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Nanotechnology in Concrete: a Bibliometric Review

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Summary: This review intends to show how nanotechnology is currently being applied in concrete. Both organic and inorganic species can be used as nanoagents, producing materials with improved properties, promoting economic and environmental gains by extending the materials' lifetime. Thus, this paper covers nanotechnology applications to improve mechanical, thermal, and corrosive properties of concrete and shows bibliometric results, proving the increase of interest in these fields. Results have shown that organic agents are more commonly used than inorganic ones, and that nanotechnology is applied mainly to improve mechanical and thermal properties.

Keywords: Bibliometric review, statistics, nanotechnology, nanoagent, concrete, construction, composite, polymer, macromolecule.

Adherence to the BJEDIS' scope: This work is closely related to the scope of BJEDIS as it presents bibliometric research regarding the most common terms in the concrete nanotechnology field.

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1. Introduction

Civil Engineering is one of the most important fields to the global economy, generating trillions of dollars annually (1). The use of construction technologies dates from antique civilizations, producing many historical monuments (2). Zabidin and collaborators affirm that, due to the Fourth Industrial Revolution, construction will play an even more relevant role in improving the world (3).

Among the challenges faced by this industry, the costs to repair or substitute concrete structures are gigantic, promoting many economic and environmental issues related to the materials' prices and the waste produced during these operations. Thus, it is necessary to develop new technologies that allow improving the life-cycle of those materials, promoting benefits to society (4).

Concrete-based materials are also needed for new specific applications since industrial applications are becoming more complex (5). Thus, it needs properties that were not possible until then, such as better thermal (6), electric (7), and anticorrosive (8) properties.

Nanotechnology has been studied to develop these new technologies (9–11), and this work is focused on the prospecting of nano-based technologies useful to the construction area. Besides, future tendencies are foreseeing, allowing us to infer how the state of the art of this field would be developed during the next future.

1.2. Methodology

For the Introduction (Section 1), current research about nanotechnology in concrete was studied to gather the necessary information that any unknowledgeable reader would need to comprehend the article.

All of the research data was gathered from Google Scholar by using certain keywords and presenting the results from research related to them for the last 20 years. This methodology was used in previous works from our research group (12, 13).

We followed the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyzes) (14) methodology when applicable: in the identification process, we did not exclude any duplicate article, since only one database was chosen (Google Scholar). In the screening process, we excluded patents – since many of them are not peer-reviewed – and quotes – which might cause duplications in the number of articles. In the eligibility process, all of the articles were chosen to be included, since our objective is to do a quantitative analysis by showing the relevance of the keywords by the number of total articles published rather than a qualitative analysis, where only the most relevant studies are selected to be evaluated.

For example: in the Relevance section (Section 1.3), we searched scientific papers in Google Scholar for the last 20 years using the terms "concrete" and "nanotechnology". Bibliometric research was made using the total of articles from each period was summed, and we presented the data in a linear model to show that this field of study is increasing steadily.

For the mechanism section (Section 2), we studied recent research about nanotechnology in concrete to see which types of materials were used and presented the most common ones. To support the information in this section, we presented bibliometric research about the use of both organic and inorganic agents in concrete nanotechnology (Section 2.1). For this, we researched the total of articles from the last 20 years containing the terms "concrete nanotechnology" + "organic" and "concrete nanotechnology" + "inorganic", presented the sum of these values for each case separately, and used an exponential model to show the geometric growth in studies related to these applications.

Lastly, we researched the most common properties improved through concrete nanotechnology applications in the last five years (2017-2021) to check new trends in the field (Section 3). We used the keywords "concrete nanotechnology" with the following keywords separately: "mechanical", "thermal", "healing", and "corrosion". We ordered them in decreasing order and presented current research related to all of those possible applications, followed by a discussion about why those topics are more or less studied.

Considering all the gathered information, we presented final considerations about the topic and where new trends can go (Section 4). Figure 1 shows a diagram containing all the topics presented in this bibliometric review.

