capsules size and shape, makes cementitious capsules equivalent to enhanced aggregates that could be used in the ordinary construction processes.

The development of the final system followed several steps, with the aim to progressively improve it through the inputs offered by the characterization of intermediate tentative systems.

For what concerns the characterization in terms of recovery of durability-related properties, the sealing efficiency was assessed through the reduction of capillary water absorption and water permeability offered by the autonomous healing system. The tests were conducted using both testing techniques present in the relevant literature and novel techniques developed in the frame of this doctoral study. Specifically, a newly developed water permeability test allowed to characterize the system efficiency using stricter testing conditions.

As regards the recovery of the mechanical properties, this was first investigated via three-point bending test in order to apply indirect tensile stresses in static loading conditions, as in most of the scientific literature. Furthermore, the mechanical behavior was also tested in repeated cyclic loading conditions until rupture in order to obtain insights regarding the seldom studied fatigue performance of the self-healing systems. In fact, this is an aspect of paramount importance to develop a reliable autonomous repair system that can be used in real field conditions.

The performances of the self-healing system using cementitious capsules were also compared with those of a system using glass capsules, which is an encapsulation technique thoroughly studied by several research groups and that served as a benchmark for the newly developed system. This comparison was obtained through the application of a test protocol developed in the framework of a European inter-laboratory testing. This allowed also to prove the protocol applicability to different self-healing cementitious materials based on the use of macro-capsules.

Visual analyses of the crack faces were also carried out to estimate the spreading of the healing agent in order to complement the previous characterizations.

In conclusion, the main objective set for this doctoral thesis was achieved, namely the development and characterization of an efficient self-healing system for cementitious materials based on the encapsulation of polyurethane in newly-designed cementitious capsules. The final self-healing system allowed to obtain almost full recovery in both durability-related and mechanical properties after damage occurrence, proving that the system is able to improve the durability of cementitious structures and has a good potential for future scale-up.