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Encapsulated polyurethane for self-healing concrete applications: prototyping, mechanical and durability characterization

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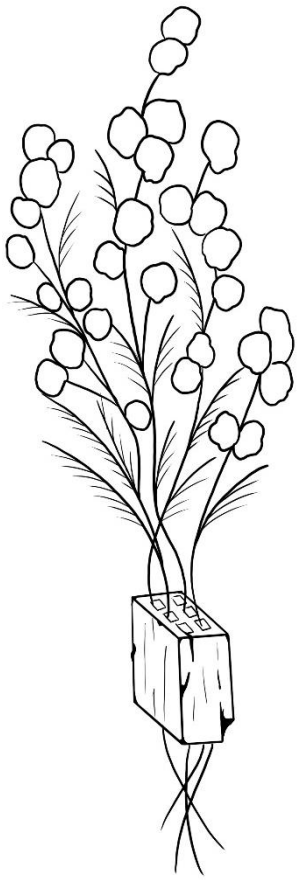

Abstract

Concrete is the most widely used material in civil and building engineer thanks to its highly cost-effective production and installation, compressive strength and durability properties, but one of the major problems that affects this type of material is the emergence of cracks which can impair its durability and mechanical characteristics, possibly leading to premature collapse of the structure. The research in this field is moving fast to improve the maintenance strategies, with the development of novel high-efficiency repairing products and the definition of innovative application techniques, in order to both guarantee and extend the structure lifetime and limit the need for demolition and production of new concrete, thus reducing the overall environmental impact of these activities. A growing attention has been addressed to the development of solutions focused on self-healing properties in cementitious materials, such as incorporated active methods that act in order to repair the cracks directly from the inside, not affecting the inner properties of the material.

The purpose of this thesis is to check the feasibility and effectiveness of an autonomous self-healing strategy based on the encapsulation of a highly moisture-reactive healing agent, in order to improve both the durability and mechanical properties after cracking due to self-repair. The first stage of the process was the production of capsules and the subsequent filling with an expansive polyurethane precursor. In a second stage, prismatic cement mortar specimens were manufactured as prototypes of the proposed self-healing system. The capsules previously produced were placed inside some of them, while other were left capsule-less for the sake of comparison. The third stage was the pre-cracking, through which a single crack with pre-defined characteristics was introduced in each specimen, in a controlled and repeatable way. Finally, the fourth and last stage consisted in testing the mortar prisms from the mechanical and durability points of view, in order to evaluate the performance recovery of the system after the autonomous repair has been completed.

The results show that the self-healing mechanism introduced via the encapsulated polyurethane generates a significant improvement in the post-crack behavior in comparison with the standard mortar.

The flexural strength was recovered almost entirely, and the same was observed for the durability, as tested in a water permeability set-up. The potentialities of the system in terms of long-term effectiveness were also preliminarily investigated on another series of specimens by means of mechanical testing under cyclic loading conditions and subsequent re-evaluation of the water permeability, until final failure of the specimen. Promising results were obtained, opening the way for future developments of the proposed self-healing system in view of its application in real field conditions.

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1. INTRODUCTION

1.1 Thesis premise and goal

Concrete is the most widely used material in civil and building engineer thanks to its highly cost-effective, production and installation, compressive strength and durability properties. However, one of the major problems that affects this type of material is the emergence of cracks which can impair its durability and mechanical characteristics, possibly leading to premature collapse of the structure.

The reasons for crack formations can be ascribed to several causes, such as poor mix design, the application of heavy and cyclic loads, adverse temperature influences, or improper maintenance of the construction.

The research field is moving to reduce the carbon footprint resulting from the concrete production cycle by replacing the ordinary Portland cement with other less polluting materials, and improve the maintenance strategies of a concrete structures by the application of repairing products and techniques in order to both guarantee and extend the structure lifetime, thus limiting the need for demolition and production of new concrete.

For this reason, a growing attention has been addressed to the development of solutions focused on self-healing properties in cementitious materials, moving from passive repair approaches, that requires the external manual intervention and only heal the surface cracks, to incorporated active methods

that are placed at the construction stage, and acts in order to repair the cracks directly from the inside, not affecting the inner properties of the material.

This goal can be achieved through several autogenous and autonomous strategies. The former can be reached by using mineral additions, crystalline admixtures, superabsorbent polymers, or other types of chemicals directly incorporated into the concrete matrix. The latter can be reached, among other possible ways, by placing in the concrete bulk capsules containing a proper healing agent.

COST (European Cooperation in Science and Technology) which is a pan-European intergovernmental framework, has the mission to enable break-through scientific and technological developments leading to new concepts and products.

In fact, the loss of performance and functionality promote an increasing investment on maintenance and/or intensive repair/strengthening works. The critical nature of such requirements is signified by their inclusion as priority challenges in the European Research Program. According to this backdrop, the "CA15202 – Self-healing As preventive Repair of COncrete Structures (SARCOS)" action was started on 2016 September 16th, which aim is to find self-healing technologies and repair solutions for extending service life of new and existing concrete structures. Studying an inter-laboratory testing procedure: the aim was to obtain sound and comparative characterization techniques for performance verification of self-healing Cementous materials.

The inter-laboratory test protocol defines the guidelines from the preparation of the specimens to the test procedures.

Partly following these guidelines, the purpose of this thesis is to check the feasibility and effectiveness of an autonomous self-healing strategy based on

the encapsulation of a highly moisture-reactive healing agent, in order to improve both the durability and mechanical properties after cracking due to self-repair. The entire production cycle of capsules and specimens has been studied, as well as the crack creation process and the testing protocols for performance assessment. The experimental data have been processed as described in the following chapters. Very positive conclusions have been drawn based on the results achieved, paving the way for future developments in view of on-field practical applications.

1.2 Experimental approach

To achieve the main goal as stated in the previous section, the following intermediate objectives were defined:

- to design and realize an easy-scalable type of capsule that fulfils the following requisites: i) mechanical and chemical compatibility with a cementitious matrix, ii) responsiveness to a mechanical stimulus, as due to cracking, and iii) capability to store and protect a liquid healing agent up to the moment in which the mechanical stimulus triggers the releasing action;
- encapsulate a fast-reacting healing agent able to fill the crack and harden in contact with air, thus sealing the fracture and partially or totally restoring the initial mechanical and water-resistance properties;
- to implement the proposed encapsulation system in a simple case study represented by lab-scale plain mortar elements with capsule addition;
- to introduce a controlled damage by means of a proper pre-cracking procedure;

- to check the system performance through mechanical and durability tests after pre-cracking and autonomous healing.

Accordingly, the experimental approach consisted in sequential steps, as described in the following.

The first step of the process was the shaping of several capsules and the subsequent filling with a highly moisture-reactive expansive polyurethane precursor.

The use of the polyurethane precursor has been chosen among other ways since it:

- is able to react very quickly;
- is a single component system that does not require special curing which is difficult to realize in real fields application, as it reacts only thanks to the moisture in the air;
- is able to fill very large cracks as it has a great expansive power;
- forms a water-resistant rigid foam, so it has the potential to contribute significantly to both waterproofing and mechanical recovery.

In a second step, prismatic mortar specimens were manufactured as prototypes of the proposed self-healing system. The capsules previously produced were placed inside some of them, while other were left capsule-less for the sake of comparison.

The third step was the pre-cracking, through which a single crack with pre-defined characteristics was introduced in each specimen, in a controlled and repeatable way.

Finally, the fourth and last stage consisted in testing the cement mortar prisms from the mechanical and durability points of view, in order to evaluate the

performance recovery of the material after the autonomous repair has been completed.

Outlining the entire process, the prisms went through:

- *Pre-cracking test* - an initial controlled cracking by three-point bending test is set up to investigate the bond between the cement mortar matrix and the capsules inserted into it, to evaluate the ability of the capsules to respond to the mechanical trigger given by the crack and to release the healing agent upon crack formation.
- *Durability test after pre-cracking* – an amount of water is pushed with constant pressure into the prisms in order to verify the sealing power of the hard foam generated by the healing agent.
- *Re-loading test* – the self-repaired specimen is resubmitted to the three-point bending test in order to check its mechanical strength recovery.
- *Mechanical dynamic loading* – dynamic actions are cyclically applied to the specimens over a short period of time, in order to evaluate the resistance of the bond between the hard foam filling the crack and the cement mortar matrix in terms of max cumulative number of cycles before cyclic failure.
- *Durability test after mechanical dynamic loading* – the water-flow procedure run after pre-cracking was run once again after prescribed numbers of dynamic reloading cycles in order to verify the overall system performance as a consequence to mechanical damaging actions.

1.3 Expected results

The purpose of the tests is to check the feasibility and effectiveness of the autonomous self-healing strategy based on the encapsulation of a highly moisture-reactive healing agent, in order to improve both the durability and mechanical properties after cracking due to self-repair.

It was expected that polyurethane generates a significant improvement in the post-crack behavior in comparison with the standard mortar, considering also cyclic loading conditions until the final failure of the specimen.

2. BACKGROUND: ORDINARY CONCRETE

2.1 Concrete manufacturing cycle and environmental impact

Concrete is the second most widely used material in the world, second only to water. It is obtained through a mixing process between cement, aggregates, additives and water.

It is characterized by a high mechanical strength and resistance to the stresses of environmental agents, including freezing and thawing cycles.

For this reason, and because of the wide availability of its constituent components, it is extensively used for most civil and building constructions.

Nevertheless, it is a material that in order to be transformed into a finished product, needs a high-temperature process that involves significant CO_2 emissions.

In fact, if cement was a country, it would be the third largest emitter of greenhouse gases, after China and the United States: it is the most used material on Earth, consumed to produce concrete at a rate of 150 tons per second.

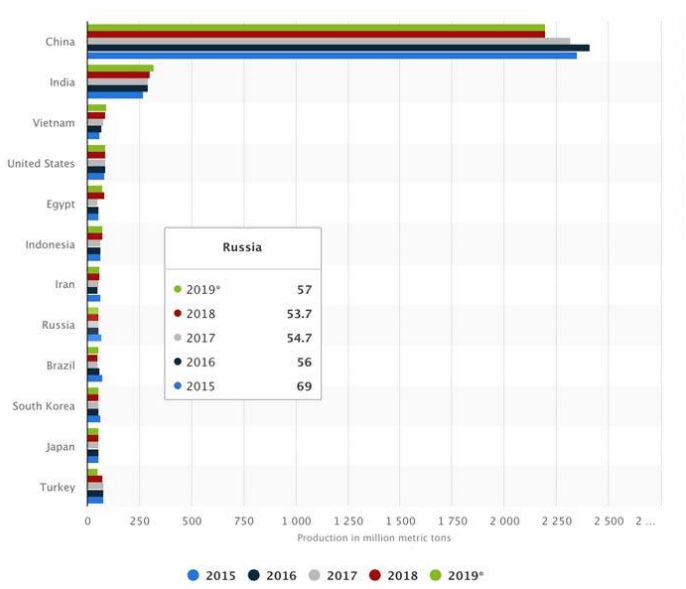


Figure 1 - Tons of concrete produced

Source: https://www.ingenio-web.it/27110-ecco-le-classifiche-mondiali-dei-produttori-di-cemento

According to the Global Cement and Concrete Association (GCCA), about 14 billion cubic meters of concrete are poured each year. In doing so, cement production is responsible for up to 7% of global emissions, which is three times the emissions produced by aviation.

Cement is the main binder in concrete, and it consists mainly of clinker, which is made by firing clay and limestone in a kiln. In the process, carbon dioxide is produced, which ends up in the atmosphere: in order to supply one ton of cement, the firing process at 1400 °C produces about one ton of CO_2.

This system, which has remained unchanged since cement was first produced over 200 years ago, is responsible for 70% of emissions, while the remaining 30% comes from the energy used to keep the kilns burning.

In order to limit the environmental impact of concrete, it will be necessary to focus not only on the decarbonization of the cement industry methods, but also on circular economy methods, which require the recycling or reuse of

materials and the design of lighter, more durable and efficient buildings based on green building techniques.

The wide use of this material in the construction field depends on:

1. easy access of raw materials,
2. low cost of materials,
3. simple production process.

However, concrete is not immune to deterioration, in fact, the phenomena of degradation leads to problems of durability that affect the service life of the structure.

The costs to repairing concrete structures, make up a large part of the maintenance effort. Moreover, these costs increase because there are no systemic approaches for the inspection of damaged structures, which compromises the evaluation of the life cycle of the structure and its serviceability and safety.

Last but not least, it is complicated to assess the actual performance of structures that have already suffered damage.

2.2 Mechanical properties

The properties of concrete in construction, were discovered as early as ancient times.

The success of concrete was due to the ease of manufacturing the mixture and the subsequent transformation into a material similar to rock. If at first it was the lime to act as a binder, with time it began to use the cement, obtaining a

significantly greater resistance and hardness, without negatively affecting the possibility of processing the compound.

The main property of concrete is its extreme workability. This depends on several factors, such as the water to cement ratio, the size and shape of the elements of the compound, temperature, climate and the presence of additives in the mixture.

Once the hydration process starts, the workability of the compound tends to decrease, until it is completely exhausted the first hour after the mixing operations start. Afterwards the concrete hardens, becoming resistant to strong compressive stresses.

Another important property of concrete is represented by the high resistance to rain infiltration, temperature changes, freezing and thawing cycles.

The tensile strength is not high, making it necessary to couple the material with steel bars.

2.3 Damage phenomena

Concrete is a material subject to progressive decay phenomena, and for this reason it is necessary to carry out periodic maintenance on concrete structures.

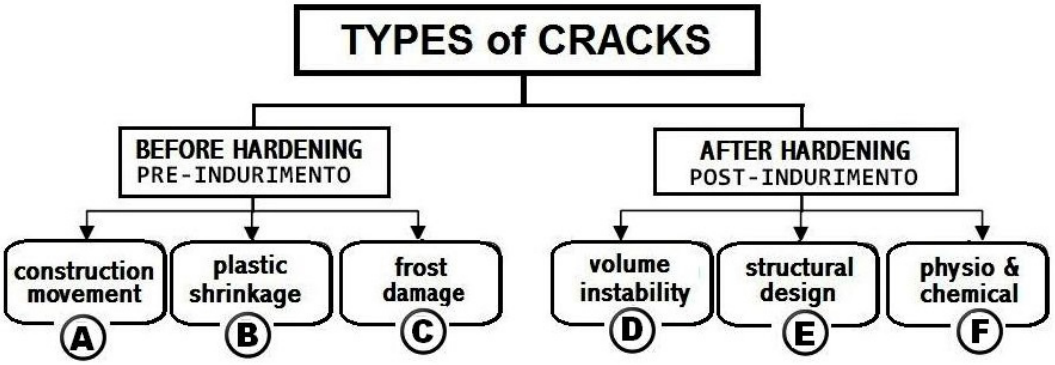


Figure 2 - Types of concrete decay phenomena

Source: https://www.azichem.it/news/calcestruzzo-difetti-superficiali-pi%C3%B9-frequenti-documento-1-2/217/

The factors that can trigger degradation in concrete are of various kinds, but the main causes can be divided into three macro categories:

- chemical causes, e.g. corrosion induced by carbonation, corrosion induced by chlorides, alkali-aggregate reactions, sulfate reactions,
- physical causes, e.g. freeze-thaw cycles, plastic shrinkage, hygrometric shrinkage, thermal movements, heat hydration,
- mechanical causes e.g. abrasion, erosion and crazing, shock, vibrations, cycling loads, overloading.

All of these causes led to the cracking of the concrete elements, and hence compromise the safety of the construction.

The beginning of crack in concrete section gets worse with the passing of time: in fact, cracks represent a vehicle for the passage of substances that could damage the reinforcement bars.

Water and humidity convey salts and dissolved gases, which lead to corrosion of the bars through the oxidation of the iron. This leads to the formation of

rust which occupies a greater volume and therefore triggers tensions in the concrete which aggravate the already existing cracks.

2.3.1 Chemical damage

The main chemical factors that affect the concrete structures are represented by:

- Carbonation,
- Chlorides corrosion,
- Alkali-aggregate reactions,
- Sulfate reactions.

Carbonation. Carbonation is the most common degradation phenomenon in concrete structures due to the penetration of carbon dioxide into the concrete.

This is a slow process in which slaked lime, made up of calcium hydroxide $(Ca(OH)_2)$, in hydrated and hardened cement reacts with the carbon dioxide (CO_2) in air, to produce calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

This reaction necessarily takes place in an aqueous medium, since carbon dioxide reacts with water to produce carbonic acid. The latter reacts with calcium hydroxide producing water and calcium carbonate.

In the presence of excess carbonic acid, the reaction progresses: calcium carbonate reacts with carbonic acid to produce calcium bicarbonate which is more soluble than calcium carbonate and therefore more vulnerable to leaching.

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2$$

The pH of a good concrete is greater than 13, and in this case, it will form a protective film of ferric oxide (Fe_3O_4) on the steel reinforcement bars which prevent the passage of oxygen and moisture.

In this strongly alkaline environment the oxide film covering the reinforcement is compact and adheres to the surface of the bars, making the reinforcement bars passivated and protected.

This process causes a significant decrease in pH: the passivating film is neutralized, leaving the iron exposed to the aggression of oxygen and humidity present in the air. The result is a loss of concrete protection against corrosion. Over time, the corrosion of the reinforcement bars, which is an expansive phenomenon, damages the concrete and reduces the load-bearing capacity of the structural elements concerned. Under these conditions, the corrosion process increases the volume of the reinforcement bars by about six times hence, the concrete cover of the reinforcement could be completely ejected.

Chlorides corrosion. Since there is an ever-increasing presence of chlorides in the atmosphere, mainly introduced by industrial discharges, there are considerable concentrations of chloridric acid in the rain, which causes chlorides corrosion phenomena in concrete structures.

Chloridric acid is a stronger acid than silicic acid and binds to the basic component of lime, that is calcium hydroxide $(Ca(OH)_2)$, producing calcium chloride $(CaCl_2)$ which is very soluble in water.

$$Ca(OH)_{2(s)} + 2HCl_{(aq)} \rightleftarrows CaCl_{2(aq)} + 2H_2O$$

Also, in this case, leaching phenomena occurs. Furthermore, oxidation-reduction reactions are triggered when chloridric acid comes into contact with iron, leading to the formation of rust due to the loss of electrons by iron.

$$2Fe^{2+} + Cl_2 \rightleftarrows 2Fe^{3+} + 2Cl^-$$

As a result of the hydration phenomenon of the cement, hydroxyl molecules are produced, which are responsible for the dissolution of the silicon dioxide (SiO_2) chains. This reaction is catalyzed at alkaline pH in the presence of sodium (Na^+) and potassium (K^+).

Alkaline-aggregate reactions. Researchers claim that calcium plays a major role in the dissolution of silicon: dissolved silicon dioxide (SiO_2) molecules

combine with hydrated calcium silicate molecules. This leads to a reduction in the silicon monoxide ions (SiO^{-}) concentration in the concrete pores and promotes a chain reaction in which silicon continues to dissolve as long as calcium is present. This phenomenon continues even after the exhaustion of calcium molecules until a balanced pH level is reached.

Two situations can occur:

- the electronegativity of the calcium silicate $(CaSiO_4)$
- increases because it incorporates the dissolved silicon molecules, to form a complex molecule of silicate, sodium and potassium,
- the dissolved silicon dioxide combines with alkali forming a hygroscopic gel with swelling capacity, responsible for the degradation of the cement.

Sulfate reactions. The pH of rainwater is about 5.5 but due to emissions from industrial activities and combustion, there are higher concentrations of sulfur dioxide (SO_2) and trioxide (SO_3), nitrogen dioxide (NO_2), carbon dioxide (CO_2) and chlorides in the atmosphere. These gases have acidic character and react with water to give the respective acids, thus creating the phenomenon of acid rain.

Moreover, sulfuric acid (H_2SO_4) with a pH of 1.7 is able to attack reinforced concrete which is made up of lime, a salt of a strong base $(Ca(OH_2))$, and a salt of a weak acid (H_4SiO_4).

The sulfation reaction occurs when sulfuric acid, which is a stronger acid than silicic acid, combines with the basic part of the cement.

$$H_2SO_4 + Ca(OH)_2 \rightleftarrows CaSO_4 + 2H_2O$$

Sulfur dioxide also attacks bricks and mortar by reacting with the tricalcium aluminate of cement mortar to produce calcium sulfur aluminate. This process is followed by an increase in volume that causes the mortar to break.

2.3.2 Mechanical damage

The main mechanical factors that affect the concrete structures are represented by:

- Abrasion, erosion and crazing,
- Shock,
- Vibrations,
- Cycling loads,
- Overloading.

Abrasion. The deterioration by abrasion occurs when the surface of concrete is subjected to friction, for example concrete pavements. In this case, the strength of the concrete depends on various factors such as the hardness of the mixture and the grip between the compound and aggregates.

Usually, the higher the compressive strength of the concrete, the higher the abrasion resistance.

Erosion. Erosion, on the other hand, can be considered as a form of abrasion of a surface, an example are hydraulic structures where there is the action of water carrying solid residues.

Cavitation. Cavitation occurs when the concrete is stressed by a non-linear flow with speeds greater than 12m/s, for example hydraulic structures subject to phenomena of swirling bubbles that generate non-linear flows.

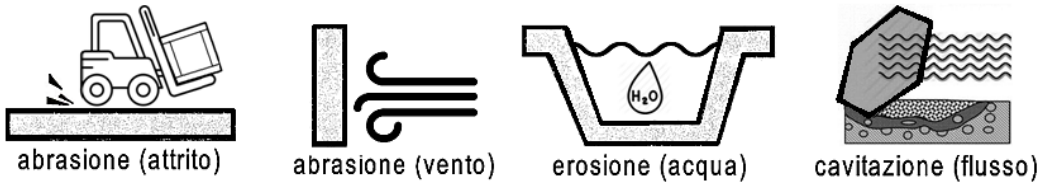


Figure 3 - Mechanical causes of decay

Source: https://www.azichem.it/news/calcestruzzo-difetti-superficiali-pi%C3%B9-frequenti-documento-1-2/217/

Impact. Impact damage occurs when concrete is subjected to localized impacts of a certain strength that generates detachments of material.

Cycling loads. When concrete is subjected to cyclic loading and unloading in strain control, the following stress-strain diagram is obtained:

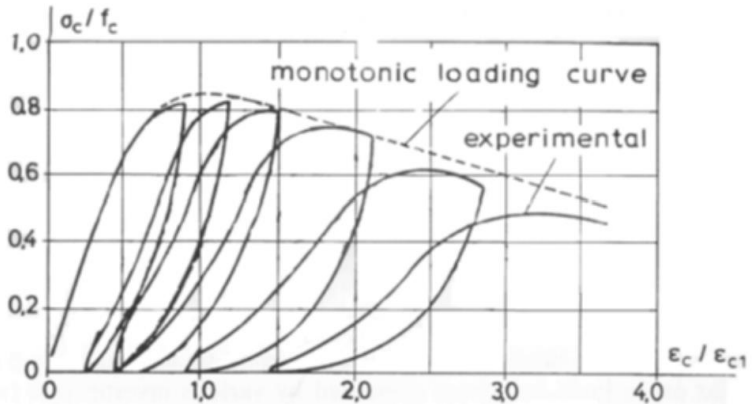


Figure 4 - Cycling load diagram

Source: ing.unipi.it

Until the maximum tension is reached, the diagram coincides with the compression curve. When the unloading phase begins, the specimen presents a lower stiffness due to the plastic deformations of the previous cycle.

Once the specimen is reloaded, there is a reduction in the slope of the curve and in strength related to the progressive damage of the internal structure of the specimen caused by the propagation of fractures in the cement.

Overloading. Overloading can lead to the fracture of the cross sections, because they are designed with a specific value of load. Once the structure is overloaded and the acting stresses are greater than the resisting ones, cracks develop and lead to the section failure.

2.3.3 Physical damage

The main physical factors that affect the concrete structures are represented by:

- Freeze-thaw cycles,

- Plastic shrinkage,
- Hygrometric shrinkage,
- Thermal movements,
- Heat hydration.

Freeze-thaw cycles. The freeze-thaw cycles are the most common cause of concrete cracking and breaking. These cause an expansion of water volume in the transformation from liquid to solid (equal to about +9.1%) which exposes the concrete to considerable stresses: if the stress developed exceeds the tensile strength of the concrete, then internal cracks may occur, chipping and even the ejection of material.

Figure 5 - Freeze-thaw phases

High temperatures. The behavior of concrete under high temperatures, including some specific operating conditions and fire exposure situations, leads to decreased functionality and collapse of the structure.

In fact, as the concrete begins to get warmer, the free water in the structure evaporates. If there is no way to convey the steam to the outside, an internal overpressure that destroys the matrix is created.

Once 350 °C is reached, the calcium hydroxide present in the concrete matrix decomposes, and when it exceeds 500 °C, the hydrated phase of the calcium silicate also decomposes releasing water vapor.

These transformations lead to an increase in the porosity of the concrete, and hence a decrease in the mechanical strength of the structure.

For these reasons, it is recommended for concrete to calculate the linear range value according to the variation of the thermal changes based on the summer and winter peak values in order to avoid injuries in the structure.

Shrinkage. Concrete is subject to two different types of shrinkage: plastic shrinkage and hygrometric shrinkage.

Plastic shrinkage occurs when concrete in its plastic phase gives up part of its moisture to the external environment due to differences in temperature, humidity or wind. This phenomenon generates surface micro-cracks.

The second phenomenon occurs when the concrete exchanges its intrinsic humidity with the external environment at a lower relative humidity. It differs from the first one because it extends over the entire service life of the structure.

2.4 Damage prevention

Since protection and repair of concrete structures requires complex design work, the UNI EN 1504 defines the principles to do that.

The key stages identified by the European standard are defined below:

- Assessment of the structure conditions,
- Identification of the deterioration causes,
- Selection of the principles and methods of protection and repair,
- Specifications of the maintenance requirements

The UNI EN 1504 is divided into 10 parts:

- UNI EN 1504-1: 2005: Definitions,
- UNI EN 1504-2: 2004: Surface protection systems for concrete. Products and systems are defined and, when applied, increase the durability of concrete structures,
- UNI EN 1504-3: 2005: Structural and non-structural repair. Products and systems are defined and, when applied, restore the geometric or aesthetic characteristics of the structure or replace damaged concrete and restore structural integrity and durability.
- UNI EN 1504-4: 2004: Structural bonding. Products and systems are defined and, when applied, provide a long-lasting bond with other applied materials.
- **UNI EN 1504-5: 2004**: Concrete injections. Products and systems are defined and, when injected, restore the strength and durability of the structure.
- UNI EN 1504-6: 2006: Anchoring of reinforcing steel bar. Products and systems are defined and, when applied, anchor the reinforcement in the concrete and fill the cavities to ensure continuity between the steel and concrete elements.
- UNI EN 1504-7: 2006: Reinforcement corrosion protection. Products and systems are defined and, when applied, increase the protection of the steel bars from decay.
- UNI EN 1504-8: 2004: Quality control and evaluation of conformity,
- **UNI EN 1504-9: 2009**: General principles for the use of products and systems.

This part defines the objectives for protecting and repairing concrete structures, sets out the minimum requirements for achieving these objectives, and finally provides guidance on the choice of materials.

- UNI EN 1504-10: 2003: Site application of products and systems and quality control of the works.

3. BACKGROUND: SELF-HEALING CONCRETE

Nature, in 3.8 billion years, has had the opportunity to improve its ability to regenerate and evolve, through a trial and error process. In fact, natural evolution has perfected over millions of years, based on the so-called principle of "minimum investment for maximum return": the minimum amount of energy possible for activities is used, in order to ensure greater performance for the perpetuation of the species.

According to Janine Benyus, an American biologist, nature has a triple role for designers: "*...it is model, measure and mentor at the same time*".

- it is a model because from nature we can abstract models (formal, structural, functional, organizational and strategic) as inspiration for technical solutions,
- it is a measure because in nature we can identify ecological standards as quantitative and qualitative references for the project,
- it is a mentor because it is a guide and teacher in the search for the most efficient solution.

Thus, was born the concept of biomimicry which is a discipline that allows to study and imitate the behaviors and structures of nature, in order to find innovative solutions to improve human activities and technologies. With biomimicry, nature is taken as a model, and from this it is possible to learn and learn continuously to create sustainable innovation and reduce energy consumption at the same time.

This technology has recently been applied into self-healing concrete field, for developing crack-treating strategies. The development of these solutions

moves from passive repair approaches, that requires the external manual intervention and only heal the surface cracks, to incorporated active methods that are placed at the construction stage, and acts in order to repair the cracks directly from the inside, not affecting the inner properties of the material.

The well-known strategies of self-healing concrete are distinguished into two main categories described below:

- **Autogenous healing**: water enters through the external cracks and hydrates the anhydrous cement present; the resulting compounds fill the crack and, if the size of the crack is small, are able to close it entirely.
- **Autonomous healing**: this strategy relies on the embedding of unconventional engineering additions to provide self-healing function. For example, encapsulated systems are the most versatile, and consist of capsules embedded in cementitious matrix that in the presence of cracks open and pour sealing material into the crack.

  Bacterial systems work by introducing bacteria into the cementitious matrix that can proliferate and live in the crack, nourishing themselves on materials present in the compound. Among these, ureolytic bacteria feed on urea, the synthesis of which forms calcium carbonate crystals that fill the crack.

  Vascular systems, which are more difficult to implement, use hollow tubes filled with the repair agent capable of sealing the crack at the time of its formation.

3.1 Autogenous strategies

Some existing materials are able to develop autogenous self-heling properties such as the reoxidation of damaged oxide steel films or recrystallization of metals to restore the initial properties.

The first example of autogenous self-healing materials dates back to 1836 at French Academy of Science.

Since this phenomenon has already been existing, it can be considered one of the reasons of ancient structures life extension, such as romans aqueduct and bridges. However, autogenous healing of cementitious materials is restricted to small cracks and water availability in the mix design.

These phenomena are mostly related to physical, chemical and mechanic processes. For example:

- Above physical processes, the main phenomenon is the swelling of the cement matrix,
- Above chemical processes, the main phenomenon is the continue hydration of unhydrated cement grains, and the precipitation on the crack faces of calcium carbonate molecules,
- Above mechanical processes, the main phenomenon is the clogging of the crack due to the production of small particles from the crack itself.

However, the most important processes are the chemical ones, since continuing hydration leads to the production of particles with a strength similar to the calcium silicate hydrate gels (CaH_2O_4Si).

Autogenous heling is strongly related to cement composition properties, such as: availability of water, age and composition of the materials, width of the cracks.

- Water: is the most important factor since it triggers the chemical processes and so the movement of particles to clogging the crack. The easier the formation of calcium carbonate, the better the healing process, in fact better healing was tested in wet-dry cycles because of the availability of carbon dioxide in the air during the dry phases.
- Composition: cement type can be considered less important than clicker content, in fact the latter is the responsible of calcium ions (Ca^{2+}) production and thereby the development of calcium carbonate precipitations $(CaCO_3)$.

  Also, aggregate type can determine the cracking pattern and shape and hence the healing process.
- Water to cement ratio: is directly related to the concrete class, as a matter of fact, low w/c ratio concrete have larger amount of unhydrated grains which stimulates a higher production of calcium silicate hydrate particles.
- Age of the material: is directly related to the hydrated amount of unhydrated particles, in fact, in early age concrete there is a higher amount of unhydrated particles, hence the calcium silicate hydrate particles is directly proportionate.

- Cracks geometry: the healing process is directly related to width, length, depth and pattern of the crack. Better self-healing process was proven for small crack from 10 to 100 µm up to 200 to 300 µm width opening.

In conclusion, autogenous healing process is more effective in presence of dry environments to develop a major amount of calcium silicate hydrate, and when small width cracks occur.

In order to reduce the crack opening, fiber-reinforced concrete (FRC) and high-performance fiber reinforced cementitious composites (HPFRCCs) can be used. Moreover, the addition of fibers in the acts as water reservoirs, absorbing it and releasing during dry periods, activating the continuous hydration of unhydrated grains.

3.2 Stimulated autogenous healing

Autogenous healing system can be improved providing water or enhancing hydration, with the addition of mineral, crystalline admixtures, superabsorbent polymers and polymer.

This systems with added elements are defined stimulated autogenous systems.

3.2.1 Mineral addictions

A way to boost the autogenous healing process in concrete structures, is the use of mineral additions in order to modify the hydration kinetics of the material.

The most of these minerals have always been already used in the building field since they reduce the cement amount in the mix design. This leads to limit the material costs and reduce the environmental footprint, since their production needs less energy and produces minor amounts of carbon dioxide.

The main minerals used in addition to the common concrete mix design are blast-furnace slag and fly-ash because of their unhydrated properties even at later ages, and their capacity to undergo delayed hydrated reactions. Obviously, there still is the need of an amount of calcium hydroxide to trigger further reactions.

However, this process can be low and slow during the first age of the material, so in order to speed up the self-healing process, alkaline solutions, higher curing temperature, higher underwater curing temperature are provided.

In particular, the alkaline activators usually used are sodium hydroxide $(NaOH)$, potassium hydroxide (KOH), calcium hydroxide $(Ca(OH)_2)$, sodium carbonate (Na_2CO_3) and sodium silicate (Na_2O_3Si).

Other minerals addition used are metakaolin, palm oil fuel ash, magnesium oxide (MgO), bentonite and quicklime (CaO). These are expansive additions that lead to the formation of brucite $(Mg(OH_2))$, portlandite $(Ca(OH_2))$ and others calcium-based hydration products.

It has to be pointed out that for stimulated autogenous self-healing process with mineral additions, the strength regain is limited to small width cracks up to 200 μm.

3.2.2 Crystalline admixtures

Crystalline admixtures as a way to boost the self-healing process have also been studied, these compounds derive from commercially available products whose elements are generally not disclosed. One way to distinguish the commercial products from supplementary cementitious materials is the quantity percentage in the mix design, for the former is about 1% by cement weight while for the latter is higher than 5%.

Generally, these products are formed by "active chemicals" mixed with cement and sand with high hydrophilic behavior, this improves the production of crack-blocking precipitates that improve the resistance to water penetration.

The improvement of concrete mechanical properties was proved for contents from 3% up to 7% of cement, subjected to moisture. Moreover, good results were reached when crystalline admixtures are combined with calcium sulfoaluminate agents, lime mortars and High-Performance Fiber Reinforced Concrete (HPFRC). Their efficiency in real scale application is currently under study.

3.2.3 Superabsorbent Polymers

Superabsorbent polymers are cross linked monopolymers or copolymers able to absorb high quantity of fluids. It mainly consists of petroleum-based monomers and synthetic cross linkers, but in order to reduce the impact on the environment researchers are developing natural and semi-synthetic superabsorbent polymers.

The performed benefits of superabsorbent polymers in the mix design, are related to the formation of macro-pores: once in the mix pour the mixing

water is absorbed, the particles swell and later shrink with the hardening of the matrix. This process generates macro-pores that trigger multiple narrow cracks easier to be cured with an autogenous self-healing process.

Since their chemical capacity to absorb and release water, their range application field extends from low water-to-binder ratio in order to reduce shrinkage, to freeze-thaw resistance.

Their ability to swell and block the cracks upon the entrance of liquid substances was proven for cracks opening width up to 150 μm.

3.2.4 Polymer Additions

This kind of products derives from a combination of cement, aggregate and organic polymers that lead to the formation of a matrix of polymer film and hydrated cement. Hence, the healing effect is based on the continuous and long-lasting hydration of cementitious materials.

In order to reach these goals, epoxy resin, ethylene vinyl acetate and shape memory polymers have been studied.

- The use of epoxy resin in cement paste is effective because of the presence of calcium hydroxide, this causes a reaction and as results the cracks healing due to the hardened resin that fills the pores,
- The ethylene vinyl acetate acts like the resin but at higher temperatures, and so act bitumen-coated steel fibers. These polymers have double effect: restrain the cracks and fill them with melted bitumen at high temperatures,
- Shape memory polymers are able to trigger the self-healing effect in a mechanical way, since are able to recover the original shape after the

deformation is applied. Another system is the hybrid one in which shape memory properties of polyethylene terephthalate (PET) is combined with pre-stressed fibers of poly-paraphenylene terephthalamide $(K29)$ – branded Kevlar.

3.3 Encapsulated autonomous strategies

These systems focus on the embedding of unconventional engineering additions to provide self-healing function. Encapsulation is the widely tested technique because of the directly providing of the healing agent at the location when the damage occurs, allowing immediately repair.

There are two main approaches in encapsulation technique, and they are distinguished because of the mechanism used to store the healing agent, thus this call for the extension of the damage that can be healed, the repeatability of the healing and the recovery rate of the healing.

The main types of encapsulated systems are distinguished between micro-encapsulation, macro-encapsulation and vascular networks.

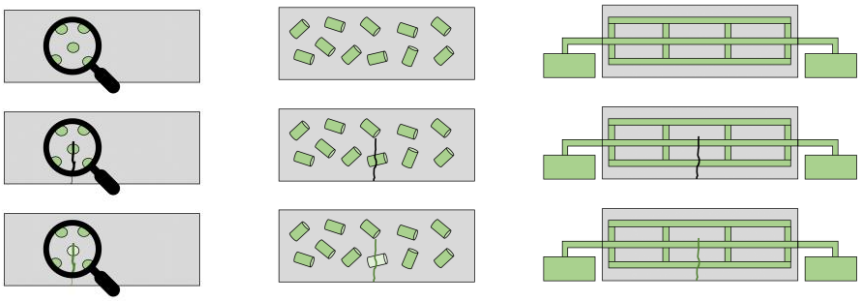


Figure 6 - Autonomous self-healing system. From left to right: micro-encapsulations, macro-encapsulation, vascular system

The system is based on the rupture of the capsules when a crack occurs, this determines the subsequent release of the healing agent in it. The healing agent reacts in different ways when in contacts with moisture, air, cement matrix or others components present in the matrix.

The key-factors for the capsules to be functional are:

- Durability of both capsule shell and core: when embedded in the matrix the capsules must resist to the mixing procedures and release the agent just when crossed by a crack, hence they must have a ductile behavior during the mixing and casting stage, and a brittle behavior in the later phases, for these reasons double-walled shells have been developed,
- The releasing of the agent: it can be mechanically or chemically induced, in fact the capsule surface can be modified, in particular pH-sensitive shell materials were developed.

3.3.1 Micro-encapsulation

Micro-capsules are characterized by < 1mm diameter width. In this mechanism the capsules are embedded in the cement matrix and release the healing agent when crossed by a fracture.

Micro-capsules are generally spherical-shaped and for this reason the adhesion with the surrounding matrix cannot be enough to allow the capsules opening when a fracture occurs.

For this reason, it is important to produce microcapsules with switchable mechanical properties to ensure both the resistance during the mixing process and the brittle glass-like behavior when crossed by a crack.

As a matter of fact, the matrix-microcapsule bonding influences the fracture mechanism, and for this reason capsules surface modification have been proposed to enhance the chemical compatibility.

In literature, many shell production techniques are studied such as emulsion polymerization, sol-gel reactions, spray drying, microfluidics.

Moreover, since the damage is connected to the decreasing of pH, and that leads to the de-passivation of the steel reinforcement bars, pH-sensitive materials are object of studies. For example, polystyrene, ethyl cellulose and chloride ion-triggered microcapsules have been proposed as shell materials. The latter, in combination with silver ion (Ag^{+}), can bind chloride ions (Cl^{-}) leading to the collapse of the shell and the subsequently releasing of the core.

Microfluidics is used to produce double emulsion: drops of core material and another fluid go through a polymerization that produces a completely closed solid microcapsule shell.

Alongside, micro-capsules can be well dispersed into the cementitious matrix, but they are characterized by a small volume of carried healing agent, frequently not enough to completely fill larger cracks.

3.3.2 Macro-encapsulation

Macro-capsules are characterized by > 1mm up to 6 mm diameter width, and as aforementioned, the capsules are embedded in the cement matrix and release the healing agent when crossed by a fracture.

The use of macro-capsules in cement composites dates back to 90s. Macro-capsules allow to store a larger amount of healing agent despite of micro-

capsules, this leads to the filling of larger cracks and even multiple healing effects by using a single capsule.

Many studies report of macro-capsules with a hollow-glass fibers structure, filled with several agents. Although glass fiber capsules can have a negative effect on concrete durability, other solutions have been tested such as ceramic or polymeric shell capsules, obtained by extrusion or additive manufacturing.

Also, cementitious hollow tubes shell was tested, coming from the extrusion of a polymer-modified cement paste. As a matter of fact, this type of encapsulation has been the starting point for the discussion of this thesis and will be better described in the following chapters.

This type of capsules is easier to produce even at lower temperature and their diameter range guarantees successfully results since the capillary attractive force of the crack and the gravitational force of the fluid mass are enough to overcome the resistive force of the capsules. This means that the healing effect is triggered even for crack width smaller than the inner diameter of the capsule.

3.3.3 Vascular healing

The fundamental principle behind vascular healing is based on the biomimetic approach, in fact many of natural systems obtain self-healing because of vascular networks they are made of.

Some examples of this phenomenon are the cardiovascular human system or the plant vascular tissue system, in both cases blood for the former and minerals for the latter are transported through a vascular network to provide the long-lasting existence of the organisms.

Based on these examples, vascular self-healing network can provide the healing agent to restore one or multiples cracks. Despite of encapsulated systems, in the vascular networks the healing agent is supplied from an external source, and so it can be continuously furnished, healing a higher cracks volume. Moreover, the healing agent can be supplied under pressure to ensure the reaching of the damaged zones.

The vascular networks that have been used in concrete, range from 1D channels to more complex 3D networks, in order to provide multiple and alternative paths for the healing agent to reach the cracks.

Some studies focused on the materials used for the channels, such as long thin glass channels, inorganic phosphate cement (IPC), polyurethane terephthalate (PET) tubes, in order to guarantee good mechanical properties during the casting phase.

Other approaches use shrinkable polyolefin tubes embedded in the concrete and then removed after casting. This method gives the system a higher placement network freedom according to the position of the steel reinforcement bars.

Another approach is the embedding of porous concrete pipes in concrete specimens with the advantage of creating a large number of paths for the healing agent, and since this requires a higher amount of agent, it produces a higher healing efficiency.

Also, the choice of the healing agent has been studied, because there is the need of a low-viscosity fluid which can easily be pumped into the network.

One of the disadvantages of the vascular system relies to the possibility of the network left exposed to the atmosphere: it could provide an easy pathway for

external materials to overpass the concrete cover and then compromise the durability of the structure.