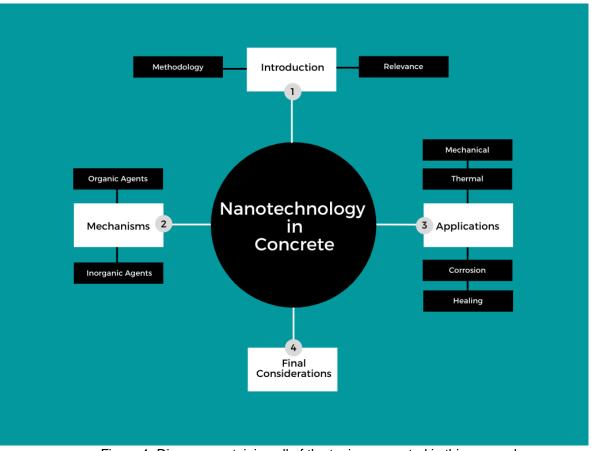


Figure 1: Diagram containing all of the topics presented in this research paper.

1.3. Relevance

Figure 2 shows the increase in nanotechnology and concrete research by searching for the keywords "nanotechnology" and "concrete" over the years. The research was done using Google Scholar. Results allowed inferring that the linear increase in published works ($R^2 = 0.9891$) proves this type of technology's relevance.

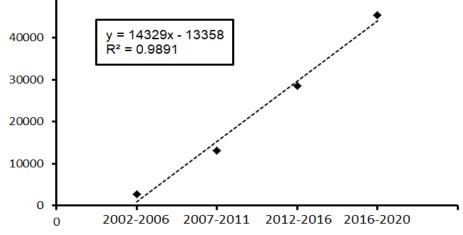


Figure 2: Number of published studies related to the terms "nanotechnology" and "concrete" in the last 20 years. Data extracted from Google Scholar on 01/29/2021.

2. Nanotechnology Mechanism in Concrete

Nanoadditives can improve concrete properties (15). As indicated by the name, those additives are in the nanometric scale (16). They provide a significant improvement in the concrete matrix properties (17). As the additives are in the nanoscale, it becomes possible to significantly increase properties with small quantities of material, avoiding compatibility issues (18). Nanoadditives can be added to cement in many different formats. Depending on the application, different types of shapes, such as nanoparticles (19), nanocapsules (20), nanotubes (21), and nanofibers (22), can be used. Besides that, many nanomaterials can be combined in the same concrete matrix, improving different properties to a certain degree (23).

2.1. Organic and Inorganic nanoadditives

Polymers are organic materials with high molar mass values, being applicable in a large set of fields, from commodities to highly technical engineering materials. Among the applications as nano additives to concrete, the use of nanofibers is the most famous. Those nanofibers can be synthetical or natural and promote a significant improvement in mechanical properties in concrete (24). However, natural fibers might need previous treatment since most natural materials have variable properties (25).

Carbon nanoadditives are also an excellent choice for concrete, both in nanotube (26) and nanofiber (27) forms. They are responsible to significantly improve concrete properties, especially in their graphene conformation, which allows an extremely resistant and lightweight material because of the hexagonal conformation of carbon atoms (28).

These nanomaterials are inorganic, composed mainly of metallic oxides (mixed or not with other molecules). Among the most important in concrete applications, it is possible to highlight: (1) silica (composed of silicon dioxide, SiO_2) (29); clay (low granulometry particles made mostly of hydrated aluminum and silicon oxides) (30); alumina (aluminum oxide, Al_2O_3) (31); and kaolin (mineral composed mostly of aluminum oxide and hydrated clay) (32). Those materials have the advantage of being available in nature.

Thus, the used materials can be organic or inorganic. Figure 3 compares research related to the "nanotechnology" and "concrete" with either the "organic" or "inorganic" keywords from 2002 to 2021. In both cases, the studies presented an exponential increase, showing the relevance of such materials. However, studies using inorganic nano additives are prevalent, with twice the amount of studies published.

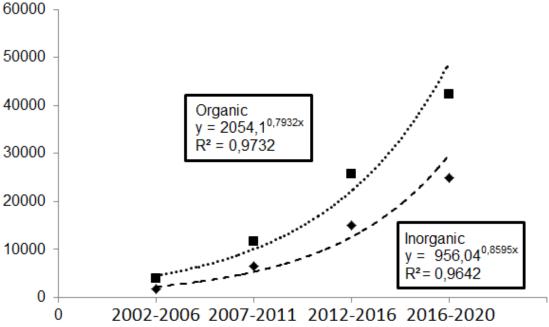


Figure 3: Number of articles related to the keywords "nanotechnology" and "concrete" with either the "organic" or "inorganic" keyword added from 2002 to 2021. Data extracted from Google Scholar on 06/02/2021.

The growth in published studies was exponential, doubling every five years for the last 20 years. It was valid for organic and inorganic agents. However, since the beginning of the measurement, inorganic agents have prevailed in the number of published studies.

