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Production of Biopolymeric Microcapsules containing Sodium Silicate for Self-Healing in Cementitious Materials

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Abstract - The storage of healing agents in capsules is one of the most promising self-healing methods in cementitious materials, becoming the most studied self-healing technique in recent years. Sodium silicate, which has many advantages as a healing agent in cementitious materials, can be encapsulated using different methods. In this work, microcapsules were produced based on the methodology developed by Kanellopoulos et al. (2017) through the complex coacervation technique in a double emulsion system water-in-oil-in-water (W/O/W), whose shell material is a crosslinked coacervate of gelatin-gum Arabic biopolymers. Initially, the methodology proposed by Kanellopoulos was replicated, performing some experimental adjustments. However, to make the process more sustainable and the microcapsules more environmentally friendly, in a second step, glutaraldehyde, known for its high toxicity, was replaced by another crosslinking agent, sodium tripolyphosphate (NaTPP), which is comparatively less toxic than glutaraldehyde. The microcapsules resulting from the two procedures were evaluated through particle size analysis and optical microscopy. Cementitious materials incorporated with the polymeric microcapsules were prepared to assess their ability to self-heal at early ages through the mechanical axial compression test. The results showed microcapsules with approximately spherical morphology and a mean diameter of around 50-100 µm. After causing small cracks in part of the samples, axial compressive strength tests showed that the microcapsules help the cementitious material perform better than the samples without the microcapsules.

Keywords**:** Polymer Encapsulation, Complex Coacervation, Self-Healing, Autonomous Healing, Sodium Silicate.

1. Introduction

Even though it is one of the most used materials in human construction, concrete is susceptible to a series of problems that impact its durability and strength. In autonomous self-healing, the cement matrix is developed to have self-healing properties, either by adding elements that chemically react with it or by elements that react only after damage by releasing a specific product inserted into the matrix at the time of manufacture. This method has been extensively studied because it is an option with good prospects for improvement in creating self-healing concrete [1].

The creation of a system based on encapsulation in the cement area was initially reported by White and collaborators in 2001 and has been adapted by several authors to obtain the restoration of mechanical properties of materials, electrical conductivity, or corrosion inhibition [2]. There are several methods and curing agents that can be used for the synthesis of microcapsules. A good choice of these can increase the stability and effectiveness of the active ingredient. The choice of method depends on the properties of the wall materials and the healing agent, the size and morphology of the desired microcapsule, and the application to which it will be submitted [3]. Among the existing methods, complex coacervation stands out due to its versatility and greater particle size control.

The principle of self-healing through microencapsulation is that the microcapsules are homogeneously incorporated into the host matrix during manufacture and trigger the release of their healing compounds after the formation of fissures with the rupture of their shell [4]. Chemical interactions between the released core material(s) and the surrounding matrix heal the crack, partially or fully restoring the material's properties. Such a system requires no external trigger, presents no restrictions on typical casting, and can handle multiple simultaneous cracks, offering greater flexibility for field applications and direct incorporation of the ubiquitous repair materials [5].

Kanellopoulos et al. (2017) and Giannaros et al. (2016) used the complex coacervation approach to develop self-healing cementitious materials by producing microcapsules containing sodium silicate as a curing agent. According to the authors, silica-based minerals are highly compatible with cementitious materials since they will react with water portlandite, calcium, or aluminum aluminate phases to form the crystalline phase/semicrystalline calcium silicate hydrate (CSH) or calcium aluminosilicate hydrate (CASH) that will precipitate and fill the cracks.

Litina and Al-Tabbaa (2020) also confirmed the curing potential of microcapsules containing sodium silicate under different cracking regimes. They investigated the effect of these additives on both fresh and hardened properties. They reinforced that incorporating mineral-based curative agents is compatible with cementitious applications, confirming that sodium silicate stands out among these. In addition to showing good compatibility with cement-based materials, it was found to considerably improve the efficiency of self-healing in terms of crack width and depth reduction, permeability, and strength recovery in mortar specimens cracks [6].

The exploration of this technique for producing this type of microcapsule has a lot of potential in self-healing materials. Still, no clear procedures available in the literature for producing microcapsules containing sodium silicate in the core were found. In Kanellopoulos et al. (2017), the microcapsule production process through complex coacervation and the materials used in the methodology were described. Still, the quantities and percentages of materials for each step were not available.

In the present work, polymeric microcapsules based on gelatine-gum Arabic were produced based on the methodology proposed by Kanellopoulos with some experimental adjustments. Once the microcapsules were produced and aiming to make the production process more sustainable, by obtaining more environmentally friendly microcapsules, glutaraldehyde, known for its high toxicity, was replaced by another crosslinking agent, sodium tripolyphosphate (NaTPP), which is non-toxic. The microcapsules resulting from the two procedures were evaluated through size analysis and optical microscopy. Then, cementitious materials incorporated with the polymeric microcapsules were prepared to assess their ability to self-heal at early ages through the mechanical axial compression test.