3.4 Bacterial self-healing

Bacterial self-healing strategy is a type of system in which concrete cracks get repaired by the deposition of calcium carbonate because of carbonation process which mainly takes place in presence of moisture. During the process, the calcium carbonate precipitates and get deposited in the cracks. The carbonation equation is reported below:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Most bacteria can induce the precipitation of calcium carbonate in appropriate conditions, however different bacteria types follow different pathways to produce calcium carbonate due to their different carbonatogenesity.

Generally, in order to obtain calcium carbonate precipitation, metabolic conversion of organic compounds by microorganisms under aerobic conditions must take place.

This phenomenon happens when the ion concentration of calcium and carbonate is higher than the calcium carbonate molecules. In fact, the presence of calcium ions allows the metabolic compounds conversion and then the carbonation.

The main chemical reactions for bacterial self-healing can occur in:

- Alkaline conditions,
- Nitrate conditions.

Alkaline conditions. Some examples of reactions in alkaline conditions are related to the development of a bacterial spore in combination with organic compound-based healing agent under aerobic conditions.

For example, the alkaline members are *Bacillus cohnii* or *Bacillus pseudofirmus* in the form of spores, and the organic compound are calcium salts or fatty acids like calcium formate $Ca(HCOO)_2$, calcium acetate $Ca(C_2H_3O_2)_2$ or calcium glutamate $Ca(C_5H_8NO_4)_2$.

When there is the occurrence of the crack, the water ingress causes the bacterial spore proliferation and the organic compound are converted to calcium carbonate and carbon dioxide.

$$CaC_6H_{10}O_6 + 6O_2 \longrightarrow CaCO_3 + 5CO_2 + 5H_2O$$

The carbon dioxide produced can promote the reaction of the calcium hydroxide already present in the cementitious matrix to produce more calcium carbonate. The reaction is reported below:

$$5CO_2 + 5Ca(OH)_2 \longrightarrow 5CaCO_3 + 5H_2O$$

Moreover, microorganisms cause the burning of oxygen and this leads to the reduction of the risk of steel reinforcement bars corrosion.

Another example of bacterial self-healing in alkaline conditions is related to ureolytic strains such as *Bacillus pasteurii, Bacillus sphaericus* or *Bacillus megaterium*. These bacteria are able to decompose urea (CH_4N_2O) into ammonia (NH_3) and carbonate ions (CO_3^{2-}).

$$CO(NH_2)_2 + 2H_2O \xrightarrow{bacterial-urease} 2NH_4^+ + CO_3^{2-}$$

This reaction leads to the production of calcium carbonate with a sufficient amount of calcium ions (Ca^{2+}).

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$$

Nitrate conditions. Some bacteria can induce self-healing effects due to the nitrate reduction caused by different strains, such as *Pseudomonas denitrificans, Castellaniella denitrificans, Pseudomonas aeruginosa.* These bacteria can run under narrowed oxygen conditions, which lead to deep crack closure.

Undergoing these conditions, denitrifiers use nitrate (NO_3^-) to produce bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}). Also, in this case, the carbon dioxide produced can promote the reaction of the calcium

hydroxide already present in the cementitious matrix to produce more calcium carbonate.

$$5HCOO^- + 2NO_3^- \longrightarrow N_2 + 3HCO_3^- + 2CO_3^{2-} + H_2O$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$$

Moreover, nitrate reduction leads to the production of nitronium ion (NO_2^-) which is a corrosion inhibitor, and so produce the counteract corrosion of steel bars in reinforced concrete.

$$2HCOO^- + 2NO_3^- + 2H^+ \longrightarrow 2CO_2 + 2H_2O + 2NO_2^-$$

It has to be pointed out that in order to trigger the self-healing action, bacteria strains must be able to produce spores. Spores are dormant cells able to resist high mechanical and chemical induced stresses and can be available up to 50 years.

Moreover, bacterial spores embedded in the concrete mixture, are subjected to a decrease in lifetime because of the hydration of the cells. So, it is important to encapsulate the spores for protecting them from the alkaline environment. To reach this aim, some strategies have been tested such as the aforementioned micro-encapsulation, macro-encapsulation or vascular networks techniques. Some other techniques studied were extrusion, spry-drying and freeze-drying process.

4. ORIGINAL EXPERIMENTAL WORK: A SELF-HEALING SYSTEM USING MACRO-ENCAPSULATED POLYURETHANE

The self-healing system used during the experimental work involves the manufacturing of macro-capsules containing a repairing agent.

The choice to use macro-capsules instead of the micro-capsules was driven by several benefits. Firstly, this system guarantees the direct delivery of the healing agent at the crack location, and it also allows the storing of a greater amount of healing agent, which can fill larger cracks and possibly offer multiple healing effects with a single capsule even in a very short period of time by selecting the appropriate healing agent.

Moreover, the use of macro-encapsulation does not present the complexity in the arrangements of the networks inside a structural element such vascular system do.

In addition, the use of macro-capsules with cementitious shell provides advantages such as the compatibility with the surrounding cementitious matrix.

In fact, the capsules used during this experimental work are characterized by an external rigid shell that meets the requirement to obtain an inherent compatibility between the capsules shell and the cementitious matrix.

The cementitious capsules are able to protect and release effectively the healing agent since they are characterized by a flexural strength comparable

to that of cementitious mortar, and the ability to survive the mixing and casting process thanks to their mechanical properties.

Finally, the rigid shell is able to get broke right when intercrossed by a fracture and hence release the healing agent in order to trigger the polymerization reaction.

4.1 Manufacturing of the shell

The capsules were produced starting from a cement base in which chemical agents were added to improve the workability of the paste.

The production of the concrete capsules took place with the following five stages, that will be better described below.

1. Mix design of the external rigid shell and later maturation of the paste;
2. Hand shaping of the tubular elements;
3. Internal and external impermeabilization;
4. Sealing of the first end;
5. Filling with self-healing agent and sealing of the second end.

The following table resumes the processing phases with the details of the activities carried out and the materials used:

Phase	Day	Description
1	23/10/2019	Mix design of the external rigid shell
2	From 23/10/2019 To 29/10/2019	Maturation

3	29/10/2019	First layer of coating
4	30/10/2019	Second layer of coating
5	31/10/2019	Sealing of the first end
6	04/11/2019	Filling with the self-healing agent Sealing of the second end

Table 1 - Time table of the phases for the shell capsules making

4.1.1 Mix design of the external rigid shell

The cementitious tubular capsules were produced using a polymer-modified cement paste. The mixture is made up of solid and liquid compounds better described below:

SOLID COMPONENTS

- 217g of ordinary Portland cement: CEM I 52.5 R;
- 3,4g of HPMC (hydrossi-propyl-methyl cellulose): added with water, it reduces segregation between the components, in order to improve homogeneity, workability and the hardened product characteristics;
- 100g of $CaCO_3$ (calcium carbonate): it is characterized by superfine aggregates, and allows the cement to demand less water and also showing higher early strength. During the hydration process, it reduces the porosity and permeability of the hardened cement paste acting like a filler. It is also used to increase the stiffness of the cementitious matrix during the creation process;
- 1,6g of Metakaolin: reacts chemically with hydrated cement in order to form a modified paste with improved workability, mechanical properties and durability. It is strongly influenced by the PH of the

mixture: in a basic environment it requires a reduced addition of water; this enhances the mechanical and porosity properties.

SOLID COMPONENTS	
Ingredient	Quantity (g)
CEM I 52.2R	217
HPMC	3,4
$CaCO_3$	100
Metakaolin	1,6

Table 2 - Solid components for the capsules shell mixture

LIQUID COMPONENTS

- 60g of demineralized water;
- 80g of PRIMAL B60A: acrylic resin in aqueous dispersion, in order to improve the workability, the density and the cohesion of the compound by reducing the water to cement ratio, the polymer modification improves the survivability of the capsules during mechanical mixing;
- 8g of PEG (poly-ethylene glycole): it has a surface-tension reducing properties, it reduces the shrinkage not affecting the strength of the paste.

LIQUID COMPONENTS	
Ingredient	Quantity (g)
Demineralized water	60
PRIMAL B60A	80
PEG	8

Table 3 - Liquid components for the capsules shell mixture

Once the quantities have been accurately weighed with the precision balance, the solid and the liquid components have been first separately mixed and then with one another. This process has been carried out by a column stirrer that produces a shear action on the final mixture.

The fresh polymer-modified cement paste was used to produce cementitious tubes, and in order to improve the compactness and the homogeneity, the fresh cement past was manually processed.

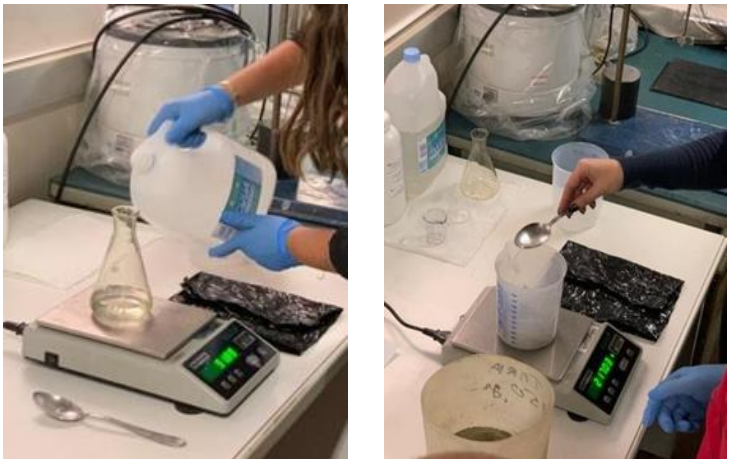


Figure 7 - Weighting of the components using a precision balance

Figure 8 - Mixing of the components using a column stirrer

4.1.2 Hand shaping of the tubular elements

The hand shaping of the capsules has been performed with the use of straws in order to give them a cylindrical shape. Specifically, the compound has been placed on a flat surface and wrapped around the straws trying to keep a constant thickness of 1mm.

During the hand shaping process, it is important to get the surface of the mixture as smooth as possible in order to avoid the occurrence of cracks; moreover, the straw's surface must not be entire covered in order to simplify the later stages of removal from the straws itself.

The final stage before the impermeabilization one, is the maturing phase: the capsules have been stored in a humid environment for 2 days, then the hardened product has been removed from the straws and the capsule has been shaped in 5 cm length tubes.

At the end the capsules have undergone completion of air curing for the next 4 days.

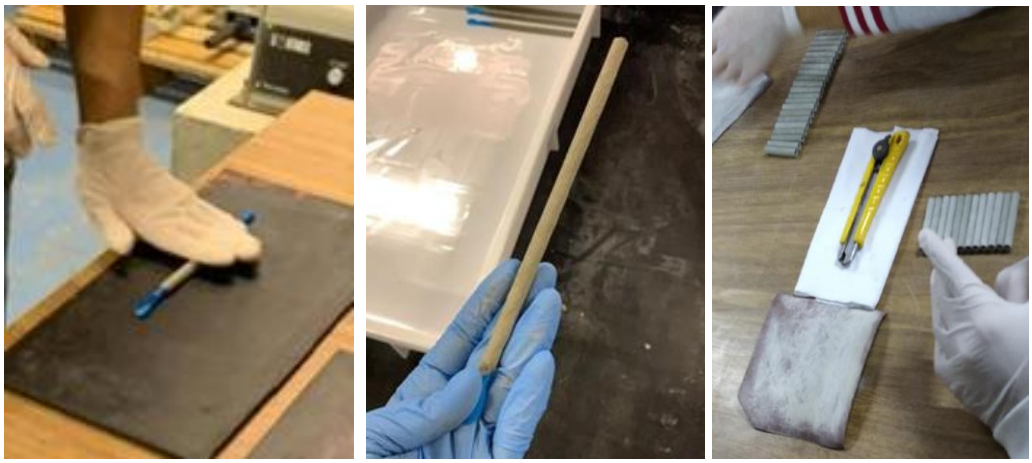


Figure 9 – Producing phases of the capsules shell. From left to right: hand shaping using a straw, after modeling shape, cutting of the hardened capsules

Figure 10 - Hardened 5 cm shell capsules

4.1.3 Internal and external impermeabilization

The cement proto-capsules obtained are characterized by an intrinsic porosity, that would allow water to enter during the casting phase. This water in contact with the repairing agent, that will be inserted later in the capsules, may compromise its performance since it is highly moisture-reactive. Also, the healing agent could leak from the shell and react with the moist of the surrounding cementitious environment.

In order to avoid the premature reaction of the healing agent it is necessary to waterproofing the surfaces of the capsules.

It was decided to use an epoxy resin in which the capsules have been dipped; the epoxy resin used is PRIMER AQ (Api S.p.a.). The dipping provides the first internal and the external protecting film in order to prepare the surfaces of the hollow capsules.

Suddenly, a second layer of coating was applied: waterproofing was carried out on the surface of the capsules using a two-component epoxy resin called PLASTIGEL (not soluble in water). This resin is usually used in naval filed for the impermeabilization of the surfaces so it has excellent waterproofing properties.

For this procedure, the compounds were mixed and introduced inside the capsule with the use of a syringe. To avoid an overabundance of product inside the capsules, and also to avoid the extremely reduction of the internal section of the capsules, hence the volume of healing agent stored, the capsules firstly have been shaken onto a polystyrene surface and then placed vertically to allow excess material to spill out from the lower end. Also, for the drying process they have been hung inside the box.

The components used for the coating are described below:

- 15g of base
- 35g of hardener
- 14g of deionized water

FIRST LAYER OF COATING	
Ingredient	Quantity (g)
Base	15
Hardener	35
Deionized water	14

Table 4 - Components for the first layer of capsules shell coating

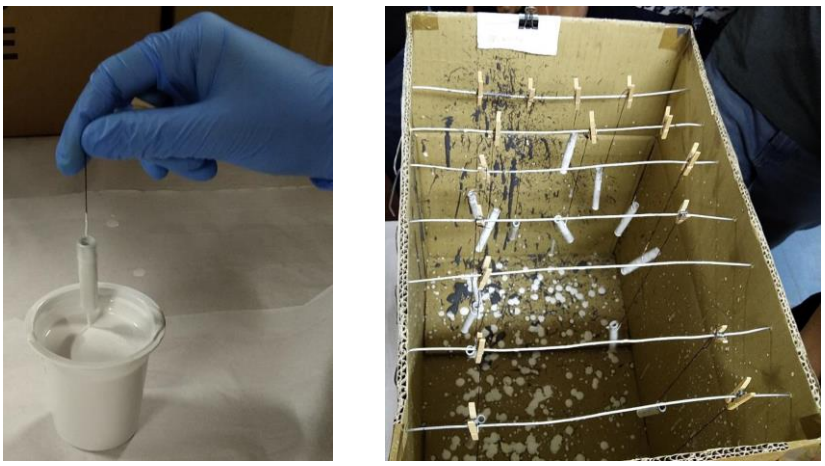


Figure 11 - First layer of coating and drying in a box

Figure 12 - Hardened capsule with the firs layer of coating

Figure 13 - Second layer of coating and drying in a box

4.1.4 Sealing of the first end

At this point the "proto-capsules" produced, according to the procedures reported in the previous sections, were simply hollow cementitious tubes with an epoxy-coated internal surface. For them to be able to be filled with a liquid, it was necessary to seal the first end, and leave the second end open for the subsequent filling operations.

For the sealing, a two-component epoxy-based tixotropic plaster called STUCCO K Api S.p.a. has been used.

The cap sealing the first end of the capsules has been created starting from a little amount of product modeled in a sphere and applied on one of the two ends. It is fundamental to properly apply the putty cap on the edge of the capsules in order to avoid any kind of leakage. For this reason, it was decided to allow a certain amount of time (approximately 30 minutes) for the plaster to settle and achieve a plastic consistency suitable for manual handling. Manual handling allows the compaction of the plaster mass, the elimination of air voids and the perfect adhesion to the capsule shell. In order to guarantee the perfect adhesion at the transition surface between the plaster and the capsule, a further coating of Plastigel has been applied.

Since handling and application of the plaster cap have been manually carried out, it was necessary to use oil to grease the gloves in order to facilitate the handling of the plaster.

FIRST END SEALING	
Ingredient	Quantity (g)
Base	16.4
Hardener	16.4

Table 5 - Components for the first capsules end sealing

Figure 14 - First end sealing

4.1.5 Filling with self-healing agent and sealing of the second end.

The filling of the capsules with the healing agent has to be done very quickly because it is essential to reduce at the minimum the exposure of the healing agent to ambient humidity, otherwise the polymerization reaction could start prematurely, creating a hardened foam. Obviously, this would invalidate the capsule functionality and the overall effectiveness of the whole system.

The healing agent must fulfill several requirements such as and adequate viscosity and thixotropy properties, or the right time of reaction. The former should not be high in order to let the healing agent easily flow out of the capsules once broken; the latter is necessary since it should not react too fast upon crack occurrence so that it has the time to flow into the crack before hardening.

For these reasons the mechanical properties of the agent are fundamental to obtain good results: it has to be flexible enough to follow the path of the cracks especially when they are expected to open and close because of the application of dynamic loads. It is also important to have both good adhesive properties between the hardened healing agent and the surrounding cement matrix, and the long-lasting effect of this conditions in order to bear freeze and thaw cycles or thermal gradients.

The self-healing agent used in this experimental work was a yellowish single component polyurethane resin called CARBOSTOP-U Orica S.p.a.; this step requires the use of a syringe to avoid the formation of air bubbles.

The final step is the second end sealing, it has to been done likewise the first one, using also the same component the two-component epoxy plaster called STUCCO K Api S.p.a. Also, in this case, it is fundamental to properly apply the plaster cap on the edge of the capsules in order to avoid any kind of leakage; once the second end was sealed a further reinforcement with the two-component epoxy resin PLASTIGEL has been done, in order to wet the stoppers and guarantee the insulation of the healing agent from the external environment.

SECOND END SEALING	
Ingredient	Quantity (g)
Base	16.4
Hardener	16.4

Table 6 - Components for the second capsules end sealing

Figure 15 - Filling of the capsules with the self-healing agent and second end sealing

Figure 16 - Second end sealing

In order to guarantee the grip between the capsules in the cement mortar prisms, the cap plasters have been covered with a layer of sand.

Figure 17 - Storing of the capsules

4.1.6 Achieved capsules list

At the end of the processing, the capsules have undergone a further quality control. During the experimental work three series of capsules were produced, that differ for the internal and external diameter, in particular 6mm diameter, 8mm diameter and 12mm dimeter capsules were produced, but just the former series was used to test the encapsulated system.

Below just the capsules belonging to the 6mm diameter series are reported, since they are ready for the next phases. The table below shows the internal diameter starting from the straw one, three measures were taken in order to define an average external diameter and the relative coefficient of variation.

Figure 18 - Final form of the hardened capsule

Φ6 DIAMETER CAPSULES							
Number [-]	Internal diameter [mm]	External diameter (measure 1) [mm]	External diameter (measure 2) [mm]	External diameter (measure 3) [mm]	**Ext. Diam. (average) [mm]**		**Coefficient of variation [mm]**
1	6.00	8.68	8.65	8.62	**8.65**		
2	6.00	8.24	8.29	8.32	**8.28**		
3	6.00	8.04	8.13	8.07	**8.08**		
4	6.00	8.04	8.13	8.07	**8.08**		
5	6.00	8.39	8.62	8.46	**8.49**		
6	6.00	8.38	8.17	7.9	**8.15**		
7	6.00	8.7	8.67	8.32	**8.56**		
8	6.00	8.03	7.99	8.98	**8.33**		
9	6.00	8.16	8.09	7.97	**8.07**		
10	6.00	8.24	8.44	8.55	**8.41**	**8.15**	**0.04**
11	6.00	7.46	7.45	7.42	**7.44**		
12	6.00	8.41	8.29	8.21	**8.30**		
13	6.00	7.8	7.7	7.74	**7.75**		
14	6.00	8.4	8.24	8.64	**8.43**		
15	6.00	8.33	8.34	8.28	**8.32**		
16	6.00	7.81	7.73	7.75	**7.76**		
17	6.00	8.4	8.46	8.64	**8.50**		
18	6.00	8.59	8.64	8.62	**8.62**		
19	6.00	8.18	8.08	8.12	**8.13**		
20	6.00	8.4	8.42	8.46	**8.43**		

21	6.00	7.7	7.75	7.71	**7.72**
22	6.00	8.1	8.15	8.23	**8.16**
23	6.00	7.79	7.81	7.73	**7.78**
24	6.00	8.34	8.83	8.32	**8.50**
25	6.00	8.29	8.23	8.31	**8.28**
26	6.00	8.03	8.07	8.07	**8.06**
27	6.00	8.26	8.11	8.24	**8.20**
28	6.00	8.8	8.66	8.65	**8.70**
29	6.00	8.04	8.06	8.06	**8.05**
30	6.00	8.01	8.01	8.06	**8.03**
31	6.00	8.06	8.08	8.16	**8.10**
32	6.00	8.01	8.02	7.94	**7.99**
33	6.00	7.89	7.85	7.81	**7.85**
34	6.00	7.81	7.94	8.08	**7.94**
35	6.00	8.35	8.29	8.16	**8.27**
36	6.00	8.16	8.19	8.14	**8.16**
37	6.00	8.08	8	7.95	**8.01**
38	6.00	8.41	8.49	8.63	**8.51**
39	6.00	8.11	8	8.03	**8.05**
40	6.00	7.79	7.82	7.92	**7.84**
41	6.00	8.07	8.06	8.03	**8.05**
42	6.00	7.86	7.77	7.85	**7.83**
43	6.00	7.63	7.71	7.6	**7.65**
44	6.00	7.95	8.19	8.19	**8.11**
45	6.00	8.4	8.43	8.42	**8.42**
46	6.00	7.76	7.59	7.59	**7.65**

Table 7 – Achieved capsules list - φ6 mm diameter

4.2 Samples manufacturing

During this phase, several series of cement mortar prisms were produced: the first series is characterized by 12 cement mortar prisms with the dimensions of 40x40x160 mm. Among the specimen of this series, 6 of them (A_REF) did not included the capsules, and were used as reference samples, while the remaining 6 samples (A_CAPS) included two capsules each. Likewise, the second of the series of specimens, is characterized by 12 cement mortar prisms with the dimensions of 40x40x160 mm, and contains 6 samples with capsules (B_CAPS) and 6 reference samples (B_REF) not containing the capsules.

During the course of the experimentation, it was considered appropriate to add a further series of specimens (CEM) to investigate the performance of encapsulated polyurethane under dynamic loads. The specimens have dimensions of 40x40x160 mm and contain a single capsule.

The production of mortar prisms instead of the concrete prisms took place since the encapsulated system studied is prototyped on a laboratory scale, according to the available devices. For the same reason, despite the dimension of the capsules fits more to the concrete prisms, cement mortar ones were manufactured.

The environment for the manufacturing of the specimens, according to the UNI EN 196-1, has to be maintained at a constant temperature of 20±2 °C and relative humidity of at least 50%. Moreover, the room for storing the samples in the mold must be maintained at a constant temperature of 20±1 °C and relative humidity not lower than 90%.

The production of the cement mortar prisms took place with the following four stages, that will be better described below.

1. Formwork preparation and capsules placement,
2. Cement mortar production,
3. Setup of the specimens for the durability test,
4. Setup of the specimens for the cracking test

The following table resumes the processing phases with the details of the activities carried out and the materials used:

Phase	Day	Description
7	06/11/2019	Cement mortar prisms production
8	From 06/11/2019 To 18/11/2019	Maturation
9	18/11/2019	Setup for the durability test
10	20/11/2019	Setup for the cracking test

Table 8 - Time table of the phases for the mortar specimens making

4.2.1 Formwork preparation and capsule placement

The formworks used during this phase, were modified than those describes in the UNI EN 192-1, in fact, according to the aforementioned regulation: the formwork must be made up of three horizontal slots to allow the simultaneous preparation of 3 specimens measuring 40x40x160 mm. It must be at least 10 mm thick and built to facilitate the demolding of the specimens without damaging them. Once the mold is assembled, it must be rigidly fixed to the base plate.

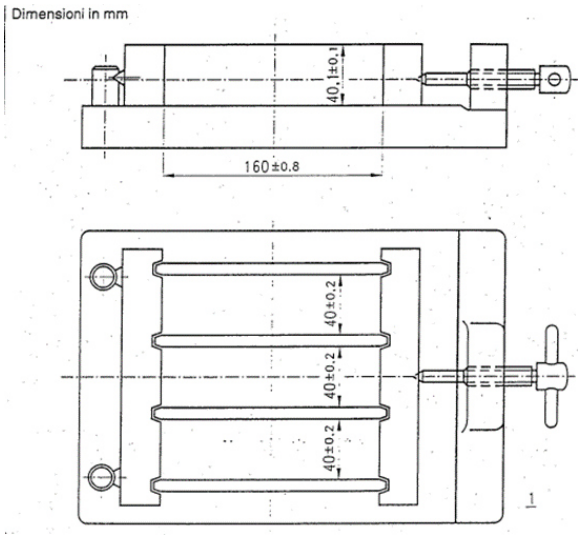


Figure 19 - Formwork dimensions according to UNI EN 196-1 for the specimens

The formwork used were modified in order to allow the creation of a notch in the middle of the specimen. Moreover, some holes were created in order to insert nylon threads necessary to correctly place in a repeatable manner the capsules in correspondence of the notch for the purpose of subsequent breakage.

Another modification concerns the insertion of a longitudinal cylindrical and properly oiled bar, which, after being removed once the samples have hardened, allows the creation of a channel necessary for the subsequent permeability tests.

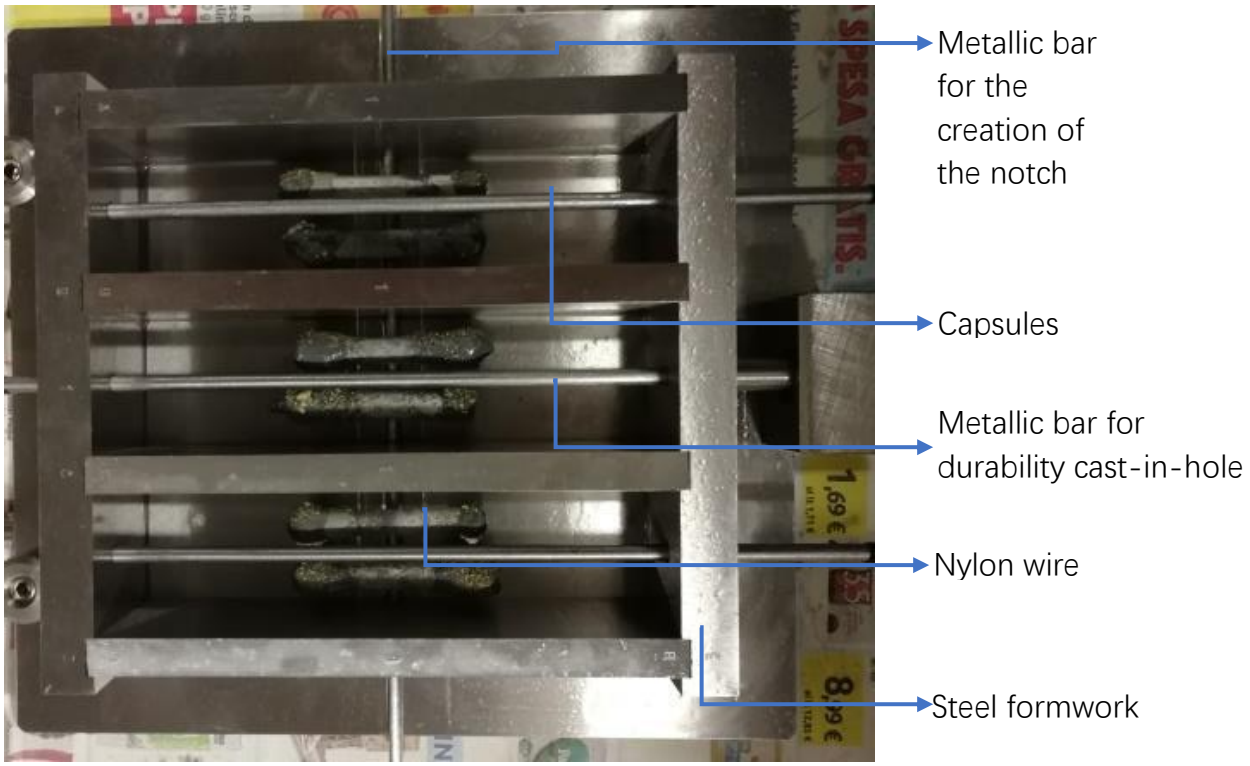


Figure 20 - Capsules placed inside the formwork

The first stage of formwork preparation was done by uniformly greasing all the surfaces with a release oil; then the capsules were manually placed inside the formwork without any additional device to fix their position but the application of a little amount of glue on the nylon threads. Also, a little piece of paper under the nylon wire was used to prevent the capsules from moving out of the defined position, once the glue hardened they were removed for not compromise the final mechanical properties of the prisms.

4.2.2 Cement mortar production

The mixture for the prisms was realized with solid and liquid compounds described below:

SOLID COMPONENTS

- 450g of CEM I 42.5 N: pure Portland concrete with standard setting time and characteristic strength of 42.5 MPa in 28 days,
- 1350g of Normalized sand: 0-2 mm diameter aggregate.

LIQUID COMPONENTS

- 250g of water: in order to provide a water/cement ratio of 0.5.

CEMENT MORTAR MIXTURE	
Ingredient	Quantity (g)
CEM I 42.5 N	450
Normalized Sand	1350
Water	250

Table 9 – Solid and liquid components for the cement mortar mixture

Once the ingredients have been weighed, the mixture is produced according to a standard procedure listed below:

- pour the water into the bowl and add the cement,
- immediately start the mixer at low speed, after 30 s add the sand with constant flow in the following 30 s,
- adjust the mixer to higher speed and continue mixing for further 30 s,
- continue mixing at the higher speed for 60 s.

According to UNI EN 196-1 the stirring machine used for mixing the compound is made up of a steel bowl with a capacity of 5 liters that must be

fixed to the structure of the stirring machine in order to set the distance between it and the machine. Moreover, a steel blade that rotates around its own axis and performs a planetary movement on the axis of the bowl was used. The blade is connected to a speed-controlled electric motor that allows the direction of rotation to be reversed.

	Rotation [min^{-1}]	Planetary movement [min^{-1}]
Low speed	140±5	62±5
High speed	285±10	125±10

Table 10 - Speed of the stirring machine blade

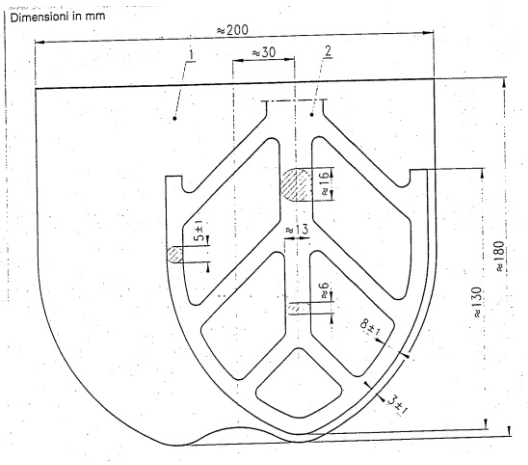


Figure 21 - Dimensions of the steel blade in the stirring machine

The shakeout equipment consists of a rectangular table rigidly connected to a pivot by two arms. During operation the table is raised and dropped from a height of 15 mm, and the position of the mold on the table must be such that the longitudinal dimension of the compartments is aligned with the direction of the arms and perpendicular to the axis of rotation of the machine. The device must be tightly secured to a concrete block which must rest on a

dampening layer itself to avoid external vibrations. The base of the equipment must be fixed by using bolts and a mortar layer to ensure vibration-free contact.

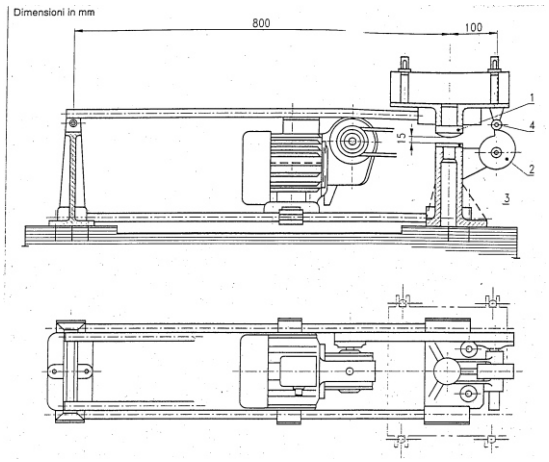


Figure 22 - Dimensions of the shakeout equipment according to UNI EN 196-1

Figure 23 - Shakeout equipment

Figure 24 - Stirring machine according to the UNI EN 196-1

The molding of the specimens takes place right after the preparation of the mortar. First of all, the mold is fixed to the shaking machine.

With a paddle the first layer of mortar (about 300 g) is introduced into the mold and then the first layer is compacted with 60 shocks. The remaining part of the mixture is introduced and compacted with other 60 shocks.

Figure 25 - Placement of the mortar mixture in the framework

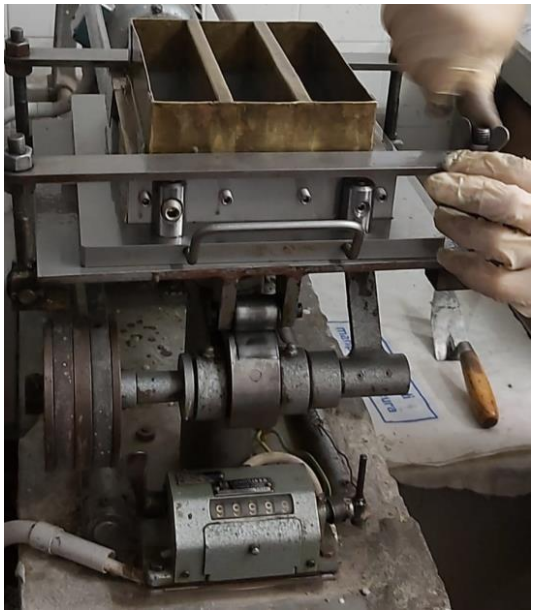


Figure 26 - Placement of the formwork on the shakeout machine

After that, the mold is lifted from the shaking machine, the excess mortar is smoothed out, and the molds marked to identify the specimens containing the capsules (CAPS) and reference specimens without capsules (REF).

Figure 27 - Smoothing of the excess mortar mixture

The molds are covered with a sheet of acetate and moved to the closet for the wet curing. After 24 hours, the specimens must be unmolded and placed in a box with water at 20±1 °C to conclude the wet curing, which can be considered completed after 28 days.

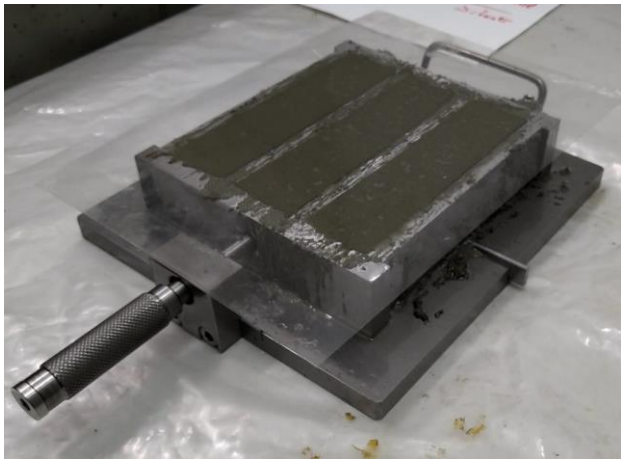


Figure 28 - Covering of the molds with a sheet of acetate

The specimens have to be well spaced so that water is in contact with all surfaces. At any time during storage, the level of water above the top sides of the specimens should be less than 5 mm. The specimens must be removed from the water no more than 15 minutes before the pre-cracking test, and must be covered with a damp towel until the test is performed.

4.2.3 Setup of the specimens for the durability test

Before crack creation, one side of the specimen was provided with a plastic tube in order to connect the specimen to the water-flow setup. In order to do this, the diameter of the hole coming from the insertion in the formwork of a longitudinal cylindrical bar was enlarged by the use of a drill. Then, the tube

was inserted and the watertight connection ensured by using silicone. On the other hand, the other side was just sealed using the same silicone.

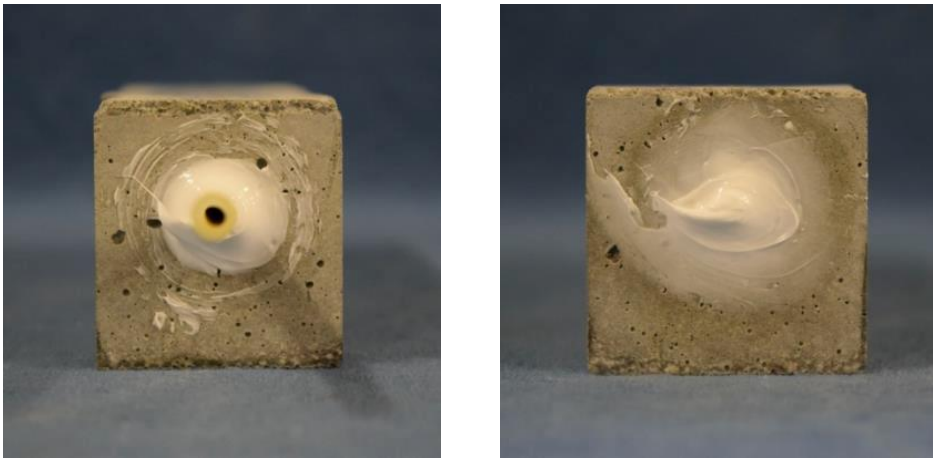


Figure 29 - Silicone sealing of the specimens

4.2.4 Setup of the specimens for the cracking test

In order to perform the pre-cracking test, each specimen was equipped, in correspondence of the notch, with small bolt nuts glued on the surface, for subsequent positioning of a displacement sensor. Before that, the surface was sanded for better bonding.

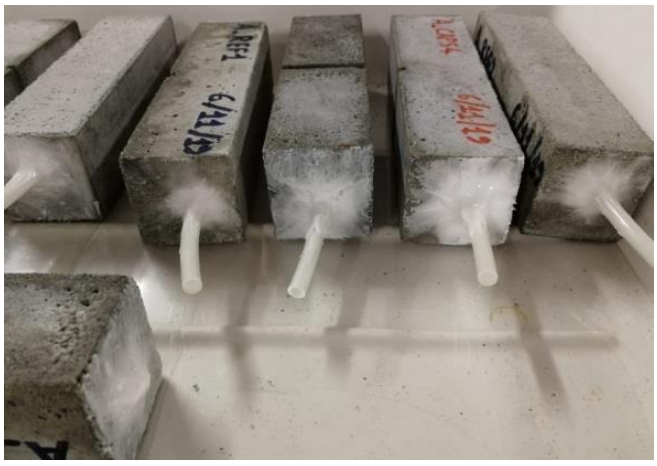


Figure 30 - Final assessment of the specimens before the tests

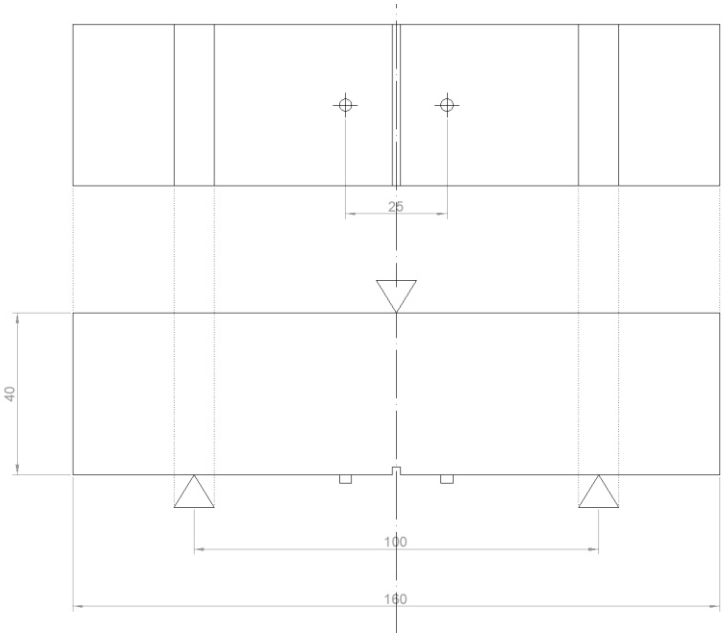


Figure 31 - Distance and positioning of the notch

4.3 Sum up of the specimen's production phases

Phase	Sub-phase	Description
1	1.1	Components weighing
	1.2	Manual mixing of solid components
	1.3	Manual mixing of liquid components
	1.4	Mixing of the components with a column stirrer
	1.5	Making of the capsules' rigid shell
2	2.1	Wet curing
	2.2	Unmolding
	2.3	Finishing (cutting and filing of the capsules)
	2.4	Air curing
3	3.1	Capsule lacing with nylon wire

	3.2	Dipping first layer of coating with PIRIMER AQ
	3.3	Air suspension for draining
4	4.1	Internal layer of coating with PLASTIGEL
	4.2	Manual capsule shaking
	4.3	Air suspension for draining
5	5.1	Weighing of components for the capsule stopper
	5.2	First end sealing with STUCCO K
6	6.1	Weighing of components for the capsule stopper
	6.2	Injection of the self-healing agent CARBOSTOP-U into the capsule
	6.3	Second end sealing with STUCCO K
	6.4	Layer of coating with PLASTIGEL
	6.5	Finishing
7	7.1	Greasing of formwork
	7.2	Placement of the capsules
	7.3	Set up formwork with nylon wire and metallic rod
	7.4	Weighing of components for the mortar mixture
	7.5	Mixing oh the mortar mixture
	7.6	Filling of formworks
	7.7	Shaking machine activation
	7.8	Finishing
8	8.1	Wet curing in formworks (2 days)
	8.2	Unmolding
	8.3	Wet curing
	8.4	Finishing
9	9.1	Set up of the specimens with the PVC pipes

	9.2	Sealing of the first end with silicon
	9.3	Sealing of the interface between the specimen and the pipe
	9.4	Hardening
10	10.1	Set up of the specimen for the pre-cracking test
	10.2	Bonding of the bolt nuts on the surface

Table 11 - Sum up of the specimen's production phases

4.4 Mechanical tests

4.4.1 Pre-cracking test

In order to evaluate the healing ability and hence the sealing efficiency provided by the use of cementitious capsules filled with polyurethane, a preliminary cracking has first to be created in the specimens.

In order to do that, the three-point bending test was run, and in order to reduce the variability of the crack width produced, the pre-cracking test has been done under controlled crack width opening.