Inorganic agents' prevalence in published studies is possibly due to the ease of obtaining inorganic materials, while the production of nanotubes and carbon nanofibers is still a more complicated process (33). In the future, it might be possible to develop the technology for the production of these organic materials, which might increase the number of studies related to the use of organic additives published. It might even be possible that investigation with organic materials passes the number of studies published with inorganic agents. However, in the short and medium-term, inorganic agents seem to prevail in the dispute.

3. Applications of Nanotechnology in Concrete

The use of nanotechnology in concrete can improve many different properties. In Figure 4, it is possible to compare published studies in Google Scholar from 2017 to 2021 using the keywords "nanotechnology" and "concrete" with those four keywords: "thermal", "mechanical", "healing" and "corrosion". It is possible to see that the studies researching improvement in mechanical properties are the most common, with thermal properties being in a close second place. Corrosion was a significant decrease in studies published, whereas healing properties is even less studied.

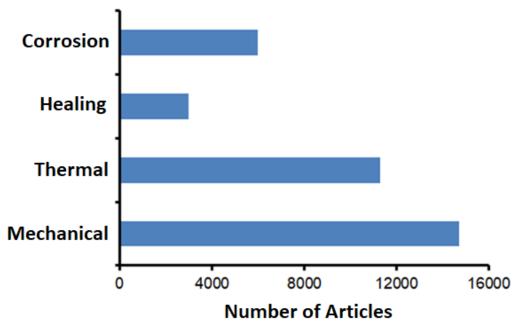


Figure 4: Studies published in Google Scholar from 2017 to 2021 using the keywords "nanotechnology" and "concrete" with either the "corrosion", "healing", thermal" and "mechanical" keywords. Data extracted from Google Scholar in 01/29/2021.

Below, the main improvements that this type of technology allowed in the cement materials are presented: **3.1. Mechanical Properties**

Costs to repair damaged concrete structures are very high (34). The cost reduction can be achieved using nanomaterials to increase these materials' mechanical resistance (35, p.). In general, fibers turn concrete more resistant to failure (36), allowing that the structures have a much longer time of application (37). Concrete-nanofiber composites tend to increase concrete mechanical properties, increase their resistance to fracture, and produce more stable fractures, according to Sharma and Lakkad (38).

Nanofibers can be natural or synthetic. The use of synthetic fibers tends to be more predictable since materials have more comparable properties (39). Among them, polymeric (especially carbon nanofibers) stand out (40). However, synthetic fibers last for a long time in nature, producing many environmental problems, as proved by Rikabi and collaborators (41). A good alternative uses recycled fibers in concrete, as Merli and collaborators explained in their extensive review about the subject (42).

On the other hand, natural nanofibers are biodegradable (43). They have variable properties depending on their source material, needing treatment before being adequately suited for this application, as pointed by Akinyemi and collaborators in a study (44). Among natural fibers, coconut (45), banana (46), bamboo (47), and others can be used.

However, probably the best material for this application are carbon-based ones. The research found that small amounts of carbon nanotubes or carbon nanofibers can improve many properties (48), even with small

amounts of the material (less than 1%) (49).

Most nanotechnology studies in concrete are related to its use in improving mechanical characteristics since nanofibers and nanotubes are relatively simple to add to cement matrices, combining numerous economic and environmental benefits with the ease of use (50). Therefore, the additives with the most potential in the construction industry are related to improving mechanical properties. Assessing the number of studies, one can imagine that the search for improvements in mechanical properties is growing as time passes. In the future, it might be possible to develop a relatively low-cost and high reproducible technology that is possible to use on a large scale in different regions of the world (51). When this technology is available, it is a matter of time before billions of dollars are saved annually in repairing concrete structures (52).

3.2. Thermal Resistance

Thermal conductivity is an important property that affects the heat transfer process in construction. Engineers need to think about it when planning their constructions (53). Many concrete materials tend to degrade themselves because of heat exposure and low thermal conductivity and resistivity (54). Thus, it is possible to change regular concrete materials to nanoadditives, improving thermal properties (55).

In general, small quantities are enough to improve those properties, but nanoadditives can go up to 5% of the total material weight (56). Mechanical properties are also improved, even it is not the original objective (57). The lower heat transfer rate, for example, is caused by the nanoparticles' small size, which favors better particle packing (Dingqiang et al., 2020).