2. Materials and Methods

2.1. Production of Biopolymeric Microcapsules

Microcapsules were produced by replicating the methodology described by Kanellopoulos et al. (2017) with some modifications. Glutaraldehyde was replaced by sodium tripolyphosphate as a crosslinking agent. Tripolyphosphate is a polyanion ($P_3O_{10}^{5-}$) and can interact with positively charged amino groups on lysine groups in the gelatin polymer by electrostatic forces to form intermolecular ionic bonds or crosslinked networks [7].

2.2. Analysis of Biopolymeric Microcapsules

The microcapsules produced were characterized for mean diameter and size distribution by laser diffraction using Malvern Mastersizer 3000, in which measurements were performed in triplicate. For morphological evaluation, the formulations were observed by optical microscopy (Leica M4000M Microscope).

2.3. Mechanical Stress Test

The microcapsules produced were incorporated (16% by volume) in cementitious materials. The specimens produced were submitted to the axial compression test, according to the guidelines of NBR 7215, at the first ages (3 and 7 days) and 28 days after loading with seven days.

3. Results and Discussion

The results obtained through particle size analysis and optical microscopy showed that most microcapsules produced have an average diameter of 50-100 µm and an approximately spherical morphology. No significant differences were observed between the microcapsules produced with glutaraldehyde and sodium tripolyphosphate, as shown in Fig. 1.

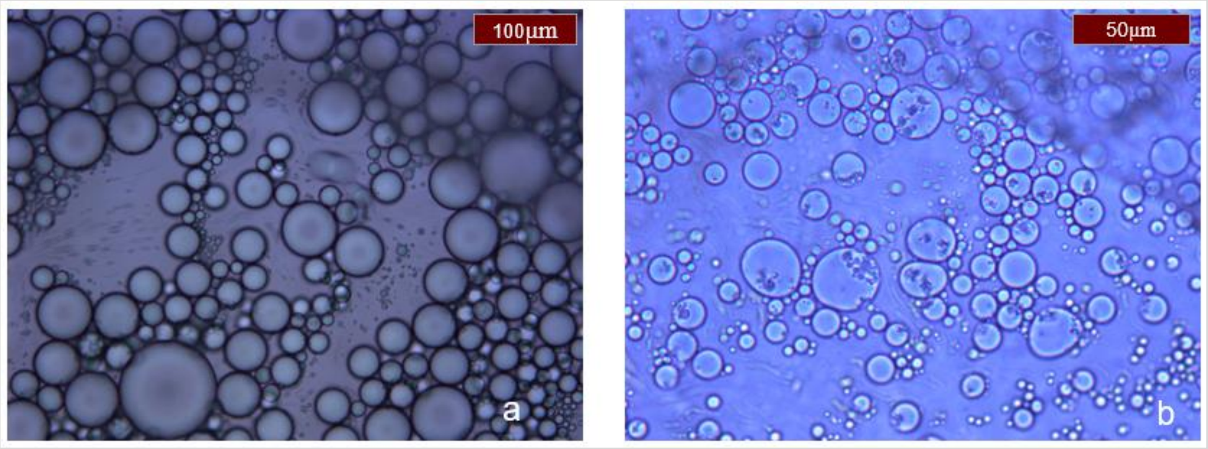

Fig. 1: Optical photomicroscopy: (a) microcapsules produced with glutaraldehyde and (b) microcapsules produced with sodium tripolyphosphate.

Generally, crosslinking with aldehydes is the primary technique to modify microparticle walls because it is fast and more efficient. However, crosslinking with glutaraldehyde has restrictions because it is a potentially toxic substance. Sodium tripolyphosphate appears as an alternative to glutaraldehyde because it is a non-toxic crosslinker that interacts well enough with positively charged amino groups (NH_3^+) in gelatin, also presenting desired controlled release properties. The size analysis results showed that the microcapsules produced by glutaraldehyde offer a polydisperse profile, with an average diameter of the largest population of approximately 100μm. The formulation prepared with sodium tripolyphosphate presented a more extensive set of smaller particles but still on the micrometric scale.