In particular, the machine is set by imposing a defined fixed-in-time law: the points connected to the glued bolt nuts move apart, and the relative distance between the points increases and so the applied load. Two behavior can be distinguished: before the first crack the machine is set by imposing a constant deformation rate, to which an elastic elongation corresponds; during this phase, a very low increasement in terms of displacement is recorded, since the material is still intact and has a high stiffness. Right after the formation of the first crack, the test machine changes the predefined law and works under controlled crack width opening; during this phase, a progressive load decrease and progressively opening width crack increase is observed.

The test machine is a closed-circuit device, controlled by the information coming from the sensor. In fact, even if the first crack is occurs, the test continues until the preset maximum opening is reached.

During the test, the fixed width opening was set to 800 μm in order to provide the maximum possible value of crack opening on specimens of these dimensions.

In addition, since the specimens are not reinforced, during the unloading phase, a snapback occurs, leading to a small closure of the crack. Moreover, this opening value is recorded during the loading phase at the height of the sensor, and since the actual opening is on a higher plane than the sensor, the actual opening of the crack is around 400 µm.

The positioning of the specimen in the three-point bending test device follows the directions of the UNI EN 196-1, which states that the three vertical planes passing through the axes of the rollers shall be parallel and shall remain equidistant and normal to the axis of the test specimen. Moreover, the lower rollers shall be provided with a tilting system capable of slightly inclining, in order to allow uniform load distribution across the width of the test specimen to avoid torsional stresses.

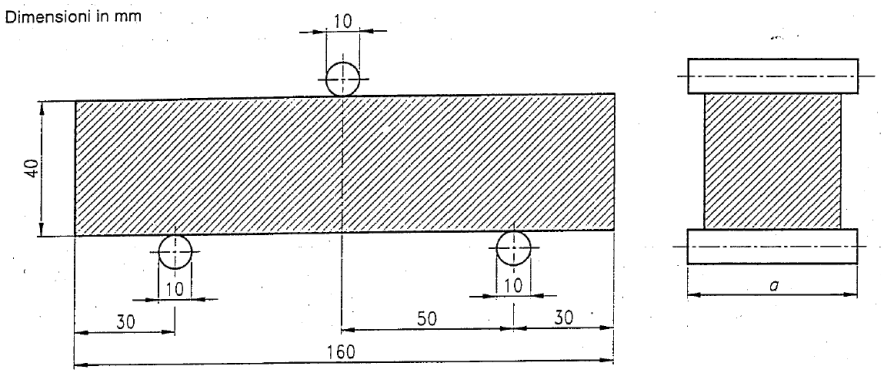


Figure 32 - Dimensions and distance of the rollers for the three-point bending test according to UNI EN 196-1

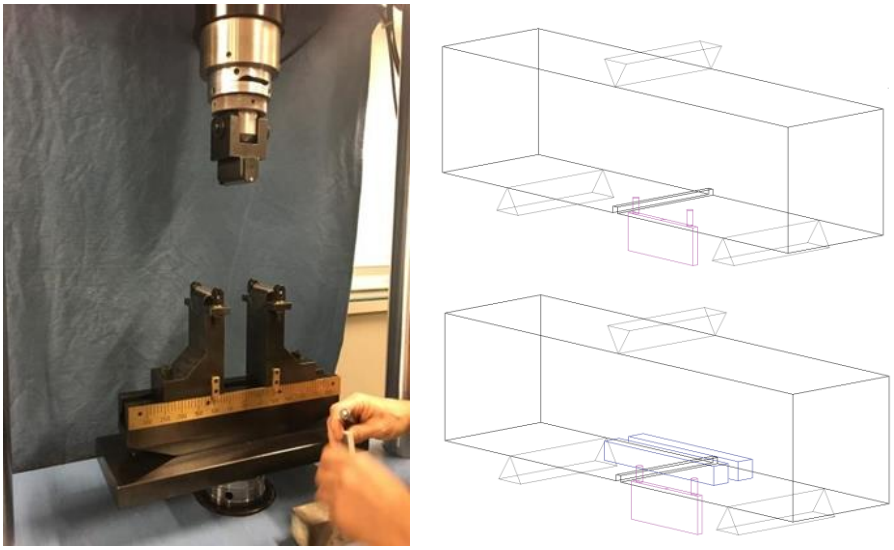


Figure 33 - Three-point bending test device

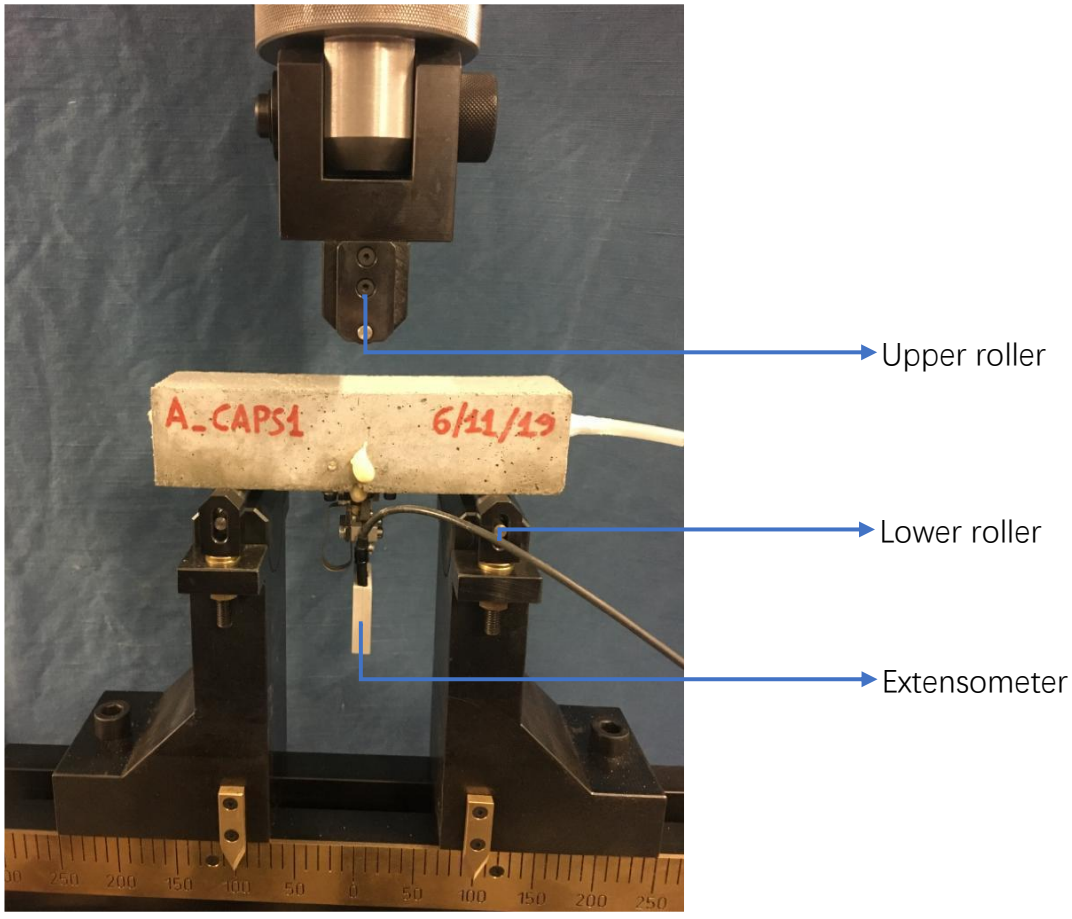


Figure 34 - Placement of the specimen in the three-point bending test device

The pre-cracking test has been done over 12 specimens without capsules called “REF” to which belongs the A_REF and B_REF series, and other 12 specimens with the capsules inside called “CAPS” to which belongs the A_REF and B_REF series.

After the pre-cracking test, all the specimens were left in the laboratory to allow the ejected polyurethane from the capsules to harden. Since the polyurethane is extremely reactive with moisture, and the hardening strongly depends on the humidity conditions of the surrounding environmental, this process can require from a few minutes to a few days.

In the study case the specimens were left to harden for 1 day.

4.4.2 Durability test

The test consists in a measurement of the amount of waterflow passing through the crack in a predefined interval time. Operating conditions have been imposed in order to uniform the durability test, by defining all the factors that may influence the outcome of the test.

In order to ensure the repeatability of the test if it were to be standardized, each specimen has been subjected to:

- Storage in water for the 24 hours before testing, in order to remove the air bubbles out of the crack and prevent water absorption through the pores of the mortar matrix during the test, so the water-flow passing through the sample will only pass through the crack and will not be able to spread in the cement matrix;

- Setting of the test time at 7 minutes, with an initial transient phase in which air bubbles created during the connection of the testing machine to the specimen must be expelled;
- Sealing with silicone so that the liquid is conveyed inside the crack. In order to avoid side effects, the openings on the side surfaces of the specimen that were produced during the three-point bending test were sealed;
- A constant water level maintained in the water tank in order to keep a constant pressure applied during the test.

This test was run differently on two different series of specimens containing the capsules.

In the first case, the A_CAPS specimens, according to SARCOS protocol, have the crack opening is facing downwards. The water-flow is one-dimensional since the lateral faces of the prisms have been sealed with silicone.

In the second case, the B_CAPS specimens, the mortar prism is rotated by 90 degrees, so as to have the water flow entering from the side surface of the specimen. In this way the water is allow to pass through the specimens following two paths: the opening mouth of the crack and the side surface crack left opened. This test, which differs from the SARCOS protocol guidelines, is more challenging because the water-flow passing through the specimen is greater. In fact, this implies that if the specimen has a good response to the passage of water in this case, it provides a more solid result on the effectiveness of the self-healing method used.

However, in both cases, during the test, the sample is connected to a graduated cylinder containing a constant level of water of about 50 cm height

with the respect to the cast-in-hole, through a small PVC pipe with a tap to allow and interrupt the flow.

The specimen is placed on a grid under which a bowl is placed and connected to a balance that measures the mass in grams of water passing through the specimen in a certain amount of time.

In particular, the leaked water was recorded over time for a minimum 5 minutes with an automated registration system. The maximum time duration of the test is 7 minutes of which the first one was not recorded to avoid the error induced by the presence of air bubbles in the pipe's testing device.

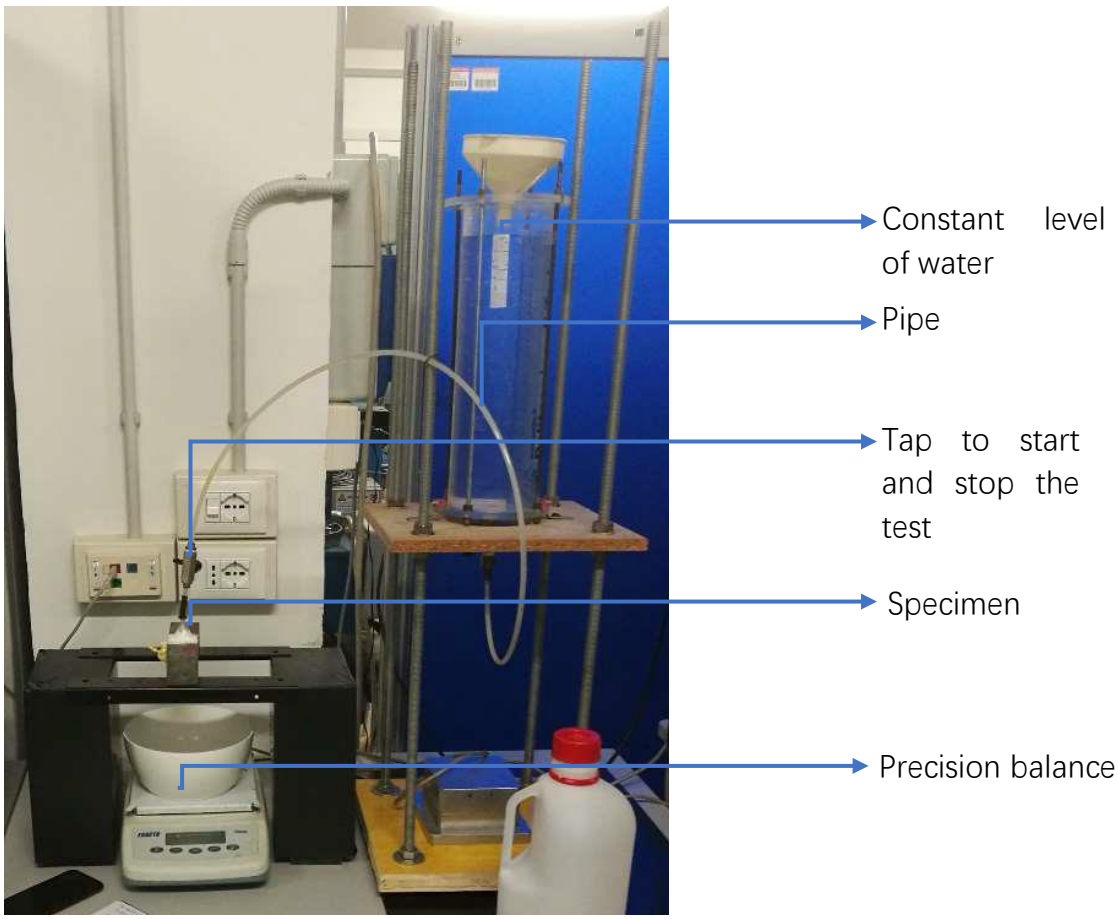


Figure 35 - Durability test device

Figure 36 - Placement of the specimen on the durability test device

With the collected data, it is possible to define the water flow rate (WF) with the following relation:

$$WF = \frac{m_2 - m_1}{t_2 - t_1} \ [g/min]$$

Starting from the water flow rate of the specimens with capsules, and the reference specimens without capsules, it is possible to define the sealing efficiency with the following relation:

$$ES(\%) = \frac{WF_{REF} - WF_{CAPS}}{WF_{REF}} \ [\%]$$

Where:

- m_2 is the mass of the water measured at the end of the test,
- m_1 is the mass of the water measured at the end of the transitional tare time
- t_2 is the time at the end of the test,
- t_1 is the time at the end of the transitional tare time
- WF_{REF} is the average water flow of the mortar prisms without capsules,
- WF_{CAPS} is the average water flow of the mortar prisms with capsules.

4.4.3 Static reloading test

The mechanical properties of the hardened polyurethane were evaluated by assessing the load-bearing capacity under static conditions.

The specimens were statically reloaded and hence subjected to the three-point bending test defined as a reloading test, following the same procedure described in the previous section. The aim of the test is to verify the mechanical recovery of the damaged mortar prisms.

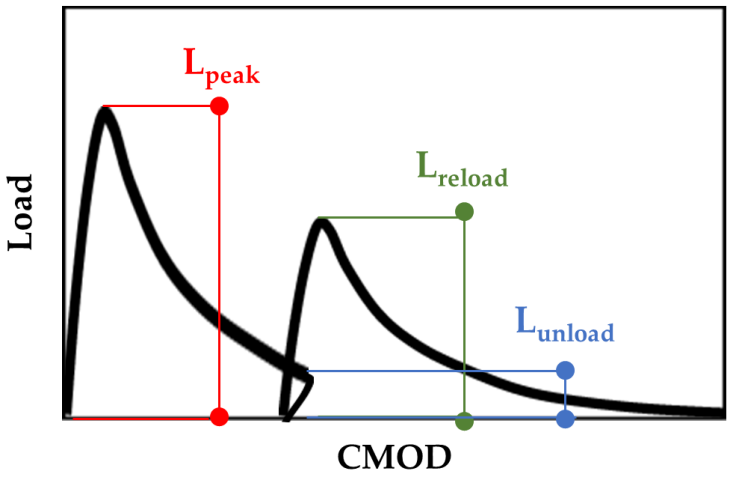


Figure 37 - Schematic load versus crack mouth opening displacement (CMOD) curves related to pre-cracking and reloading tests

The previous figure shows a graphical illustration of the pre-cracking load curve and the static-reloading one versus crack mouth opening displacement.

In particular, starting from left to right, the first peak (in red) corresponds to the moment in which the matrix cracks and so the reaching of the mechanical strength of the mortar prisms in reached. The second peak (in green) corresponds to the maximum value of load applied during the static reloading test when the healing agent is already hardened. The trend is more or less similar to the pre-cracking curve as the healing agent has returned a resistance capacity.

The last peak (in blue) corresponds to the residual load-bearing capacity at the end of the pre-cracking test in which the maximum established opening is reached and the machine releases the piston.

The impact of the self-healing agent is only noticeable during the reloading phase with the comparison of the peaks between the loading and the reloading curve: if the latter has a greater peak than the former, then the agent has restored the same initial mechanical properties.

It is possible to define a load recovery index (LRI) expressed as a function of the maximum load-bearing capacity of the specimens in the pre-cracking phase and the static reloading one, moreover is dependent on the residual bearing capacity at the end of the pre-cracking test. It is defined as follow:

$$LRI = \frac{L_{reload} - L_{unload}}{L_{peak} - L_{unload}} \ [\%]$$

Where:

- L_{peak} is the peak load during the pre-cracking test
- L_{reload} is the peak load during the reloading test
- L_{unload} is the leftover load during the pre-cracking test.

Since the opening we have reached in the samples is very wide, the residual load resistance is negligible, in fact it turns out to be substantially zero.

For this reason, we can rewrite the previous equation as follow:

$$LRI = \frac{L_{reload}}{L_{peak}} [\%]$$

Using this relationship, it is possible to obtain an average value for all the specimens analyzed, considering in separate way the self-repairing ones from the reference ones.

4.4.4 Dynamic reload test and durability test

One of the main sources of stress on concrete structures can be ascribed to dynamic actions: cyclically repeated over short periods of time, or with increasing intensity over longer periods of time.

The cyclic actions cause the repeated opening and closing of healed cracks: the overall system composed by the cementitious matrix and the healing agent is subjected to strains that could cause damages on the individual parts of the system but also compromise the bonding between these two different

materials. For this reason, it is important to investigate the bonding between the hardened healing agent and the surrounding cement matrix for characterizing their behavior in real field conditions, and allow the use of the system with the certainty of ensuring the structural safety and durability.

As written in the previous section, during the course of the experimentation, it was considered appropriate to investigate a different series of specimens for this test. The specimens belonging to groups A and B were not used as they had already been tested at final break with the reloading test to evaluate mechanical recovery. Considering the good response to the other tests of the specimens of groups A and B containing two capsules, the CEM series of specimens was produced containing only one capsule.

The force-controlled three-point bending test was run using the same setup and the same closed-loop servo-controlled hydraulic press, but using a sinusoidal load in order to make possible to investigate the mechanical behavior of the specimens until rupture, of the healed system in dynamic conditions.

The test was performed by applying a number of cycles with a fixed load value based on the average value of the peaks load obtained during the reloading test. During the loading phase the load applied reaches to the maximum value with a 10 N/s speed. Once the load comes to the max value, then a sinusoidal load is applied with a 3 Hz frequency, with the peak loads equal to the maximum load (L_{max}) and the minimum value equal to the minimum load (L_{min}).

At the end of each series of cycle, the durability test was performed again in order to evaluate the water-tightness of the specimens, with the aim of checking whether the degree of water tightness of the specimens has been

maintained or negatively affected by the cyclic mechanical stress to which they have been subjected to.

The upper and lower limit of the reloading test have been defined as the fraction of the average bearing capacity obtained during the static reloading test. In particular, they have been set according to the following equation:

$$L_{min} = 0.1 \cdot L_{reload}$$

$$L_{max} = S \cdot L_{reload}$$

Where:

- L_{min} is the minimum applied load
- L_{max} is the maximum applied load
- S is the percentage of the peak load during the reloading test
- L_{reload} is the peak load during the reloading test

The percentage of the peak load during the reloading test (S) is set to 0.75: this means that the load applied during the test is equal or greater of the expected strength of the specimens during the reloading test.

The upper and the lower limit of the dynamic reloading test are equal to 80 N and 600 N and match to 10% and 75% of the expected bearing capacity for self-repaired specimens.

These settings were used in order to induce a high stress on the healed material, in order to provide initial feedback on how these types of self-repairing systems might behave in real field application.

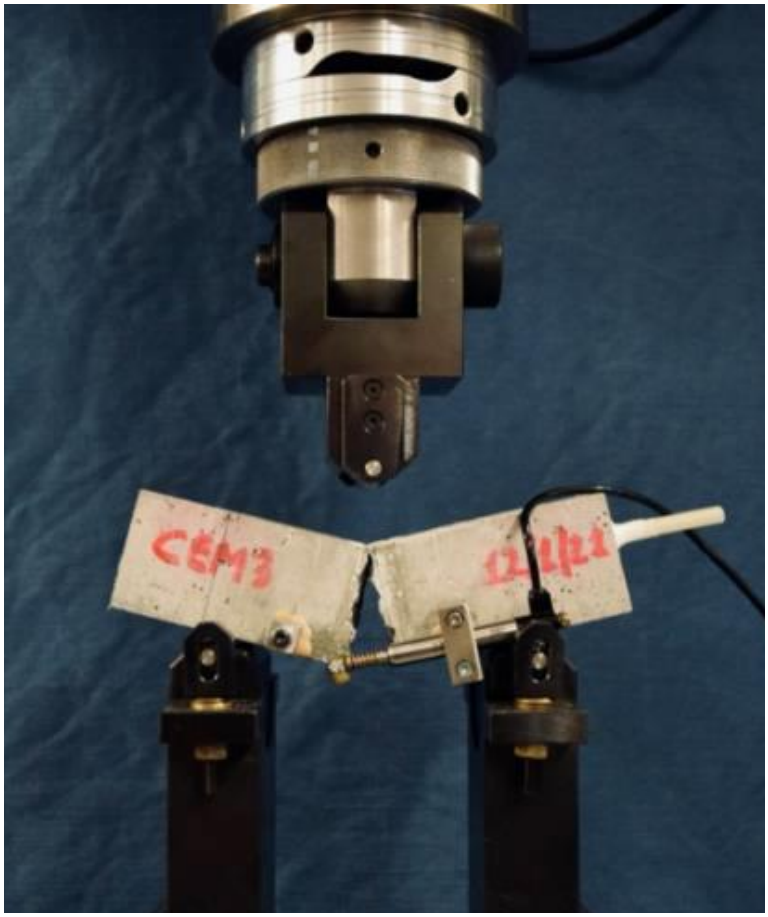


Figure 38 – Tested specimen during the dynamic reloading test

5. RESULTS

5.1 Pre-cracking test

5.1.1 REF specimens

The REF specimens of both series A_REF and B_REF, are characterized with the first line by an elastic-linear trend, suddenly a change in slope occurs due to the starting of the first micro-crack that progressively increases until its maximum opening mouth is reached.

The elastic-linear trend is followed with a curve called softening branch: the spreading of the crack leads to a reduction in the cross-section of the specimen and hence in its stiffness. During this stage, the load decreases but the displacement continues to grow until it reaches the target value of 800 μm since the test is run in CMOD control; then the specimen is unloaded and a partial elastic recovery can be observed.

With the data acquired during the test, it was possible to obtain the charts load versus time and load versus crack opening for each specimen. For the sake of clarity, only the curves related to the load versus crack opening are displayed.

The data collected are reported below:

TESTED SPECIMEN	MAXIMUM LOAD [N]	AVERAGE LOAD [N]	DISPERSION [N]	VARIATION COEFFICIENT
A_REF1	1729.17	1535.22	90.67	6%
A_REF2	1476.74			
A_REF3	1498.86			
A_REF4	1459.53			
A_REF5	1501.59			
A_REF6	1545.45			
B_REF1	1839.89	1886.43	90.36	5%
B_REF2	1909.19			
B_REF3	1952.5			
B_REF4	2035.67			
B_REF5	1816.3			
B_REF6	1765			

Table 12 – Tested specimens during the pre-cracking test - REF

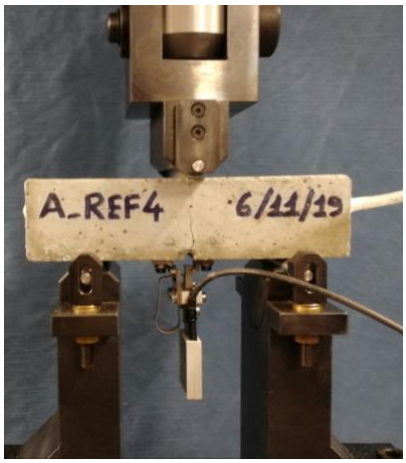
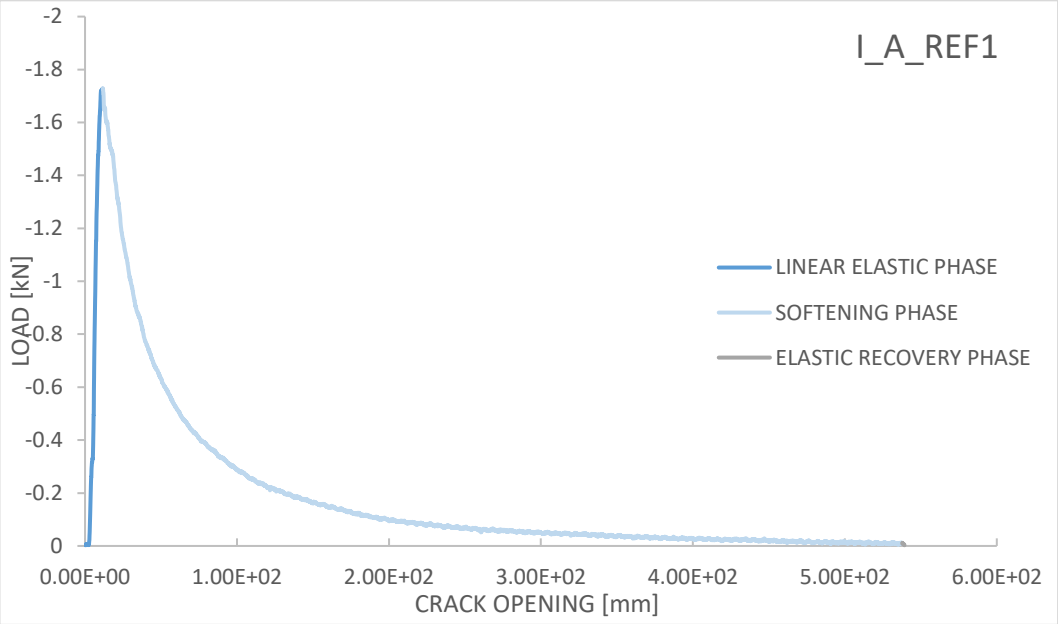


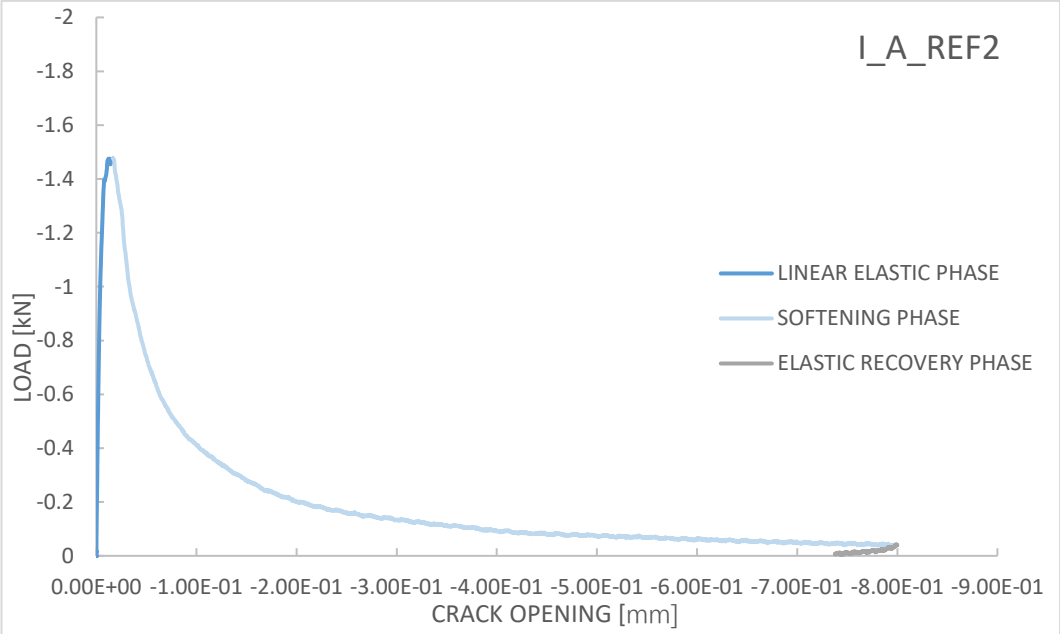
Figure 39 - Cracking of the REF specimens

According to the breaking behavior of the concrete, evidence shows that the first crack in the specimens without capsules was developed in a fast manner: analyzing the load curve of the specimen, and considering that a severe maximum crack opening mouth has been imposed, the end of the elastic trend and therefore the triggering of the first crack has a very small range compared to the whole test one. The chart shows a peak load and right after the decline in load which corresponds to the softening branch.

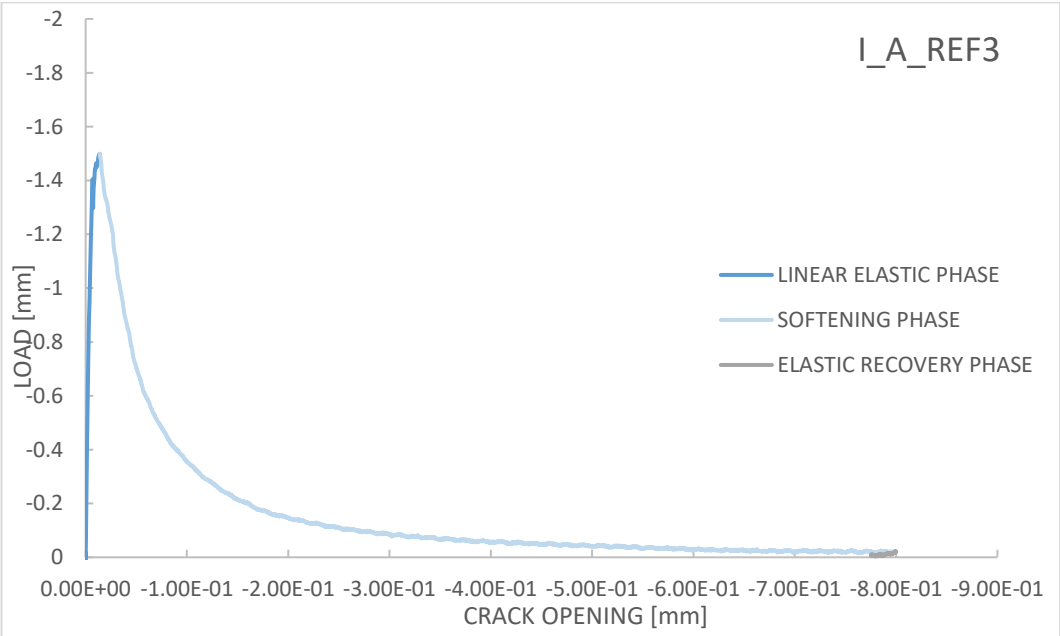
The following, are the charts load versus crack opening obtained for each specimen belonging to the A_REF and B_REF series.



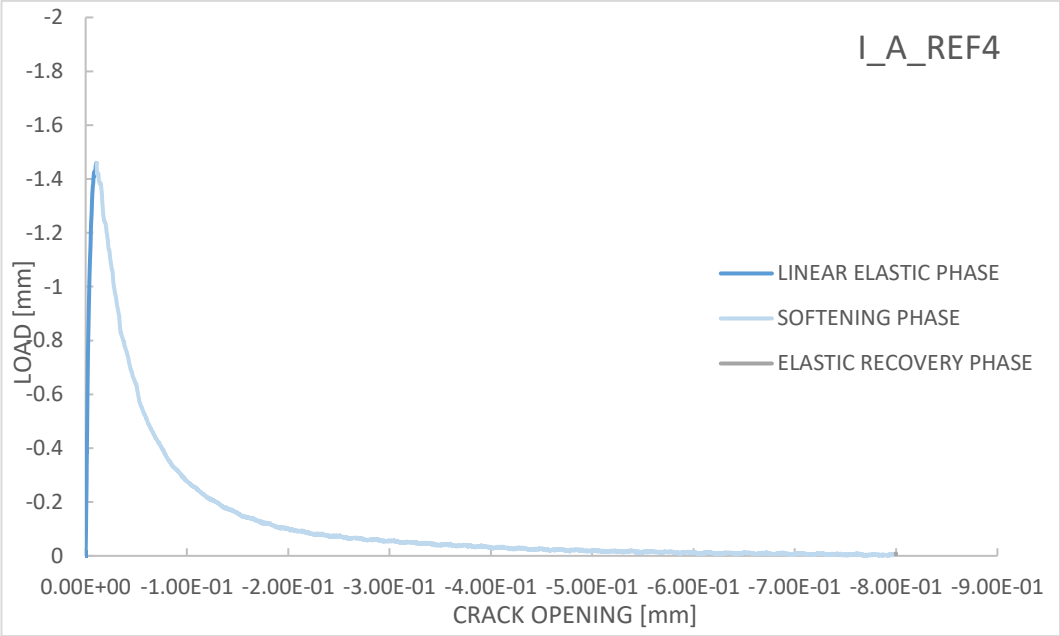
Graph 1 - Pre-cracking test upon the specimen without capsules - A_REF1



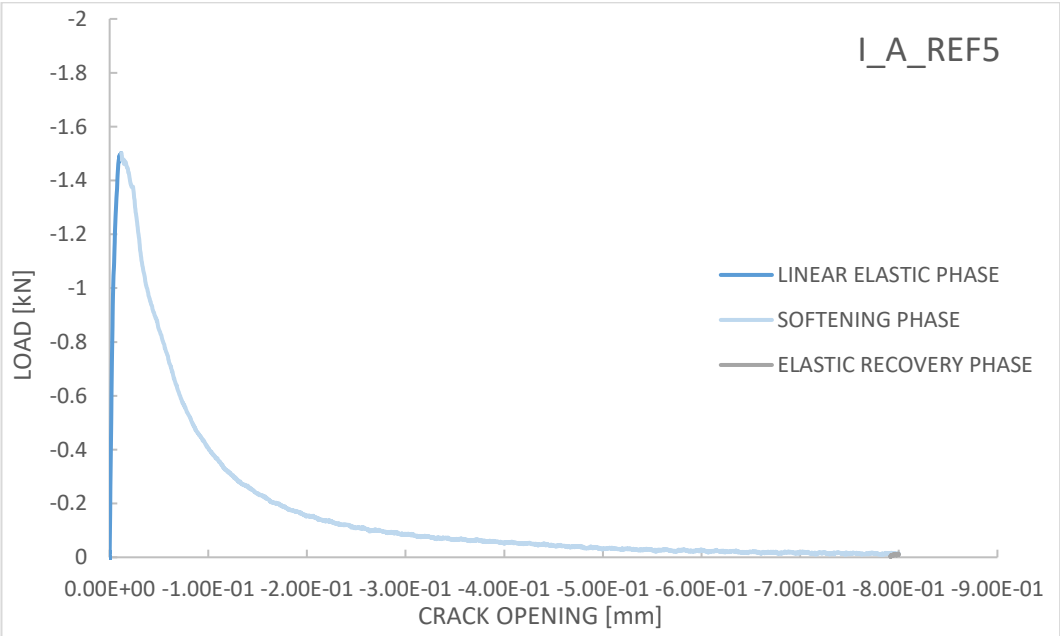
Graph 2 - Pre-cracking test upon the specimen without capsules - A_REF2



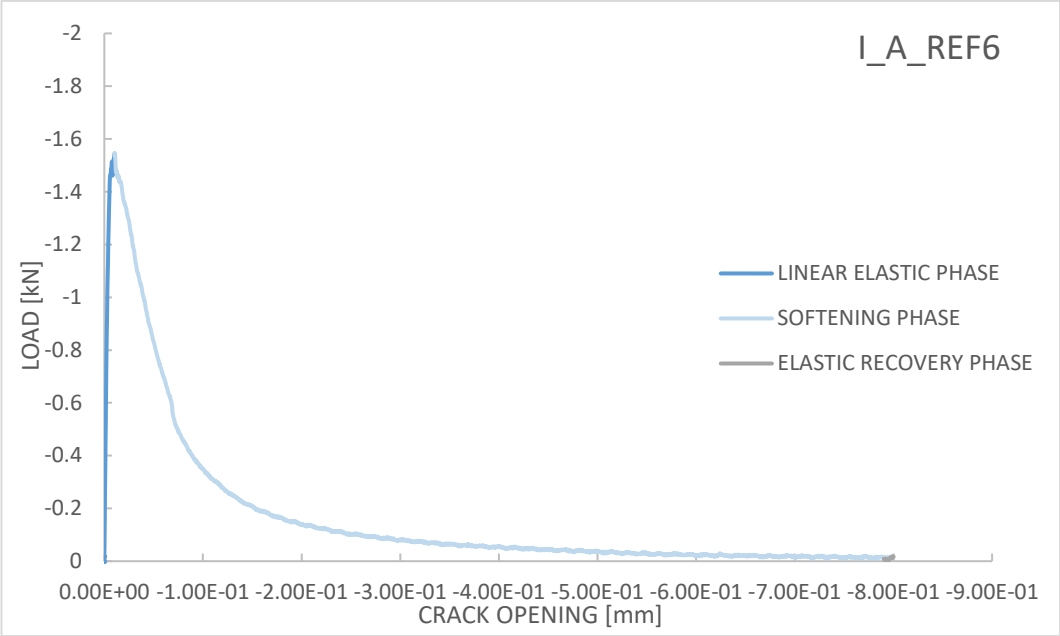
Graph 3 - Pre-cracking test upon the specimen without capsules - A_REF3



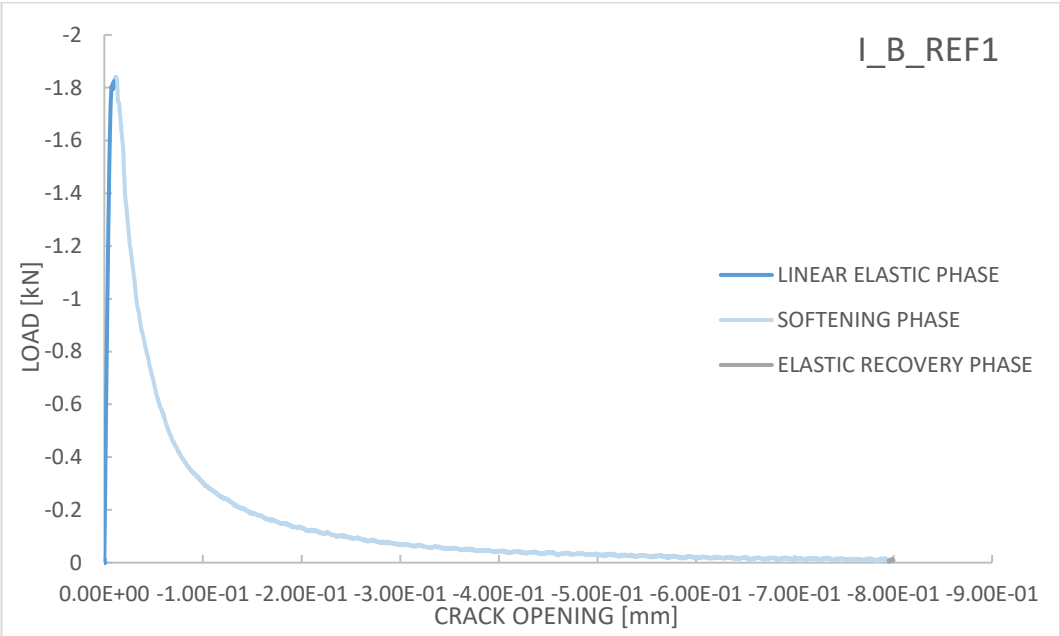
Graph 4 - Pre-cracking test upon the specimen without capsules - A_REF4



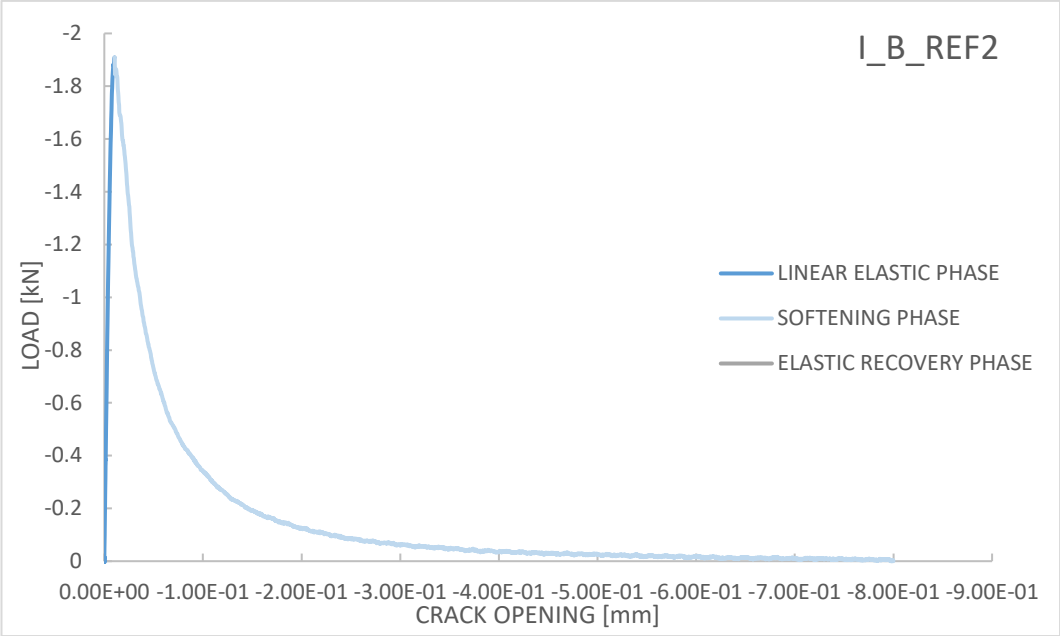
Graph 5 - Pre-cracking test upon the specimen without capsules - A_REF5