The thermal properties can be improved using phase-change materials (PCMs). A PCM is a component that can be added to concrete to improve its thermal properties (59). A PCM can absorb and liberate heat instead of concrete, changing its physical state and avoiding any damage done in the concrete material, extending its lifespan and performance (60). A PCM can store and liberate heat repeatedly, promoting many heating-cooling cycles (61).

Biodegradable PCMs (also called Bio-PCMs) tend to have better properties: they are less dangerous, are accessible, have adjustable features, and allow thousands of heating-cooling cycles, according to a comparative study (62). Materials of this type are tested in concrete to improve their thermal properties and cool the environment (63).

Experimental study shows that nanoparticles-based PCMs are capable of reducing indoor temperature fluctuations (64) in construction while also improving the thermal conductivity of the materials (65), making it a positive alternative to improve thermal properties in concrete materials (66).

Researches using nanotechnology to improve thermal properties are in second place among collected data. The development of nanotechnology materials that can improve thermal properties will allow using a great range of materials in different regions, especially those with more extreme thermal conditions, such as very cold or hot areas (67). It is possible to apply Bio-PCMs in tropicals (68) or cold regions (69), developing the construction industry.

3.3. Corrosion Resistance

The material surface can significantly influence the resistance to corrosion of concrete, its structure, and, thus, its lifetime (70). It is heavily influenced by the environment, as it can degrade the concrete surface as time goes by (71). Many factors that tend to decrease concrete lifetime comes through the surface, such as the exchange of liquid/gas phase with the environment (72), acoustic absorption (73), and others (74). Having good surface properties is determinant to the concrete application, having a direct relation to its lifetime. Thus, surface treatment is needed to enhance concrete structure (75).

The surface treatment of concrete was always essential to improve the material properties. In this application, nanoparticles can be a potent ally, improving the related properties (76). For this, many organic agents, such as polymers (77), and inorganic agents, such as minerals (78), can be used. Coatings containing nano agents are also a form to promote corrosion resistance (Sharma et al., 2020).

Research studying anti-corrosion properties in concrete comes in third when it comes to relevance in studies. Corrosion is a very worrying factor in civil construction, especially considering reinforced concrete applications (80). With the development of nanotechnologies that can improve these properties, it will be possible to develop more resistant constructions in environments that favor corrosion, such as humid locations or even on the ocean floor (81).

3.4. Healing Properties

Self-healing systems (SHS) allow concrete to regenerate by itself when damaged. SHS consists of a self-healing agent present in concrete that can restore cracks (82). There are four types of agents: (1) autogenous (materials found naturally in concrete); (2) minerals; (3) bacteria and (4) adhesive materials (polymers, in most of

the cases, such as epoxy resins, polyurethanes, or superabsorbent polymers), according to Huang and collaborators (83). The combined use of different self-healing agents is commonly performed to improve the regeneration capability (84).

Recent studies tend to apply this technology outside laboratories, on larger scales, as shown by Seifan and Berenjian in a review (85). Polymeric materials tend to be preferred to promote concrete self-healing. They can regenerate more significant cracks, although it is not recommended for underground and underwater applications, as explained by Danish in a critical review about concrete self-healing efficacy (86)

Nanosize applications in self-healing concrete can be made mostly by mineral agents: carbon nanotubes (87), silica (88), and others (89). However, polymer applications as nanoadditives are also possible, both as the healing agent (90) or as an encapsulation material (91) that protects the agent until the crack happens. In both cases, many cracking-restoring mechanisms can happen (92).

Applications of nanotechnology-based self-healing systems are less common since the concept of self-healing is still not widespread in large-scale applications, although it is changing (93). In general, materials with these properties are found only in engineering materials, as they have high costs to be applied in regular applications (94, 94, 95). Although cheaper self-healing systems in civil construction already exist (Vermeer et al., 2021), this type of application is still relatively unknown.

4. Conclusions

The number of studies about nanotechnology in concrete increases significantly over time, showing the relevance of this theme. Both the use of organic agents and inorganic agents have increased exponentially for the last 20 years. However, inorganic agents remain the most applied due to their greater ease of production and reproducibility concerning organic agents.

Nanotechnology can improve the mechanical and thermal properties of concrete. It also can act as anticorrosion and self-healing agents as technologies become accessible. These are the most relevant fields where nanotechnology can impart relevant new properties, reducing construction costs.

With the correct development in technologies, using nano additives might allow the application of materials with a much longer life cycle and an increase in performance, which results in many long-term economic and environmental benefits.

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