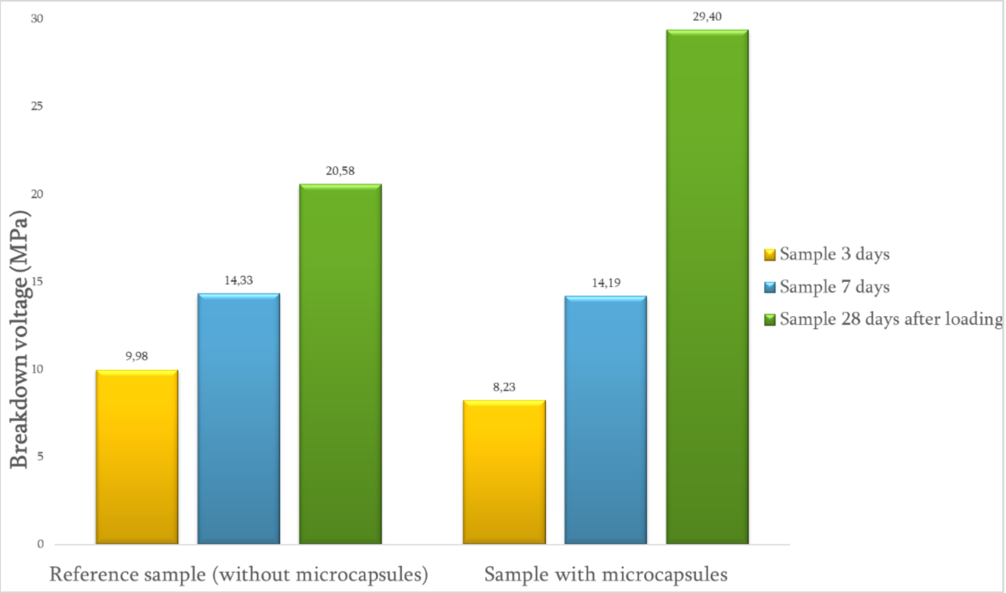

Fig. 2: Axial Compression test of biopolymeric microcapsules entrapped sodium silicate and reference into cementitious material (time: 3, 7, and 28 days after loading).

The results of the axial strength tests are shown in Fig. 2, for samples with addition of microcapsules and whitout addition. As expected and consistent with the literature, incorporating microcapsules in the mixture reduced the compressive strength of the samples when tested on 3rd day. In the sample overloaded with seven days and submitted to the axial compression test after 28 days, it was verified that the specimen with microcapsules not only recovered but also to have acquired superior resistance to the reference sample (without microcapsule) in the same period. This study proves the microcapsules' efficiency in the generated cracks' healing process.

3. Conclusion

This study showed that sodium silicate incorporated in biopolymeric microcapsules showed promise for autonomous self-healing of cementitious materials. There were no significant differences between the microcapsules produced with glutaraldehyde and sodium tripolyphosphate concerning morphology, size, and axial compression tests. The inclusion of microcapsules in the mixture substantially increases compressive strength after inducing small cracks. This study demonstrates that these microcapsules containing 20% (w/v) of sodium silicate as a healing agent help the cementitious material to perform better when compared to the same material without the microcapsules.

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References

[1] V. G. Cappellesso, “Avaliação da autocicatrização de fissuras em concretos com diferentes cimentos,” Dissertação apresentada ao Programa de Pós-Graduação em Engenharia Civil: Construção e Infraestrutura. Universidade Federal Do Rio Grande Do Sul, 2018.

[2] W. H. Binder, *Self-Healing Polymers: From Principles to Applications*. Weinheim: Wiley-VCH, 2013.

[3] A. Kanellopoulos, P. Giannaros, D. Palmer, A. Kerr, and A. Al-Tabbaa, “Polymeric microcapsules with switchable mechanical properties for self-healing concrete: Synthesis, characterisation and proof of concept,” *Smart Mater. Struct.*, vol. 26, no. 4, 2017, doi: 10.1088/1361-665X/aa516c.

[4] M. Rajczakowska, K. Habermehl-Cwirzen, H. Hedlund, and A. Cwirzen, “Autogenous Self-Healing: A Better Solution for Concrete,” *J. Mater. Civ. Eng.*, vol. 31, no. 9, p. 03119001, 2019, doi: 10.1061/(asce)mt.1943-5533.0002764.

[5] C. Litina and A. Al-Tabbaa, “First generation microcapsule-based self-healing cementitious construction repair materials,” *Constr. Build. Mater.*, vol. 255, 2020.

[6] P. Giannaros, A. Kanellopoulos, and A. Al-Tabbaa, “Sealing of cracks in cement using microencapsulated sodium silicate,” *Smart Mater. Struct.*, vol. 25, no. 8, 2016, doi: 10.1088/0964-1726/25/8/084005.

[7] C. Butstraen and F. Salaün, “Preparation of microcapsules by complex coacervation of gum Arabic and chitosan,” *Carbohydr. Polym.*, vol. 99, pp. 608–616, 2014, doi: 10.1016/j.carbpol.2013.09.006.