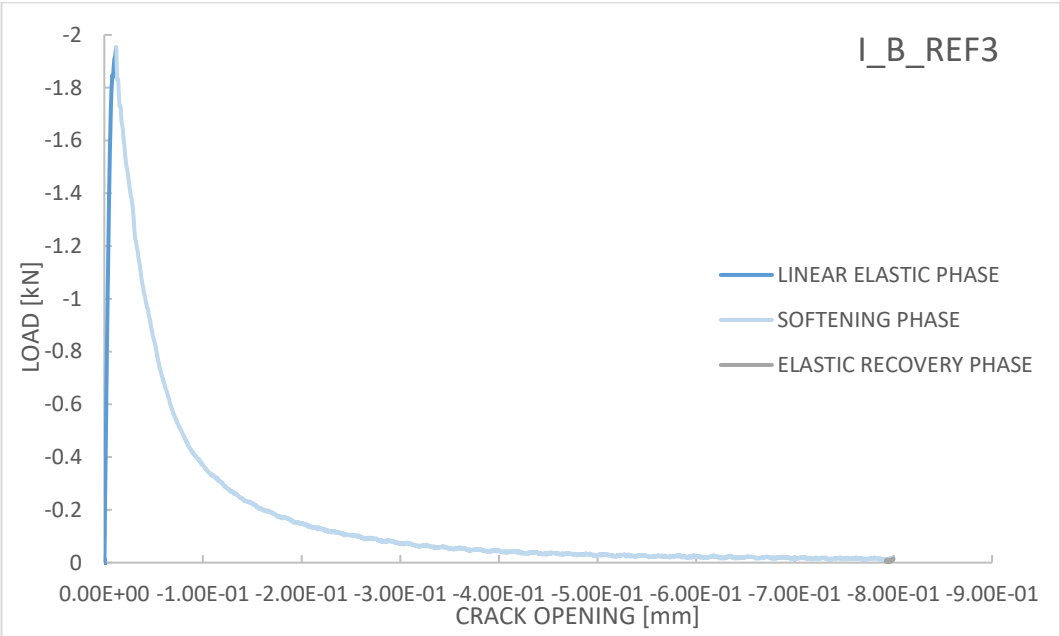
Graph 6 - Pre-cracking test upon the specimen without capsules - A_REF6



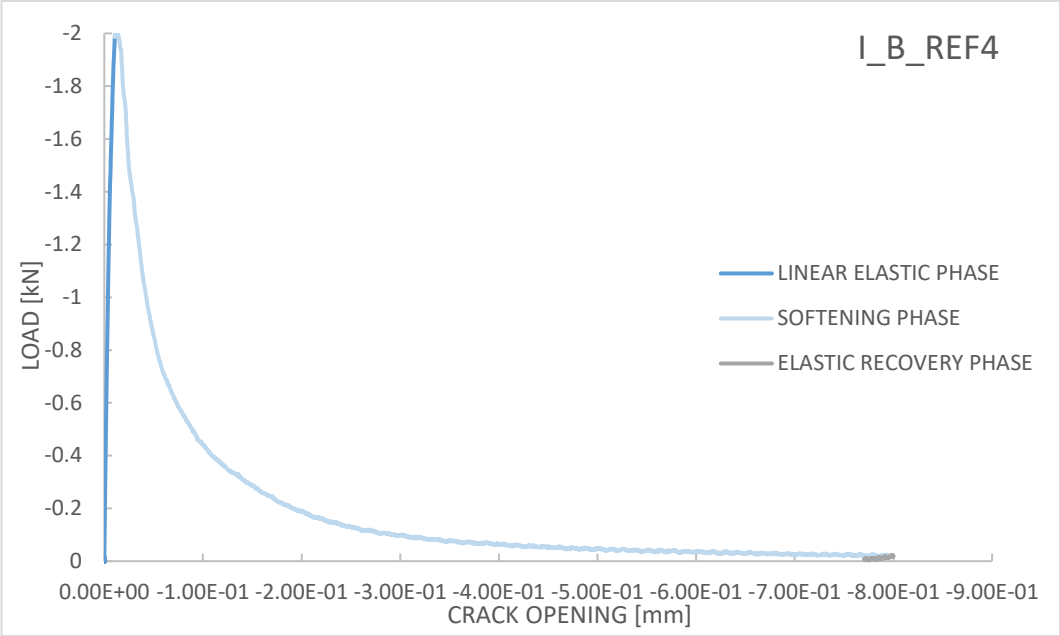
Graph 7 - Pre-cracking test upon the specimen without capsules - B_REF1



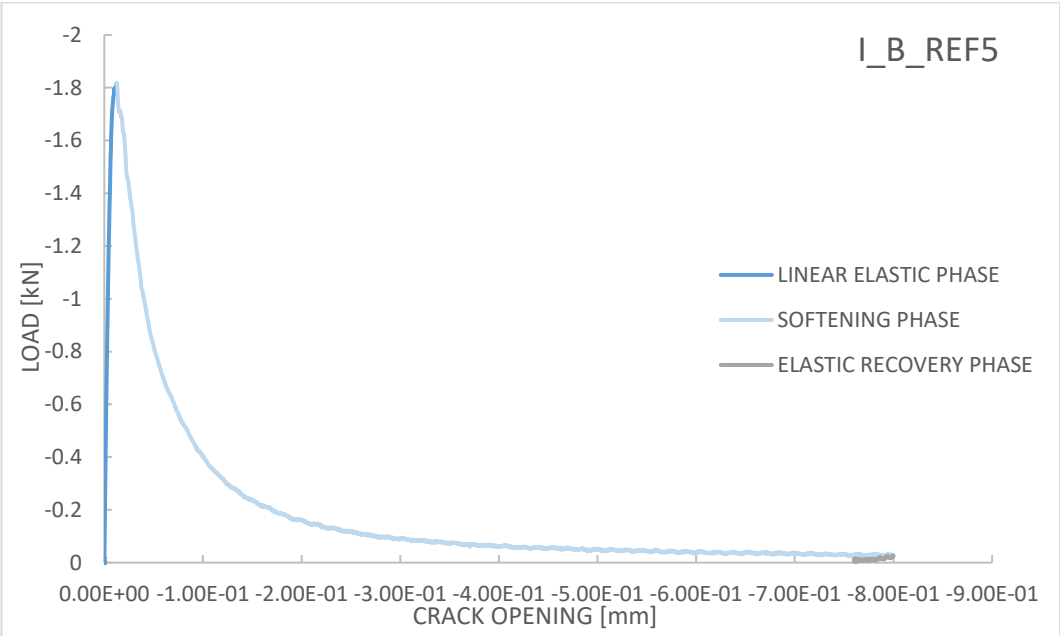
Graph 8 - Pre-cracking test upon the specimen without capsules - B_REF2



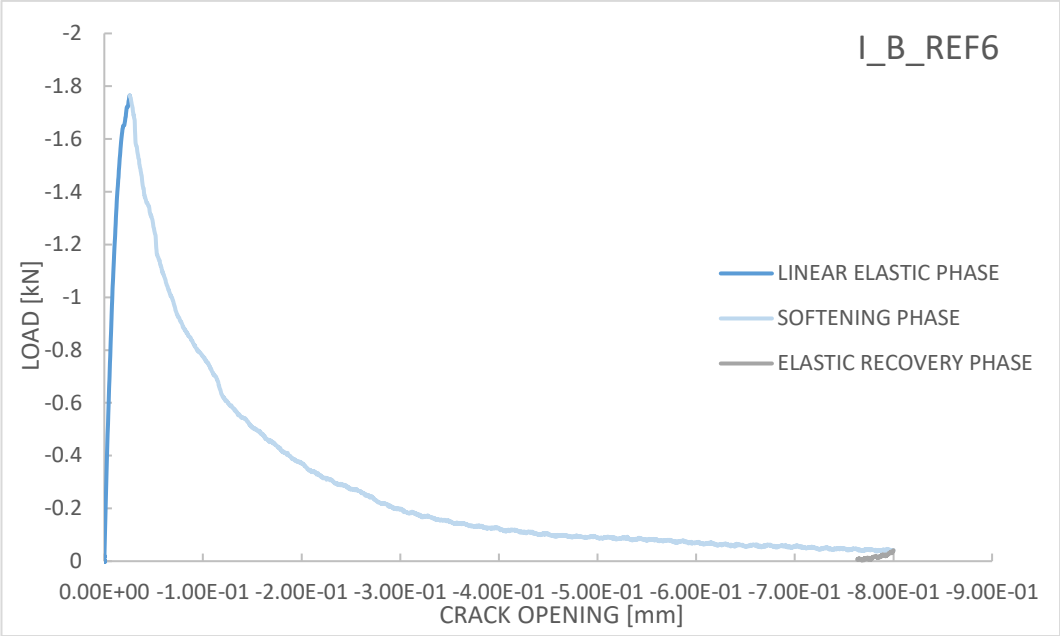
Graph 9 - Pre-cracking test upon the specimen without capsules - B_REF3



Graph 10 - Pre-cracking test upon the specimen without capsules - B_REF4



Graph 11 - Pre-cracking test upon the specimen without capsules - B_REF5

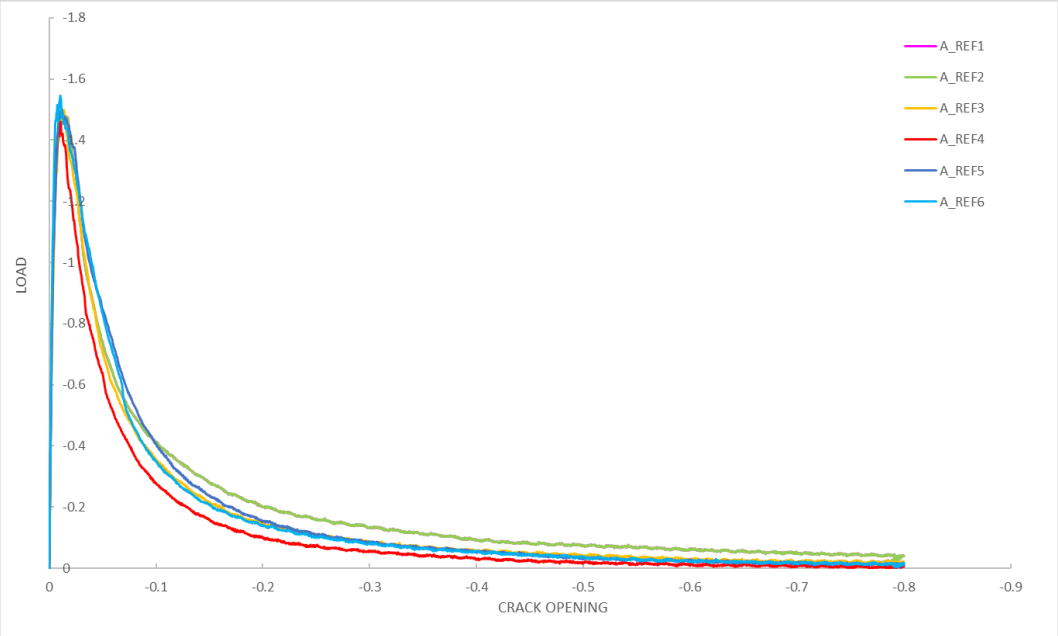


Graph 12 - Pre-cracking test upon the specimen without capsules - B_REF6

For the sake of comparison, all the curves belonging to the A_REF and B_REF series of the reference specimens have been reported and superposed.

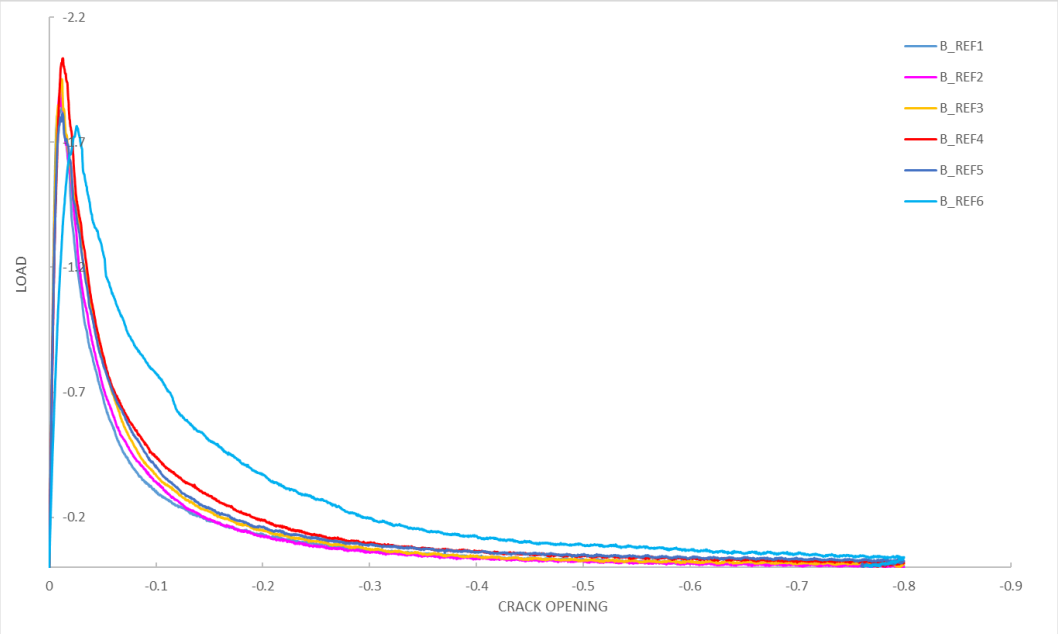
With this superposition, it is noticeable that the behavior of all the specimens was the same unless the maximum load values reached, which however remains similar on all the samples as shown in the previous table. In fact, for the first series of specimens, the average value of load reached during the pre-cracking phase was about 1535 N with a dispersion of 90 N and hence a 6% of variation.

Therefore, the following graph highlights the repeatability of operations and results on samples that are all the same.



Graph 13 - Superposition of the load curves for the group A of the specimens without the capsules

Similarly, the same observations can be stated for the second series of specimens not containing the capsules. For the B_REF series too, it is noticeable that the behavior of all the specimens was the same unless the maximum load values reached, which remarks the repeatability of operations and results. In fact, for the second series of specimens, the average value of load reached during the pre-cracking phase was about 1886 N with a dispersion of 90 N and hence a 5% of variation.



Graph 14 - Superposition of the load curves for the group B of the specimens without the capsules

5.1.2 CAPS specimens

The CAPS specimens are characterized by four type of trends, best described below:

- The first line is characterized by a linear elastic trend;
- First peak load to which corresponds the maximum material strength and the development of the first micro-cracks;
- Softening branch: the spreading of the crack in the specimen leads to a reduction in its cross-section and hence in its stiffness. During this phase, the fracture of the capsules occurs too, since they have similar mechanical properties in comparison to the surrounding matrix. The capsules fracture occurs when the crack, which starts from the edge of the notch, reaches the height of the capsules. The fracture of the capsules is sometimes followed by a sudden load drop, if the capsules

do not break simultaneously, there could be more than one load drop corresponding to the fracture of each capsule;

- Unloading phase: during this stage the 800 µm width opening mouth is reached and the load decreases, the specimen is unloaded and a partial elastic recovery can be observed.

It has to be pointed out that due to the heterogeneity inside the matrix during the breaking phase, the machine may lose control and a sudden a load drop may be recorded.

This phenomenon happened to three specimens of the first group, in detail to the specimens called I_A_CAPS2, I_A_CAPS5, I_A_CAPS6.

With the data acquired during the test, it was possible to obtain the charts load versus crack opening obtained for each specimen belonging to the A_CAPS and B_CAPS series.

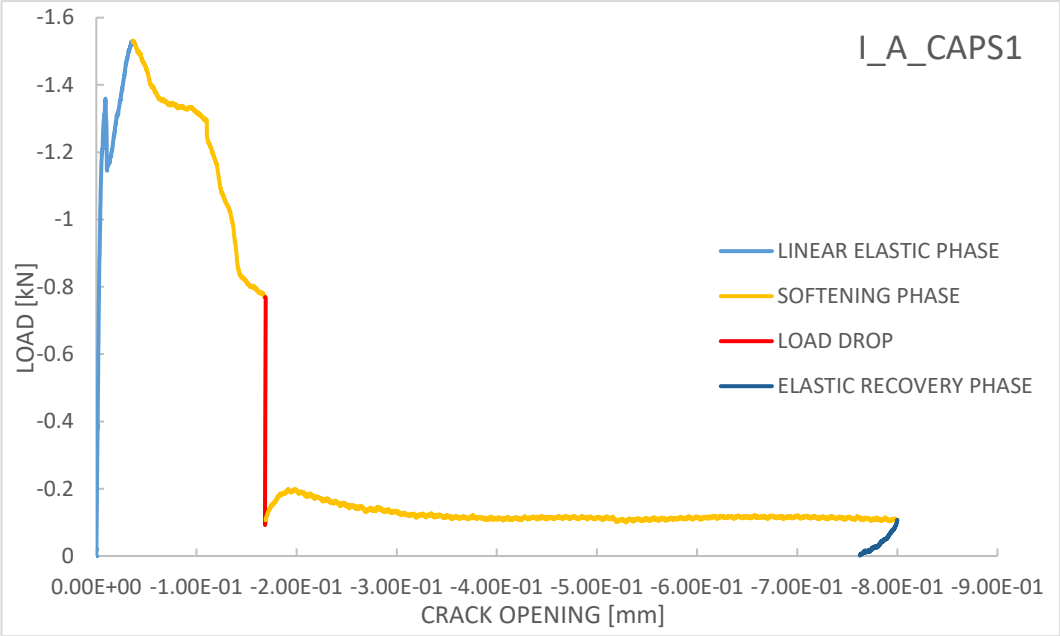
The data collected are reported below:

TESTED SPECIMENS	MAXIMUM LOAD [N]	AVERAGE LOAD [N]	DISPERSION	VARIATION COEFFICIENT [%]
I_A_CAPS1	1531.22	1420.19	90.03	6%
I_A_CAPS2	1511.49			
I_A_CAPS3	1285.49			
I_A_CAPS4	1326.65			
I_A_CAPS5	1452.34			
I_A_CAPS6	1413.95			
I_B_CAPS1	1429.63	1536.46	75.54	5%
I_B_CAPS2	1470.06			
I_B_CAPS3	1617.80			
I_B_CAPS4	1541.84			
I_B_CAPS5	1516.37			
I_B_CAPS6	1643.07			

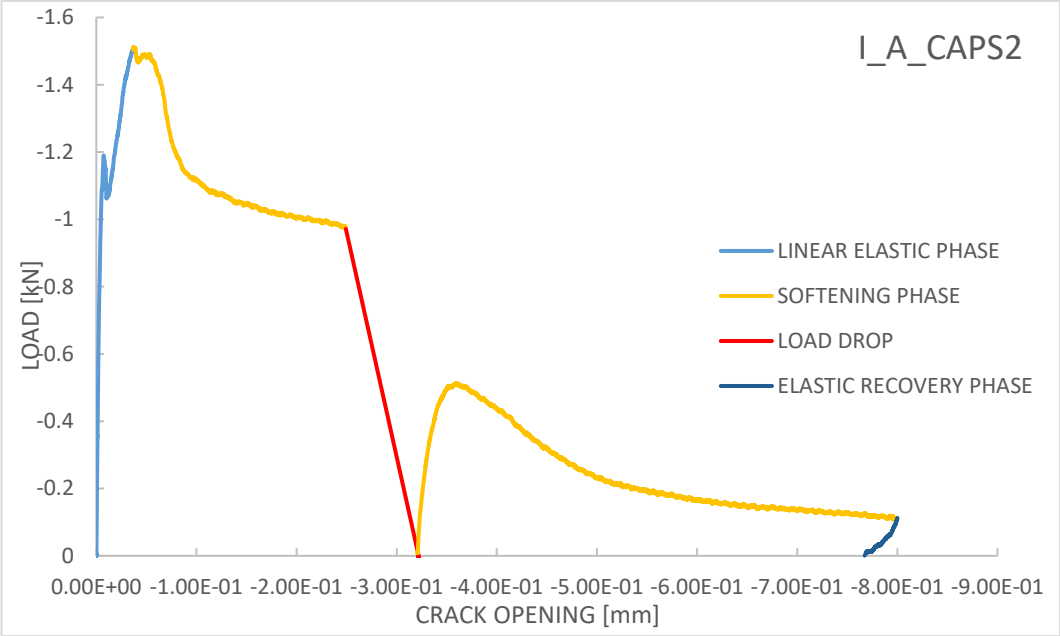
Table 13 – Tested specimens during the pre-cracking test - CAPS

Figure 40 - Cracking of the CAPS specimen

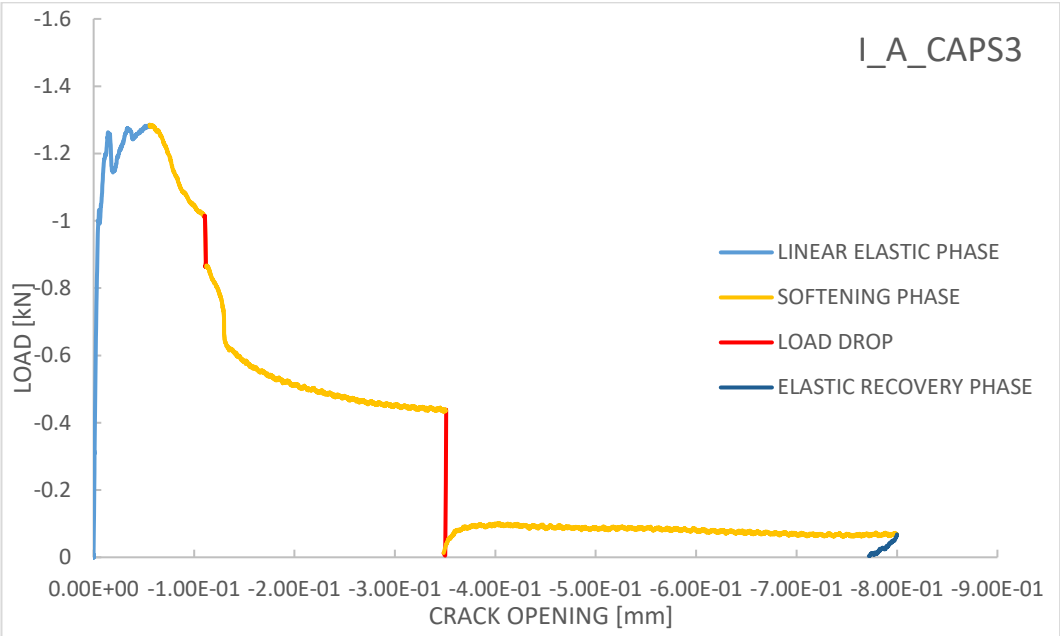
The following are charts load versus crack opening obtained with the data collected for the samples with capsules.



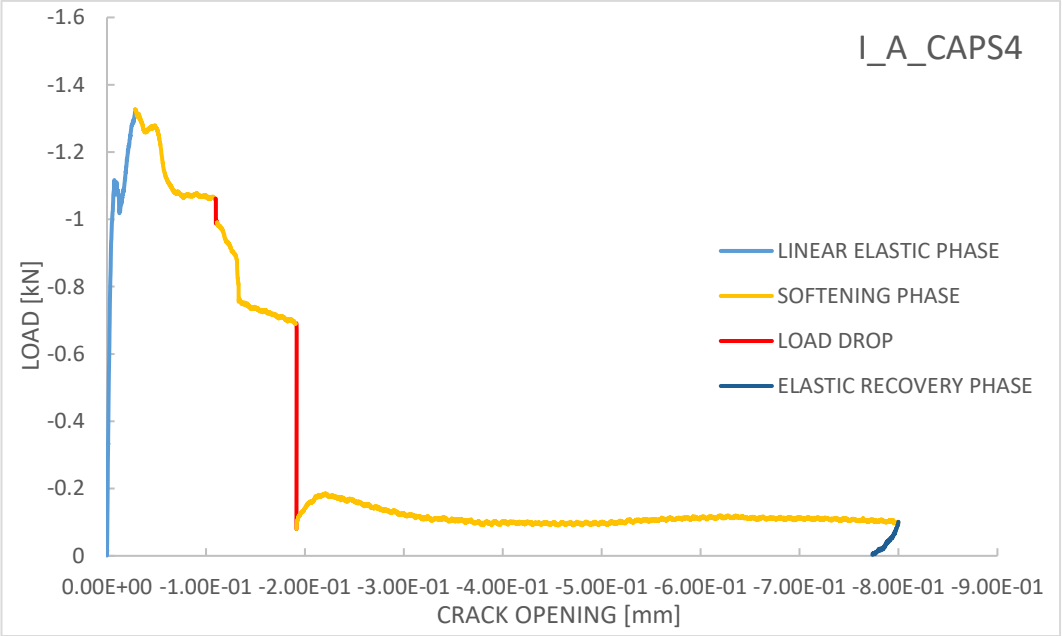
Graph 15 - Pre-cracking test upon the specimen with capsules - A_CAPS1



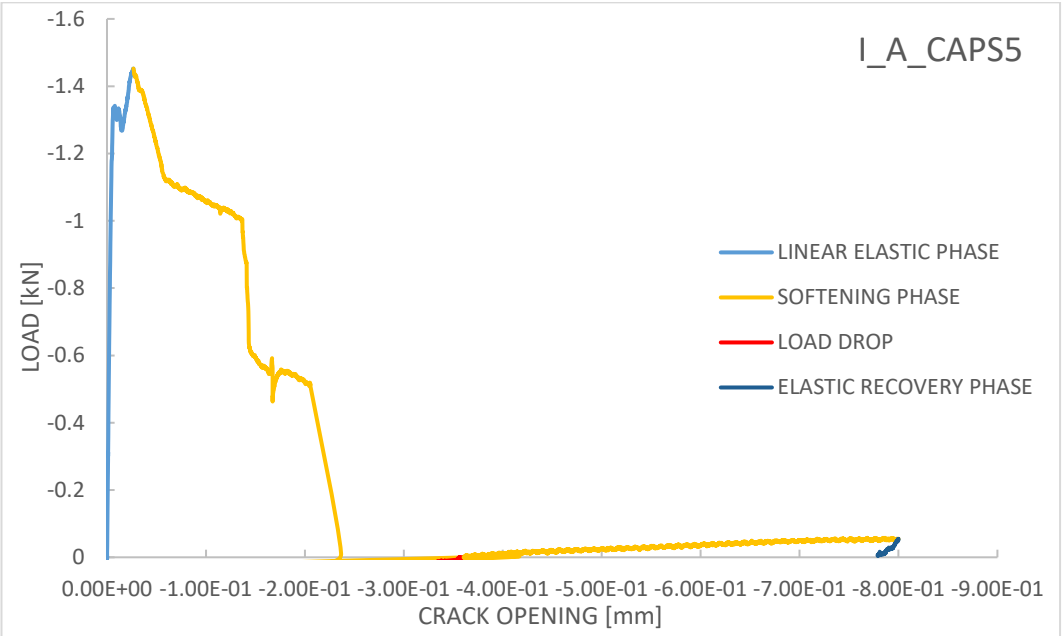
Graph 16 - Pre-cracking test upon the specimen with capsules - A_CAPS2



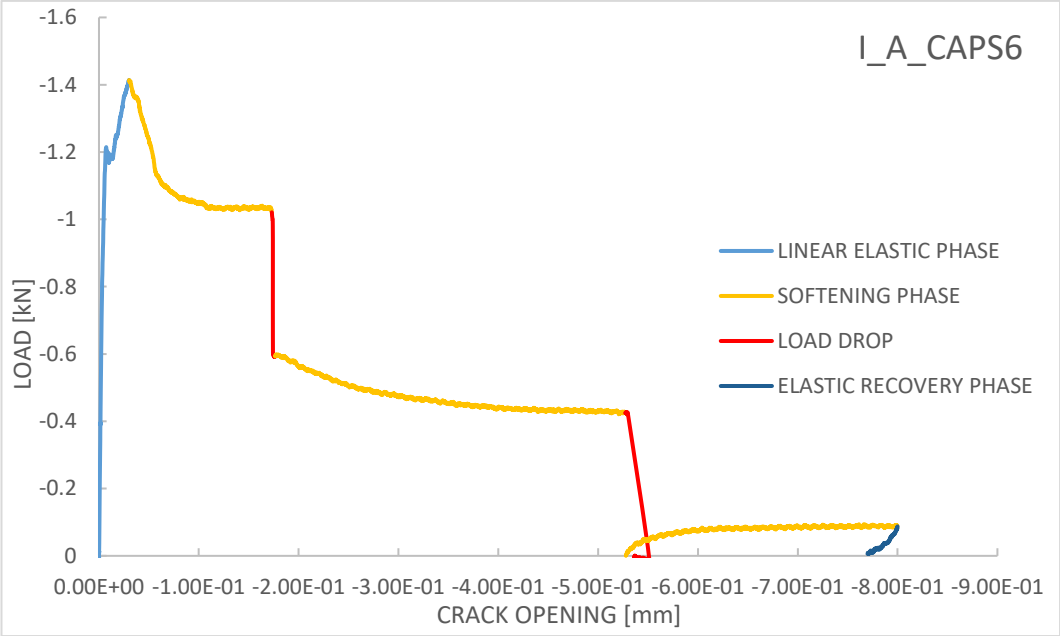
Graph 17 - Pre-cracking test upon the specimen with capsules - A_CAPS3



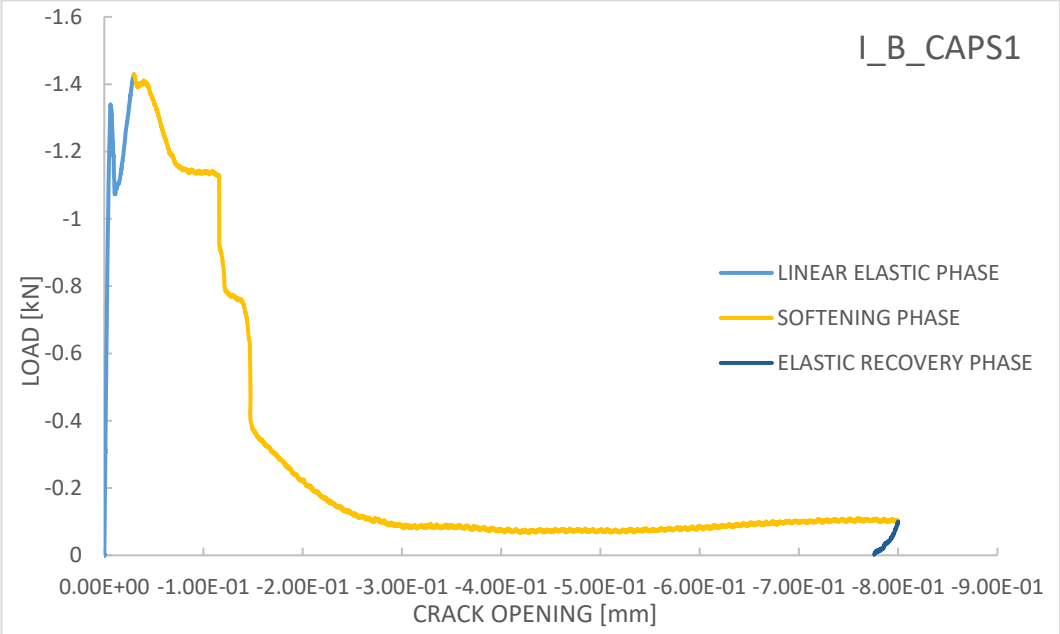
Graph 18 - Pre-cracking test upon the specimen with capsules - A_CAPS4



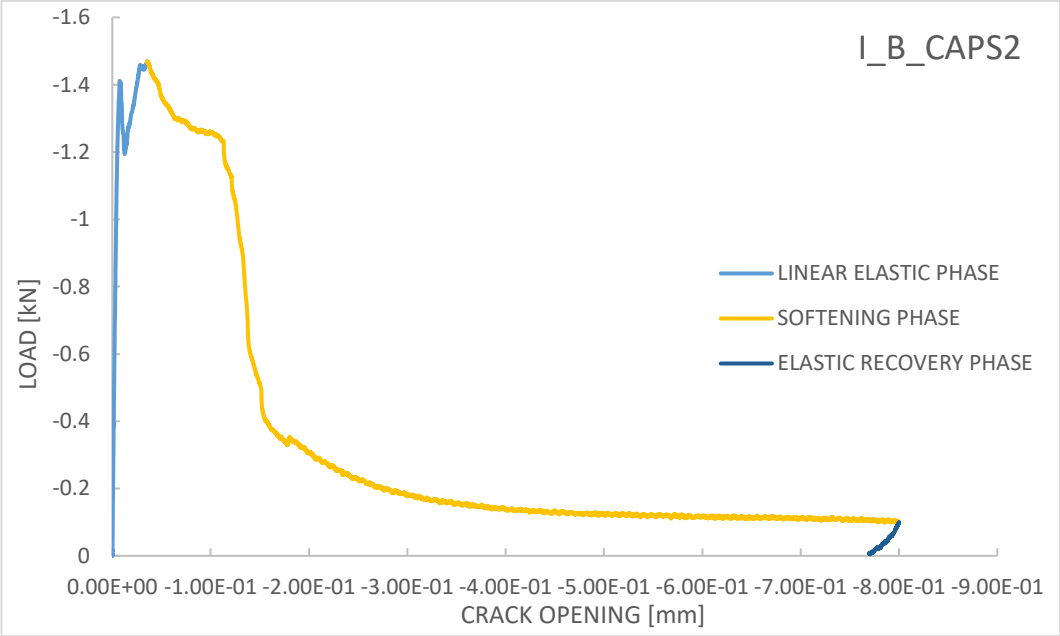
Graph 19 - Pre-cracking test upon the specimen with capsules - A_CAPS5



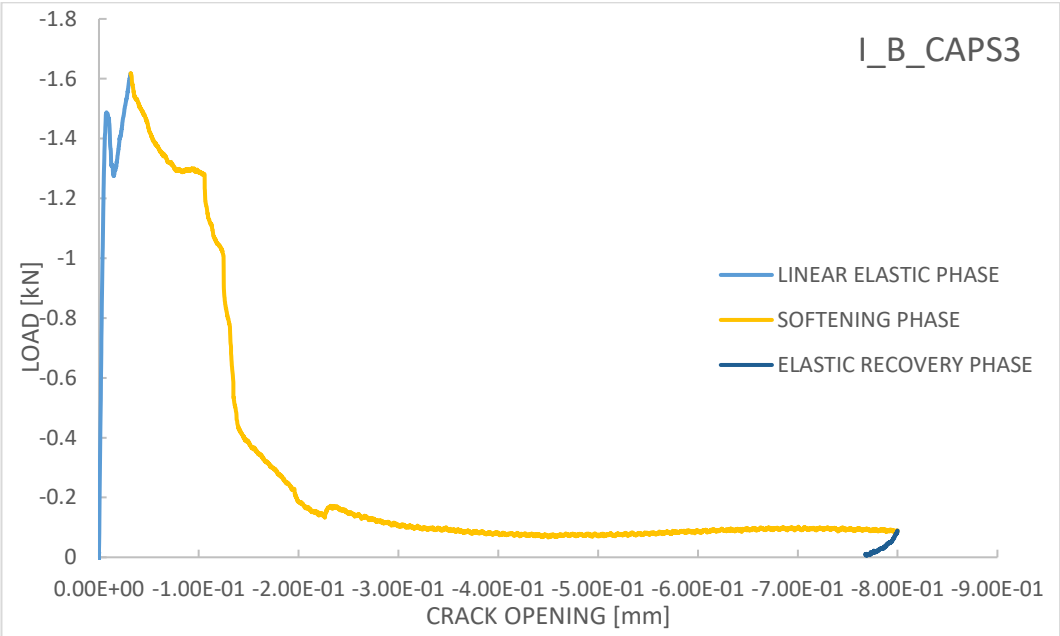
Graph 20 - Pre-cracking test upon the specimen with capsules - A_CAPS6



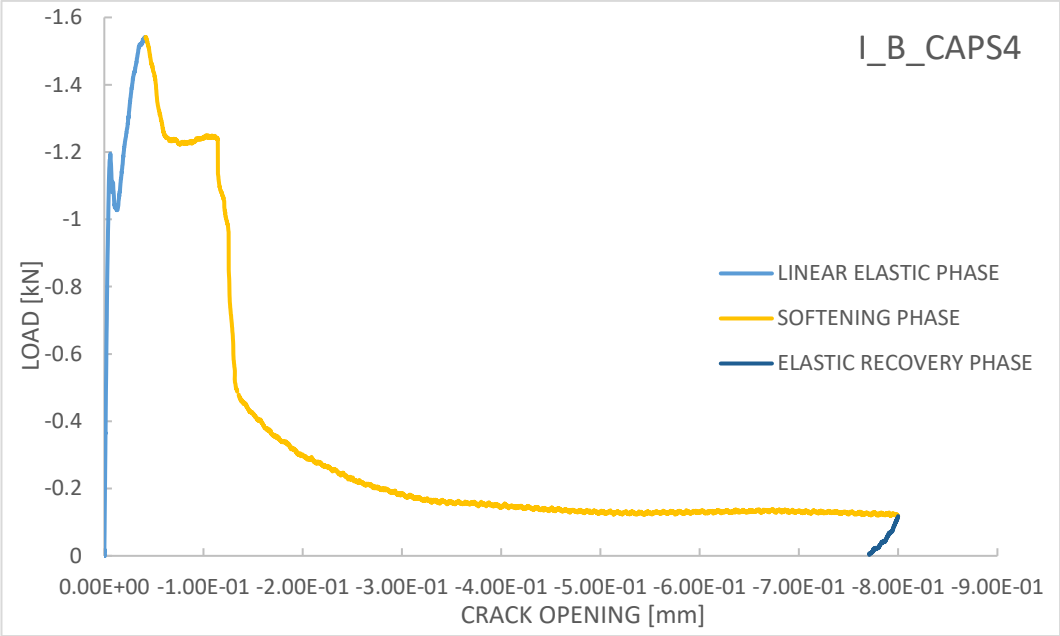
Graph 21 - Pre-cracking test upon the specimen with capsules - B_CAPS1



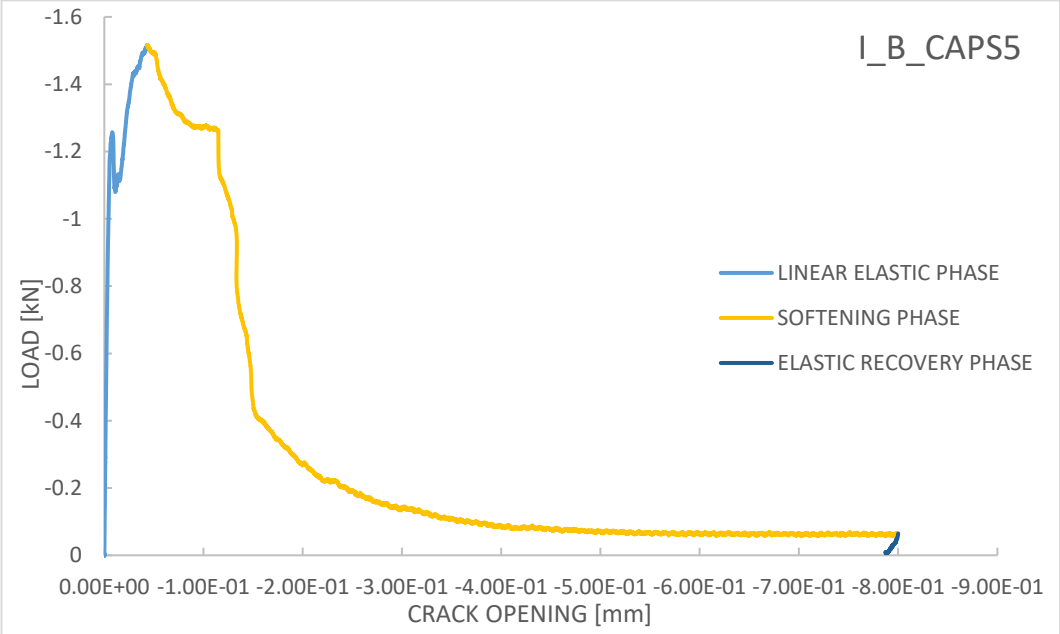
Graph 22 - Pre-cracking test upon the specimen with capsules - B_CAPS2



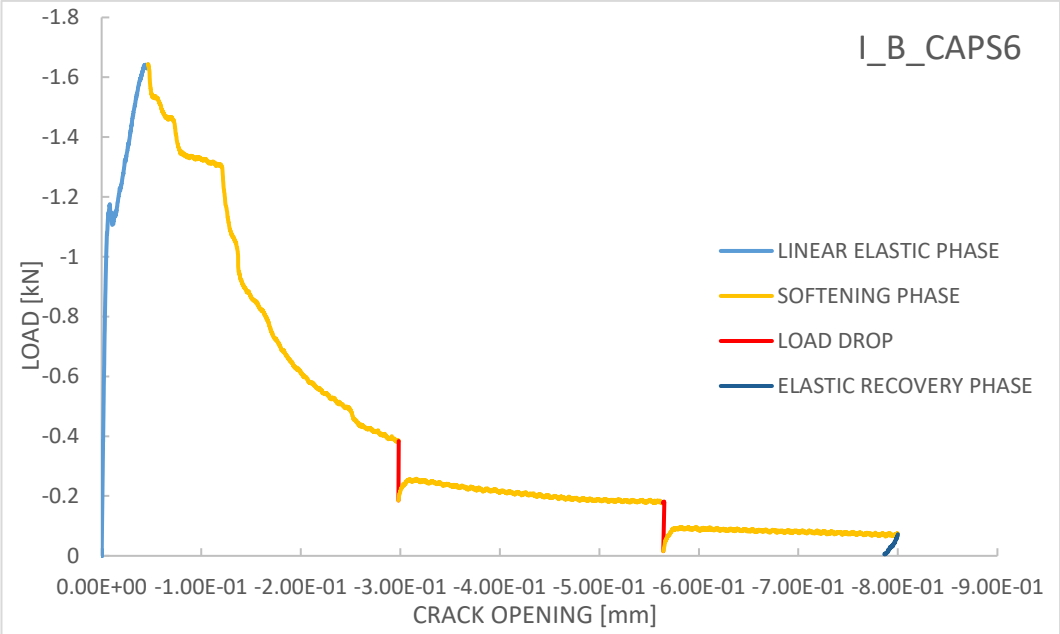
Graph 23 - Pre-cracking test upon the specimen with capsules - B_CAPS3



Graph 24 - Pre-cracking test upon the specimen with capsules - B_CAPS4



Graph 25 - Pre-cracking test upon the specimen with capsules - B_CAPS5

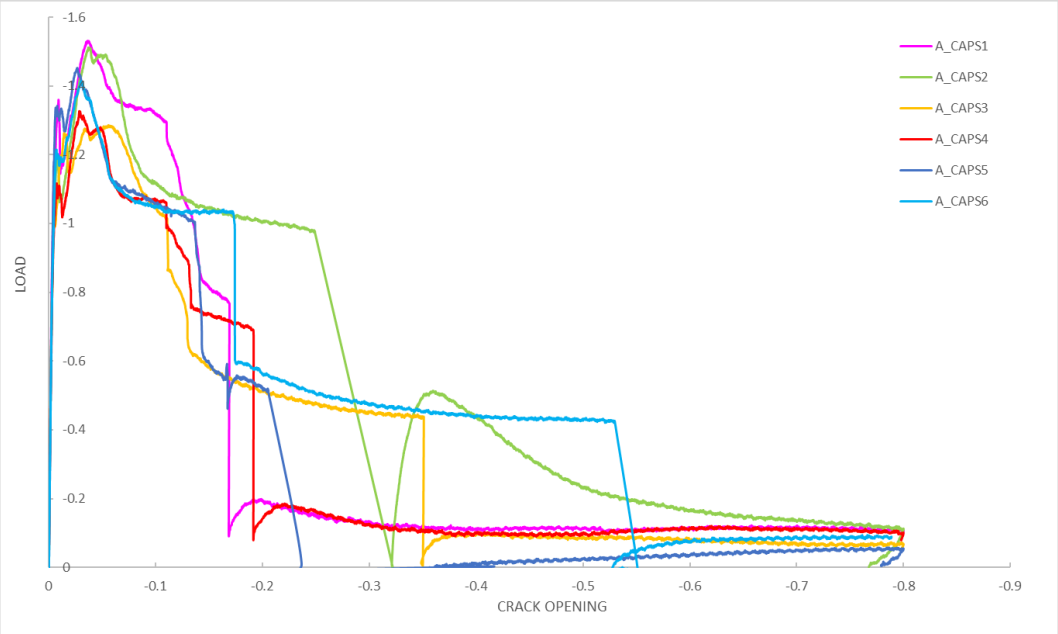


Graph 26 - Pre-cracking test upon the specimen with capsules - B_CAPS6

For the sake of comparison, all the curves belonging to the A_CAPS and B_CAPS series of the specimens with capsules have been reported and superposed.

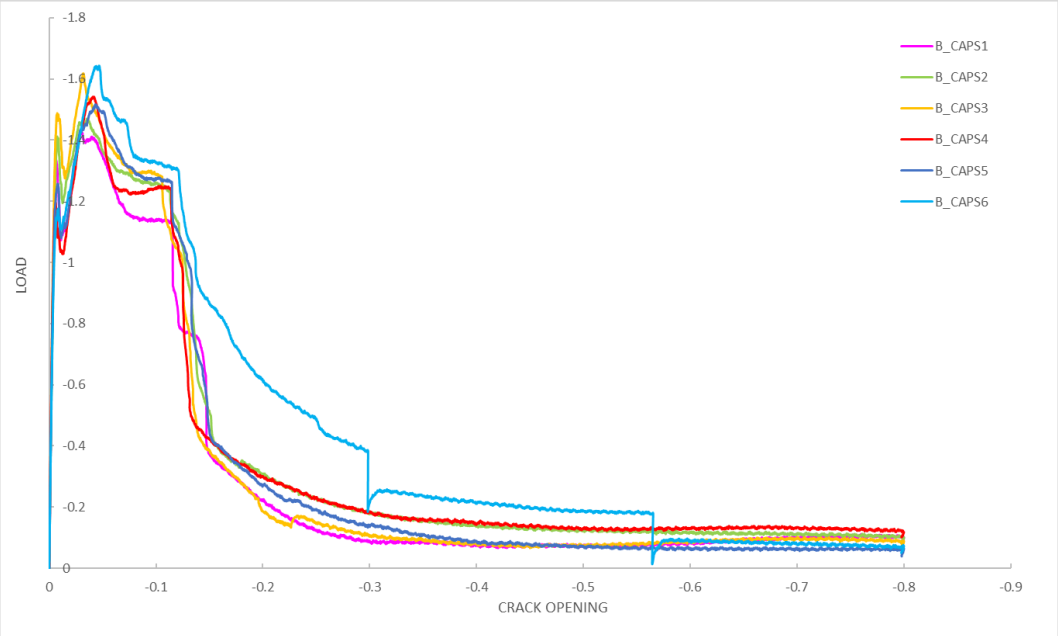
With this superposition, it is noticeable also in the case of encapsulated polyurethane specimens, how the behavior of all the specimens was the same unless the maximum load values reached, which however remains similar on all the samples as shown in the previous table. In fact, for the first series of specimens, the average value of load reached during the pre-cracking phase was about 1420 N with a dispersion of 90 N and hence a 6% of variation.

Therefore, the following graph highlights the repeatability of operations and results on samples that are all the same.



Graph 27 - Superposition of the load curves for the group A of the specimens with the capsules

Similarly, the same observations can be stated for the second series of specimens containing the capsules. For the B_CAPS series too, it is noticeable that the behavior of all the specimens was the same unless the maximum load values reached, which remarks the repeatability of operations and results. In fact, for this second series of specimens, the average value of load reached during the pre-cracking phase was about 1536 N with a dispersion of 75 N and hence a 5% of variation.



Graph 28 - Superposition of the load curves for the group B of the specimens with the capsules

5.2 Durability test

As mentioned in the previous section, the durability test was run differently between the two groups of encapsulated specimens. All the specimens belonging to the A group (A_REF and A_CAPS) were tested using the SARCOS protocol procedure, while all the specimens belonging to the B group (B_REF and B_CAPS) were tested using a brand-new procedure taking inspiration from the literature.

This choice was driven from the necessity to provide comparisons between different types of water permeability tests, using different conditions in order to disprove that the results could depend on the testing conditions rather than the effective sealing power of the healing agent.

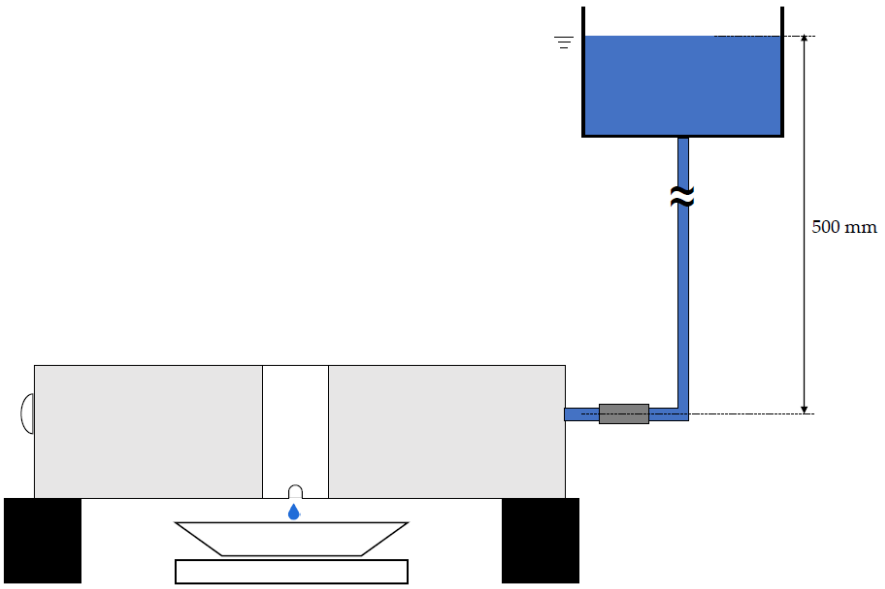


Figure 41 - Test setup for the water-flow test used for the A group of specimens (SARCOS protocol)

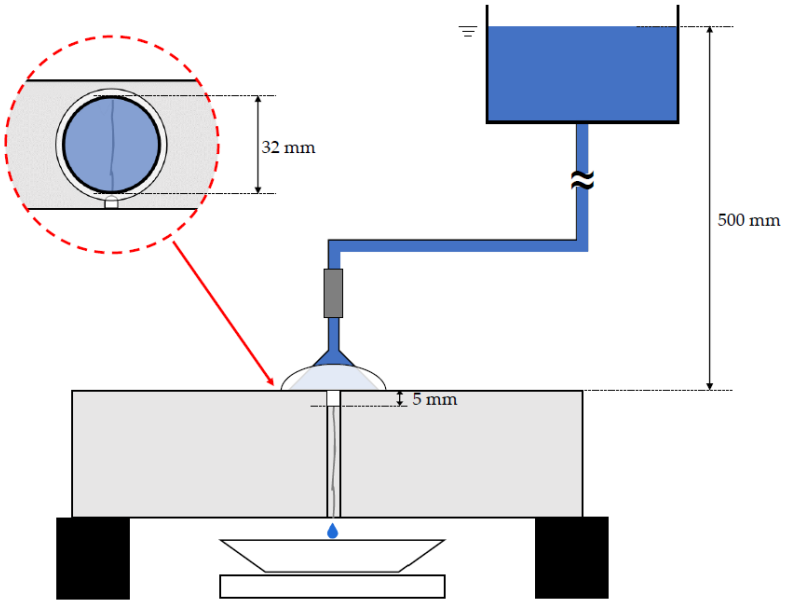


Figure 42 - Test setup for the water-flow test used for the B group of specimens

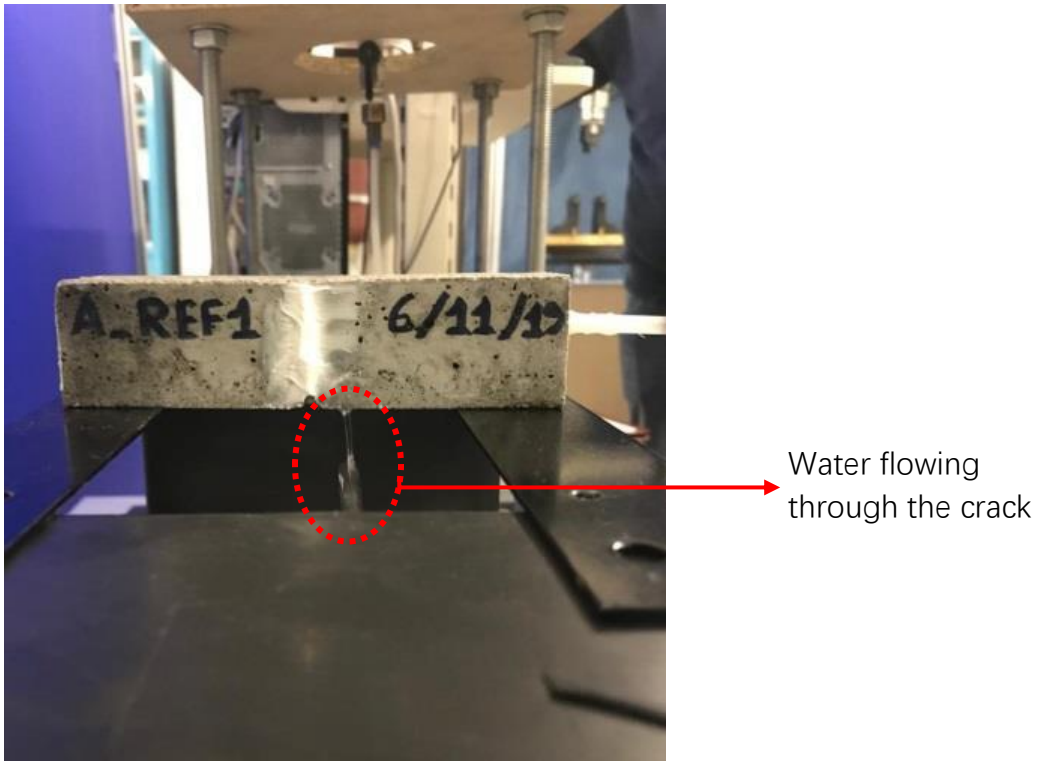


Figure 43 - Water passing through the cracked specimen

5.2.1 REF specimens

As for concerns the REF specimens the data collected are reported below:

TESTED SPECIMEN	T_1	M_1	T_2	M_2
	[h]	[g]	[h]	[g]
A_REF1	09.36.10	40.3	09.42.10	279.1
A_REF2	09.46.47	21.9	09.52.47	145.6
A_REF3	10.19.13	12.1	10.25.13	60.3
A_REF4	10.28.44	87.3	10.34.44	658.7
A_REF5	11.06.06	130.5	11.12.06	1178.3
A_REF6	11.16.39	56.1	11.22.39	394.9
B_REF1	09.56.22	101.2	10.02.22	768.4
B_REF2	10.16.21	244.6	10.21.21	1484.8
B_REF3	10.44.57	89.4	10.50.57	655.1
B_REF4	10.55.19	57.9	11.01.19	547.7
B_REF5	11.24.34	19.0	11.30.34	267.3
B_REF6	11.34.48	48.9	11.40.48	467.9

Table 14 - Tested specimens during the durability test - REF weighted mass

For each specimen, the water flow and the sealing effectiveness index have been calculated according to the equations described in the previous chapter.

The results are reported below:

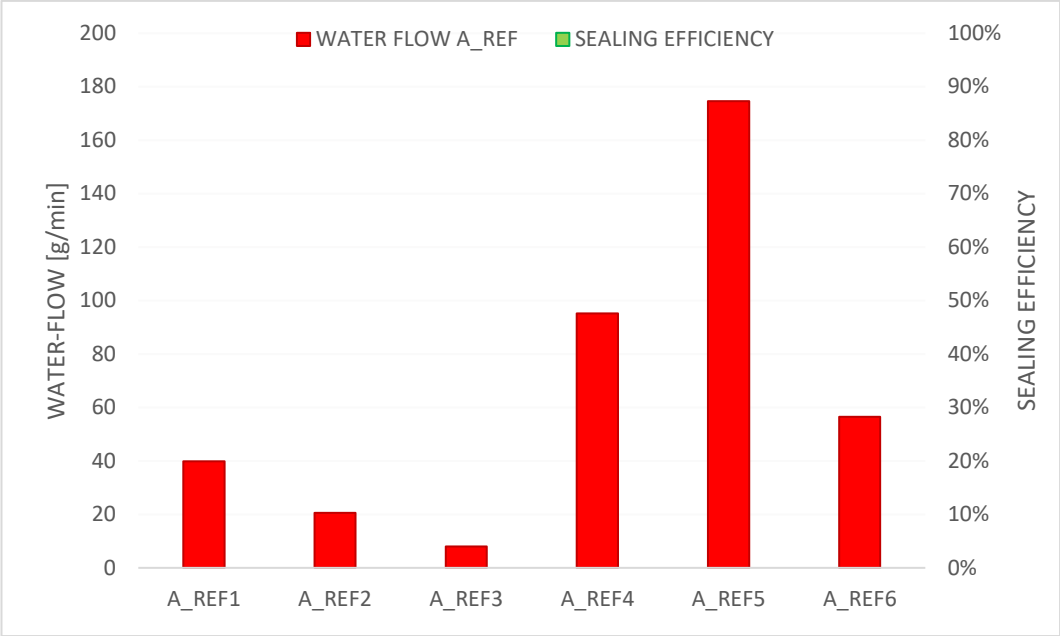
TESTED SPECIMEN	ΔT	ΔM	WF	ES
	[min]	[g]	[g/min]	[%]
A_REF1	6	238.8	39.8	0
A_REF2	6	123.7	20.6	0
A_REF3	6	48.2	8.0	0
A_REF4	6	571.4	95.2	0
A_REF5	6	1047.8	174.6	0
A_REF6	6	338.8	56.5	0
B_REF1	6	667.2	111.2	0
B_REF2	5	1240.2	248.0	0
B_REF3	6	565.7	94.3	0
B_REF4	6	489.8	81.6	0
B_REF5	6	248.3	41.4	0
B_REF6	6	419.0	69.8	0

Table 15 - Tested specimens during the durability test - REF sealing efficiency

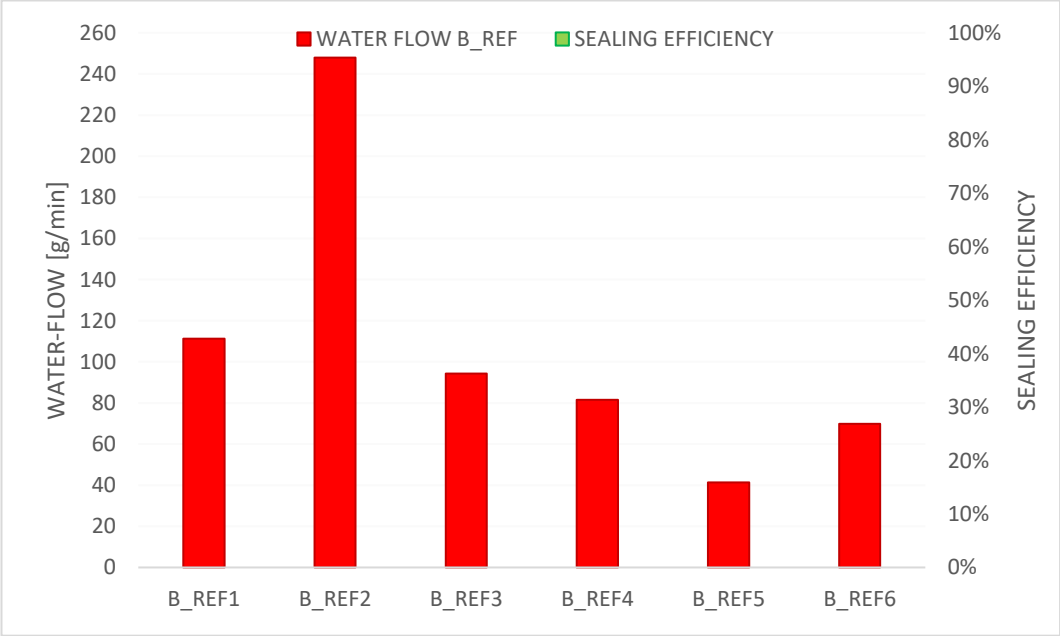
During the execution of the test on the specimens A_REF4 and A_REF5, water also leaked from the upper face of the specimen, a clear sign that they were completely cracked.

For the B_REF2 specimen the test was stopped before the expiration of the 7 minutes because the amount of water that passed through it was such that completely filled the container for the measurement before the expiration of the limit time.

Obviously, for all the specimens regardless of the type of test performed, the sealing efficiency was nil since the prisms did not contain any healing agent, as shown in the following graphs.



Graph 29 - Comparison between water flow and sealing efficiency of the specimens without capsules for the group A



Graph 30 - Comparison between water flow and sealing efficiency of the specimens without capsules for the group B

5.2.2 CAPS specimens

As for concerns the CAPS specimens the data collected are reported below:

TESTED SPECIMEN	T_1	M_1	T_2	M_2
	[h]	[g]	[h]	[g]
A_CAPS1	09.55.45	0	10.01.45	0
A_CAPS2	10.05.00	0	10.11.00	0
A_CAPS3	10.39.41	0	10.45.41	0
A_CAPS4	10.47.56	0	10.53.56	0
A_CAPS5	11.25.59	0	11.31.59	0
A_CAPS6	11.44.00	0	11.50.00	0
B_CAPS1	10.06.08	0	10.12.08	0
B_CAPS2	10.28.41	0	10.34.41	22.2
B_CAPS3	11.05.16	0.5	11.11.16	0.9
B_CAPS4	11.15.50	2.3	11.21.50	4.2
B_CAPS5	11.44.08	0.8	11.50.08	2.3
B_CAPS6	11.52.45	115.9	11.58.45	884.7

Table 16 - Tested specimens during the durability test - CAPS weighted mass

For each specimen the water flow and the sealing effectiveness index have been calculated according to the equations described in the previous chapter.

The results are reported below:

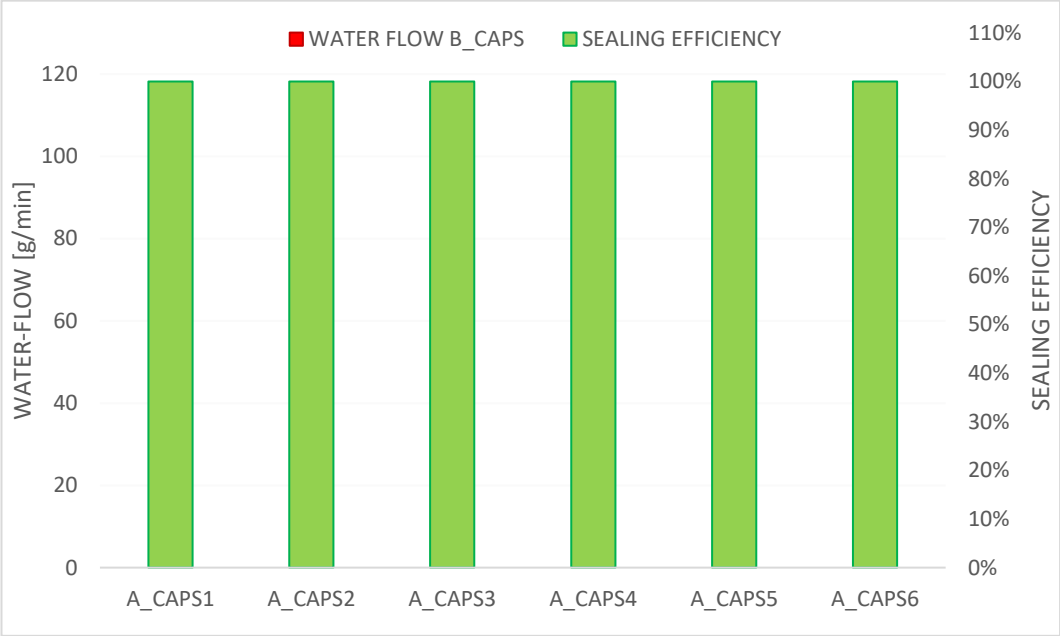
TESTED SPECIMEN	ΔT	ΔM	WF	ES
	[min]	[g]	[g/min]	[%]
A_CAPS1	6	0	0	100
A_CAPS2	6	0	0	100
A_CAPS3	6	0	0	100
A_CAPS4	6	0	0	100
A_CAPS5	6	0	0	100
A_CAPS6	6	0	0	100
B_CAPS1	6	0	0	100
B_CAPS2	6	22.2	3.7	96.6
B_CAPS3	6	0.4	0.1	99.9
B_CAPS4	6	1.9	0.3	99.7
B_CAPS5	6	1.5	0.3	99.8
B_CAPS6	6	768.8	128.1	-18.9

Table 17 – Tested specimens during the durability test - CAPS sealing efficiency

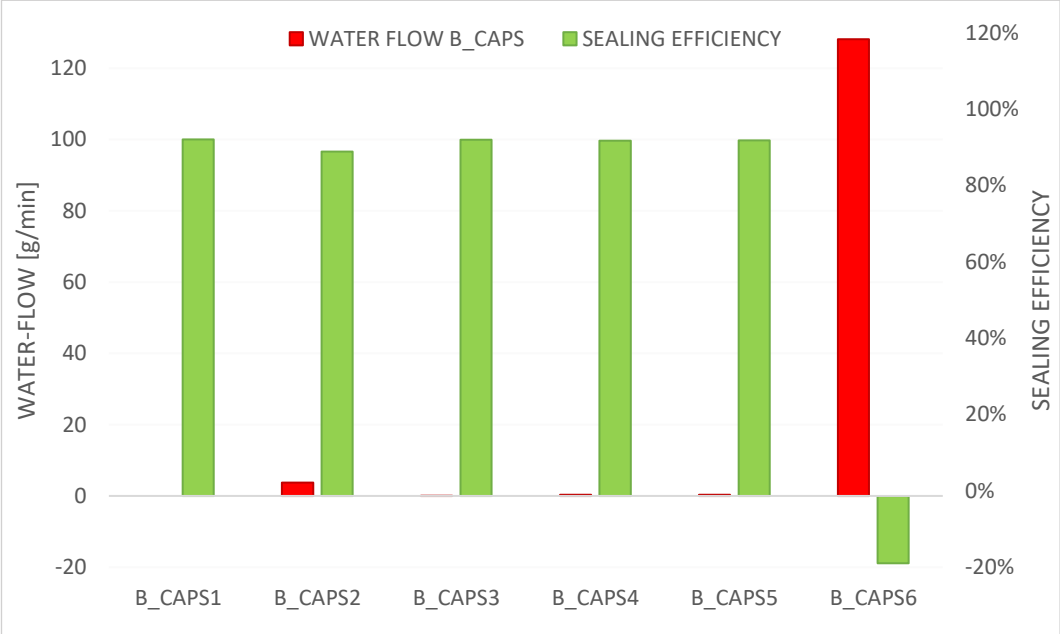
For the first group of specimens, the waterflow recorded was nil and as a result the sealing efficiency equal to 100%.

For the second group of specimens, the water passed through the crack was higher due to the respect of the first group, because the conditions of the test itself were more severe, nevertheless, the results obtained are excellent as the sealing efficiency calculated exceeds the 95% on all the samples. The only anomaly is noted for the specimen B_CAPS6, because the recorded water flow is elevated: this is due because the capsules inserted inside did not completely release the polyurethane during the first load test, leaving many opened cracks.

There results are shown in the following graphs.



Graph 31 - Comparison between water flow and sealing efficiency of the specimens with capsules for the group A



Graph 32 - Comparison between water flow and sealing efficiency of the specimens with capsules for the group B

5.3 Static reloading test

The aim of the test is to evaluate the load recovery index (LRI) expressed as a function of the maximum load-bearing capacity of the specimens in the pre-cracking phase and the static reloading one, and dependent to the leftover bearing capacity at the end of the pre-cracking test.

This index is valid for single specimens since both the initial pre-cracking curve and the subsequent reloading curves are unique for each of them.

Consequently, it is not possible to obtain an average index considering components and data referred to different samples, unless the residual load resistance may be considered as negligible, in fact it turns out to be a very small value.

5.3.1 REF specimens

It can be seen that the specimen without the capsule does not resume the behavior it should have, since small manipulations and displacements on an already cracked element lead to a decrease in the residual load capacity PR.

Using the following relationship, it is possible to obtain an average value for all the specimens analyzed, considering separately the self-repairing ones from the reference ones.

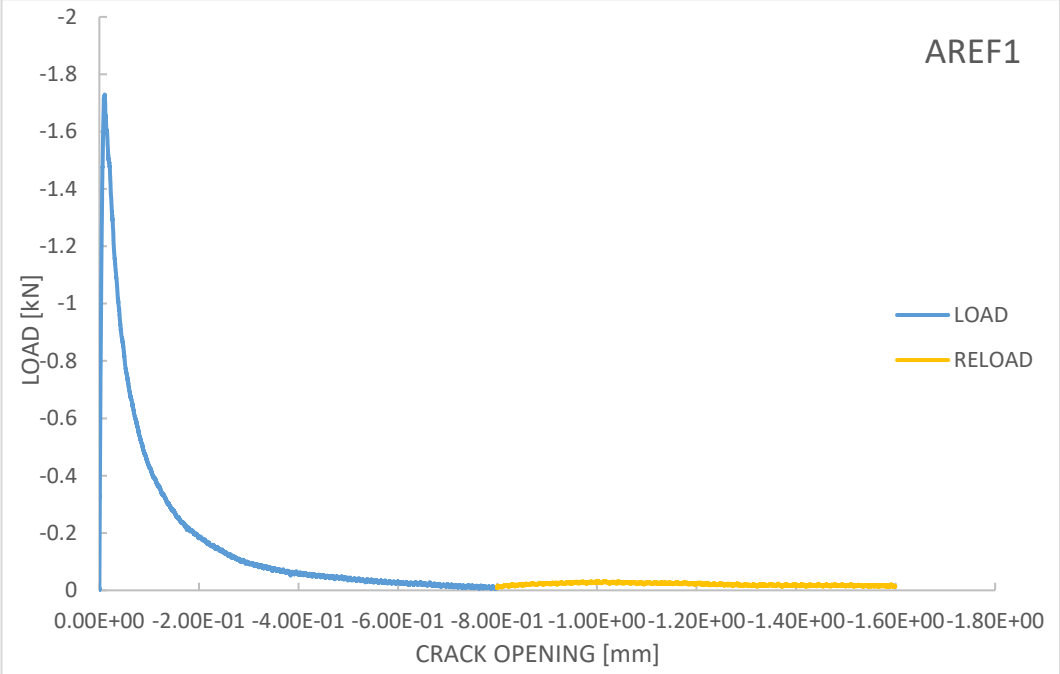
$$LRI = \frac{L_{reload}}{L_{peak}} \ [\%]$$

Graphically, this results in a peak P'' lower than PR. In some cases, P'' is even zero, such as for AREF4, AREF5, BREF2 and BREF4, as it fails even before being tested.

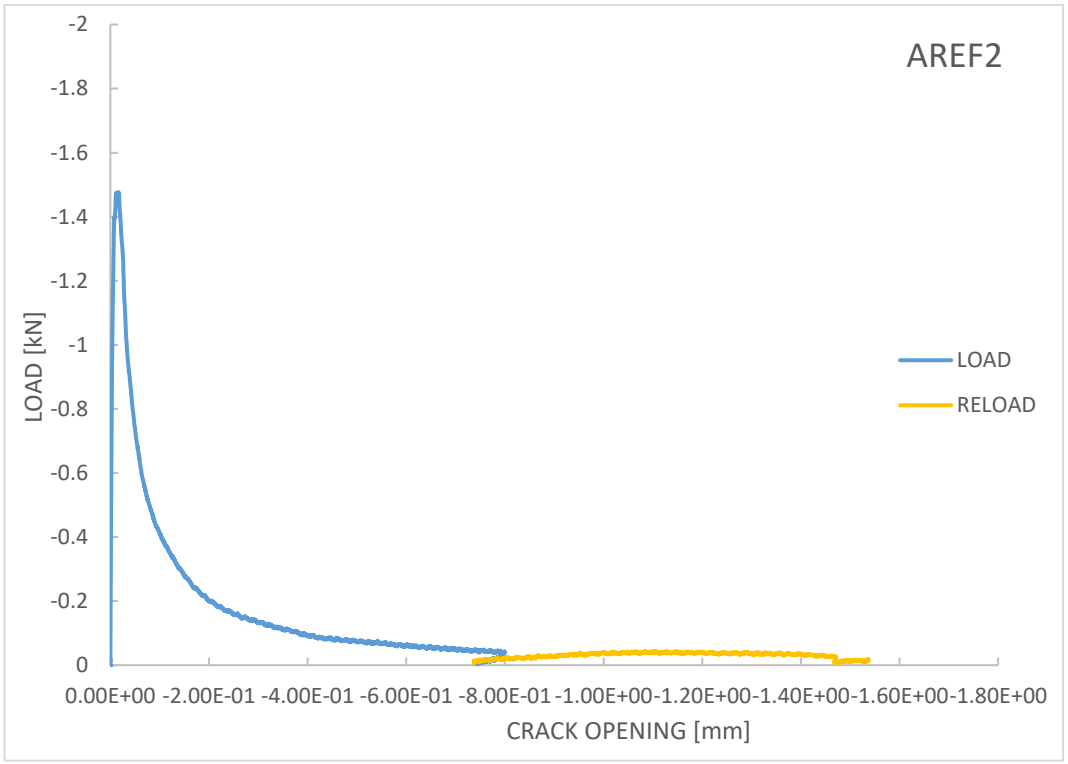
For each specimen, the peak during the load phase and the peak during the reloading phase have been analyzed and are reported below:

TESTED SPECIMEN	L_{PEAK}	L_{RELOAD}
	[N]	[N]
A_REF1	1729.17	21.05
A_REF2	1476.74	37.41
A_REF3	1498.86	37.41
A_REF4	1459.53	Invalid
A_REF5	1501.59	Invalid
A_REF6	1545.45	20.23
B_REF1	1839.89	13.18
B_REF2	1909.19	Invalid
B_REF3	1952.50	11.49
B_REF4	2035.67	Invalid
B_REF5	1816.30	19.00
B_REF6	1765.00	38.89

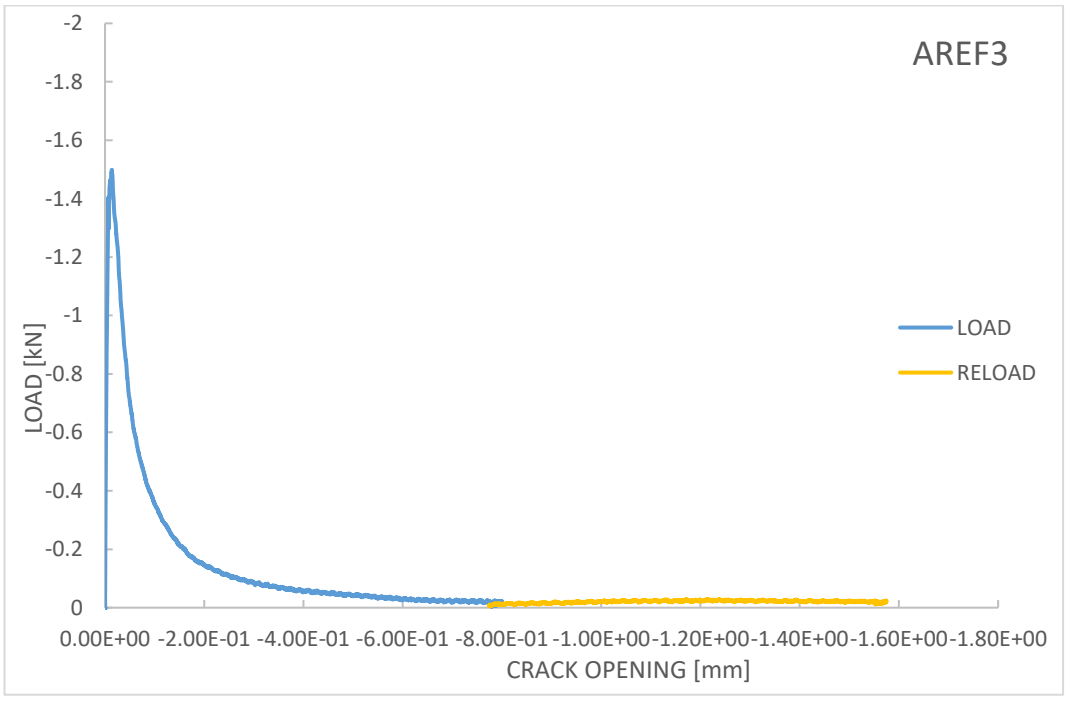
Table 18 - Tested specimens during the reloading test - REF



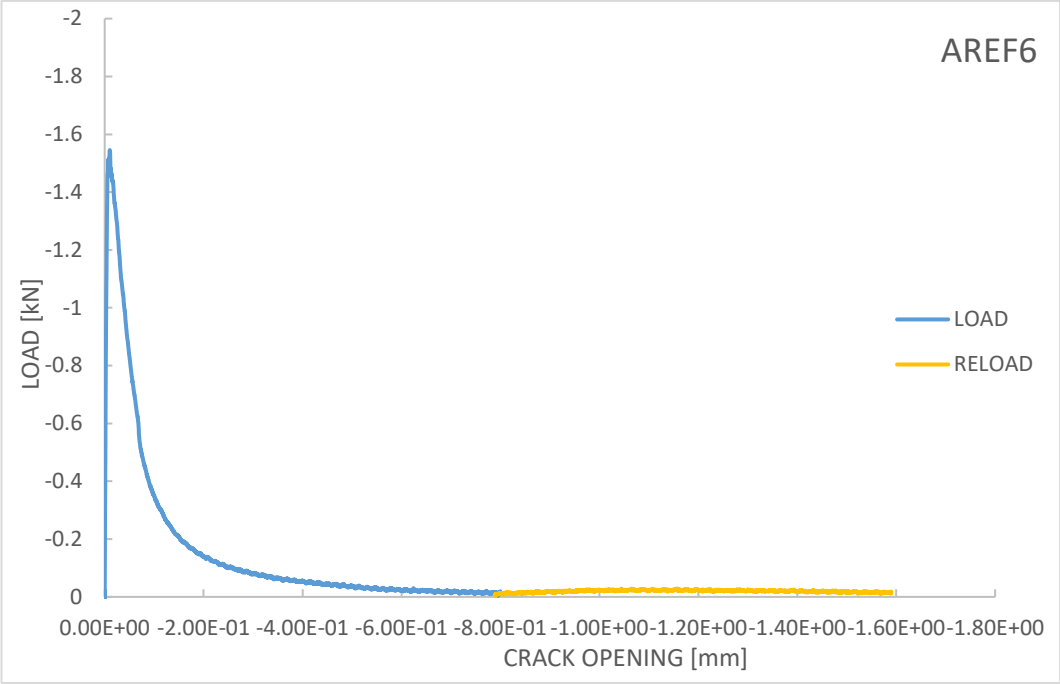
Graph 33 - Reloading test upon the specimen without capsules - A_REF1



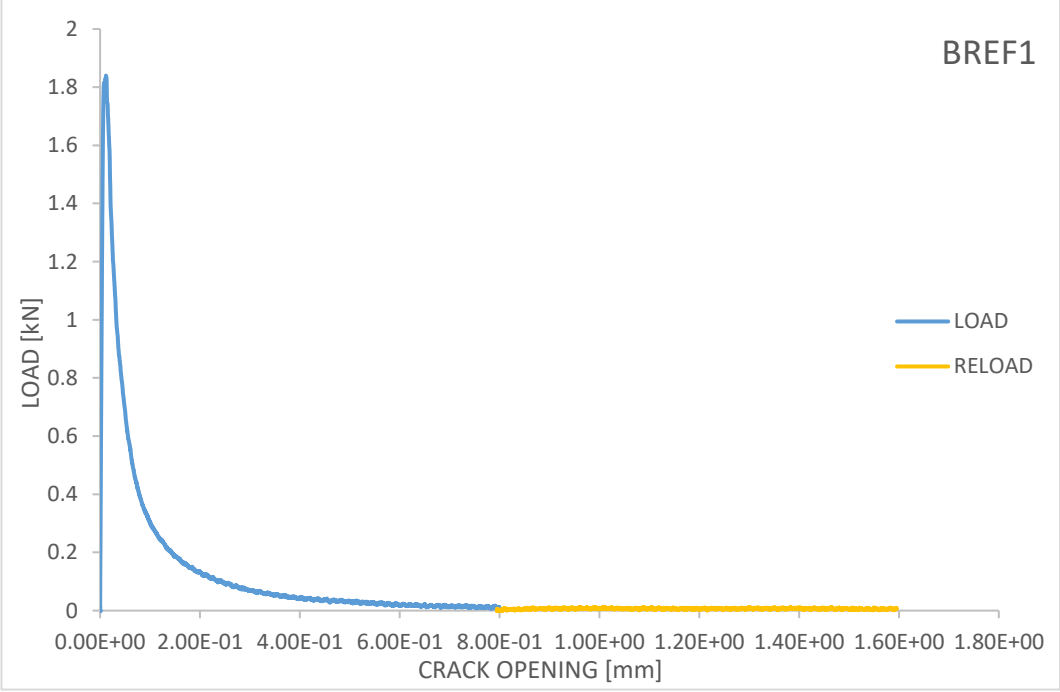
Graph 34 - Reloading test upon the specimen without capsules - A_REF2



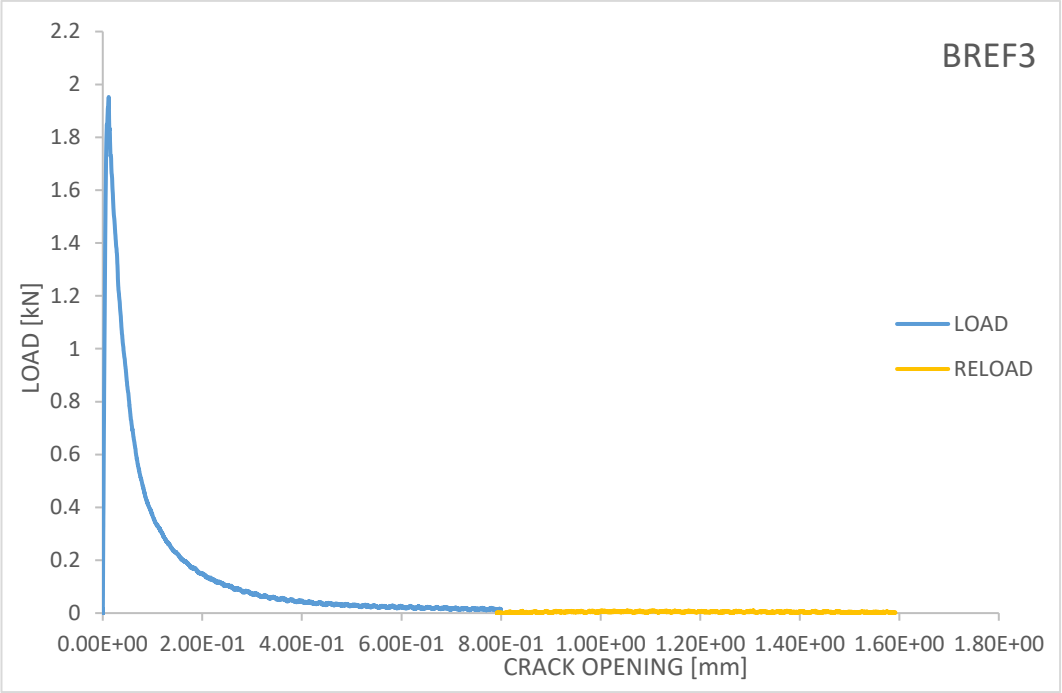
Graph 35 - Reloading test upon the specimen without capsules - A_REF3



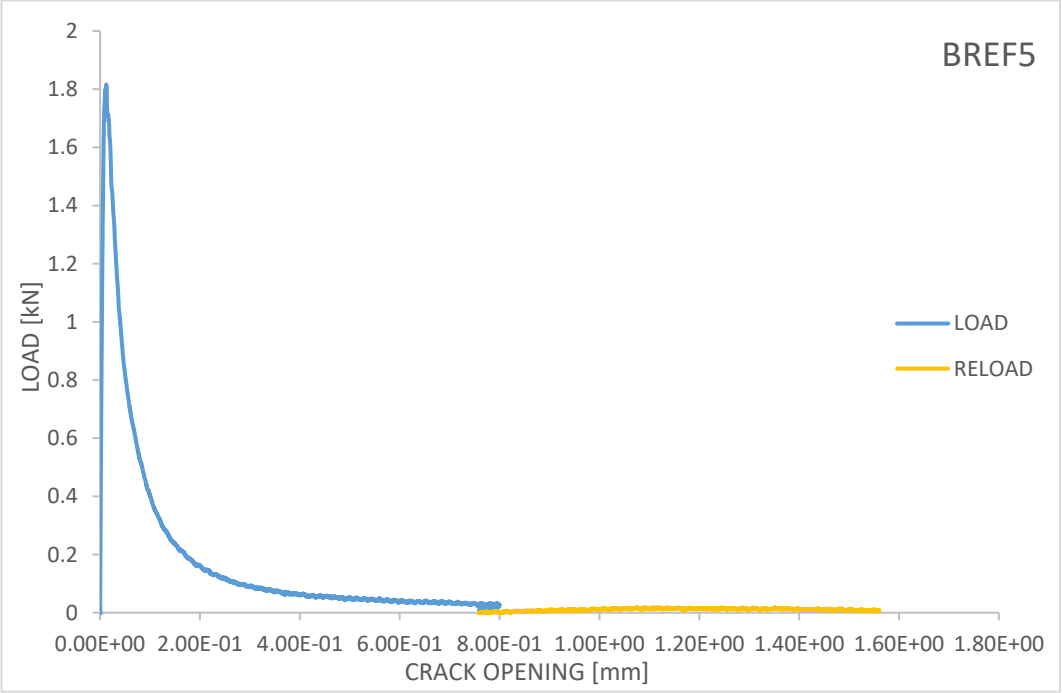
Graph 36 - Reloading test upon the specimen without capsules - A_REF6



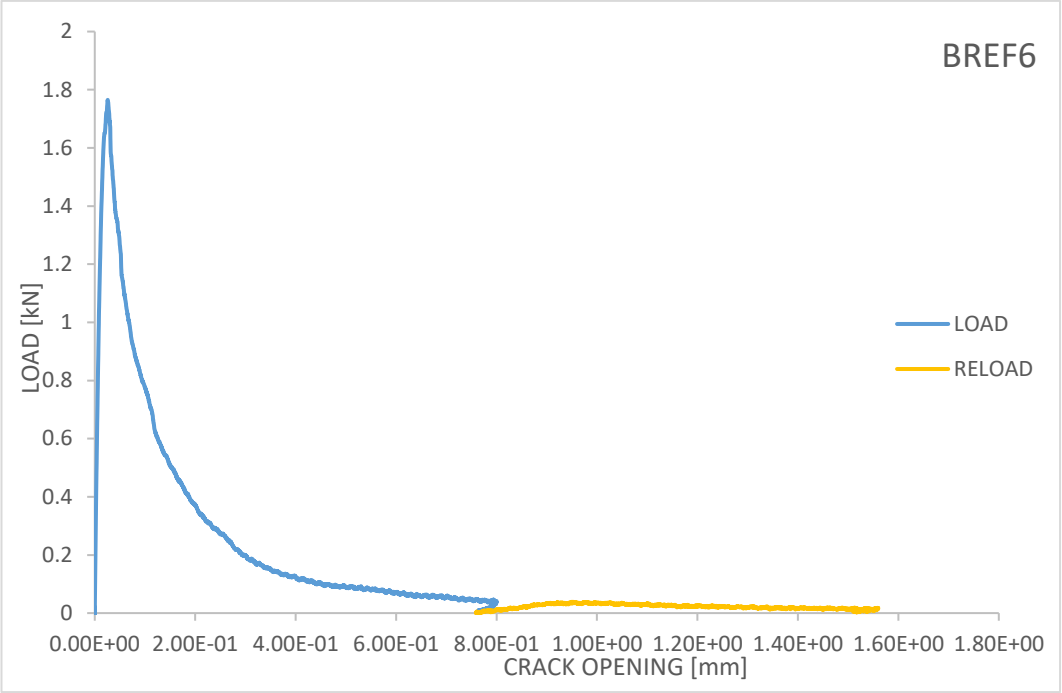
Graph 37 - Reloading test upon the specimen without capsules - B_REF1



Graph 38 - Reloading test upon the specimen without capsules - B_REF3



Graph 39 - Reloading test upon the specimen without capsules - B_REF5

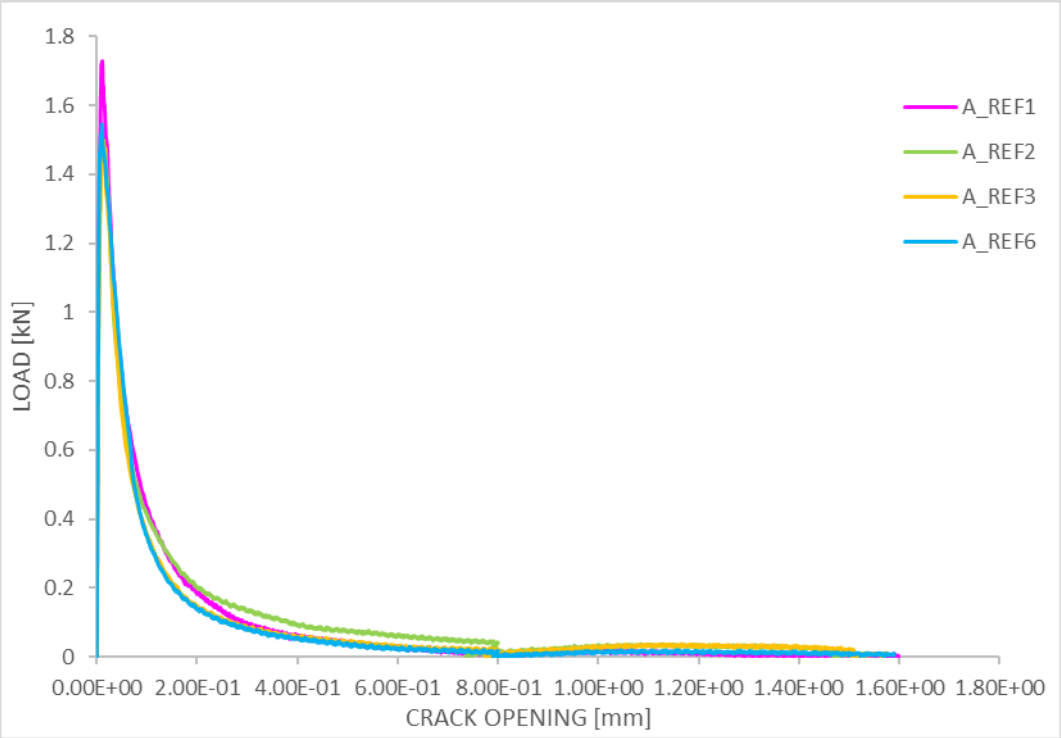


Graph 40 - Reloading test upon the specimen without capsules - B_REF6

For the sake of comparison, all the curves belonging to the A_REF and B_REF series of the reference specimens have been reported and superposed.

With this superposition, it is noticeable that the behavior of all the specimens was the same unless the load values reached, which however remains similar on all the samples ah shown in the previous table.

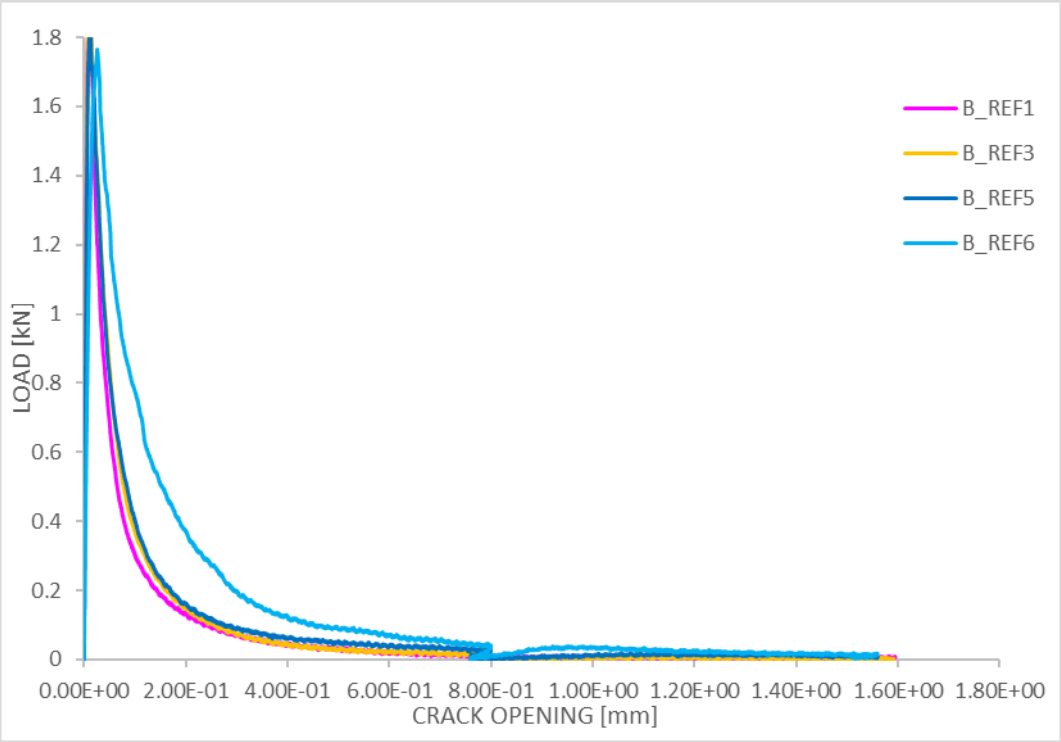
Therefore, the following graph highlights the repeatability of operations and results on samples that are all the same. During the reloading test, all the REF specimens had a significant decrease in peak load as expected since they do not have the capsules inside.



Graph 41 - Superposition of the load and reload curves for the group A of the specimens without the capsules

In the previous graph are reported just the specimens that were tested during the static reloading test, in fact, the A_REF4 and A_REF5 specimens broke during the pre-cracking test.

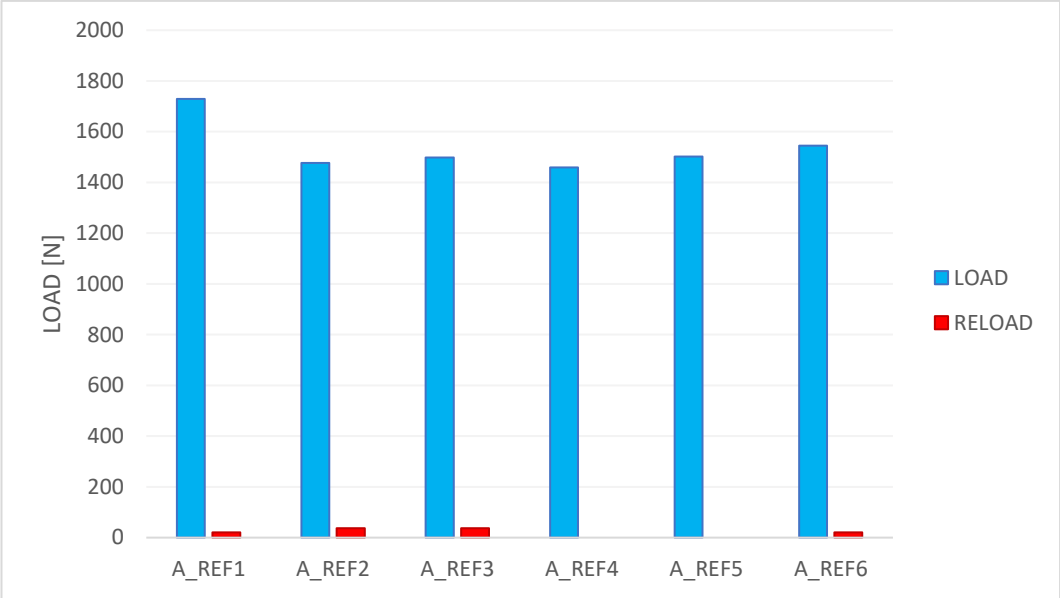
Similarly, the same observations can be stated for the second series of specimens not containing the capsules. For the B_REF series too, it is noticeable that the behavior of all the specimens was the same unless the load values reached, which remarks the repeatability of operations and results.



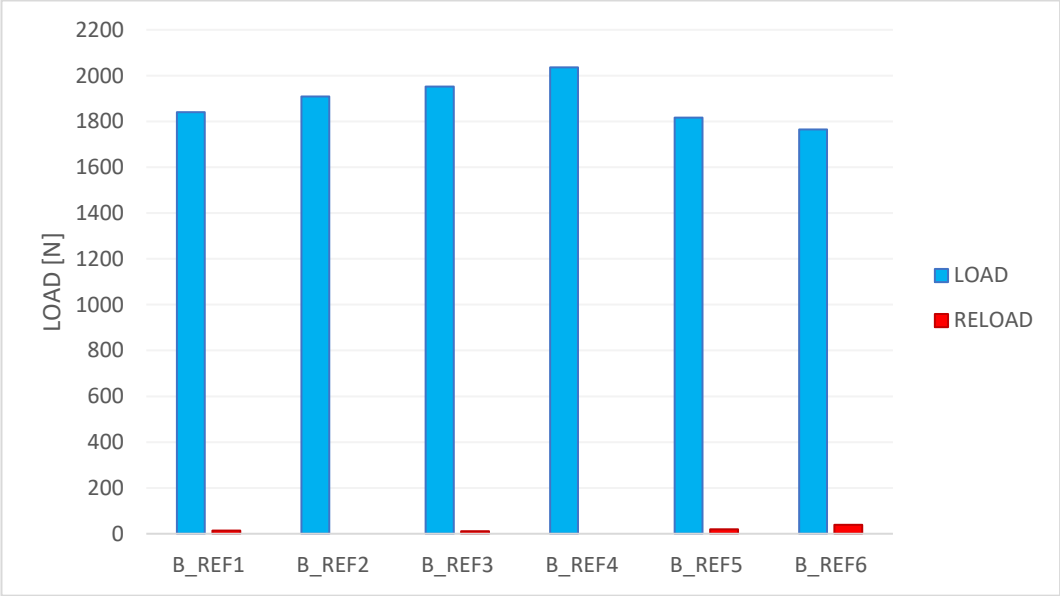
Graph 42 - Superposition of the load and reload curves for the group B of the specimens without the capsules

In the previous graph are reported just the specimens that were tested during the static reloading test, in fact, the B_REF2 and B_REF4 specimens broke during the pre-cracking test.

The following graphs show the comparison of the peak load values obtained during the loading tests for the two groups of reference specimens: the peak load during the reloading test is significantly lower than the pre-cracking phase.



Graph 43 - Peak load reached during the pre-cracking and reloading tests for the group A of the specimens without the capsules



Graph 44 - Peak load reached during the pre-cracking and reloading tests for the group B of the specimens without the capsules

5.3.2 CAPS specimens

On the other hand, for the specimens with capsules, the healing process due to the presence of polyurethane is involved, and leads to an improvement in strength.

The reloading curve presents a peak P'' higher than the residual load capacity value PR, and results to be softer, with a more ductile behavior.

Due to the presence of a different material from the cementitious matrix, which is instead a more fragile material, the two materials result complementary.

On the other hand, polyurethane has a lower mechanical resistance, but gives other properties, including impermeability and ductility, that the cementitious material usually does not have.

It can also be highlighted that the higher ductility during the reloading phase implies a higher dissipation of energy, in fact the area under the curve is higher than during the pre-cracking test.

Using the following relationship, it is possible to obtain an average value for all the specimens analyzed:

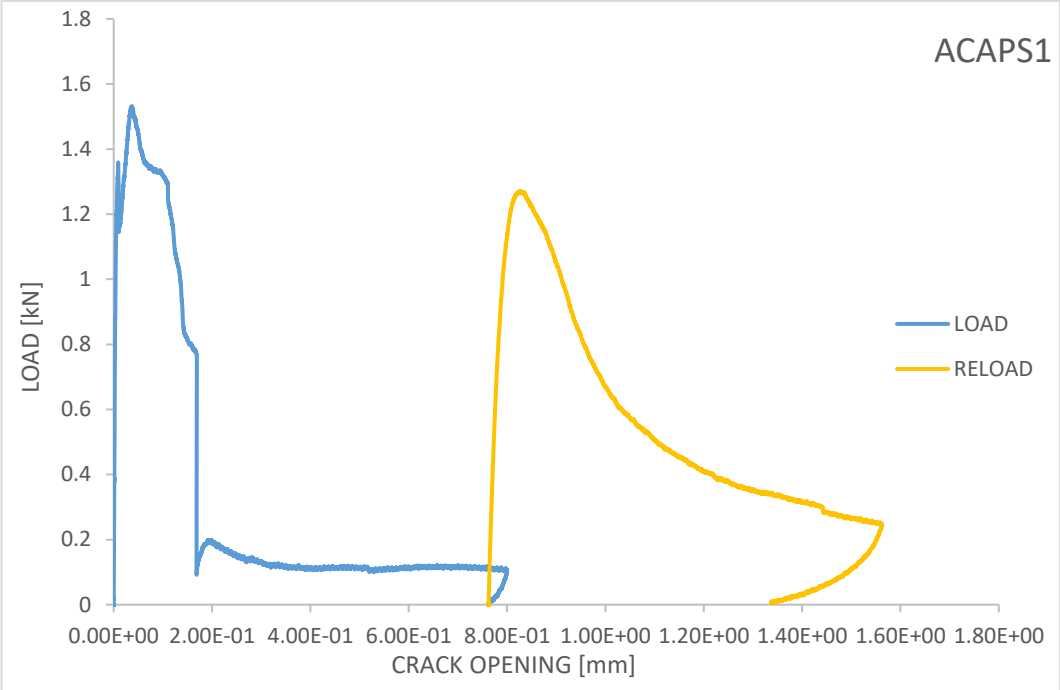
$$LRI = \frac{L_{reload} - L_{unload}}{L_{peak} - L_{unload}} \ [\%]$$

For each specimen, the peak during the load phase and the peak during the reloading phase have been analyzed and are reported below:

TESTED SPECIMEN	L_{PEAK}	L_{RELOAD}	L_{UNLOAD}
	[N]	[N]	[N]
A_CAPS1	1531.22	1270.44	107.24
A_CAPS2	1511.49	1453.44	112.63
A_CAPS3	1285.49	1311.91	68.08
A_CAPS4	1326.65	1332.94	101.12
A_CAPS5	1452.34	893.39	54.74
A_CAPS6	1413.95	1127.92	87.46
B_CAPS1	1429.63	1178.20	100.62
B_CAPS2	1470.06	806.13	100.04
B_CAPS3	1617.80	1254.01	89.30
B_CAPS4	1541.84	1265.52	117.93
B_CAPS5	1516.37	948.75	64.51
B_CAPS6	1643.07	340.57	72.38

Table 19 – Tested specimens during the reloading test - CAPS

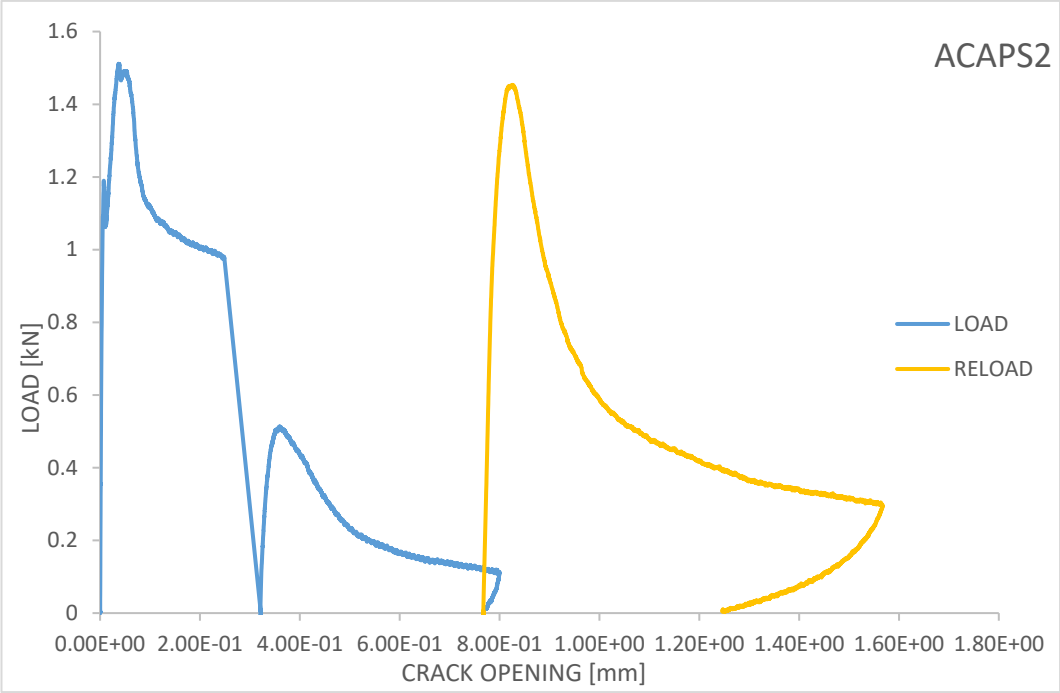
For each specimen, also the LRI (load recovery index) has been calculated and all of the results are reported below:



Graph 45 - Reloading test upon the specimen with capsules - A_CAPS1

A_CAPS1	LPEAK	1531.22	82%
	LRELOAD	1270.44	
	LUNLOAD	107.24	

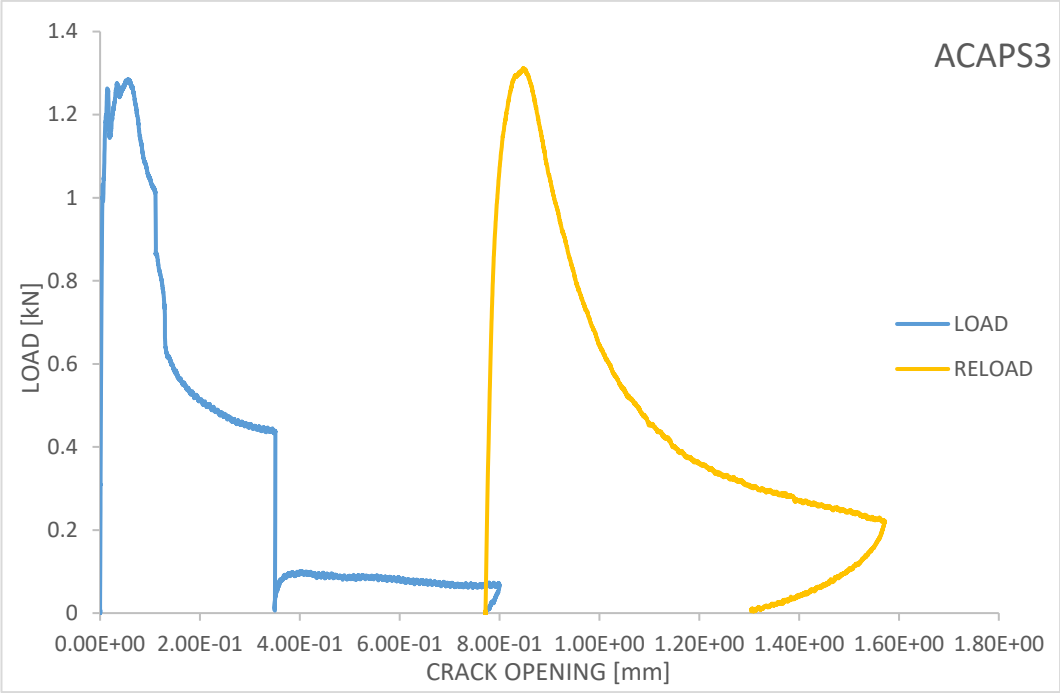
Table 20 - Values of load reached during the tests, and LRI obtained - A_CAPS1



Graph 46 - Reloading test upon the specimen with capsules - A_CAPS2

A_CAPS2	LPEAK	1511.49	96%
	LRELOAD	1453.44	
	LUNLOAD	112.63	

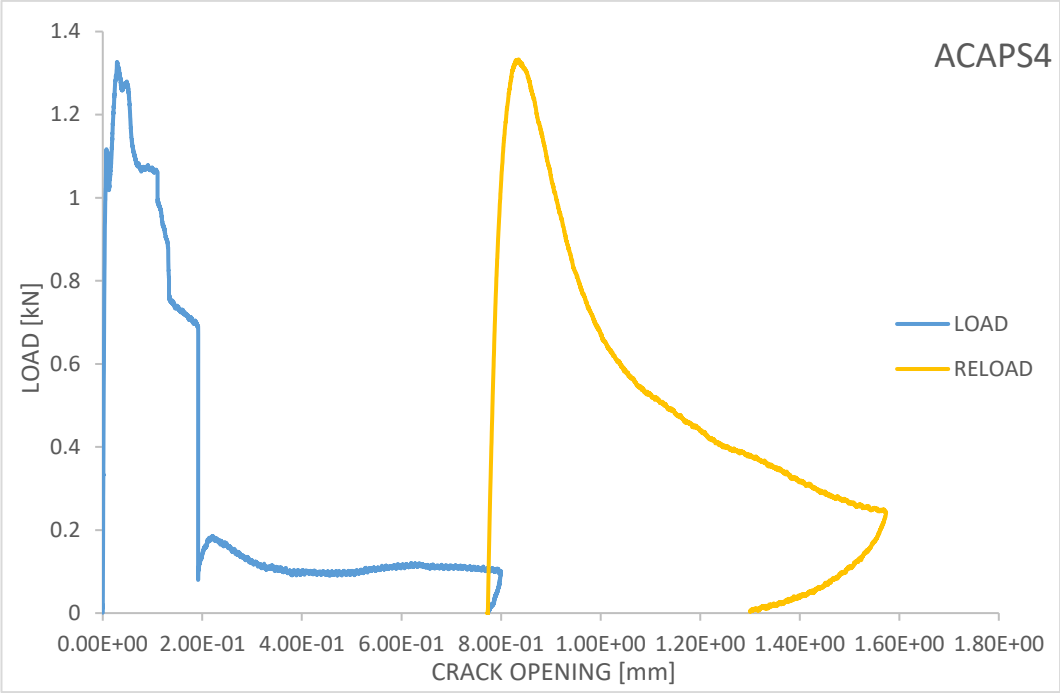
Table 21 - Values of load reached during the tests, and LRI obtained - A_CAPS2



Graph 47 - Reloading test upon the specimen with capsules - A_CAPS3

A_CAPS3	LPEAK	1285.49	102%
	LRELOAD	1311.91	
	LUNLOAD	68.08	

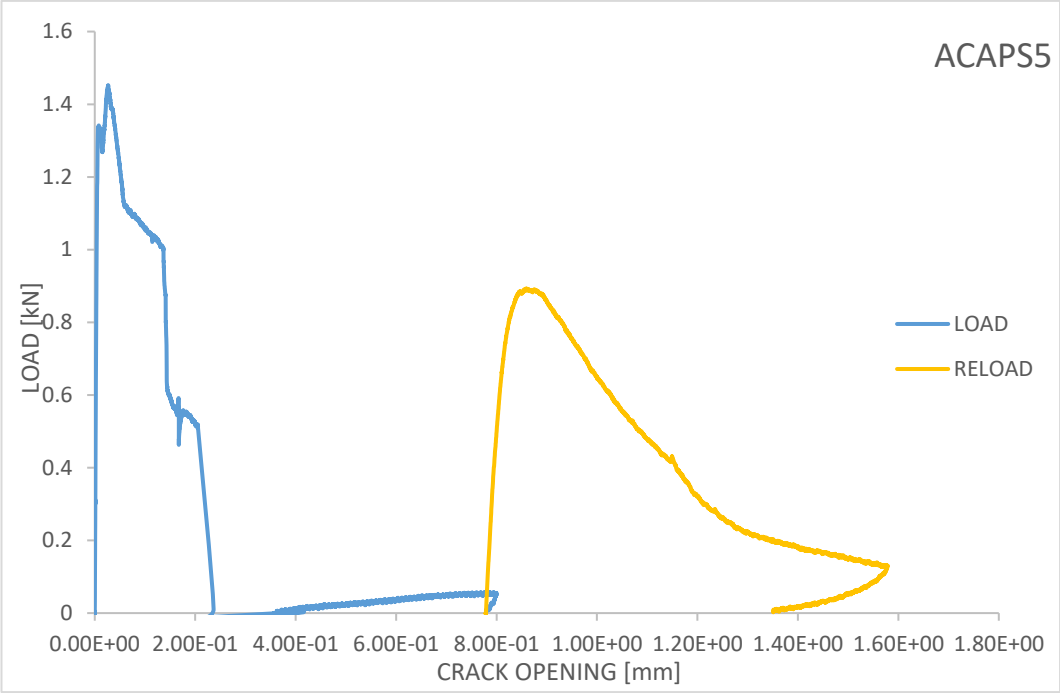
Table 22 - Values of load reached during the tests, and LRI obtained - A_CAPS3



Graph 48 - Reloading test upon the specimen with capsules - A_CAPS4

A_CAPS4	LPEAK	1326.65	101%
	LRELOAD	1332.94	
	LUNLOAD	101.12	

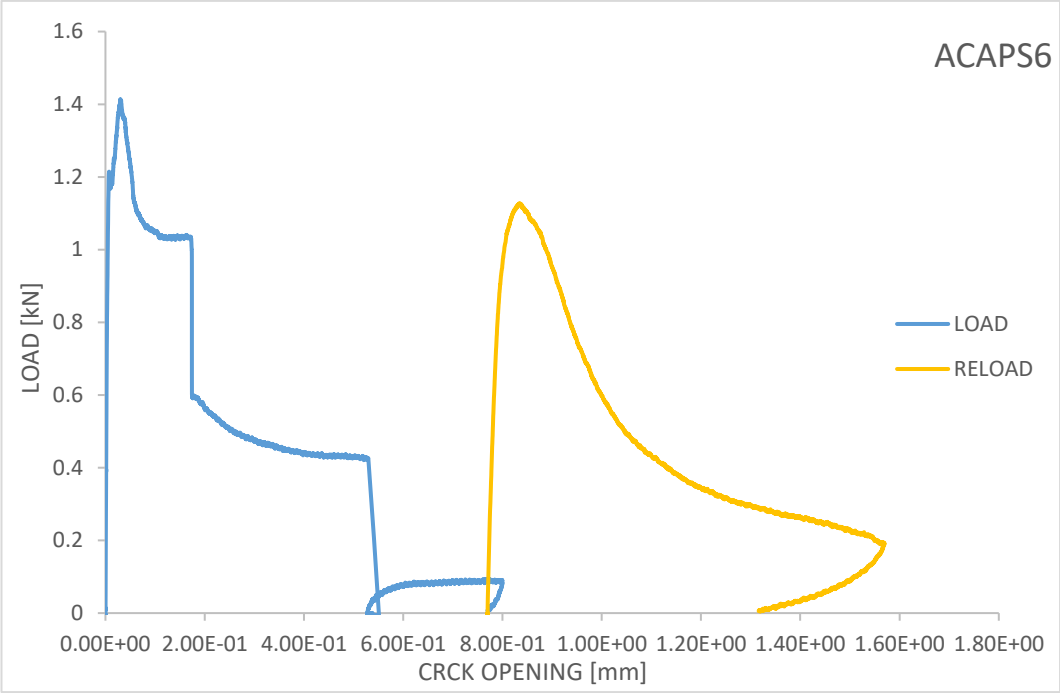
Table 23 - Values of load reached during the tests, and LRI obtained - A_CAPS4



Graph 49 - Reloading test upon the specimen with capsules - A_CAPS5

A_CAPS5	LPEAK	1452.34	60%
	LRELOAD	893.39	
	LUNLOAD	54.74	

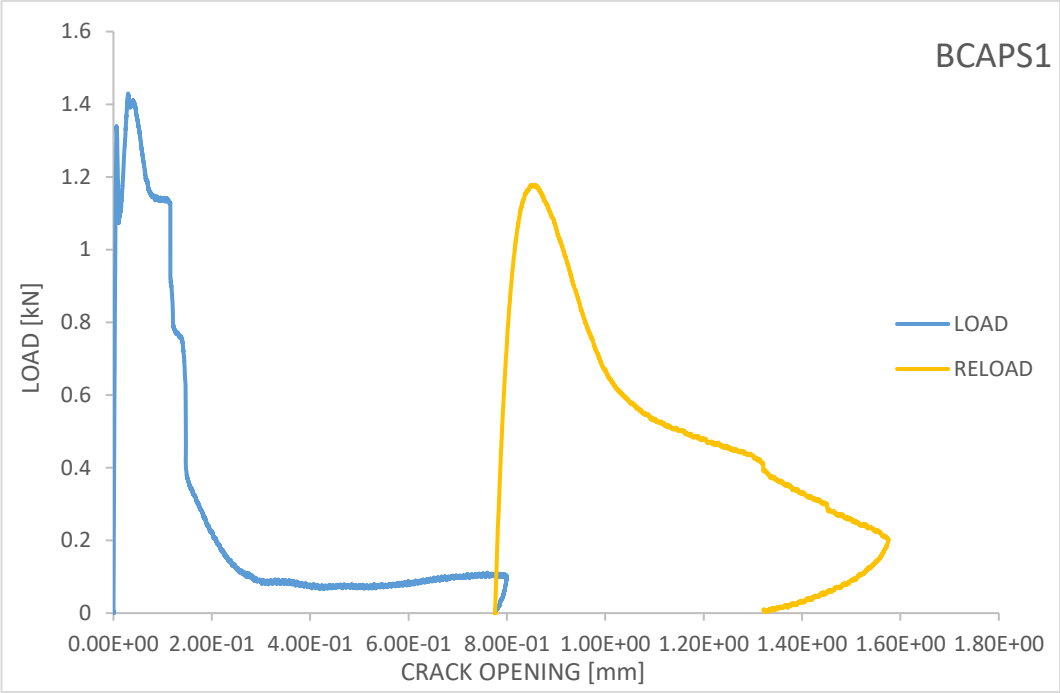
Table 24 - Values of load reached during the tests, and LRI obtained - A_CAPS5



Graph 50 - Reloading test upon the specimen with capsules - A_CAPS6

A_CAPS6	LPEAK	1413.95	78%
	LRELOAD	1127.92	
	LUNLOAD	87.46	

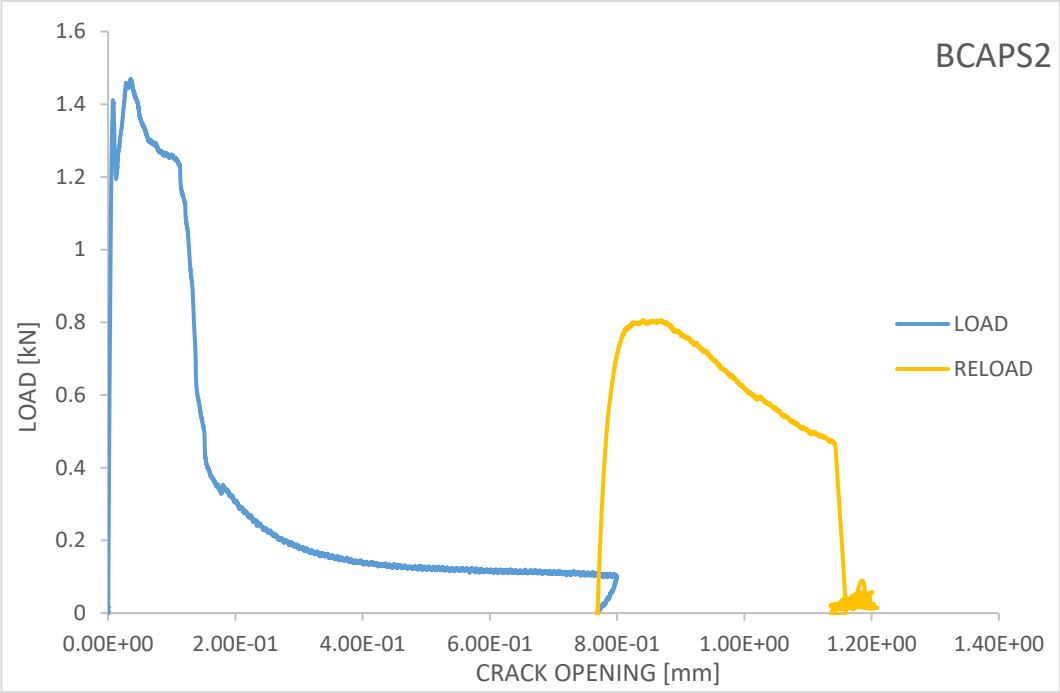
Table 25 – Values of load reached during the tests, and LRI obtained - A_CAPS6



Graph 51 - Reloading test upon the specimen with capsules - B_CAPS1

B_CAPS1	LPEAK	1429.63	81%
	LRELOAD	1178.2	
	LUNLOAD	100.62	

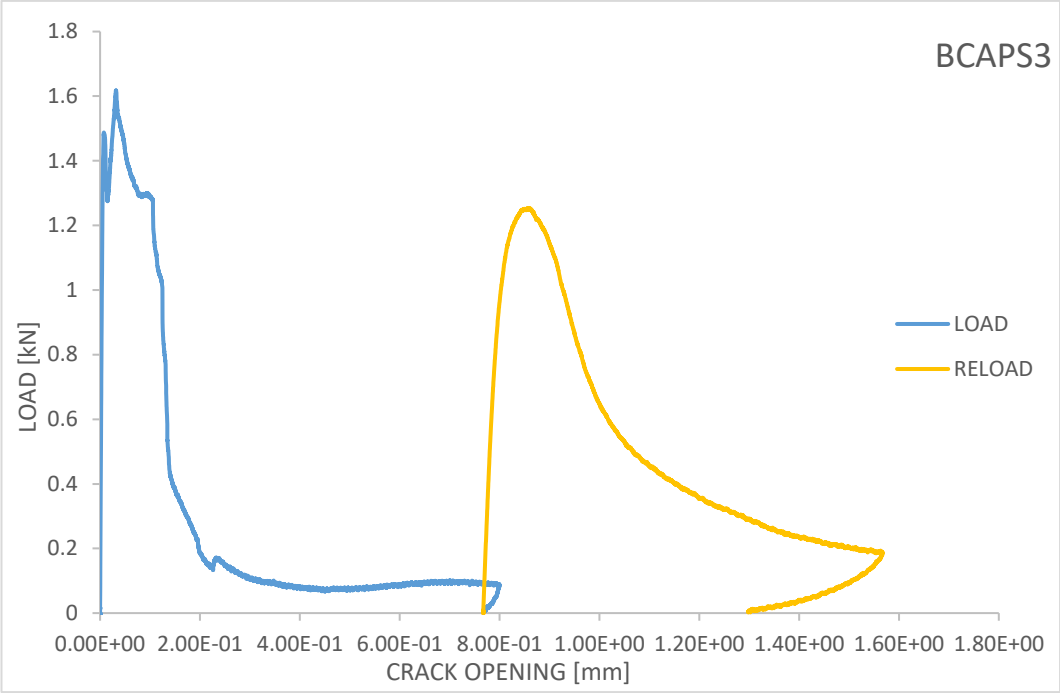
Table 26 - Values of load reached during the tests, and LRI obtained - B_CAPS1



Graph 52 - Reloading test upon the specimen with capsules - B_CAPS2

B_CAPS2	LPEAK	1470.06	52%
	LRELOAD	806.13	
	LUNLOAD	100.04	

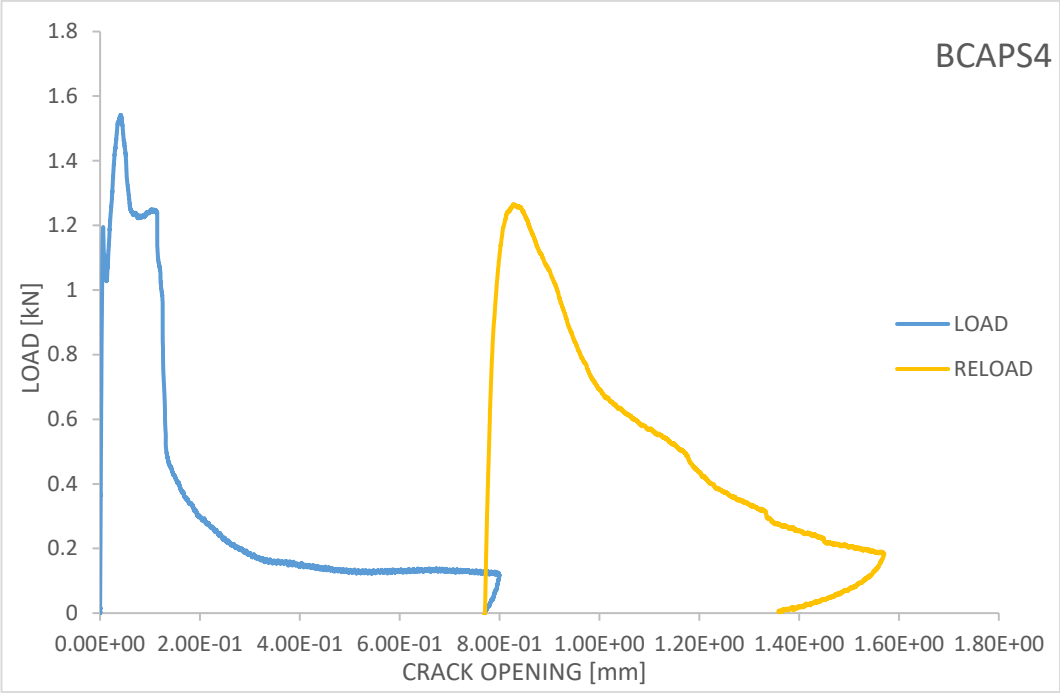
Table 27 - Values of load reached during the tests, and LRI obtained - B_CAPS2



Graph 53 - Reloading test upon the specimen with capsules - B_CAPS3

B_CAPS3	LPEAK	1617.8	76%
	LRELOAD	1254.01	
	LUNLOAD	89.3	

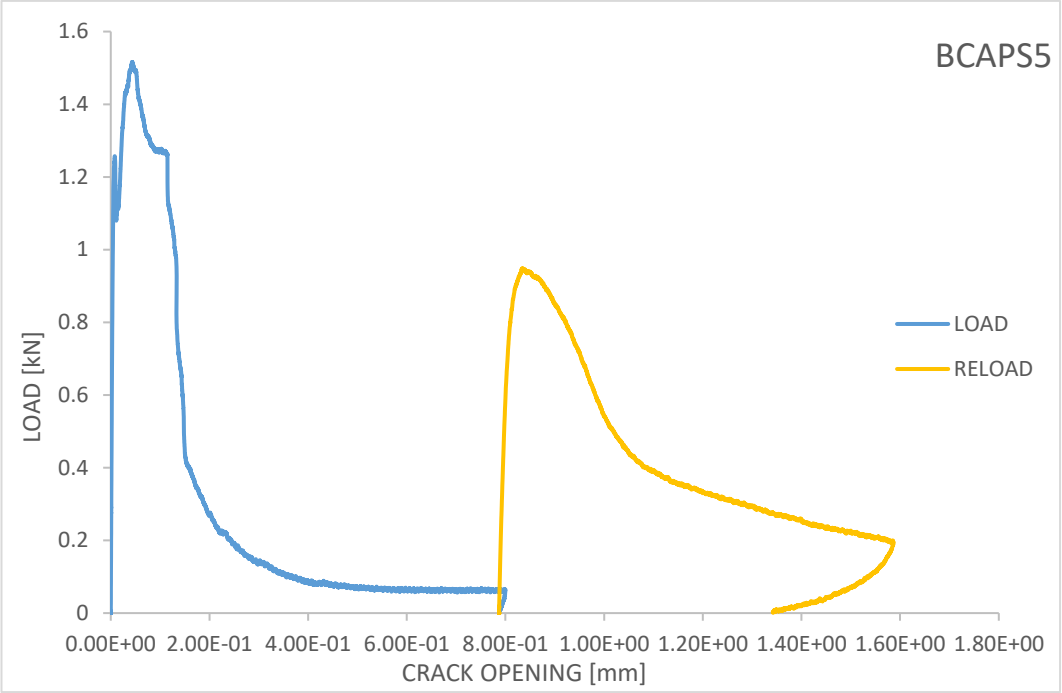
Table 28 - Values of load reached during the tests, and LRI obtained - B_CAPS3



Graph 54 - Reloading test upon the specimen with capsules - B_CAPS4

B_CAPS4	LPEAK	1541.84	81%
	LRELOAD	1265.52	
	LUNLOAD	117.93	

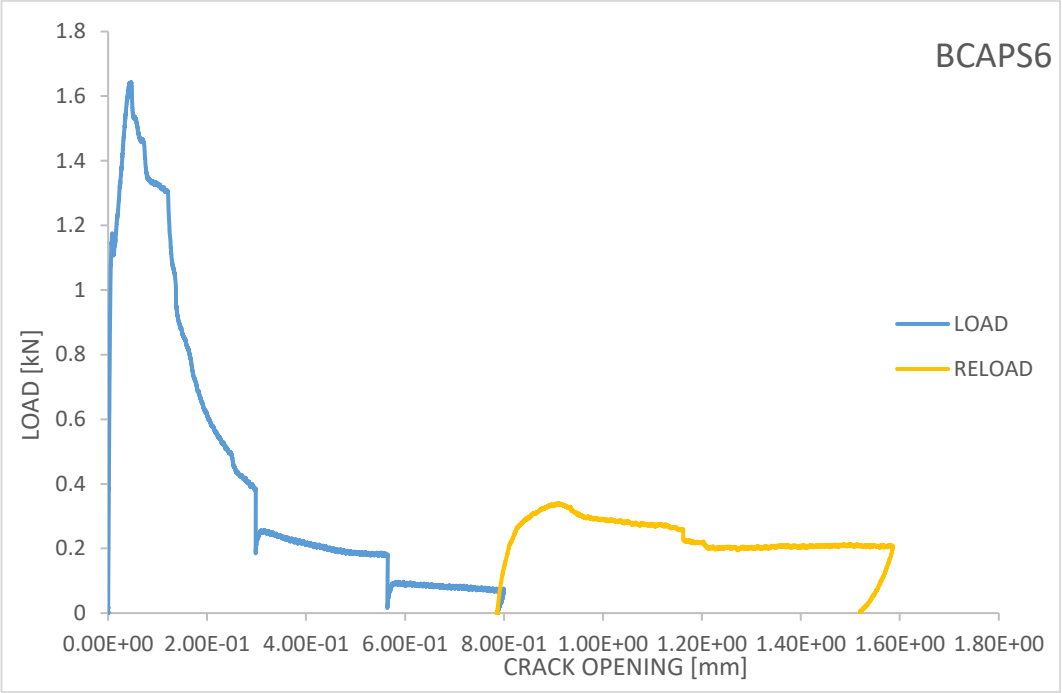
Table 29 - Values of load reached during the tests, and LRI obtained - B_CAPS4



Graph 55 - Reloading test upon the specimen with capsules - B_CAPS5

B_CAPS5	LPEAK	1516.37	61%
	LRELOAD	948.75	
	LUNLOAD	64.51	

Table 30 - Values of load reached during the tests, and LRI obtained - B_CAPS5



Graph 56 - Reloading test upon the specimen with capsules - B_CAPS6

B_CAPS6	LPEAK	1643.07	17%
	LRELOAD	340.57	
	LUNLOAD	72.38	

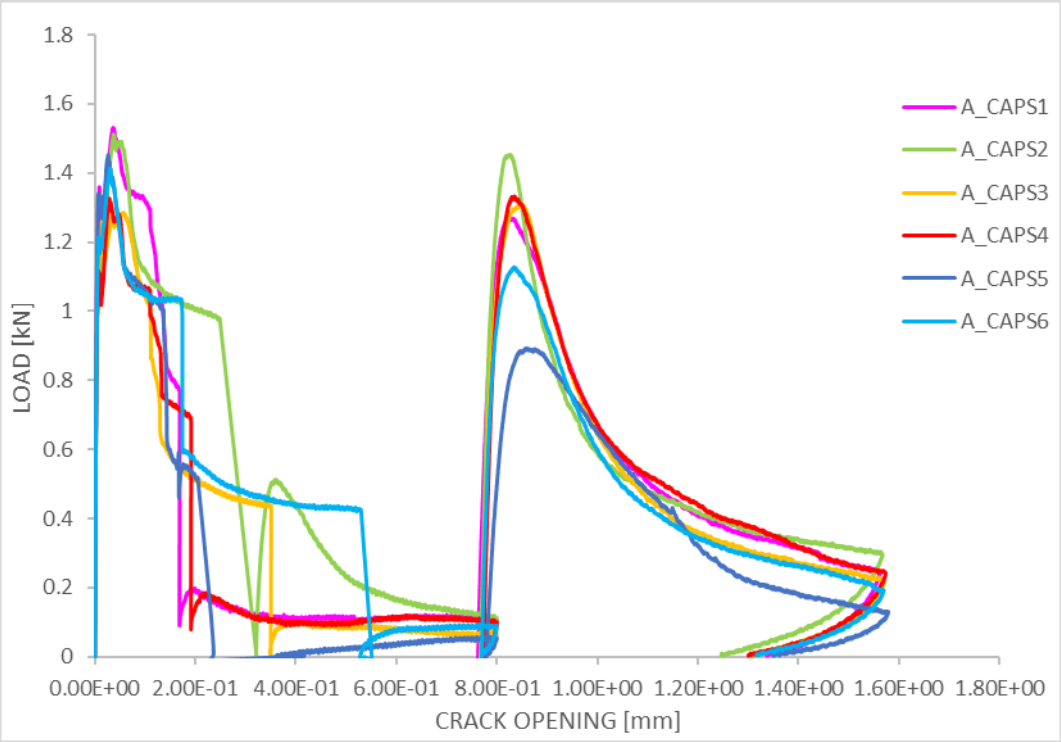
Table 31 - Values of load reached during the tests, and LRI obtained - B_CAPS6

For the sake of comparison, all the curves belonging to the A_CAPS and B_CAPS series of the specimens with capsules have been reported and superposed.

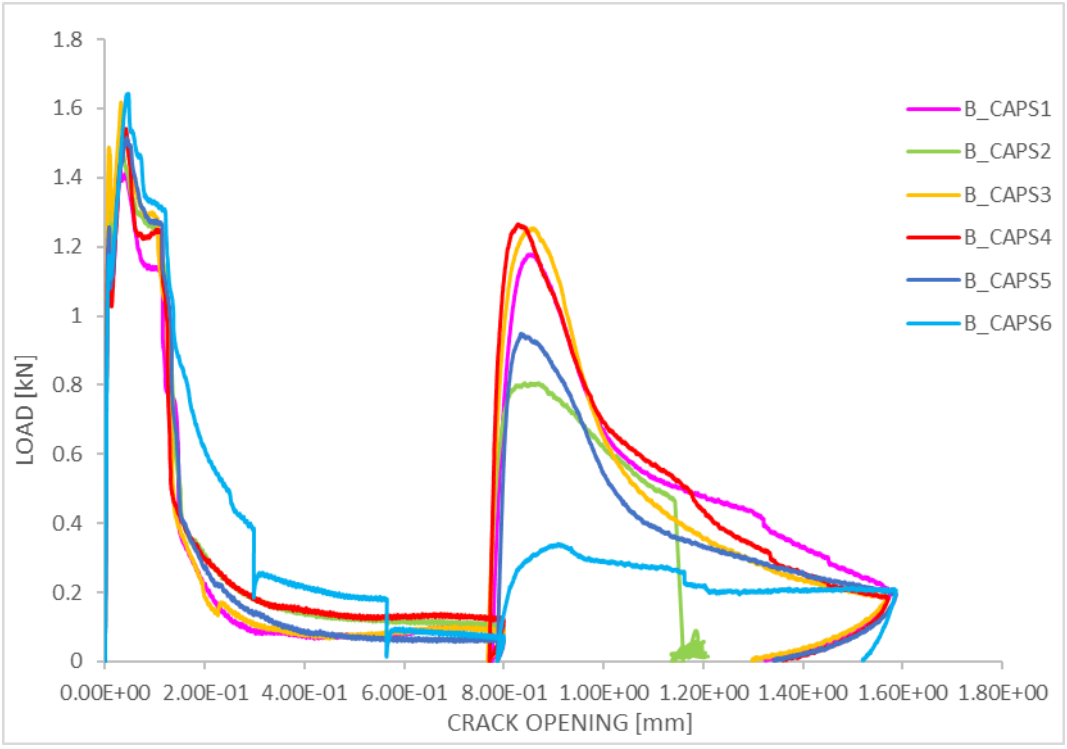
With this superposition, it is noticeable that the behavior of all the specimens was the same unless the load values reached, which however remains similar on all the samples as shown in the previous tables.

Therefore, the following graph highlights the repeatability of operations and results on samples that are all the same. During the reloading test, all the CAPS

specimens had a significant recover in peak load as expected since the hardened polyurethane in the capsules.



Graph 57 - Superposition of the load and reload curves for the group A of the specimens with the capsules



Graph 58 - Superposition of the load and reload curves for the group B of the specimens with the capsules

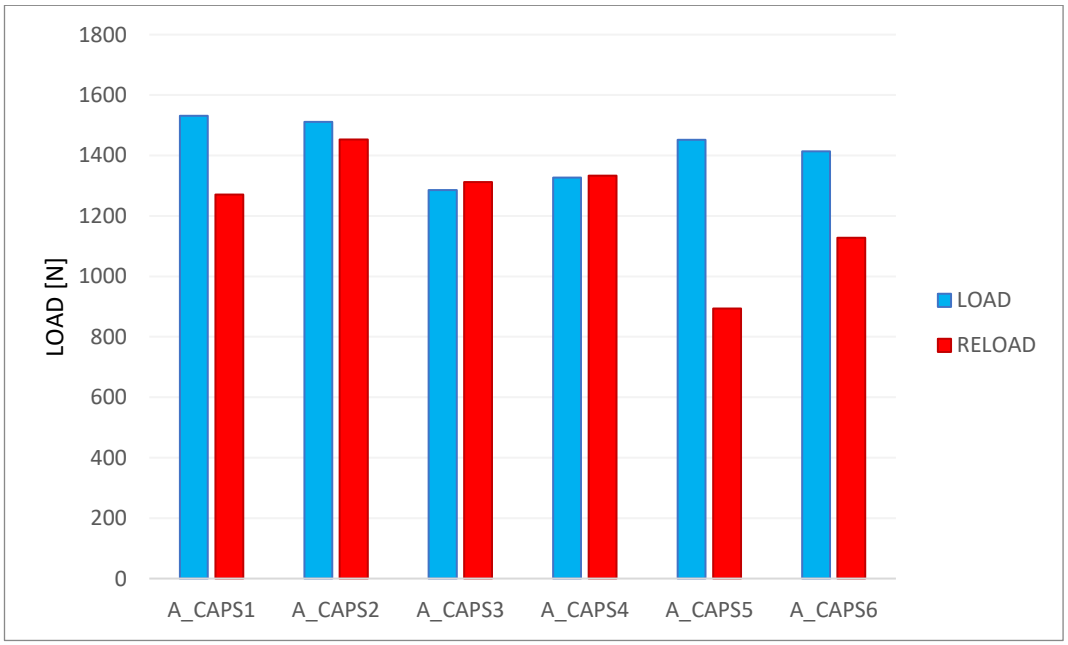
The following table summarizes the obtained results for the two groups of specimens.

TESTED SPECIMEN	L_{PEAK}	L_{RELOAD}	L_{UNLOAD}	LRI
	[N]	[N]	[N]	
A_CAPS1	1531.22	1270.44	107.24	82%
A_CAPS2	1511.49	1453.44	112.63	96%
A_CAPS3	1285.49	1311.91	68.08	102%
A_CAPS4	1326.65	1332.94	101.12	101%
A_CAPS5	1452.34	893.39	54.74	60%
A_CAPS6	1413.95	1127.92	87.46	78%

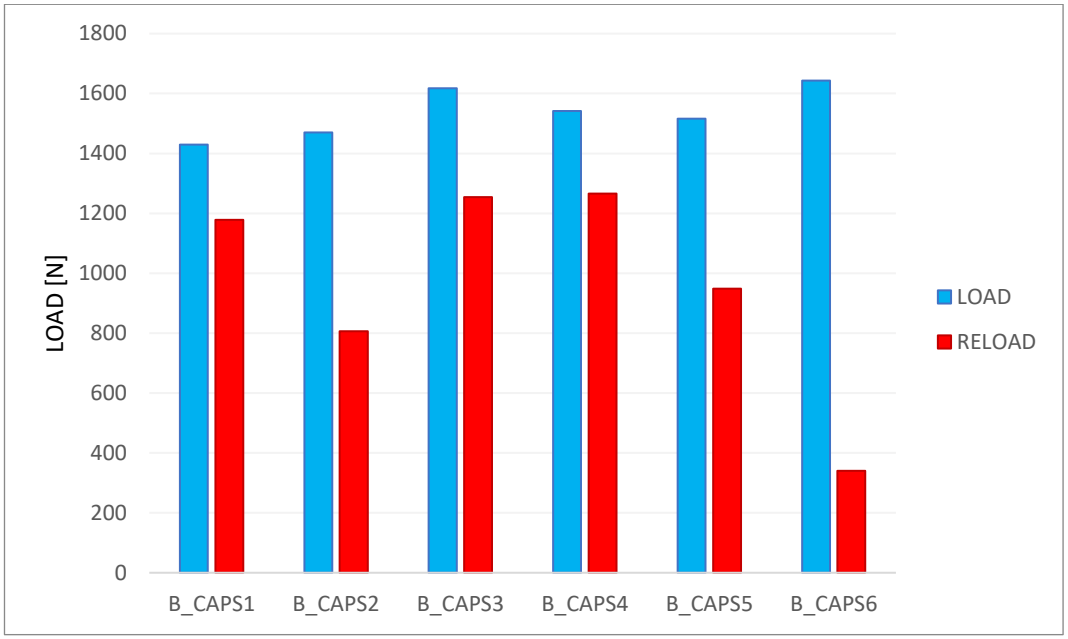
B_CAPS1	1429.63	1178.2	100.62	81%
B_CAPS2	1470.06	806.13	100.04	52%
B_CAPS3	1617.8	1254.01	89.3	76%
B_CAPS4	1541.84	1265.52	117.93	81%
B_CAPS5	1516.37	948.75	64.51	61%
B_CAPS6	1643.07	340.57	72.38	17%

Table 32 - Load Recovery Index (LRI) for the specimens with the capsules

The following graphs show the comparison of the peak load values obtained during the loading tests for the two groups of specimens with the capsules: for some of the CAPS specimens the peak load during the reloading test reached values equal to or even higher than the peak load during the pre-cracking phase.

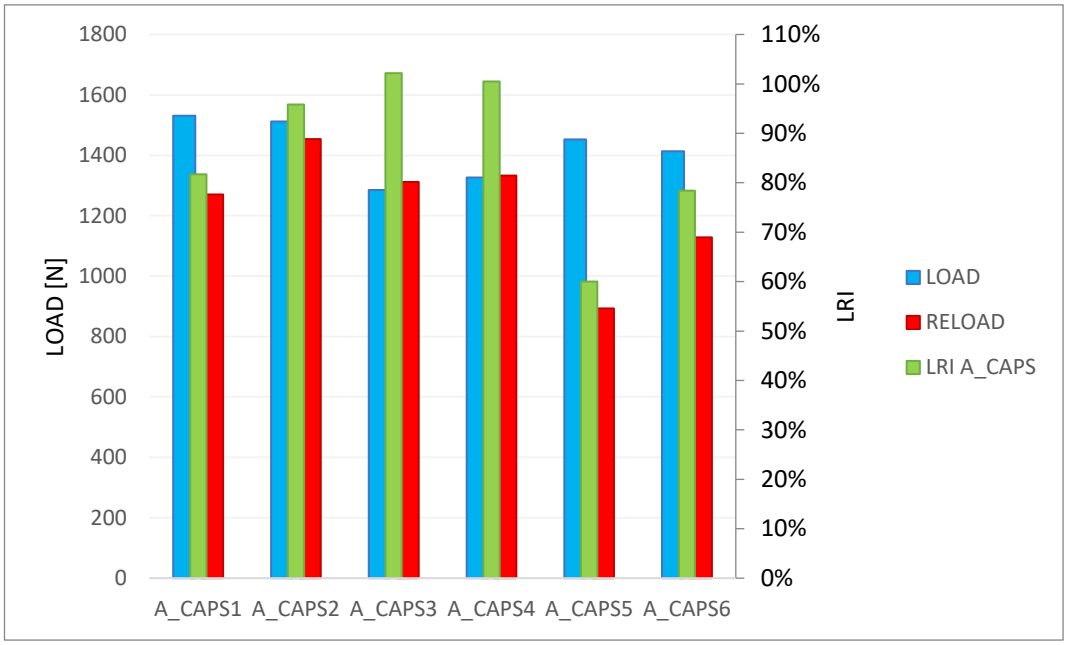


Graph 59 - Peak load reached during the pre-cracking and reloading tests for the group A of the specimens with the capsules

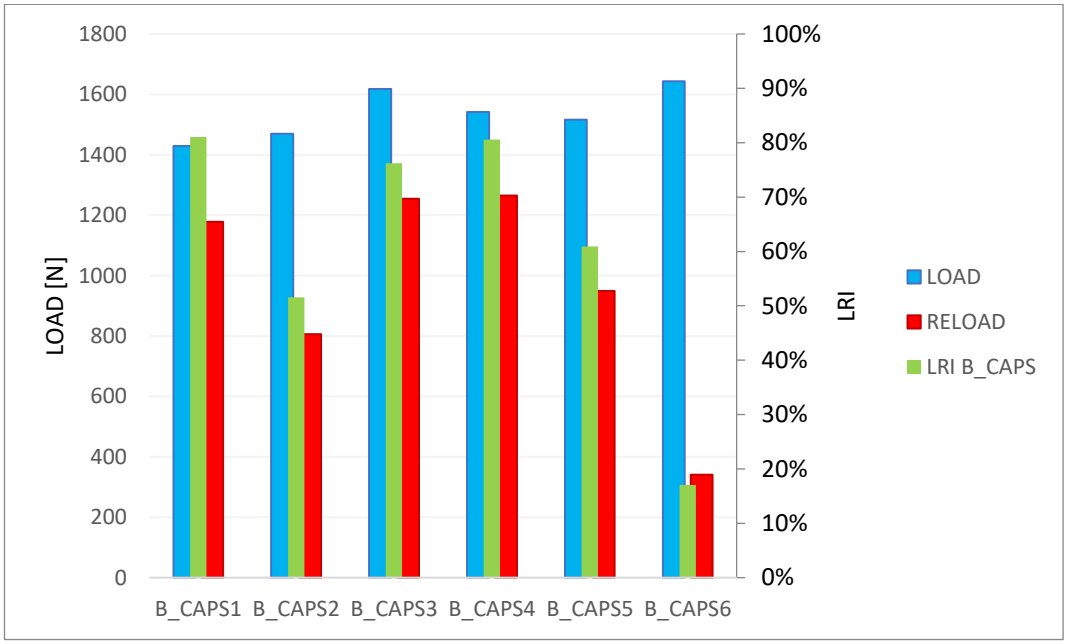


Graph 60 - Peak load reached during the pre-cracking and reloading tests for the group B of the specimens with the capsules

In the following graphs the LRI – load recovery index – are reported for each specimen of the two groups of cement mortar prisms.



Graph 61 - Load Recovery Index (LRI) for the group A of the specimens with the capsules



Graph 62 - Load Recovery Index (LRI) for the group B of the specimens with the capsules

Results show that the healing process due to the presence of polyurethane generates an improvement in residual load capacity. If the specimen is

reloaded under the same loading conditions as pre-cracking, there will be an increasing of the peak load.

This is due to the complementarity between the cementitious matrix and the polyurethane, which although having a lower mechanical resistance, gives the system new properties, including impermeability and ductility, which are characteristics that the cementitious material usually does not have.

5.4 Dynamic reloading test and durability test

As written in the previous sections, the different series of specimens (CEM) was tested to dynamic reloading test. As expected, the healing agent in the capsule allowed in most cases to perform the cyclic test until a high number of cycles was reached.

During the test, the specimens went through different phases:

- In the first phase the micro-crack occurs, suddenly an increasing opening of the crack during the loading stage was observed;
- In the second phase a slow and steady growth of the micro-crack was observed;
- In the final stage the crack develops unsteadily until the fatigue failure is observed. The result is the complete break-up of the specimen, hence the total separation between the two sides of the fracture.

The number of cycles for each specimen are reported below:

Tested Specimen	Number of cycles						
Test	500	1000	2000	5000	10000	20000	
Progressive	500	1500	3500	8500	18500	38500	
CEM_1	500	1000	2000	5000	10000	-	18500
CEM_3	69	-	-	-	-	-	69
CEM_4	500	1000	216	-	-	-	1716
CEM_5	500	869	-	-	-	-	1369
CEM_6	21	-	-	-	-	-	21
CEM_8	500	1000	2000	5000	10000	20000	38500
CEM_9	500	1000	2000	5000	10000	-	18500
CEM_11	500	1000	2000	5000	10000	-	18500

Table 33 – Number of cycles during the dynamic reloading test

As reported in the table above, good results were reached for the specimens CEM1, CEM8, CEM9, CEM11; while the specimens CEM3, CEM4, CEM5, CEM6 broke-up during the test. Finally, the specimens CEM2, CEM7, CEM12 failed the test at the starting of it.

After each cycle of the dynamic reloading test, the durability test was run in order to evaluate the conditions of the crack-opening and the mass of water passing through it.

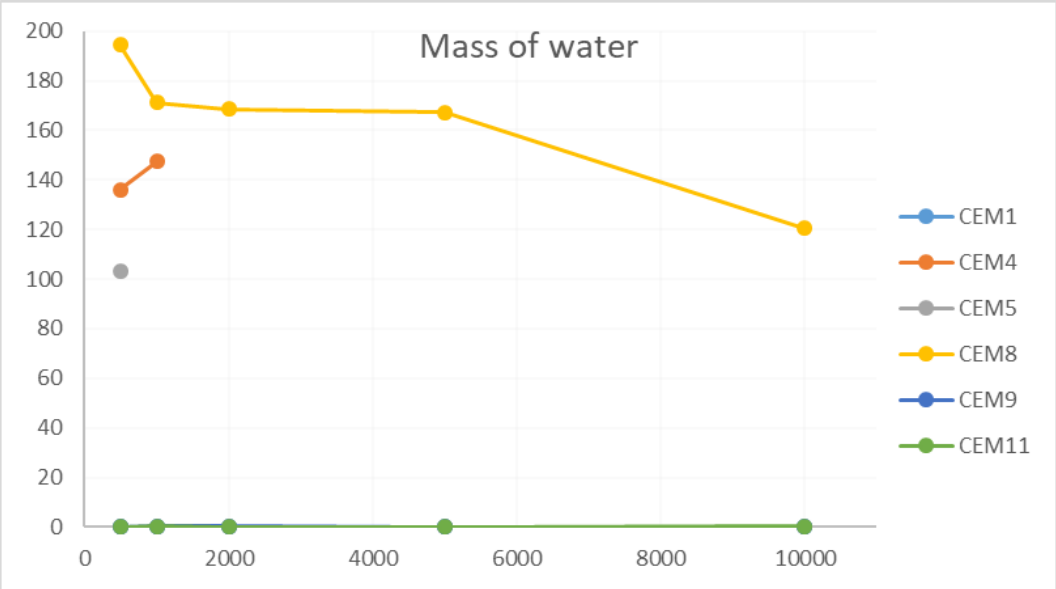
The self-healing specimens were able to sustain a satisfactory amount of cycles before failure. This result is consistent with the self-healing system in restoring the mechanical properties of the damaged cementitious material.

Moreover, considering the mass of water registered during the durability test following the dynamic reloading test, it is possible to notice that for some of the specimens the amount of water registered was negligible.

In the table below, these results are reported:

Tested Specimen	Number of cycles				
	500	1000	2000	5000	10000
CEM_1	0	0.1	0.2	0	0
CEM_4	136.2	147.4	-	-	-
CEM_5	103.3	-	-	-	-
CEM_8	194.3	171.2	168.6	167.2	120.5
CEM_9	0	0.4	0.3	0	0.2
CEM_11	0	0.3	0.1	0	0.3

Table 34 – Mass of water registered during the durability test for each step of dynamic reload test



Graph 63 - Mass of water registered during the durability test for the CEM specimens

As reported in the table and the graph above, good results were reached for the specimens: as the number of cycles increases it was expected that the mass of water passing through the crack would also increase, and that the action of the cycles would damage the interface between the cured polyurethane and the surrounding matrix. This phenomenon is only recorded for one of the CEM_4 specimens.

Unexpected results were recorded, however, for the other specimens: as the number of cycles applied increased, the mass of water passing through the specimen, recorded by the balance, became progressively lower.

This phenomenon shows an improvement of the durability of the system subjected to mechanical action, since has caused a further release of the encapsulated polyurethane. It can be said that the dynamic action produces a sort of pump effect of the air into the crack causing a further reaction of the unreacted polyurethane.

6. CONCLUSIONS

The use of cementitious macro-capsules to develop autonomous self-healing cement-based materials was investigated in this thesis.

Taking into account the advantages and limitations of each self-healing technique, the macro-encapsulation was selected as the focus of this thesis due to several benefits offered by this technology. This system in fact, allows to *directly provide the healing agent at the crack location* since the capsules are embedded in the cement matrix; also, macro-encapsulation allows to *heal large crack widths* with the respect to other strategies in *short time periods* selecting the appropriate healing agent. Finally, the macro-encapsulation system *does not present a high complexity in the arrangements*, indeed all the processes that led to the production of the encapsulated system were carried out in a laboratory scale using simple and commonly used tools.

Based on these premises, the objective of the thesis was to assess the long-term durability of encapsulated polyurethane in cement mortar prisms subjected to mechanical stresses.

In order to reach this goal *cement-based capsules* were produced, filled with polyurethane, and inserted in cement mortar prisms. Several intermediate objectives had to be fulfilled:

- capsules should be compatible with concrete, they should resist the concrete mixing and casting processes and also be crack-responsive when intercrossed by a fracture;

- capsules have to be compatible with the encapsulated healing agent in order to protect it for a long time, and releasing it to fill and repair the cracks;
- capsules should not affect significantly the mechanical properties of the environment in which they are inserted.

The cementitious hollow tubes used in this experimental work, totally meet the aforementioned requirements, since they proved to be mechanical and chemical compatible with the surrounding cementitious matrix, responsive to a mechanical stimulus, as due to cracking, and capable to store and protect a liquid healing agent up to the moment in which the mechanical stimulus triggers the releasing action.

Since the cement-based capsules are characterized by an intrinsic porosity, that would allow water to enter during the casting phase, the capsules were coated internally and externally with epoxy resins used in naval field: PRIMAL B60 A is the first film of coating and PLASTIGEL is the second one used in order to waterproofing the entire surface of the capsules. The coat was added in order to protect and release the heling agent.

The *healing agent* must fulfill several requirements such as and adequate viscosity and thixotropy properties, or the right time of reaction. The agent:

- should easily flow out of the capsules once broken;
- should not react too fast upon crack occurrence so that it has the time to flow into the crack before hardening;
- has to be flexible enough to follow the path of the cracks,
- should have good adhesive properties with the surrounding cement matrix, and the long-lasting effect of this conditions.

The self-healing agent used in this experimental work was a yellowish single component polyurethane resin called CARBOSTOP-U Orica S.p.a. highly moisture-reactive.

Once the healing agent was selected, in order to guarantee a good self-healing performance, the *test of the mechanical recovery of the system* has to be fixed as another intermediate objective. This aspect was analyzed both under static and dynamic conditions in order to evaluate the applicability of the system in real fields conditions.

In order to pursue the aforementioned intermediate objectives, cement mortar prisms with and without capsules were produced and suddenly tested.

The first thing was to *induce a fracture* on the specimens in order to release the polyurethane contained in the capsules in order to trigger the self-healing process.

Through the pre-cracking test, the bond between the cement mortar matrix and the capsules inserted was investigated. Suddenly, in order to verify the sealing power of the hard foam generated by the healing agent, a durability test was run. Finally, in order to check the mechanical strength recovery of the self-repaired system, the specimen is resubmitted to the three-point bending test. For the sake of comparison, cement mortar prisms with and without capsules were tested.

As expected, the specimens without the capsules failed the durability test with 0% of sealing efficiency recorded, since there was no repairing action. The self-repaired specimens have shown great results both for the durability test and the static reloading one: the former returned sealing efficiency values not lower than 95% in all cases, the latter returned load recovery index values close to 100% in the majority of the tested cases.

Another aspect investigated during the experimental work upon another series of specimens, has been the evaluation of the bond between the hard foam filling the crack and the cement mortar matrix in terms of max cumulative number of cycles before cyclic failure and relative water tightness, in order to evaluate the dynamic actions that may affect a structure in real field applications.

These tests provided unexpected results: as the number of cycles increases it was expected that the mass of water passing through the crack would also increase, and that the action of the cycles would damage the interface between the cured polyurethane and the surrounding matrix. Nonetheless, for most of the tested specimens, the mass of water passing through the crack, became progressively lower. This phenomenon shows an improvement of the durability of the system subjected to mechanical action, since dynamic actions caused a further release of the encapsulated polyurethane causing a further reaction of the unreacted polyurethane.

Even though the system has shown very good performances both on mechanical and durability behavior, *further research* is need to be done in order to implement the system in practice.

For example, all the tests were performed on cement mortar specimen instead of concrete ones: even if the reaction of the healing agent stored in the capsules does not depend on the surrounding matrix, but only on the presence of moisture in the air, it would be relevant to test the efficiency of the encapsulated polyurethane system among concrete elements in order to test the system in full-scale reinforced concrete elements. In fact, the presence

of reinforcement bars may have an effect on crack development, and hence a different behavior of the encapsulated polyurethane system.

Another relevant aspect is the stability of the healing agent through the time: the crack occurrence could happen in very long period of time, and the healing agent should save its properties until the crack occurrence. Likewise, another aspect that requires a further research is the durability of the bonding between the hardened agent and the surrounding matrix which can be compromise by several actions during the real structure service life.

Also, all the test was run over small scale specimens, using a limit number of capsules. In real field applications, should be relevant to further investigate the right positioning and number of capsules to be adopted as well as the random orientation of the macro-capsules in the concrete mix during the mixing and casting process.

Finally, it is important to develop design criteria for the dosage and characterization of the capsules in order to use them in the structural elements. The last but not the least aspect to consider, is the possibility to industrialize the process of production of the capsules with their relative coating, filling and sealing, in order to realize the scale-up of the system in real concrete structures.

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Acknowledgements

(in Italian because my grandparents do not know English)

Oops! I did it again...diceva Britney

E a questo punto penso di doverlo dire anche io.

Non mi sembra vero, eppure se mi tiro un pizzicotto non sto dormendo...e menomale direi!

Sarebbe stato uno di quei sogni in cui cerchi disperatamente di svegliarti ma il tuo inconscio ti obbliga a non farlo e ad affrontare tutte le cose scomode che da sveglio eviteresti.

Mamma, Papà mi trasferisco a Torino per fare la magistrale, però state tranquilli, cosa volete che succeda?

La risposta?

Una pandemia globale, una guerra mondiale, ci sono più rinoceronti oggi che 100 anni fa, la Francia ha aperto la prima casa di riposo per elefanti in Europa...mi sa che ci faccio un salto appena potrò, d'altronde la Francia è proprio qui dietro l'angolo, bello no?

Forse è questo il senso di tutto: per ogni cosa brutta che succede ce ne sono altre belle che passano in sordina. Sembra una cosa banale, ma è una conclusione a cui non sempre sono giunta senza prima passare dei periodi che Schopenhauer scansati.

Ed effettivamente durante questo percorso di cose belle ne sono successe.

Sia chiaro, non ricordo quasi nulla di tutto quello che è successo, come dopo una brutta sbronza, però proprio come dopo una sbronza, la mattina dopo ti svegli e ti sono rimaste sensazioni positive della sera prima e un gran mal di testa.

Le mie sensazioni positive?

La Vigiless, U Maresciall e Zus oltre che un numero indefinito di parenti che puntualmente chiamavano quando ero più indaffarata tra relazioni, progetti e cercare di sopravvivere alla vita da studentessa fuorisede alimentata a scatolette di tonno e bestemmie.

"Ci sentiamo più tardi, adesso sono super occupata, vi richiamo io dopo."

E chiaramente non richiamavo mai, e nonostante tutto non mi hanno diseredata e hanno continuato a pagarmi le tasse per permettermi di continuare a studiare. Carini no?

Poi ci sono quelle persone che sono nella tua stessa situazione (di merda), e che proprio come te hanno scelto di fare la magistrale di ingegneria anziché i travel-blogger (potessi parlare alla me stessa del passato gliene direi quattro!). Quelle persone con cui condividi tutte le cose per cui non riesci a richiamare i tuoi genitori, i parenti, gli amici che hai lasciato lontano, Mattarella o il Papa che ci tenevano tanto a sentire come stessi.

Quelle persone con cui condividi maccaroni cheese mentre scherzi sulla chiusura del Politecnico per pochi giorni (ancora rimpiango quelle parole!). Quelle con cui passi serate infinite a bere birre al Comala appena riaprono le gabbie e c'è il liberi tutti. Quelle persone con cui fai discorsi che andrebbero censurati anche nel più progressista dei paesi, ma vabbè tutti abbiamo quei momenti così. Quelle persone che conosci da poco ma con cui ti senti libero di essere senza filtri e censure perché sai che non ti giudicheranno mai (e perché loro sono uguali!).

Poi ci sono quelle persone che percorrono la tua stessa strada da anni e anni e nonostante le deviazioni, i fossi, le corsie bloccate e le corse saltate dei tram o dei pullman notturni, le ritrovi sempre lì a un passo da te pronte a FARE LA BALDORIAAAA, prendere un caffè, (perché ormai abbiamo una certa età!), parlare di cucine e tatuaggi o di discorsi esistenziali mentre bevi Gin Tonic. Quelle persone con cui programmi viaggi in tempi da record, o talmente minuziosamente da sembrare pazza, ma tanto sai che alla fine non andrà niente come da programma, l'importante è la compagnia no?

Quelle persone su cui sai di poter contare perché tanto dove vuoi che vadano?! Non ci hai firmato un patto di sangue per carità, ma è quel tipo di legame difficile da dissolvere, perché ormai è parte di te e ti ha plasmata senza che te ne rendessi conto, come quella storia dei sistemi che interagiscono tra loro per un certo periodo di tempo e poi vengono separati, ma non possono più essere descritti come due sistemi distinti, e in qualche modo sottile diventano un unico sistema.

Poi ci sono quelle persone che ti deludono, tanto, per più di una volta, magari sei stata tu a farti aspettative sbagliate o a fraintendere situazioni e discorsi (la colpa sta sempre nel mezzo, si sa), però a loro modo fanno parte del percorso e ti insegnano a prendere i pali in faccia...tanti pali in faccia, tantissimi pali in faccia e in altre parti, ma vabbè è la vita, e se c'è qualcosa che ho imparato è che i lividi a volte servono e che comunque raccontano una storia.

A loro modo anche loro sono utili a crescere, certo, non in uno dei modi migliori che conosca, però il mondo è bello perché è vario...dicono.

Poi ci sono quelle persone con cui non penseresti mai di creare un legame, perché le circostanze non lo dovrebbero richiedere, ma che contro tutte le aspettative diventano la tua famiglia, anche perché ci passi insieme 15 ore al giorno che, diciamocelo, non sono mica una passeggiata in riva al mare mentre sorseggi birra fresca.

Sono quelle persone con cui passi dal venerdì pomeriggio al sabato mattina senza rendertene conto, anzi forse l'unico ad avere un sospetto è il portafoglio che puntualmente il sabato mattina è lì in un angolo, svuotato, che piange.

Quelle persone con cui fai gite, sciate, viaggi a caso, i giovedì pizza, vendita di rose abusive in giro per la città, Superga, ti perdi sotto gli occhi degli altri e con cui crei ricordi e sensazioni che sono difficili da dimenticare, almeno per alcuni, almeno per me.

Quelle persone che per aiutarti o sollevarti il morale spaccherebbero il mondo, ma non lo dicono, perché queste cose non si dicono ma si fanno.

Quelle persone a cui ti sei legata in un lasso di tempo talmente breve da farti girare la testa, ma va bene così.

Poi ci sono loro, quelle persone che sai che non ci saranno per sempre, ma tu un po' ci speri, e quando ti rendi conto che non è così decidi di portartele sottopelle così almeno lì sai che ci rimarranno per un po'.

Sono quelle persone da cui impari cosa significhi davvero essere forti e come reagire alle batoste (ma quelle vere eh!) che ti capitano, quelle persone da cui bisognerebbe solo che imparare a vivere.

Sono quelle persone che profumano di torte e biscotti, che quando raggiungi degli obiettivi hanno il cuore che esplode di gioia, e che fanno esplodere il tuo nel vedere la loro gioia, e lo so, lo so, che non è un buon momento per parlare di esplosioni, ma è l'unica parola che esprime la sensazione che si prova quando vedi quel sorriso sul loro volto, o almeno lo immagini.

E poi ci sono io, che troppo spesso non credo in me stessa, ma che ho incontrato per fortuna (o sfortuna, boh) tutte queste persone, che nel bene e nel male mi circondano e mi ricordano che forse qualcosa in fondo in fondo c'è.

Dovrei dirvi grazie, ma sinceramente mi sembra un po' banale, quindi non dirò niente, mi limiterò a offrirvi da bere quando ci vedremo.

24/03/2022

Attachment - Product data sheets

TP 1372 TECNO PIEMONTE
PROVE E CERTIFICAZIONI

ORGANISMO NOTIFICATO n° 1372

Sede legale: Via C. Pizzorno, 12 - 28078 ROMAGNANO SESIA (NO) *Sede operativa:* Statale Valsesia, 20 - 13035 LENTA (VC)

CERTIFICATO DI COSTANZA DELLA PRESTAZIONE 1372-CPR-2782

In conformità al Regolamento (UE) 305/2011 del Parlamento Europeo e del Consiglio del 9 marzo 2011 (Regolamento Prodotti da Costruzione – CPR), questo certificato si applica al prodotto da costruzione:

Dati del prodotto:

Descrizione: **Cemento comune**

Denominazione: **Cemento Portland CEM I 52.5 R**

immesso sul mercato sotto il nome:

Ragione sociale: **BUZZI UNICEM S.p.A.**

Sede Legale: **Via Luigi Buzzi, 6 - 15033 CASALE MONFERRATO (AL)**

e prodotto nello stabilimento:

identificazione/indirizzo: **Strada Piansottano,1 - 12017 ROBILANTE (CN)**

Questo certificato attesta che tutte le disposizioni riguardanti la valutazione e la verifica della costanza della prestazione descritte nell'allegato ZA della norma

EN 197-1:2011

nell'ambito del sistema 1+ per le prestazioni indicate in questo certificato sono applicate e che il controllo di produzione in fabbrica condotto dal fabbricante è valutato assicurare la

costanza della prestazione del prodotto da costruzione.

Questo certificato è stato emesso per la prima volta il 15/11/2018 e ha validità sino a che la norma armonizzata, il prodotto da costruzione, i metodi di AVCP o le condizioni di produzione nello stabilimento non siano modificate in modo significativo, a meno che non sia sospeso o ritirato dall'Organismo Notificato di certificazione di prodotto (Tecno Piemonte S.p.A.).

Emissione corrente: Lenta, 15/11/2018

Revisione: 0

Il Direttore Tecnico
Dott. Ing. Sergio Beltrame

TP 1372 TECNO PIEMONTE
PROVE E CERTIFICAZIONI

ORGANISMO NOTIFICATO n° 1372

Sede legale: Via C. Pizzorno, 12 - 28078 ROMAGNANO SESIA (NO) *Sede operativa:* Statale Valsesia, 20 - 13035 LENTA (VC)

CERTIFICATO DI COSTANZA DELLA PRESTAZIONE 1372-CPR-2782

In accordo alla norma EN 197-1:2011, sono state eseguite le prove di controllo per la valutazione della prestazione del prodotto con Sistema di Valutazione e Verifica della Costanza della Prestazione 1+, ottenendo le prestazioni sotto riportate:

Requisito dal Mandato	Punti della norma EN 197-1:2011	Esito ottenuto
Resistenza alla compressione (iniziale e normalizzata)	7.1, 8, 9	Passa
Tempo di presa	7.2, 9	Passa
Residuo insolubile	7.3, 9	Passa
Perdita al fuoco	7.3, 9	Passa
Stabilità (espansione)	7.2, 9	Passa
Stabilità (tenore di SO_3)	7.3, 9	Passa
Tenore di cloruro	7.3, 9	Passa

L'esito sopra riportato dovrà essere confermato dai risultati delle prove di controllo ispettivo eseguite periodicamente su campioni prelevati in fabbrica/deposito dall'Organismo Notificato di certificazione di prodotto (Tecno Piemonte S.p.A.).

Buzzi Unicem

DICHIARAZIONE DI PRESTAZIONE
N° 1372-CPR-2782
Ai sensi del REGOLAMENTO DELEGATO (UE) n° 574/2014 del 21 febbraio 2014

1. Codice di identificazione unico del prodotto-tipo:

Cemento Portland EN 197-1 – CEM I 52,5 R

2. Usi previsti:

Preparazione di calcestruzzo, malta, malta per iniezione o altre miscele per costruzione e fabbricazione di prodotti da costruzione, etc.

3. Fabbricante:

BUZZI UNICEM S.p.A. – Via L. Buzzi 6 – 15033 Casale Monferrato (AL) – ITALIA

4. Mandatario:

Non applicabile

5. Sistema di VVCP: (Valutazione e Verifica della Costanza della Prestazione)

Sistema 1+

6.a Norma armonizzata:

UNI EN 197-1:2011

Organismi notificati:

TECNO PIEMONTE, notificato con il numero 1372, ha effettuato la determinazione di prodotto-tipo sulla base delle prove (compreso il campionamento), l'ispezione iniziale dello stabilimento e del controllo di produzione della fabbrica, la sorveglianza, la valutazione e la verifica continue del controllo di produzione di fabbrica, e le prove di verifica di tipo dei campioni prelevati prima della immissione sul mercato del prodotto sotto il sistema 1+ e ha rilasciato il relativo certificato.

7. Prestazioni dichiarate

Caratteristiche essenziali	Prestazione
Costituenti e composizione del cemento comune	CEM I
Resistenza a compressione (normalizzata e iniziale)	52,5 R
Tempo di presa	*Passa*
Residuo insolubile	*Passa*
Perdita al fuoco	*Passa*
Stabilità - Espansione - Contenuto di SO_3	 *Passa* *Passa*
Contenuto di cloruro	*Passa*

8. Documentazione tecnica appropriata e/o documentazione tecnica specifica:

Non applicabile

La prestazione del prodotto sopra identificato è conforme all'insieme delle prestazioni dichiarate. La presente dichiarazione di prestazione viene emessa, in conformità al regolamento (UE) n. 305/2011, sotto la sola responsabilità del fabbricante sopra identificato.

Firmato a nome e per conto del fabbricante da:

Antonio Buzzi – Direttore Operativo Cemento Italia

Casale Monferrato, 01.01.2019

Rev. 1

SIGMA-ALDRICH

3050 Spruce Street
Saint Louis, Missouri 63103 USA
Telephone 800-325-5832 • (314) 771-5765
Fax (314) 286-7828
email: techserv@sial.com
sigma-aldrich.com

ProductInformation

(Hydroxypropyl)methyl cellulose

Product Number **H 7509**
Store at Room Temperature
Replacement for Product Code 20,032-8

Product Description
CAS Number: 9004-65-3
Molecular weight: approximately 86 kDa.

Hydroxypropylmethylcelluloses are water soluble polymers derived from cellulose. They are typically used as thickeners, binders, film formers, and water retention agents. They also function as suspension aids, surfactants, lubricants, protective colloids, and emulsifiers. In addition, solutions of these polymers thermally gel.[1,2]

These polymers are prepared by reacting wood or cotton cellulose fibers with propylene oxide and methyl chloride in the presence of caustic soda.

This product has a methoxyl content of 28-30% and a hydroxypropoxyl content of 7-12%.

Precautions and Disclaimer
For Laboratory Use Only. Not for drug, household or other uses.

Preparation Instructions
This product is soluble in water (10 mg/ml). However, it is very important to thoroughly disperse the particles in water with agitation before they will dissolve. Otherwise, they will lump and form a gelatinous membrane around the internal particles, preventing them from wetting completely. There are four dispersion techniques commonly used to prepare solutions of hydroxypropylmethylcellulose: dispersion in hot water, dry blending, dispersion in non-solvent medium, and dispersion of surface-treated powders. (The last method is only for surface-treated powders).

Dispersion in hot water:
1. Heat approximately 1/3 the required volume of water to at least 90 °C.
2. Add the powder to the heated water with stirring or agitation.
3. Agitate the mixture until the particles are thoroughly wetted and evenly dispersed.
4. Add the remainder of the water (cold water) to lower the temperature of the dispersion. As the product cools, it will reach a temperature at which it becomes water soluble. It will then begin to hydrate and dissolve, increasing the viscosity of the solution.
5. Continue agitation for at least 30 minutes after the proper temperature is reached for solubility. The solution is now ready to use.

Dry blending:
1. Combine powder with other dry ingredients. The suggested ratio of dry powder to hydroxypropylmethylcellulose is 7:1 to 3:1.
2. Thoroughly blend the dry ingredients.
3. Add the dry mixture to water with agitation.
4. Agitate until the product has completed hydrated and the solution is consistently smooth. The solution is now ready for further processing/use.

Dispersion in non-solvent medium:
1. Hydroxypropylmethylcellulose may be dispersed in non-solvent media such as vegetable oil, polyethylene glycol, glycerin, corn syrup, and concentrated salt solutions. A ratio of 5-8 parts non-solvent to 1 part hydroxypropylmethylcellulose is recommended to obtain a liquid slurry.
2. Agitate the mixture until the particles are evenly dispersed.
3. This dispersion may be added to cold water or cold water may be added to the dispersion.
4. Continue mixing until the powder is completely hydrated and the solution is smooth. Additional ingredients may now be added to the formulation.

References

1. Savage, A. B., Encyclopedia of Polymer Science and Technology, vol. 3, Interscience (New York, 1965), p. 496-511.
2. Greminger, G. K., Savage, A. B., Industrial Gums, R. L. Whistler, Ed., Academic Press (New York, 1973), p. 619-647.

CMH/RXR 6/03

PRIMAL B 60 A

SCHEDA

RESINA ACRILICA IN EMULSIONE COPOLIMERO DI ETILACRILATO E METILMETACRILATO EA/MMA

CARATTERISTICHE CHIMICO-FISICHE

ASPETTO: liquido lattiginoso
COLORE: bianco
ODORE: ammoniacale
PESO SPECIFICO: 1,07
RESIDUO NON VOLATILE: 46 -48%
Ph: 9,0 - 9,9
VISCOSITA'(BROOKFIELD No2,30 giri/min): 800 - 3000 mPas .
PUNTO DI EBOLLIZIONE: 100°C/212°F Acqua
SOLUBILITA' IN ACQUA: diluibile
PERCENTUALE DI VOLATILI: 52 - 55% Acqua
VEL. EVAP. (BAc = 1): < 1 Acqua
TMF: 9° C

INDICAZIONI

Il PRIMAL B 60 A appartiene ad una generazione di resine acriliche introdotte sul mercato dalla Rohm & Haas di Filadelfia fin dal 1953 . Da allora l'esperienza ha dimostrato che si tratta di prodotti di qualità superiore per pitture all'acqua e fissativi murali per interno ed esterno. Infatti da oltre 15 anni vengono fabbricati ed applicati sui più svariati supporti in tutte le parti del mondo, dimostrando una eccezionale resistenza in tutti i climi alle più severe condizioni atmosferiche.

PROPRIETA':
- Eccellente stabilità al gelo
- Grande compatibilità con pigmenti e cariche
- Ottima resistenza ai sali solubili compresi quelli bivalenti
- Ampia compatibilità con altre emulsioni
- Finissima dispersione
- Buona stabilità del Ph

PROPRIETA' DEL FILM:
- Buona stabilità meccanica
- Elevata resistenza all'ingiallimento
- Buona trasparenza
- Eccellente resistenza ai raggi ultravioletti
- Permanente flessibilità ed elasticità
- Resistenza agli agenti chimici e ai grassi
- Ottimo potere legante
- Grande resistenza agli alcali
- Permeabilità al vapore acqueo: buona traspirabilità

CARATTERISTICHE DELLE PITTURE E CONSOLIDAMENTO DELLE SUPERFICI PITTORICHE A BASE DI PRIMAL:
Grazie alle citate proprietà, le pitture a base di PRIMAL sono adatte alla verniciatura di superfici a calce, gesso, legno, agglomerati, carta, tessuti, ecc. Inoltre le pitture a base di PRIMAL si distinguono per queste particolari caratteristiche:
- rapidità di essicazione: circa 30', per cui è possibile applicare diverse mani nella stessa giornata
- dilatazione
- resistenza allo sfarinamento
- resistenza alla efflorescenza ed alla formazione di macchie;
- aderenza ad ogni tipo di supporto
- facilità di applicazione
- resistenza al lavaggio

Ultimo aggiornamento Aprile 2000

ANTICHITA' BELSITO s.r.l.
Via Prisciano, 22/a 00136 Roma
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Web : www.antichitabelsito.it

SCHEDA DI DATI DI SICUREZZA

secondo il Regolamento (CE) Num. 1907/2006

Versione 6.1
Data di revisione 30.01.2019
Data di stampa 04.02.2020

SEZIONE 1: identificazione della sostanza/miscela e della società/impresa

1.1 Identificatori del prodotto

Nome del prodotto	:	Polietilenglicole
Codice del prodotto	:	P3015
Marca	:	Sigma-Aldrich
Num. REACH	:	Per questa sostanza non è disponibile un numero di registrazione in quanto la sostanza o i suoi usi sono esentati da registrazione, il tonnellaggio annuale non richiede registrazione oppure la registrazione è prevista ad una scadenza successiva.
N. CAS	:	25322-68-3

1.2 Usi identificati pertinenti della sostanza o della miscela e usi sconsigliati

Usi identificati	:	Chimici di laboratorio, Produzione di sostanze chimiche

1.3 Informazioni sul fornitore della scheda di dati di sicurezza

Società	:	Merck Life Science S.r.l. Via Monte Rosa 93 I-20149 MILANO
Telefono	:	+39 02 3341 7340
Fax	:	+39 02 3801 0737
Indirizzo e-mail	:	serviziotecnico@merckgroup.com

1.4 Numero telefonico di emergenza

Telefono per le emergenze	:	800-789-767 (CHEMTREC Italia) +39-02-4555-7031 (CHEMTREC chiamate internazionali) +39 02-6610-1029 (Centro Antiveleni Niguarda Ca' Granda - Milano)

SEZIONE 2: identificazione dei pericoli

2.1 Classificazione della sostanza o della miscela

Sostanza o miscela non pericolosa secondo la regolamentazione (CE) N. 1272/2008.

2.2 Elementi dell'etichetta

Sostanza o miscela non pericolosa.

2.3 Altri pericoli

Questa sostanza/miscela non contiene componenti considerati sia persistenti, bioaccumulabili che tossici (PBT), oppure molto persistenti e molto bioaccumulabili (vPvB) a concentrazioni di 0.1% o superiori.

SEZIONE 3: composizione/informazioni sugli ingredienti

3.1 Sostanze

Formula	:	(C2H4O)nH2O
N. CAS	:	25322-68-3
N. CE	:	500-038-2

Secondo la normativa applicabile non è necessario dichiarare alcun componente.

SEZIONE 4: misure di primo soccorso

4.1 Descrizione delle misure di primo soccorso

Se inalato
Se viene respirato, trasportare la persona all'aria fresca. Se non respira, somministrare respirazione artificiale.

In caso di contatto con la pelle
Lavare con sapone e molta acqua.

In caso di contatto con gli occhi
Come precauzione sciacquare gli occhi con acqua.

Se ingerito
Non somministrare alcunchè a persone svenute. Sciacquare la bocca con acqua.

4.2 Principali sintomi ed effetti, sia acuti che ritardati

I più importanti sintomi ed effetti conosciuti sono descritti nella sezione 2.2 sull'etichettatura e/o nella sezione 11.

4.3 Indicazione dell'eventuale necessità di consultare immediatamente un medico e di trattamenti speciali

Nessun dato disponibile

SEZIONE 5: misure antincendio

5.1 Mezzi di estinzione

Mezzi di estinzione idonei
Utilizzare acqua nebulizzata, schiuma alcool resistente, prodotti chimici asciutti o anidride carbonica.

5.2 Pericoli speciali derivanti dalla sostanza o dalla miscela

5.3 Raccomandazioni per gli addetti all'estinzione degli incendi

Se necessario, indossare un respiratore autonomo per spegnere l'incendio.

5.4 Ulteriori informazioni

Nessun dato disponibile

SEZIONE 6: misure in caso di rilascio accidentale

6.1 Precauzioni personali, dispositivi di protezione e procedure in caso di emergenza

Evitare di respirare vapori/nebbia/gas.
Vedere Sezione 8 per i dispositivi di protezione individuale.

6.2 Precauzioni ambientali

Non sono richieste particolari misure precauzionali per la salvaguardia dell'ambiente.

6.3 Metodi e materiali per il contenimento e per la bonifica
Conservare in contenitori adatti e chiusi per lo smaltimento.

6.4 Riferimento ad altre sezioni
Per lo smaltimento riferirsi alla sezione 13.

SEZIONE 7: manipolazione e immagazzinamento

7.1 Precauzioni per la manipolazione sicura
Per le precauzioni vedere la sezione 2.2.

7.2 Condizioni per lo stoccaggio sicuro, comprese eventuali incompatibilità
Immagazzinare in luogo fresco. Tenere il contenitore ermeticamente chiuso in un ambiente secco e ben ventilato.

7.3 Usi finali particolari
A parte gli usi descritti nella sezione 1.2 non sono contemplati altri usi specifici.

SEZIONE 8: controllo dell'esposizione/protezione individuale

8.1 Parametri di controllo

Componenti con limiti di esposizione
Non contiene sostanze con valore limite di esposizione professionale.

8.2 Controlli dell'esposizione

Controlli tecnici idonei
Prassi generale di igiene industriale.

Protezione individuale

Protezioni per occhi/volto
Utilizzare dispositivi per la protezione oculare testati e approvati secondo i requisiti di adeguate norme tecniche come NIOSH (USA) o EN 166 (EU)

Protezione della pelle
Manipolare con guanti. I guanti devono essere controllati prima di essere usati. Usare una tecnica adeguata per la rimozione dei guanti (senza toccare la superficie esterna del guanto) per evitare il contatto della pelle con questo prodotto Smaltire i guanti contaminati dopo l'uso in accordo con la normativa vigente e le buone pratiche di laboratorio. Lavare e asciugare le mani.

I guanti di protezione selezionati devono soddisfare le esigenze della direttiva (UE) 2016/425 e gli standard EN 374 che ne derivano.

Pieno contatto
Materiale: Gomma nitrilica
spessore minimo: 0,11 mm
Tempo di permeazione: 480 min
Materiale testato:Dermatril® (KCL 740 / Aldrich Z677272, Taglia M)

Contatto da spruzzo
Materiale: Gomma nitrilica
spessore minimo: 0,11 mm
Tempo di permeazione: 480 min
Materiale testato:Dermatril® (KCL 740 / Aldrich Z677272, Taglia M)

Fonte dei dati: KCL GmbH, D-36124 Eichenzell, tel. +49 (0)6659 87300, e-mail sales@kcl.de, metodo di prova: EN374
Se usato in soluzione, o mischiato con altre sostanze, e in condizioni diverse da quelle menzionate nella norma EN 374, contattare il fornitore di guanti approvati

dalla CE. Questa raccomandazione vale a titolo di consiglio e dev'essere valutata da un igienista industriale e da un responsabile della sicurezza al corrente della situazione specifica dell'uso previsto dai nostri clienti. Non si deve interpretare come un'approvazione di uno specifico scenario di esposizione.

Protezione fisica
Indumenti impermeabili, Il tipo di attrezzatura di protezione deve essere selezionato in funzione della concentrazione e la quantità di sostanza pericolosa al posto di lavoro.

Protezione respiratoria
Non è richiesta la protezione respiratoria. Per bassi livelli di esposizione utilizzare cartucce per respiratori di tipo OV/AG (US) o di tipo ABEK (EU EN 14387). Utilizzare respiratori e componenti testati e approvati dai competenti organismi di normazione, quali il NIOSH (USA) il CEN (UE).

Controllo dell'esposizione ambientale
Non sono richieste particolari misure precauzionali per la salvaguardia dell'ambiente.

SEZIONE 9: proprietà fisiche e chimiche

9.1 Informazioni sulle proprietà fisiche e chimiche fondamentali

a)	Aspetto	Stato fisico: liquido
b)	Odore	Nessun dato disponibile
c)	Soglia olfattiva	Nessun dato disponibile
d)	pH	Nessun dato disponibile
e)	Punto di fusione/punto di congelamento	Punto/intervallo di fusione: -65 °C
f)	Punto di ebollizione iniziale e intervallo di ebollizione.	Nessun dato disponibile
g)	Punto di infiammabilità	Nessun dato disponibile
h)	Velocità di evaporazione	Nessun dato disponibile
i)	Infiammabilità (solidi, gas)	Nessun dato disponibile
j)	Infiammabilità superiore/inferiore o limiti di esplosività	Nessun dato disponibile
k)	Tensione di vapore	< 0,01 mmHg a 20 °C
l)	Densità di vapore	Nessun dato disponibile
m)	Densità relativa	1,127 g/cm 3
n)	Idrosolubilità	Nessun dato disponibile
o)	Coefficiente di ripartizione: n-ottanolo/acqua	Nessun dato disponibile
p)	Temperatura di	Nessun dato disponibile

	autoaccensione	
q)	Temperatura di decomposizione	Nessun dato disponibile
r)	Viscosità	Nessun dato disponibile
s)	Proprietà esplosive	Nessun dato disponibile
t)	Proprietà ossidanti	Nessun dato disponibile

9.2 Altre informazioni sulla sicurezza
Nessun dato disponibile

SEZIONE 10: stabilità e reattività

10.1 Reattività
Nessun dato disponibile

10.2 Stabilità chimica
Stabile nelle condizioni di stoccaggio raccomandate.

10.3 Possibilità di reazioni pericolose
Nessun dato disponibile

10.4 Condizioni da evitare
Nessun dato disponibile

10.5 Materiali incompatibili
Agenti ossidanti forti

10.6 Prodotti di decomposizione pericolosi
Prodotti di decomposizione pericolosi in caso d'incendio. - Ossidi di carbonio
Altre prodotti di decomposizione pericolosi - Nessun dato disponibile
In caso di incendio: vedere la sezione 5

SEZIONE 11: informazioni tossicologiche

11.1 Informazioni sugli effetti tossicologici

Tossicità acuta
DL50 Orale - Ratto - 30.200 mg/kg
DL50 Dermico - Su coniglio - > 20.000 mg/kg

Corrosione/irritazione cutanea
Nessun dato disponibile

Lesioni oculari gravi/irritazioni oculari gravi
Occhi - Su coniglio
Risultato: Leggera irritazione agli occhi

Sensibilizzazione respiratoria o cutanea
Nessun dato disponibile

Mutagenicità delle cellule germinali
Nessun dato disponibile

Cancerogenicità

IARC: Nessun componente di questo prodotto presente a livelli maggiori o uguali allo 0.1% è identificato come cancerogeno conosciuto o previsto dallo IARC.

Tossicità riproduttiva
Nessun dato disponibile

Tossicità specifica per organi bersaglio - esposizione singola
Nessun dato disponibile

Tossicità specifica per organi bersaglio - esposizione ripetuta
Nessun dato disponibile

Pericolo in caso di aspirazione
Nessun dato disponibile

ulteriori informazioni
RTECS: nessun dato disponibile

Al meglio della nostra conoscenza, le proprietà chimiche, fisiche e tossicologiche non sono state oggetto di studi approfonditi.

SEZIONE 12: informazioni ecologiche

12.1 Tossicità
Nessun dato disponibile

12.2 Persistenza e degradabilità
Nessun dato disponibile

12.3 Potenziale di bioaccumulo
Nessun dato disponibile

12.4 Mobilità nel suolo
Nessun dato disponibile

12.5 Risultati della valutazione PBT e vPvB
Questa sostanza/miscela non contiene componenti considerati sia persistenti, bioaccumulabili che tossici (PBT), oppure molto persistenti e molto bioaccumulabili (vPvB) a concentrazioni di 0.1% o superiori.

12.6 Altri effetti avversi
Nessun dato disponibile

SEZIONE 13: considerazioni sullo smaltimento

13.1 Metodi di trattamento dei rifiuti

Prodotto
Conferire le soluzioni non riciclabili e le eccedenze ad una società di smaltimento rifiuti autorizzata.

Contenitori contaminati
Smaltire come prodotto inutilizzato.

SEZIONE 14: informazioni sul trasporto

14.1 Numero ONU
ADR/RID: - IMDG: - IATA: -

14.2 Nome di spedizione dell'ONU

ADR/RID: Merci non pericolose
IMDG: Not dangerous goods
IATA: Not dangerous goods

14.3 Classi di pericolo connesso al trasporto

ADR/RID: - IMDG: - IATA: -

14.4 Gruppo d'imballaggio

ADR/RID: - IMDG: - IATA: -

14.5 Pericoli per l'ambiente

ADR/RID: no IMDG Inquinante marino: no IATA: no

14.6 Precauzioni speciali per gli utilizzatori

Nessun dato disponibile

SEZIONE 15: informazioni sulla regolamentazione

15.1 Disposizioni legislative e regolamentari su salute, sicurezza e ambiente specifiche per la sostanza o la miscela

Questa scheda di sicurezza rispetta le prescrizioni del Regolamento (CE) Num. 1907/2006.

15.2 Valutazione della sicurezza chimica

Per questo prodotto non è stata effettuata una valutazione della sicurezza chimica.

SEZIONE 16: altre informazioni

Ulteriori informazioni

Le informazioni di cui sopra sono ritenute corrette, tuttavia non possono essere esaurienti e dovranno pertanto essere considerate puramente indicative. La Sigma-Aldrich Corporation e le suo filiali non potranno essere ritenute responsabili per qualsiasi danno derivante dall'impiego o dal contatto con il prodotto di cui sopra. Per ulteriori termini e condizioni di vendita fare riferimento al sito www.sigma-aldrich.com e/o al retro della fattura o della bolla di accompagnamento.
Il marchio riportato nell'intestazione e/o a piè di pagina del presente documento potrebbe momentaneamente differire visivamente da quello del prodotto acquistato, per via della transizione dei nostri marchi. Tuttavia, tutte le informazioni relative al prodotto contenute in questo documento rimangono inalterate e si riferiscono al prodotto ordinato. Per ulteriori informazioni, si prega di contattare mlsbranding@sial.com.

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www.api-spa.com

primer aq

Prodotto a due componenti, a base di resine epossidiche in veicolo acquoso, compatibile con leganti idraulici (cemento)

Dati tecnici

Natura del veicolo epossidico
Contenuto in solidi in volume 60%
Punto di infiammabilità non infiammabile
Peso specifico 1,16 kg/dm^3
Colore neutro
Rapporti di impiego in peso base 30 - indurente 70
Pot-life a 23°C 60 minuti
Spessore film secco dell'impasto con cemento 0,180 mm
(rapporto resina-cemento 1:1)
Consumo d'impasto 0,400 kg/m^2
Tempo aperto a 23°C, 60% U.R. min. 5 minuti, max. 1 ora
Tempo di copertura con rivestimenti resinosi a 23°C, 60% U.R.
min. 20 ore, max. 48 ore
Adesione al calcestruzzo > 3 N/mm^2
Indurimento completo a 23°C 7 giorni
Solvente per pulizia attrezzi acqua

Campi principali di impiego

Viene impiegato quale promotore di adesione per rivestimenti resinosi, malte cementizie, calcestruzzi freschi su superfici cementizie invecchiate anche lisce. È impiegato anche quale promotore di adesione per cicli epossidici su fondi umidi.
Il prodotto può essere applicato tal quale o mescolato con cemento Ptl 325 o Ptl 425 e/o quarzo.
Il prodotto si applica sempre su superfici compatte e pulite, prive di boiacche, parti friabili, oli disarmanti.

Preparazione delle superfici

L'individuazione della metodologia di preparazione del supporto deve essere fatta tenendo conto della natura e consistenza del supporto e delle successive fasi lavorative.
La superficie, in ogni caso, dopo la preparazione non dovrà presentare parti incoerenti o distaccate, vecchie vernici e/o sostanze che potrebbero compromettere l'adesione.
Sistemi di preparazione sono: idrosabbiatura, pallinatura, fresatura.

Modalità di applicazione

a) Applicazione a rullo:
il prodotto può essere applicato tal quale, dopo miscelazione dei due componenti (base + indurente), oppure con aggiunta di cemento Ptl 325 o 425 in rapporto 1:1 in peso.
Quando l'applicazione, oltre alla funzione di promuovere l'adesione degli strati successivi, ha anche la funzione di barriera vapore, il prodotto va utilizzato sempre addizionato con cemento e si consiglia l'applicazione con spazzolone.
b) Applicazione a spatola:
il prodotto può essere applicato per la realizzazione di strati con spessori variabili compresi tra 1-2 mm, in relazione alla granulometria di quarzo impiegata nella miscelazione.
Si consiglia di non eccedere con gli spessori oltre quelli indicati in quanto potrebbero aversi fessurazioni per evaporazione dell'acqua.
Quando viene applicato a spatola, il *Primer aq* deve essere miscelato con cemento Ptl 325 o 425 e quarzo nei rapporti in peso 1:1:1 resina, inerte, cemento.
Per migliorare la scorrevolezza dell'impasto e la sua applicabilità, aggiungere fino a un massimo del 30% di acqua pulita.

Two-component product, based on epoxy resins in acqueous vehicle and hydraulic binders (concrete) compatible

Technical data

Vehicle type epoxy
Solids content in volume 60%
Flash point not flammable
Specific gravity 1,16 kg/dm^3
Colour neutral
Mixing ratio by weight base 30 - hardener 70
Pot-life at 23°C 60 minutes
Dry film thickness of the mixture with concrete 0,180 mm
(ratio resin-concrete 1:1)
Coverage of mixture 0,400 kg/m^2
Open time at 23°C, 60% R.H. 5 minutes min.,1 hour max.
Overcoating time with resin coatings at 23°C, 60% R.H.
min. 20 hours, max. 48 hours
Adhesion to concrete > 3 N/mm^2
Full cure at 23°C 7 days
Tool cleaner water

Main use

It is used as adhesion promoter for resin coatings, cement mortars, wet concretes on aged, also smooth, cement surfaces. It is also used as adhesion promoter for epoxy systems on damp substrates.
This product can be applied as it is, or mixed with cement Ptl 325 or Ptl 425 and/or quartz. Always apply the product on surfaces that are compact and clean, without cement puddles, loose parts, disbonding oils.

Surface preparation

The choice of the surface preparation method must be done checking the nature and consistency of the substrate and the subsequent working phases. In any case, after preparation the surface must not have loose parts, old paints and/or materials which can compromise adhesion. Sand blasting, shot blasting, milling are some of methods used to prepare surface before application of Primer aq.

Application method

a) Application by roller:
the product can be applied either as is, after mixing the two components (base + hardener), or with the addition of Ptl 325 or 425 cement in a ratio of 1:1 by weight.
When the product is applied not only to promote the adhesion of subsequent layers, but also as a steam barrier, cement should be always added to the product and we recommend application by brush.
b) Application by spatula:
the product can be applied by spatula in layers 1-2 mm thick, depending on the quartz particle size used in mixture. We do not advise applying thicker layers because water evaporation may cause cracking. When applied by spatula, the *Primer aq* must be mixed with Ptl 325 or 425 cement and quartz sand in a resin, sand, cement ratio of 1:1:1. To improve the fluidity of the paste and ease of application, add up to 30% clean water.

api
protective coatings
and resin flooring

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Quando il *Primer aq* viene impiegato come promotore di adesione nelle riprese di getto e/o malte cementizie, l'applicazione del nuovo getto o della malta deve avvenire entro il "tempo aperto", ovvero il tempo massimo decorrente tra l'applicazione e la ricopertura con l'impasto cementizio.
Dipende dalle condizioni ambientali: un'alta temperatura del supporto, una atmosfera molto secca e una forte ventilazione, tendono a ridurre il tempo aperto. Un criterio empirico di valutazione consiste nel toccare, con leggera pressione del dito, l'adesivo applicato: quando il dito non viene più sporcato il tempo aperto è terminato. A 20°C e 60% U.R., in assenza di ventilazione, il tempo aperto è di circa 1 ora.

Temperatura di applicazione

Non è consigliabile applicare il materiale sotto i 10°C ed al di sopra dei 35°C. In nessun caso si deve applicare al di sotto dei 5°C.

Confezionamento

Latte da kg 10 peso netto (base + indurente).

Norme di igiene e sicurezza

Materiali nocivi per ingestione e prolungato contatto con la pelle. Evitare pertanto questi contatti, utilizzando indumenti protettivi durante l'uso.

When *Primer aq* is used as adhesion promoter for construction joints and/or cement mortars, application of the new casting or of the mortar have to be done within the "open time", that is maximum time from the application to the overcoating with the cement mixture. It depends on the environmental conditions: high surface temperature, very dry atmosphere and strong ventilation, tends to decrease the open time. An empirical criterion of evaluation is to touch, with a slight pressure of the finger, the adhesive applied: when the finger does not get dirty any more, the open time has finished. At 20°C and 60% R.H., with no ventilation, the open time is approx. 1 hour.

Application temperature

Application when temperature is below 10° C and above 35° C is not advisable. In no cases it should be applied when temperature is below 5° C.

Pack size

Kg 10 cans net weight (base + hardener).

Safety precautions

Harmful for ingestion and prolonged contact with skin. Avoid this kind of contacts, wearing protective garments during use.

PLASTIGEL3220SIGILLANTE
Sigillante impermeabile a base di thiokol

descrizioneprodotto

Prodotto elastomerico a due componenti predosati.
Disponibile nella versione **fluido** per superfici orizzontali o **tixo** per superfici verticali
Perfetta adesione a tutti i materiali: legno, ferro, lega leggera, vetro, tutti i tipi di plastica, ecc. opportunamente puliti e trattati.
Facile applicabilità, indurimento (vulcanizzazione) senza variazione apprezzabile di volume (ritiro).
Elasticità inalterabile nel tempo in quanto inattaccabile dall'ossigeno e dall'ozono.
Dopo l'indurimento si presenta come una gomma elastica, tenace, dotata di straordinarie caratteristiche che praticamente non variano tra i -30 e +80°C.

Campi principali di impiego:
Per sigillare opere in calcestruzzo e per sigillare e impermeabilizzare vetrate, finestre, strutture in legno, parquet all'esterno, ed inoltre per impedire corrosioni dovute a formazione di micropile che si realizzano in presenza di acqua, per contatto di metalli di natura diversa (es. leghe leggere, rame, bronzo, ecc. con acciaio).

cicloapplicativo

Preparazione delle superfici
Le superfici da sigillare devono essere accuratamente pulite e perfettamente asciutte. Pece, grassi, ruggine, residui di vecchie vernici devono essere completamente asportati.
Applicare a pennello una mano di PRIMER ETO, per superfici di calcestruzzo, legno e acciaio. Applicare una mano di PRIMER CINQUE, per superfici di vetro o leghe leggere.
Dopo i tempi previsti di sovrapposizione dei primers (v. Schede Tecniche relative) applicare il PLASTIGEL 3220 SIGILLANTE. Se trascorressero più di 24 ore, dall'applicazione del PRIMER ETO o più di 5 ore dall'applicazione del PRIMER CINQUE, riapplicare i primers, prima di applicare il PLASTIGEL 3220 SIGILLANTE.

Modalità di applicazione
Versare il contenuto della latta di indurente nella latta di base avendo cura di rimuovere tutto il prodotto dalle pareti e fondo della latta.
Procedere ad una accurata miscelazione (circa 5 minuti) con un'opportuna girante (chiedere uff. tecnico API).
L'applicazione viene fatta mediante una pistola ad estrusione a mano, su superficie trattata con i primers, nel rispetto dei tempi previsti (vedi Schede Tecniche relative).

Temperatura di applicazione
Temperature e umidità elevate accelerano l'indurimento. In condizioni normali (ca. 23°C e 50% UR) il tempo a disposizione per l'applicazione è di circa 1 ora. Dopo 24 ore dall'applicazione, in condizioni normali, le superfici sono pedonabili (assenza di appiccicosità). L'indurimento si completa entro 10-12 giorni. Dopodiché si possono tagliare eventuali sbavature e/o effettuare la carteggiatura.
Non è consigliabile applicare il materiale con temperature inferiori a 10°C e superiori a 35°C. In nessun caso si deve applicare al di sotto dei 5°C. La temperatura del supporto deve essere almeno 3°C al di sopra del punto di rugiada.

normegenerali

Confezionamento
latte da kg 1 e kg 5 peso netto (base + indurente)

Solventi per pulizia attrezzi
SOLVENTE N.1076

Norme di immagazzinaggio
Il materiale può essere conservato per 12 mesi se mantenuto in recipienti chiusi ed originali, in ambiente asciutto ed a temperatura compresa tra i 5°C e i 20°C.

Attrezzature
La ns. Società può fornire a richiesta le seguenti attrezzature:
1) Pistola a mano
2) Girante per sigillante
3) Pistole a mano per cartucce in plastica
4) Cartucce vuotein plastica
5) Controcoperchi per caricamento cartucce in plastica

Norme di igiene e Sicurezza
Materiali nocivi per ingestione, inalazione e prolungato contatto con la pelle.

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PLASTIGEL3220SIGILLANTE

Sigillante impermeabile a base di thiokol

caratteristichetecniche

Caratteristiche chimico/fisiche:

Natura chimica:	*polisolfurico bicomponente*
Peso specifico:	*1,55±0,05 kg/dm³*
Colore:	*nero*

Dati tecnici

Rapporti di impiego in peso:	*base 94 - indurente 6*
Pot-life a 23°C e 50% UR:	*60 min. Utilizzare l'indurente estivo lento per temperature > 27°C*
Consumo (sezione di 1 cm²):	*circa 0,160 kg/m*
Indurimento completo a 23°C:	*7 giorni*
Temperatura di esercizio:	*da -30°C a +80°C*
Riduzione volumetrica dopo indurimento:	*< 4%*

Caratteristiche meccaniche

Allungamento a rottura:	*> 450%*
Allungamento massimo in esercizio:	*circa 25%*
Durezza (ISO 868):	*35±3 Shore A*

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STUCCOK

descrizioneprodotto

Adesivo epossidico bicomponente tissotropico senza solventi.

Campi principali di impiego
E' adatto come adesivo per incollaggio e piccole riparazioni su calcestruzzo, inghisaggi. Presenta caratteristiche di resistenza meccanica e di adesione superiori a quelle del calcestruzzo e presenta elevata resistenza agli alcali e ai solventi.

normegenerali

Confezionamento
Confezioni: kg. 6 peso netto
(3 kg. ciascun componente)

Solventi per pulizia attrezzi
SOLVENTE N.1080 (infiammabile).

Norme di igiene e sicurezza
Evitare il contatto
con la pelle e con gli occhi.
Durante l'applicazione
usare creme barriera.

cicloapplicativo

Preparazione delle superfici
Si consiglia di eseguire una molatura con mezzi meccanici.
Dopo tale trattamento la superficie deve risultare compatta, asciutta, pulita e senza polvere.
La compatezza di supporti porosi può essere migliorata usando, prima della stuccatura, il PRIMER DUE.

Modalità di applicazione
Il prodotto previa accurata mescolazione della base con l'indurente, si applica mediante spatola dentata o a filo diritto.

Temperatura di applicazione
Non è consigliabile applicare il materiale sotto i 5°C ed al di sopra dei 35°C. La temperatura del supporto deve essere almeno 3°C al di sopra del punto di rugiada.

caratteristichetecniche

Caratteristiche chimico fisiche

Natura del veicolo	*:epossidico*
Contenuto in solidi	*:100%*
Peso specifico	*:1,7 kg/dm^3*
Colore	*:Componenti: bianco e grigio scuro*
	Miscela: grigio chiaro

Dati tecnici

Pot-life a 23°C	*:60 min*
Rapporto impiego	*:1 a 1 in peso e in volume*
Primo indurimento a 23°C	*:10 h circa*
Indurimento completo a 23°C	*:4 giorni circa*

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CarboStop U

Monocomponente!
Pronto all'uso senza miscelazione

Descrizione

Resina poliuretanica monocomponente, reattiva all´acqua, esente da CFC e plastificanti. Pronta all'uso senza miscelazione.
Viene utilizzato per:

- blocco di trasudamenti d'acqua, anche marina, in fessure
- sigillatura in galleria
- consolidamento di sabbia ghiaiosa
- sigillatura di fori

Applicabile a temperature ambiente comprese tra 0 e 40 °C.
CarboStop U è approvato sulla base della normativa tedesca ZTV-RISS come presigillante per la sigillatura di strutture in calcestruzzo.

Caratteristiche Tecniche

I dati di seguito elencati sono relativi a valori ottenuti in laboratorio in reazione non contrastata. Nella messa in opera in cantiere essi possono subire variazioni dovute a scambi di calore fra la resina e l´ambiente circostante, in funzione delle caratteristiche della roccia o del terreno, dell´umidità, della pressione e di altri fattori.

Dati dei Componenti

		CarboStop U
Densità a 25 °C	kg/m³	1100 -1140
Colore		marrone
Punto di Infiammabilità	°C	> 100
Viscosità a 5 °C	mPa*s	2500 - 6000
Viscosità a 10 °C	mPa*s	1900 - 4500
Viscosità a 15 °C	mPa*s	1100 - 2500
Viscosità a 25 °C	mPa*s	270 - 1000

Dati della miscela

Temperatura	5 °C	10 °C	15 °C	20 °C	25 °C	
Inizio	27”	26”	24”	22”	20”	± 5”
Fine	4’20”	3’20”	2’50”	2’20’’	2’00”	± 15”
Fattore di schiumatura	30 - 60				30 - 50	

La reazione avviene con l'aggiunta del 10% di acqua alla miscela appena preparata
Se necessario la reazione può essere accelerata con CarboAdd X.

CarboStop U

Composizione e Caratteristiche

Componenti

CarboStop U è composto da isocianati modificati con plastificanti e additivi.

Sistema

CarboStop U reagisce a contatto con l'acqua creando una schiuma poliuretanica/poliurea. Il tasso di espansione della schiuma dipende in primo luogo dalla pressione di ritorno provocata dalla propagazione della resina nella struttura da sigillare, perciò fessure ampie o ghiaia daranno luogo a un elevato fattore di schiumatura, mentre fessure strette o sabbia fine daranno luogo a un basso fattore di espansione e ad un'elevata resistenza meccanica.

Prodotto Finale

CarboStop U ferma venute d'acqua e fornisce una sigillatura temporanea, che spesso è sufficiente per la sigillatura di scavi durante i lavori di costruzione. CarboStop U è usato anche come presigillante secondo la normativa tedesca ZTV-ING (sigillatura e giuntura estendibile di fessure in cemento armato). Dopo l'iniezione di CarboStop U, iniettare CarboCrackSeal H nella schiuma non ancora completamente indurita. 2,3
Il CarboStop U indurito non si restringe né si gonfia a contatto con l'acqua.
CarboStop U è stato testato in merito alla compatibilità con acqua di falda secondo le direttive ufficiali dell'Istituto Tedesco per la Tecnologia di Costruzione (DIBt); è stata rilevata solo una minima alterazione della qualità dell'acqua.[1]

Messa in opera

CarboStop U reagisce a contatto con l'acqua. È quindi possibile che si formi una pellicola sulla superficie del liquido a causa della reazione con l'umidità presente nell'aria; questo, tuttavia, non ha nessuna influenza negativa sulla pompabilità della miscela stessa.
La miscela CarboStop/CarboAdd viene convogliata analogamente a un materiale monocomponente, con pompa a mano o meccanica, e iniettata tramite packer all´interno della zona da trattare. La miscela aumenta di volume (schiumatura) al contatto con l´acqua e indurisce.
Nel caso all´interno della zona iniettata non esistesse acqua in quantità sufficiente, questa può essere immessa posteriormente all´iniezione del CarboStop/CarboAdd. Contrariamente ai sistemi bicomponenti, CarboStop U non indurisce all´interno dei tubi di caricamento una volta che la sua reazione dipende dal contatto con l´acqua nella zona iniettata.
Subito dopo il termine dell'attività di iniezione sciacquare la pompa con CarboSolv D, per prevenire la formazione di ostruzioni. In seguito a periodi di pausa della durata superiore a un giorno, riempire la pompa con CarboSolv S.

Avvertenze

Prima della messa in opera si raccomanda di conservare i prodotti per almeno 12 ore ad una temperatura minima di 15°C, in modo da ottenere la temperatura di lavorazione ideale (fra 15 e 30 °C). Nel riscaldare evitare assolutamente l'impiego di fiamma diretta sui contenitori.

Indicazioni di Sicurezza e Manipolazione per l'Impiego di CarboStop U

Osservare le regole generali di sicurezza mentre si manipolano i prodotti chimici.

CarboStop U

CarboStop U
Simbolo: Xn (nocivo).
R20 Nocivo per inalazione. R36/37/38 Irritante per gli occhi, le vie respiratorie e la pelle. R42/43 Può provocare sensibilizzazione per inalazione e contatto con la pelle. R48/20 Nocivo: pericolo di gravi danni alla salute in caso di esposizione prolungata per inalazione.
S9 Conservare il recipiente in luogo ben ventilato. S23 Non respirare i fumi/aerosol. S26 In caso di contatto con gli occhi, lavare immediatamene e abbondantemente con acqua e consultare il medico. S36/37 Usare indumenti protettivi e guanti adatti. S45 In caso di incidente o di malessere consultare immediatamente il medico. S60 Questo materiale e il suo contenitore devono essere smaltiti come rifiuti pericolosi.
Z1 Contiene isocianati: vedi informazioni fornite dal produttore

Ulteriori informazioni sulle schede di sicurezza fornite dl produttore.

Imballi
5,5 kg in latte metalliche
22 kg in latte metalliche

Altri imballi su richiesta.

Stoccaggio e Conservazione
Almeno 6 mesi dalla data di consegna o 12 mesi dalla data di produzione se conservati in ambiento asciutto fra 10 °C e 30 °C. In questo periodo è possibile che la viscosità aumenti di circa 100%; questo non influisce sulla messa in funzione del prodotto. Le condizioni legali di stoccaggio devono essere osservate. Nell'impiego di prodotti stoccati a lungo, prima della messa in opera, si consiglia di verificare presso la Minova CarboTech le effettive caratteristiche del prodotto come da specifica.

Smaltimento
Vedere le normative locali. I prodotti liquidi possono essere smaltiti presso un impianto inceneritore (codice UE 080501).
Il CarboStop U indurito può essere smaltito come rifiuto urbano (codice UE 200139).

Certificazioni Disponibili
1. Valutazione d'igiene nel rispetto dell'acqua di falda (Istituto di Igiene, Gelsenkirchen, 2006)
2. Relazione su iniezioni di CarboCrackSeal H / CarboStop U in base alla normativa ZTV-RISS (Institut für Massivbau, Essen, 2003)
3. Certificato di conformità Ü-399 (ibac Aachen, 2011)
4. Numero di registrazione KR07-887 (Registro dei prodotti, Svezia 2008)
5. Certificato conforme alle direttive KTW (LADR GmbH, 2010)

Disconoscimento

CarboStop U

responsabile di, eventuali danni risultanti dall'avere utilizzato o prestato fede alle informazioni contenute nel presente documento.

Per ulteriori informazioni visitate il nostro sito web: www.orica.com

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